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Observational Study of Black Carbon in the North Suburb of Nanjing, China

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1. Introduction

Black carbon is a kind of amorphous carbon particles, which was formed by incomplete combustion of carbonaceous substance (Andreae et al., 1984; Bond and Bergstrom, 2006; Hansen and Rosen, 1984; Hansen et al., 1988; Penner et al., 1993). The main natural sources of black carbon are volcanic eruptions, forest fires, etc. Its shape, size and origins are extremely variable depending on the different type of fuels, combustion processes, and the age and history of air masses. It mainly resides in the submicron particle size range. This aerosol is usually separated into two main components: one is called the organic carbon (OC) and the other the black carbon (BC) component. Emissions from natural sources such as forest fires are localized and incidental (Bai and Wang, 2005), whereas anthropogenic emissions are widespread and continuous (Liu et al., 2010; Streets et al., 2001; Xu et al., 2006). The increasing demand for energy in the past century has led to a great increase in the rate of BC emissions. Black carbon particles have received increased interest recently since Hansen et al.(Hansen et al., 2000) indicate that it is perhaps more cost effective to control black carbon particles than CO_2 at the present time. Black carbon has many effects (IPCC 2001; Lary et al., 1999), such as harming to human health, changing climatic characteristics, reducing visibility, affecting the atmospheric chemical reaction process, which has become a focus of scientific research in recent years.

Although the effect of increasing BC in the atmosphere may be considerable, knowledge of BC concentrations, distributions, characteristics, and potential effects is still seriously lacking. Moreover, the surface of BC particles contains numerous adsorption sites that are capable of enhancing catalytic processes. As the result of its catalytic properties, BC may intervene in some important chemical reactions involving atmospheric sulfur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and other gaseous compounds (Gundel et al., 1989). Despite the evident significances of BC in air chemistry and physics, information concerning their spatial and temporal variability is still quite limited.

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Considering the global distribution of black carbon, the black carbon concentrations in the northern hemisphere were significantly higher than that in the southern hemisphere, as well as there is higher black carbon concentration value in eastern China (Streets et al., 2001). Of both natural and anthropogenic origin, emissions of black carbon recently have been estimated at 24Tg per year (Penner et al., 1993). China has higher black carbon emissions in recent years. We must make observation of black carbon in order to grasp the first primary data. The research work about the systematic observation of black carbon begun from 1990s in China, which had been carried out in most areas of China after 21 century.

Nanjing is located in the center of Yangtze River Delta region, which has developed petrochemical, steel and other heavy industries. The air pollution in Nanjing is very serious, but the observations of black carbon have not been reported. The observational results of black carbon in fine particulate matter from November 2008 to April 2010 in the north suburb of Nanjing were used to study the evolution law of black carbon aerosol. The observational data of SO_2, NO_2, HNO_2 and O_3 in October 2009 was also used to analyze the correlations between black carbon aerosols and SO_2; to discuss the complex-phase photochemical reaction between black carbon aerosols and gas. Moreover, the findings may also be useful in the formulation of strategic air pollution control in China and other rapidly developing countries. To understand anthropogenic air pollutant sources, loading, and their fate in the region, it is important to measure BC for different seasons and compare their characteristics. In this paper, an intensive air pollution health effects study was conducted. The characteristics of spatial variations of BC in $PM_{2.5}$ concentrations during one more year are summarized, and the relationships between gas and BC in $PM_{2.5}$ are discussed.

2. Experimental methods

2.1 Measurement site description

The field study was conducted in north suburb area of Nanjing City which is located in Jiangsu Province, 290 km east of Shanghai, and 10 km south-southeast of the Yangtze River. There are large regional sources that can impact this site, including Yangzi Petrochemical Industries Company, Nanjing steel plant, Nanjing chemistry plant and Huaneng electric generating station (5-10 km to the east and northeast). The No. 328 national highway is just 1 km in the east of measurement site. Average daily traffic flow is over 42,000 on this highway. The dominant local sources of BC are expected to be vehicular emissions, incomplete combustion of fossil fuels and biomass burning.

Measurements were taken at a university 10 km north of the center of Nanjing city in a residential area, near the top of automatic meteorological observation station (elevation 5m). Samples were collected 4.5 m above the ground.

2.2 Sample collection and analysis

$PM_{2.5}$ aerosol samples were collected from November 2008 to April 2010. Sampling started and ended at around 8 a.m. and 8 p.m. every week; each sample was collected for 12 h. The sampler (Andersen Instruments, Smyrna, GA, USA) was equipped with a slot inlet of 2.5 μm cut size and operated at a flow rate of 1.11m^3/min. All the collection substrates were 20×25 cm quartz fiber filters, prebaked at 550 ℃ overnight to remove any absorbed organic materials. The filters were stored and transported to the field in annealed aluminum foil pouches. After the sampling was completed, the 20×25 cm filters were folded in half such

that the side with the sample on it was folded onto itself and stored in the annealed aluminum pouches. All the filter samples were stored at -4 ℃ in a freezer until analysis.
OC and EC concentrations were determined using a thermal/optical aerosol carbon analyzer (Sunset Laboratory, Forest Grove, OR, USA) (Birch and Cary, 1996). For the determination of OC and EC concentrations, a filter punch 1.45 cm^2 in size was removed from the 20×25 cm filter and loaded into the aerosol carbon analyzer. The thermal analysis conditions (i.e., temperature program and the type of atmosphere) employed were similar to those adopted by all research groups that participated in the carbon analysis of the ACE-Asia samples (Schauer et al., 2003). Duplicate measurements of OC and EC were made on every sample, and the average relative standard deviations were 4% and 9% for OC and EC, respectively. Laboratory and field blanks were collected at a rate of 10% to determine the limit of detection (LOD); collocated samples were collected at a rate of 10% to determine precision; replicate analysis was performed on 10% of the samples to determine analytical precision.

