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Chemical characteristics of $PM_{2.5}$ during a typical haze episode in Guangzhou

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Abstract

The chemical characteristics (water-soluble ions and carbonaceous species) of $PM_{2.5}$ in Guangzhou were measured during a typical haze episode. Most of the chemical species in $PM_{2.5}$ showed significant difference between normal and haze days. The highest contributors to $PM_{2.5}$ were organic carbon (OC), nitrate, and sulfate in haze days and were OC, sulfate, and elemental carbon (EC) in normal days. The concentrations of secondary species such as, NO_3^-, SO_4^{2-}, and NH_4^+ in haze days were 6.5, 3.9, and 5.3 times higher than those in normal days, respectively, while primary species (EC, Ca^{2+}, K^+) show similar increase from normal to haze days by a factor about 2.2–2.4. OC/EC ratio ranged from 2.8 to 6.2 with an average of 4.7 and the estimation on a minimum OC/EC ratio showed that SOC (secondary organic carbon) accounted more than 36.6% for the total organic carbon in haze days. The significantly increase in the secondary species (SOC, NO_3^-, SO_4^{2-}, and NH_4^+), especially in NO_3^-, caused the worst air quality in this region. Simultaneously, the result illustrated that the serious air pollution in haze episodes was strongly correlated with the meteorological conditions. During the sampling periods, air pollution and visibility had a good relationship with the air mass transport distance; the shorter air masses transport distance, the worse air quality and visibility in Guangzhou, indicating the strong domination of local sources contributing to haze formation. High concentration of the secondary aerosol in haze episodes was likely due to the higher oxidation rates of sulfur and nitrogen species.

Key words: $PM_{2.5}$; haze episode; water-soluble inorganic ions; organic carbon; elemental carbon; Guangzhou
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Introduction

Guangzhou (23°1′N and 113°2′E) is the political, economic and cultural center of Guangdong Province with a population of around 11 million. It is located in a transitional zone of the East Asian monsoon system, where the southeaster summer monsoon comes from South China Sea, and the northeaster winter monsoon comes from Mainland China. The air pollution in city is aggravated by the topography of basin which traps pollutants easily. The meteorological conditions which promote poor air quality often occur during autumn and winter (Tan *et al*., 2006) and result in visibility deterioration. With the rapid development of economy over the past 30 years, Guangzhou has experienced haze conditions that range from slight transient haze episodes to severe haze episodes, with a sharp increase in air pollutant emissions (Streets *et al*., 2008). In the past four decades, atmospheric visibility has been significantly degraded in Guangzhou, with a visibility decline rate of 0.22 km per year (Lin, 1995). Currently, the annual average visibility has been declined to about 5.4 km, which was much lower than most large cities in the world (Horvath, 1995). The recent satellite (MODIS) data show that the aerosol optical depth is often higher than 0.6 in this area (Wu *et al*., 2006).

Ambient aerosols play important roles in global radiative forcing by scattering or absorbing light directly or indirectly and consequently have an impact on climate change (IPCC, 2001). $PM_{2.5}$ (aerosols aerodynamically < 2.5 μm) has attracted world wide attention due to their adverse impacts on visibility reduction (Watson, 2002), human health (NRC, 1998) and global climate (Okada *et al*., 2001). Urban haze is defined as the weather phenomenon which leads to atmospheric daily average visibility less than 10 km, due to suspended solid, liquid particles, smoke, and vapor in atmosphere and closely related to meteorological conditions and air pollution (Sun *et al*., 2006; Lee and Sequeira, 2001). Urban haze is generally resulted from high level of air particles emitted from anthropogenic sources and gas-to-particle conversion (Watson *et al*., 2002). More emissions of pollutants and stagnant conditions favor haze formation and hence haze alters the composition of the aerosols through the aqueous-phase reactions (Sun *et al*., 2006).