2.3 The aethalometer

A model AE-21 Aethalometer (Magee Scientific Inc., Berkeley CA) was used to measure aerosol black carbon (BC) in real time (Lavanchy et al., 1999; Liousse et al., 1993; Petzold and Niessner,1995; Ruellan and Cachier,2000; Sharma et al.,2002). It measures the attenuation of light transmitted through particles that accumulate on a quartz fiber filter (Hansen et al., 1984). A vacuum pump draws air through the instrument so that the particles continuously accumulate on the filter while being illuminated by visible light (incandescent light source). The effective operational wavelength of the aethalometer is 880 nm (Bodhaine 1995; Lavanchy et al., 1999). The measurement of BC by this technique is controversial since this optical technique is based on light absorption of atmospheric particles sampled on filters and Mie theory to estimate BC mass concentrations in the atmosphere. This method is similar in principle to the Coefficient of Haze monitors developed over 40 years ago (Hemeon et al., 1953), but is more sensitive and stable. Optical attenuation from BC is calculated using the decrease in light transmission through the filter and the sample volume. The Aethalometer is not designed to measure either aerosol organic carbon or atmospheric light extinction from particles. The principle of the method is described in detail elsewhere (Hansen et al., 1984; Hansen and McMurry1990). The Aethalometer sample flow rate was 4 $L\text{-}min^{-1}$. An 2.5μm size inlet fraction was used. The disk aging, power failure and other reason cause some data loss in the observation process, neglecting whole day data less than 18 hours per day (Lou et al., 2005), the effective data is 285 days.
This study was also conducted to determine the relationship between light absorption measurements of an aethalometer and thermally derived black carbon concentrations.

2.4 Observation of SO_2, NO_2, O_3 and HNO_2

AR500 system was used to determine the concentration of four kinds of gases, which has double optical DOAS AQM system and produced by Swedish OPSIS AB. High-pressure xenon lamp (B class) was used as launchers light. A smooth spectrum emitted by the xenon lamp can covere the wavelength. The wavelength of UV and visible light is about 200 ~ 400 nm and about 400 ~ 700 nm, respectively. The measured gases are O_3, SO_2, NO_2 and HNO_2. Observation date was from 1 October to 31 October of 2009. According to 75% of data capture rate, excluding whole hour data less than 45 min per hour and whole day date less than 18 h per day.

Meteorological and air quality data are monitored continuously at this location by the Office of Atmospheric Environment Observatory.

3. Results and discussion

3.1 Methods comparison: elemental carbon and black carbon

Comparison between the Aethalometer BC data and the EC component of the EC/OC sampler data should show good agreement, since EC is expected to be the principal (visible) light absorbing component in ambient air (Gundel et al., 1984; Hansen et al., 1984; Hansen and Rosen, 1990). Five minutes Aethalometer BC data were averaged into twelve hour values temporally matching the 61 EC/OC samples. The relationship between BC and EC is shown in Figure 1. The two methods were found to be highly correlated (R^2=0.9492). It is said that particulate black carbon measured by the Aethalometer method has been shown to be a reliable surrogate for particulate elemental carbon measured by Thermo/Optical Reflectance at this location and time of year.

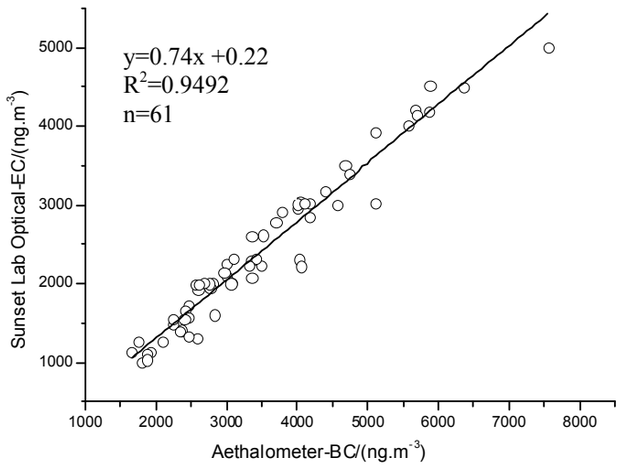


Fig. 1. Comparison between BC measurements made by EC/OC Analyzer and Aethalometer

3.2 Monthly variation of BC concentration

Fig. 2 shows the variation of monthly average black carbon aerosol concentrations during the observation period. The Black carbon aerosol concentration in autumn and winter is higher than that in spring and summer. Take the year 2009 as example, variation order (from high to low) of black carbon aerosol concentrations is October> May> November> February> December> June> April> September> August> July.