Haze is a worldwide phenomenon and has caught great

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attention for its great effects on visibility, cloud formation, public health, and even global climate (Okada *et al*., 2001; Yadav *et al*., 2003; Thurston *et al*., 1994; Menon *et al*., 2002). Water soluble inorganic ions (NO_3^-, SO_4^{2-}, and NH_4^+) and carbonaceous species are considered as important contributor to visibility impairment (Brown *et al*., 2002; Jacobson *et al*., 2001; Kang *et al*., 2004). Schichte *et al*. (2001) presented the patterns and trends of haze over the United States and found that the haze decline was consistent with the reductions in $PM_{2.5}$ and sulfur emissions. Chen *et al*. (2003) studied the haze formation in summertime in the mid-Atlantic region, and evaluated the role of SO_4^{2-} in haze formation. Senaratne and Shooter (2004) found that the accumulation of diesel emissions contributed most to the appearance of brown haze in Auckland. Sun *et al*. (2006) investigated chemical characteristics of $PM_{2.5}$ and PM_{10} in haze-fog episodes in Beijing and the serious haze pollution was strongly correlated with the meteorological conditions and the emissions of pollutants from anthropogenic activities. Raloff (1999) suggested that the decrease of photosysnthesis, due to the haze in China, could reduced the farmers' grain by more than the entire nation imports.

Although several studies on the spatial variation of visibility and climatic characteristics of haze have been carried out in Guangzhou (Liu *et al*., 2004; Lee and Sequeira, 2001; Cheung *et al*., 2005; Wu *et al*., 2006), the chemical characteristics and sources of haze have not been investigated. Evidence showed that haze days were characterized by symmetric peak shape cycles (haze episode) through the year (especially in autumn and winter). The air quality was influenced greatly by this kind of haze episodes. To better understand haze formation, this study aims to: characterize carbonaceous and water soluble inorganic ions of $PM_{2.5}$ during a typical haze episode; compare the difference between haze and normal days and identify possible sources. This kind of haze episode has not been reported elsewhere and the results are very important to assess and refine pollution reduction measures for $PM_{2.5}$.

1 Experiment

1.1 Filter sampling

$PM_{2.5}$ was collected using a sampler (Graseby-Andersen, GMW High Volume Air Sampler) at a flow rate 1.13 m^3/min in Wushan site. Fifteen samples together with 2 field blanks were collected from 2007/12/31 to 2008/1/12. Wushan site is located on the rooftop of a 15-m height building in Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The most area of Wushan is covered with schools, residences, office buildings and highways. Meteorological data including wind speed, temperature, relative humidity, dew point, pressure, and visibility were obtained from Weather Underground (http://www.underground.com/) and data of SO_2 and NOx were obtained from the website http://www.gzepb.gov.cn/.

The sampler trapped $PM_{2.5}$ on quartz fiber filters (Whatman, 20.3 cm × 25.4 cm) for 24 h. All quartz fiber filters were annealed at 450°C for 4 h to remove trace organics before use. After sampling, the filters were folded and sealed in aluminum foil envelopes until weighing for mass determination of $PM_{2.5}$. Before and after collection, filters were wrapped in baked aluminum foil. The mass was determined by weighing the filters before and after exposure. Prior to weighing, the filters were placed at 25°C with humidity 50% for 24 h. After weighing, the samples were wrapped in aluminum foils and stored at –30°C until analysis. All procedures were strictly quality controlled to avoid any possible contamination of the samples.

1.2 Carbonaceous species

A thermal/optical carbon aerosol analyzer (Sunset Laboratory, Forest Grove, USA) operated with the IMPROVE thermal/optical reflectance protocol was used for the carbon analysis (Chow *et al*., 1996). A 1.5-cm^2 punch of a sample quartz filter was heated stepwise at 310, 475, 615, and 840°C in a nonoxidizing helium atmosphere, and 550, 625, 700, 775, and 850°C in an oxidizing atmosphere of 2% oxygen in a balance of helium. The analyzer was calibrated daily with known quantities of methane and replicate analyses were performed for each sample with < 3.7% error. The results were corrected by the average value of field blanks. The detection limit is below 0.1 μg/cm^3.