The monthly average black carbon aerosol concentration in Nanjing reaches maximum in September 2009 in the whole observation process. It is earlier comparing with other areas of the country (Qin et al., 2007; Zhao et al., 2008) The rainfall in Nanjing is very low in October 2009, and it is controlled by the high atmospheric pressure. These reasons lead to air pollutants concentrate and difficult to spread and eliminate. Moreover Nanjing was located in the transition zone between subtropical zone and temperate zone and doesn't adopt large-scale unified heating measures like north cities of China in winter. The emission inventory of black carbon aerosol won't increase sharply because of heating, which is another reason for the relative higher monthly average concentration of black carbon

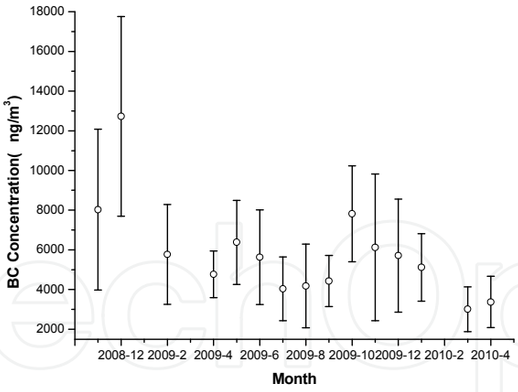


Fig. 2. Variation of BC average concentration in $PM_{2.5}$ in the air of north suburb of Nanjing

aerosol in October. By contrast, the black carbon monthly average concentrations in November and December 2009 decrease by 23.7% and 55.1% respectively over the same periods, which indicates that "on the promotion of crop straw integrated reuse decision" issued by Jiangsu Environmental Protection Administration and a series of air pollution control policies in the practical application has gained tangible effects. However, the black carbon aerosol concentration is still higher in Nanjing, the black carbon aerocolloidal concentrations in November and December 2009 are (6127 ± 3689) ng/m^3 and (5714 ± 2849) ng/m^3 respectively. It is still necessary to reduce emissions of industrial waste gas, vehicular exhaust and to prohibit straw incineration strictly.

The minimum of monthly average black carbon aerosol concentration appeared in March 2010 in the whole observation process. The precipitation in March 2010 increases by 40% over the same period, reaching 118mm, 16 precipitation days, black carbon aerosol was significantly removed by rain. Wu et al (Wu et al., 2009) found in the Pearl River Delta of China that black carbon aerosol concentrations in the rainy season were significantly lower than that in dry seasons in Panyu district of Guangzhou city. From 2004 to 2007, black carbon aerosol concentrations in the dry seasons is 10.4% higher than that in the rainy seasons (Wu et al., 2009). From the beginning of March, the amount of solar radiation reaching the ground increases with the gradual increase of sunlight hours and the atmospheric convection become strong. The black carbon aerosol concentrations decrease because of the diffusion of black carbon aerosol with atmospheric convection.

3.3 Seasonal variation of BC concentration

Nanjing is located between subtropical and temperate transition zone, which has four distinctive seasons. Therefore the criteria for the classification of astronomy is used to differentiate the Four Seasons, March, April and May are classified as spring, June, July and August are classified as summer, September, October and November are classified as fall, December and January, February in the following year are classified as winter. Fig. 3 shows the seasonal variation of black carbon aerosol concentration, where 1 to 7 in x-axis represents different seasons from the fall in 2008 to the spring in 2010. From the Fig. 3, black carbon aerosol concentrations in fall and winter were significantly higher than that in spring and summer, which is consistent with variation characterization of monthly average black carbon aerosol concentrations. The maximum of black carbon aerosol concentration appeared in the fall of 2008 during the whole observation period. It is the peak time of straw

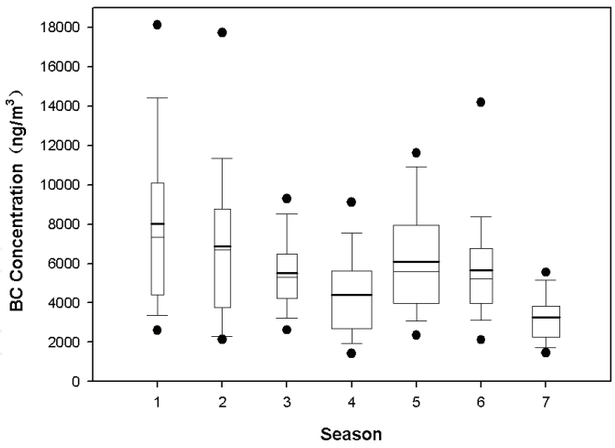


Fig. 3. Variation of seasonal average BC concentrations in $PM_{2.5}$ in the north suburb of Nanjing

incineration from the November 12 to November 31. The straw incineration attributes to the increase of the black carbon aerosol concentration. The concentrations of black carbon aerosols is relatively lower while without straw incineration. Hence the variation of daily black carbon aerosol concentration is greater in the fall of 2008 and the data has a higher dispersion degree. The concentration is 18000ng /m^3 at 95%, but less than 3000ng/m^3 at 5% with no difference in other seasons.

3.4 Diurnal variation of BC concentration

The diurnal variation of BC concentration is characterized by a special pronounced double-peak patterns during the observation period in Fig 4. In the case of temperature inversion persisting, human activities starting from 5 a.m. lead to the increase of black carbon aerosols emissions, and centralization and no diffusion of a large number of pollutants near the ground. Black carbon aerosol concentration in the air began to increase at the same time. Auromeet et al (Auromeet and Serge 2009) found that transportation was an important

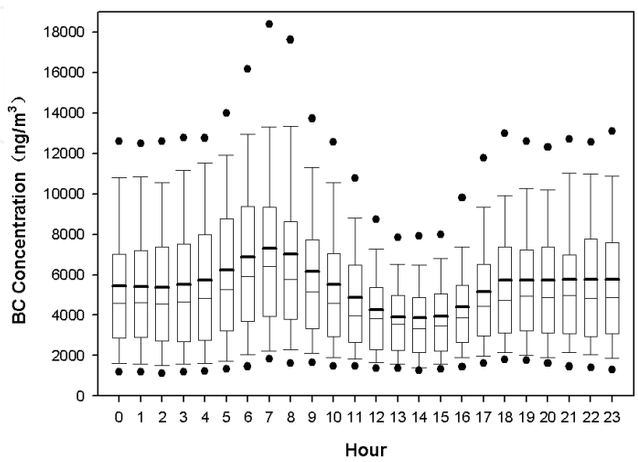


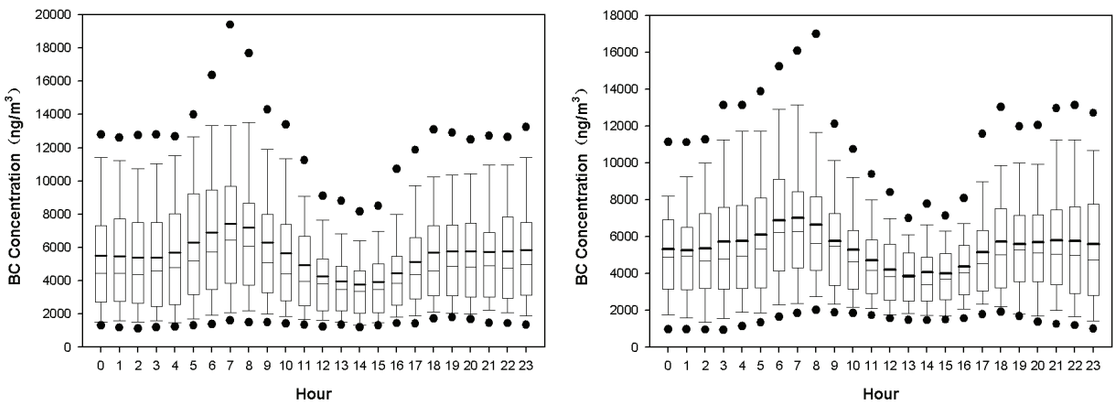
Fig. 4. Diurnal variation of BC concentration in $PM_{2.5}$ in the air of north suburb of Nanjing

source to the black carbon aerosol in Toulon region of France. In this study, the 328 national highway is just 1 km far away from observation site, so the vehicular exhaust make a greater contribution to the concentration of black carbon aerosol.

After 7 a.m., with the increase of solar radiation, temperature inversion structure was destroyed and atmospheric convection was enhanced, black carbon aerosol concentration decreases gradually. The strongest solar radiation and most intense atmospheric convection appear from 13 p.m. to 15 p.m., so the aerosol particle is not easy to concentrate. Hence the minimum of black carbon aerosol concentrations occurs at this time.

Black carbon aerosol concentration gradually increased after 16 p.m., reached maximum again at 18 p.m. Solar radiation was gradually decreased, and convection was weakened during this period. Meanwhile, a large number of black carbon aerosols were emitted to the atmosphere again by human activities; black carbon aerosol concentration begins to increase.

These changes of Black carbon aerosol concentration have similarity with other previous reports (Qin 2001; Zhao et al., 2008). But the maximum of the black carbon aerosol concentration at 18 p.m. will last until the dawn of the following day and does not decrease with the reduction of human activity during this period, which is different with other reports. It is because of the particular weather conditions in Nanjing. The book "Jiangsu weather" published by Jiangsu Province Bureau of Meteorology 90 years in the 20th century (Jiangsu Climate 1991) described that Nanjing has a high frequency of temperature inversion. The day of temperature inversion was defined that it appeared temperature inversion one time in a day, which has strong temperature inversion frequency. The structure of temperature inversion layer can be formed at toward evening in the Nanjing region. As the time passed by, strength of temperature inversion was continually increasing. The presence of strong temperature inversion layer caused that black carbon aerosols were not easy to diffuse and maintained at a stable concentrations level.



(a) (b)

Fig. 5. Variation of diurnal BC concentration in $PM_{2.5}$ on weekdays(a) and weekend(b) in the air of north suburb of Nanjing

The hourly average concentrations of black carbon aerosol on weekdays and weekend are discussed respectively. Fig. 5 shows the variation of hourly average black carbon aerosols concentration on weekdays. The tendency of black carbon aerosol concentration in Fig. 5 is consistent with the observation period, but the concentration value has more dramatic

change. While the tendency of black carbon aerosol concentration given in Fig. 5 has some differences, the appearing time of maximum of black carbon aerosol concentration at 95% is put off one hour; the appearing time of maximum of black carbon aerosol concentration at 75% is still at 7 a.m. The different concentration among different numbers demonstrated that human activities are random on weekend and it is irregular about black carbon aerosols emission. However, the maximum of black carbon aerosols concentration still appears at 6 a.m. to 8 a.m. and after 5 p.m. due to the variation of temperature. The appearing time of afternoon maximum of black carbon aerosols concentration is delayed three hours on weekend, which is related that people enjoy some form of recreation and go home late.