1.3 Ion analysis

Water inorganic soluble ions (NO_3^-, SO_4^{2-}, Cl^-, F^-, NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) were analyzed in Beijing Normal University by ion chromatography (IC, Dionex 2000, USA). The filter (3.14 cm^2) was submerged in a vial with 20 mL ultra pure water, sealed and sonicated for 20 min for extraction. The details were given elsewhere (Wang *et al*., 2006).

1.4 Meteorological condition

The serious air pollution in haze episodes between 2008/1/3 and 2008/1/12 was strongly correlated with meteorological conditions (Fig. 1). Temperature, pressure, and relative humidity (RH) tended to increase during 1-Jan to 12-Jan, whereas visibility and wind speed decreased, except a little increase at the last four days. During sampling periods, stagnation condition dominated under the alternation of northern winds and southern winds. Surface winds from north were dry with lower temperature and RH, which indicate the north continental air; and surface winds from south with higher temperature and RH indicative of maritime air, which could be confirmed by the back trajectories conducted in sampling period (Fig. 2). When wind comes from north China and South Ocean, the relatively clean air blow off the pollutants and is not favorable for the formation of secondary aerosol. However, when the stagnation condition occurs, pollutants begin to accumulate and form secondary aerosol.

In order to better understand the transport of airborne particles from distant sources, the HYSPLIT model was

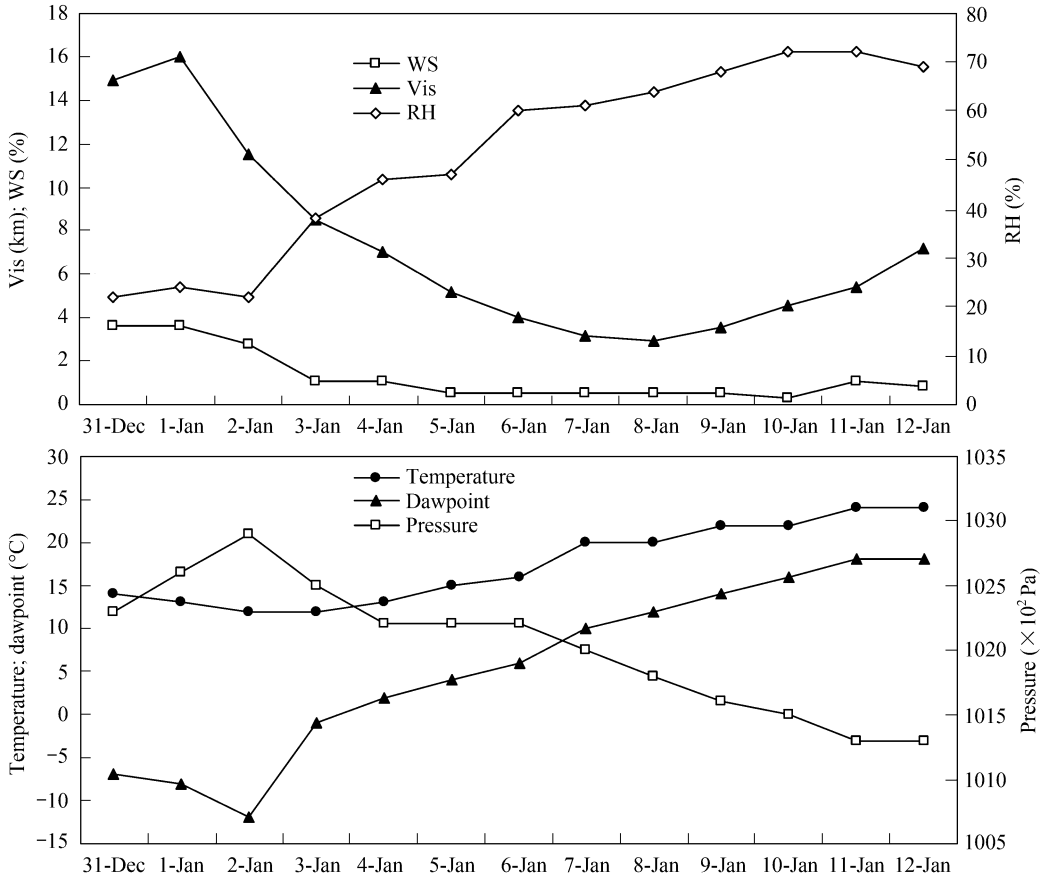

Fig. 1 Meteorological data during the period of study. WS: wind speed; RH: relative humidity; Vis: visibility.