3.5 The pollution character of BC concentration in the north of Nanjing

From Fig. 4, black carbon aerosol concentration has no significant difference with its average value, which indicates the concentration of black carbon aerosols is not a normal distribution. It is not scientific to use average value to represent the background value. Considering the request of atmospheric background, we define the concentration having maximum frequency as the background concentration of black carbon aerosols (Tang et al., 1999). Taking 100ng/m^3 as frequency statistics step, draw the frequency distribution map of hourly average concentration of black carbon aerosol. From Fig. 6, the frequency distribution of hourly average black carbon aerosol does not have normal characterization, using the log-normal distribution function to fit the frequency distribution characteristics, results show that hourly average concentration of black carbon aerosols at 2920ng/m^3 appeared maximum frequency. The observation site is located in the campus of Nanjing University of Information Science & Technology in the north suburb of Nanjing, we can conclude the background concentration of black carbon aerosol is approximately 2920ng/m^3 in the north suburb of Nanjing. The statistics data are not affected by a small number of polluted air masses and do not appear extremely high concentration of black carbon, therefore the value is most representative to the black carbon aerosols in the north suburb of Nanjing.

The background concentrations of black carbon aerosols in different areas of China have significant differences. The detailed results are listed in Tab. 1. The black carbon in $PM_{2.5}$ was studied in this paper, which is the main difference with other papers. Li Yang et al (Li et al., 2005) observed the black carbon in $PM_{2.5}$ in Xi'an, and the results showed that

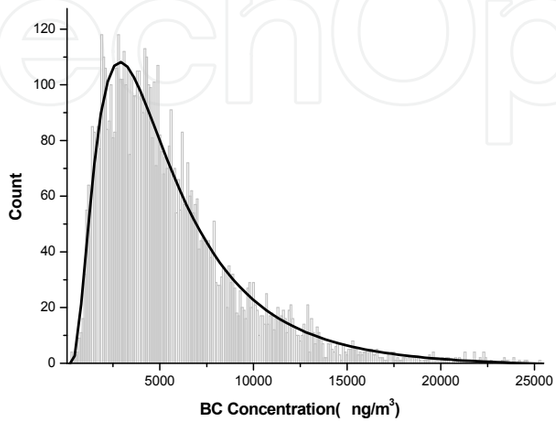


Fig. 6. Count distribution of hourly mean of BC in $PM_{2.5}$ in the air of north suburb of Nanjing

background concentration of black carbon in $PM_{2.5}$ is as high as 4500ng/m^3, but the value only reflects the black carbon concentration levels in $PM_{2.5}$ of the fall in Xi'an region. There is a higher value of the black carbon aerosol concentration in the fall. It can be inferred that the whole-year background concentration in Xi'an region is lower than the value in the fall. Lou Shujuan et al (Lou et al., 2005) found that 90% of black carbon exists in the aerosol particles with the diameter less than 10μm, while 82.16% of black carbon exists in the aerosol particles with the diameter less than 2.5μm in Beijing region. Taking 80% as conversion factor between the black carbon in TSP and the black carbon in $PM_{2.5}$ in Nanjing, background concentration of black carbon in TSP is up to 3650ng/m^3 in this study. The value is much higher than that in other studies. The air pollution by black carbon aerosol is very serious in Nanjing.

Site name in China	Location	Date	Position	Background concentration (ng/m^3)	Literature
Wa liguan, Qinhai	Global background	September 1994-November 1995	TSP	63	Tangjie et al. (1999)
Wenjiang, Sichuan	Suburb of city	September 1999-August 2000	TSP	2890	Qin Shiguang (2001)
Lasa, Tibetan	Suburb of city	June 1998-September 1998	TSP	400	Qin Shiguang (2001)
Lin'an,Zhejiang	Region background	August 2000-February 2001	TSP	2350	Qin Shiguang (2001)
Shang dianzi, Beijing	Region background	August 1999-September 2000	TSP	222	Qin Shiguang (2001)
Xi'an, Shanxi	Suburb of city	September 2003-November 2003	$PM_{2.5}$	4500	Liyang et al. (2005)
Xining, Qinghai	Suburb of city	September 2005-February 2006	TSP	2300	Zhao Yucheng et al. (2008)
Nanjing, Jiangsu	Suburb of city	November 2008-April 2010	$PM_{2.5}$	2920	This paper

Table 1. The background concentration of BC in other areas of China

3.6 A case study

Nanjing municipal government had instituted the blue sky plan in order to control the air pollution and ameliorate the air quality since 2003. The aim of blue sky plan for 2009 is to have 320 days achieving superior rank of the atmospheric status (API ≤ 100). Considering from the whole year of 2009, there are only 14 pollution days with the help of further some weather conditions in the first six months. But from the beginning of October, due to the increasingly deterioration of atmospheric status, there are 16 pollution days within October in Nanjing. There into, it appears 15 consecutive pollution days from October 16 to October 30 in Nanjing.

The air condition of Pukou district in which observation site is located is better than whole Nanjing region, but there are nine days with air pollution index exceeding 100, slight pollution, and there are many days with the air pollution index around 95 in Fig. 7. There

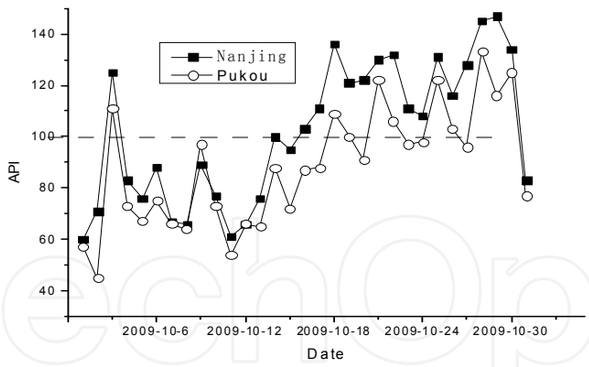


Fig. 7. The comparison of air pollution in two different site

are no large-scale infrastructural construction in Pukou district, but there are many large industries, such as Yangzi Petrochemical, Nanjing Chemical, Nanjing steel and so on in the north suburb of Nanjing. Therefore black carbon aerosols make an important contribution to air pollution in the north suburb of Nanjing.

Fig. 8 shows the evolution sequence of hourly average black carbon aerosol concentration in October, the data of October 10 and 11 were lost. From Fig. 8, the concentration of black carbon aerosol has significant changes. The air pollution is most serious in late October, the variation scope of diurnal black carbon aerosol concentrations can reach 20000ng/m^3, the maximum (26701ng/m^3) occurred at 8 p.m. on October 26. These are determined by the boundary layer structure and the emissions of pollution sources in Nanjing region. The north cold air arrived at Nanjing on October 31, black carbon aerosol concentration simultaneously decreased to 964ng/m^3 at 20 p.m. In Fig. 9, correlation analysis was used between the air pollution index and black carbon aerosol concentration. The result of correlation analysis shows that they have positive relationship (the correlation coefficient $R = 0.689$; $p < 0.05$), also proved that black carbon aerosol is an important component in the atmospherically particles.

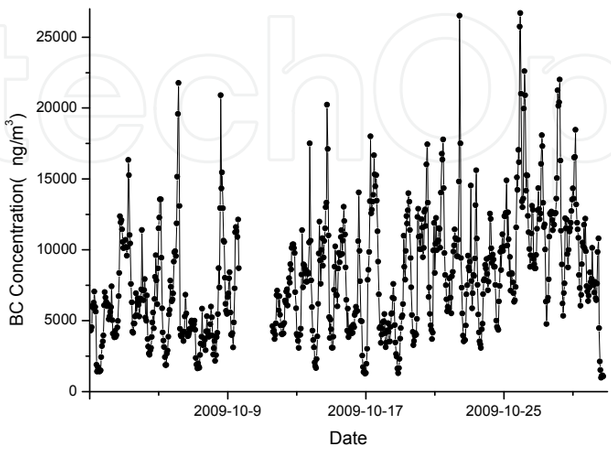


Fig. 8. Sequence of hourly average BC concentration in $PM_{2.5}$ in October 2009 in north suburb of Nanjing

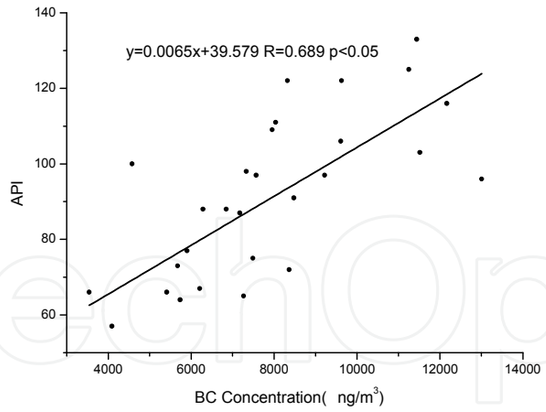


Fig. 9. Correlation between the API and diurnal average BC

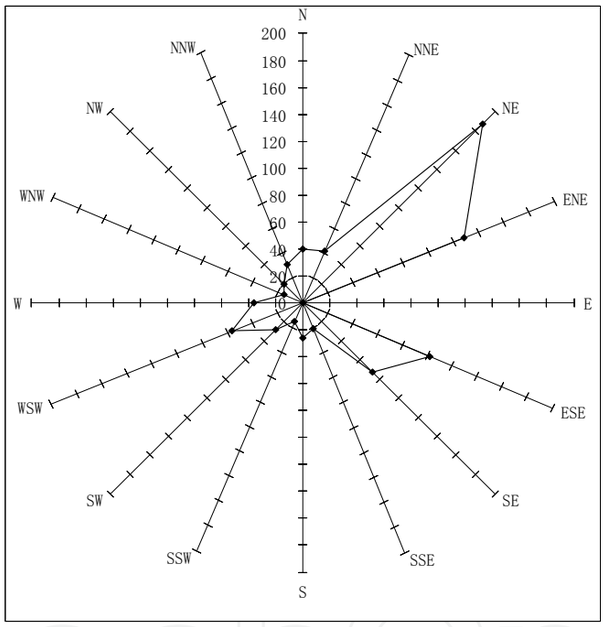


Fig. 10. Wind Rose in the north suburb of Nanjing during Oct.2009

There was no significant rainfall in October 2009 in Nanjing. The cumulative rainfall was only 8.3 mm, which decreases by 90% over the same period. Most areas of Jiangsu province have shown a meteorological drought. From Fig. 10, the dominant wind direction was northeast in October 2009 in Nanjing. There are industrial areas along the Yangtze River in this direction, where is a large emission sources of black carbon aerosol. In addition, after the harvest of crops, phenomenon of straw incineration still exists partially, and incomplete burning of biomass is also an important source of black carbon aerosols. The static wind frequency was 116 hours in October 2009 in Nanjing. The black carbon aerosol is not easy to diffuse because of the higher static wind frequency. The black carbon aerosols centralized gradually on the condition of low rainfall and higher static wind frequency, and formed a high value and serious pollution at last.

3.7 Relationship between BC and different gas

Black carbon aerosols were formed only by the incomplete combustion of carbonaceous material. Nitrogen oxides and sulfur oxides were generated with the formation of black carbon aerosols. Penner et al (Penner et al., 1993) pointed out that there are good correlation between SO_2 and black carbon aerosols in most places, and according to the correlation to calculate the global emission inventory of black carbon aerosol. Fig. 11 shows the hourly average concentration and daily average concentration of SO_2 in October 2009 and correlations between them and the Black carbon aerosol concentration. The results of correlation analysis show there is higher positive relationship between daily average concentration of SO_2 and black carbon aerosols (correlation coefficient= 0.627; $p < 0.05$), which demonstrate that it is operational to calculate the emission inventory of black carbon aerosols according to the emission inventory of SO_2 in the north suburb of Nanjing. But there is no good relationship between hourly average concentration of SO_2 and black carbon aerosols (the correlation coefficient= 0.290; $p < 0.05$), which shows that average concentration of SO_2 and black carbon aerosols concentration do not have complete consistency. So the emission inventory of SO_2 was not applied to reflecting the real emission inventory of black carbon aerosols. It is necessary to consider various factors when the emission inventory of black carbon aerosols is calculated.

Fig. 12 shows variation sequences of hourly average NO_2, HNO_2 and O_3 concentration in October 2009. Fig. 13 shows correlations between black carbon aerosol and these three kinds of gas. The results showed that black carbon aerosol has good positive relationship with NO_2 and HNO_2; correlation coefficients are 0.615 and 0.676 respectively. Nitrogen oxides in the atmosphere are mainly from fuel combustion. NO generated firstly in the combustion process was emitted into atmosphere and was oxidized to NO_2 gradually. The good relationship between NO_2 and black carbon aerosol demonstrates that air pollution in the north suburb of Nanjing presents complex features.

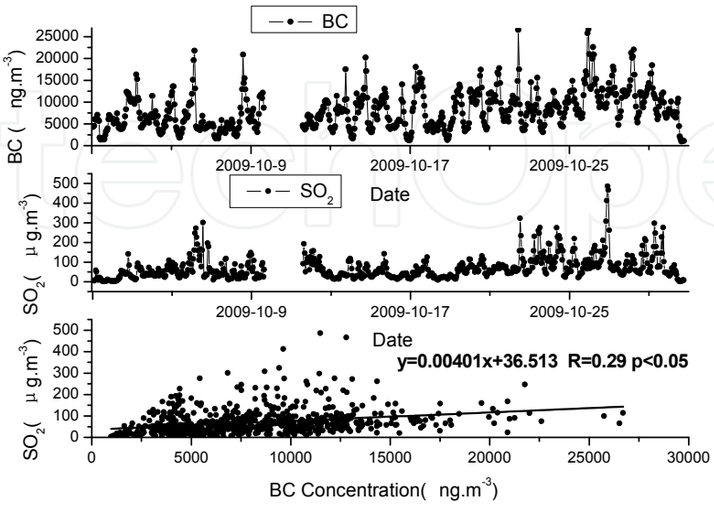


Fig. 11. Hourly mean variation series of SO_2 concentration in the north suburb of Nanjing during Oct.2009 and correlation character between SO_2 and BC

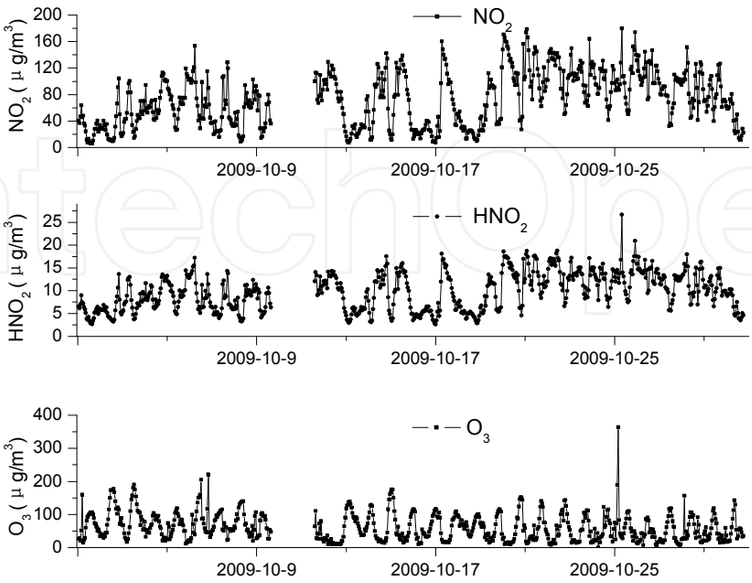


Fig. 12. Variation series of NO_2, HNO_2, O_3 concentration in the north suburb of Nanjing during Oct.2009

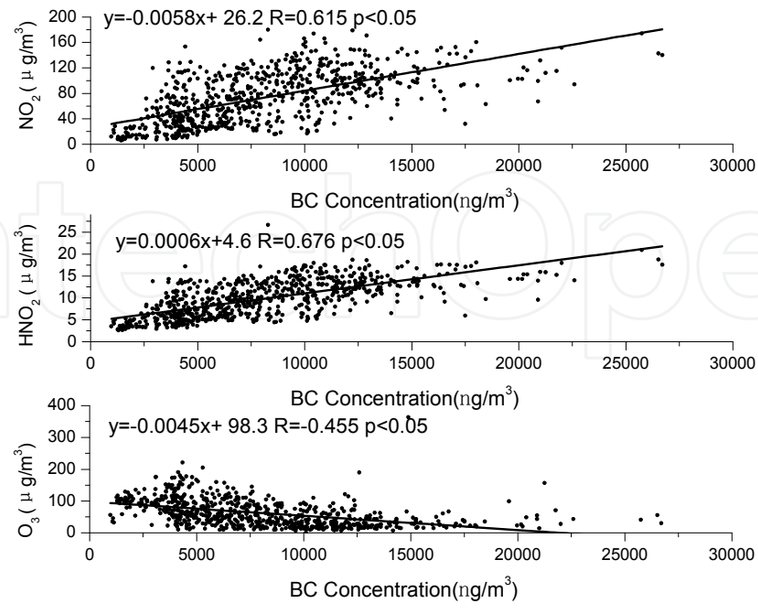


Fig. 13. Correlation character between NO_2, HNO_2, O_3 and BC

HNO_2 plays a dominated chemistry role in atmosphere. The diurnal variation tendency of HNO_2 and black carbon aerosol has good consistency and the most significant relationship. The major production of HNO_2 is from heterogeneous chemical reaction in the atmosphere, and the conversion rate of NO_2/HNO_2 was enhanced by the black Carbon Aerosol (Ammann et al., 1998; Kalberer et al., 1999; Tang et al., 2006). At the same time, HNO_2 is very unstable in the atmosphere and is accumulated only at night. The maximum concentration of HNO_2 occurs at early morning before sunrise. HNO_2 is quickly converted to OH free radicals rapidly by photolysis after sunrise. A series of photochemical reaction are initiated by the reaction of OH radicals and organic pollutants, and a large number of secondary pollutants, such as PAN, O_3 and so on, are generated in the reaction process. The migration and transformation of HNO_2 was an important reason why the concentration of HNO_2 and black carbon aerosol concentration has high correlation coefficient.

O_3 has the typical negative relationship with black carbon aerosols (correlation coefficient = -0.455; $p < 0.05$). This shows that the black carbon aerosols in the atmosphere can promote the loss of tropospheric O_3, which is consistent with observations got by Latha et al (Latha et al., 2004) in the Indian Hyderabad region. Fendel et al (Fendel et al., 1995) inferred that the black carbon aerosols contribute to break the π bond of O_3 molecule, O_2 molecules and atomic oxygen were generated in the reaction. O_2 molecules generated was released into the atmosphere directly , while atomic oxygen is able to combine with another atomic oxygen and form O_2 molecules, or react with black carbon aerosol and form carbon oxides. Meanwhile, black carbon aerosol concentration is some extent determined by the atmospheric convective activity determined by the solar radiation intensity. There is the strongest solar radiation at noon, black carbon aerosol are not easy to concentrate due to strong convective activity. But at the same time, strong solar radiation provides more energy for atmospheric photochemical reactions and promote the reactions. O_3 concentration will therefore increase. In summary, the negative relationship between O_3 concentration and black carbon aerosol concentration is determined by the two factors.

4. Conclusions

Particulate black carbon measured by the Aethalometer method has been shown to be a reliable surrogate for particulate elemental carbon measured by Thermo/Optical Reflectance at this location and time of year. The variation of diurnal black carbon aerosol concentration in Nanjing showed unique bimodal structure, high frequency of the inversion temperature lead to black carbon aerosol concentration maintaining the maximum at night.

There is a dramatic variation in the diurnal average concentrations of black carbon aerosols in Nanjing, varied from 1114 to 19408 ng/m^3 during the observation period, the concentration of black carbon aerosol in autumn and winter is higher than in spring and summer. The background concentration of black carbon in $PM_{2.5}$ is 2920ng/m^3 during observation period, air pollution is serious. The major factors which determine black carbon aerosol concentration are the structure of boundary layer temperature profiles, wind speed, wind direction, precipitation and other meteorological factors and emission intensity of sources.

The black carbon aerosols have positively correlated with SO_2, NO_2 and HNO_2. It is operational to calculate the emission inventory of black carbon aerosol according to the emission inventory of SO_2 in the north suburb of Nanjing. The black carbon aerosol in the

atmosphere has certain catalysis to the formation of HNO_2. The concentration of black carbon aerosol concentration has negative relationship with O_3 concentration. Black carbon aerosol on the consumption of O_3 and meteorological factors are the main causes of this negative relationship.

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