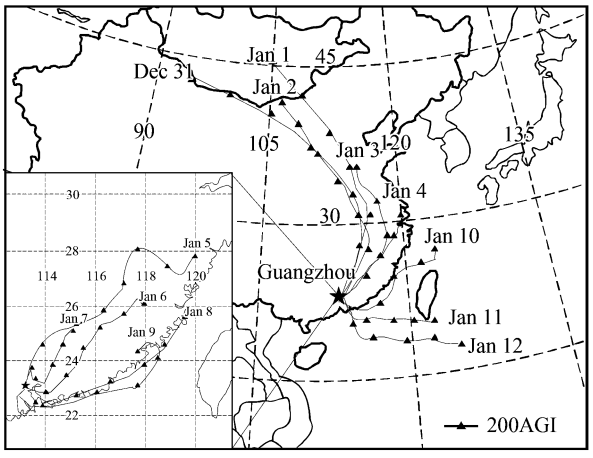

Fig. 2 A 72-h backward air trajectories arriving at Guangzhou during the sampling period.

used to generate 72-h backward trajectories at an altitude of 200 m above ground level (AGL). The results revealed that air quality had a relationship with transport pathways of the air masses. During haze period, the air masses originated from inner China, its pathways covered highly industrialized, densely populated areas of South China and emissions from those regions would be transported to Guangzhou. Through sampling period, air pollution and visibility have a good relationship with the distance of air masses transport pathway. The longer air masses transported, the better air quality and visibility was, no matter whether the air masses came from northerly or southerly direction. The air masses on January 7 originated from Guangdong Province and its transport pathways covered the shortest distance (190 km) through the period, resulting in the worst air quality. Thus, during this period it suggests that local emission sources mainly contributed to the enhanced pollutants concentrations and poorer visibility.

2 Results and discussion

2.1 Concentrations and sources of water-soluble ions

Water soluble inorganic ions (WSII) are important species of atmospheric particles. The concentrations of WSII ions in $PM_{2.5}$ in haze episode were significantly higher than those in normal days (Table 1). The total concentrations of ions accounted for (44.9 ± 8.7)% of the total $PM_{2.5}$ in haze episode, and (24.7 ± 4.9)% in normal days. The major cations (NH_4^+, Ca^{2+}, and K^+) and anions (NO_3^-, SO_4^{2-}, and Cl^-) contributed 95.6% of the total ions in $PM_{2.5}$ in haze episode, and 91.5% of those in normal days. SO_4^{2-} was the highest WSII species in normal days, followed by NO_3^- and NH_4^+, while NO_3^- was the highest WSII species in haze days under stagnation condition, followed by SO_4^{2-} and NH_4^+. The highest daily concentrations of major WSII species (NO_3^-, SO_4^{2-}, and NH_4^+) were 56.1, 11.7, and 13.7 times higher than the lowest value. During haze episode, the concentration of WSII species showed a significant difference between northerly

Table 1 Average concentration ($\mu g/m^3$) of $PM_{2.5}$, water soluble inorganic ions (WSII), carbonaceous species and ratios during the sampling period

Wind direction	Normal day	Haze day			
	North	North	Stagnation	Southeast	Average
$PM_{2.5}$	94.7	188.7	292.5	111.0	235.5
NO_3^-	4.68	19.16	42.27	5.95	30.38
SO_4^{2-}	8.27	26.47	41.84	13.09	33.02
Cl^-	1.19	5.31	10.90	3.86	8.37
F^-	0.50	0.93	1.03	0.37	0.88
NH_4^+	3.40	12.33	24.46	5.21	18.18
Na^+	0.82	2.01	3.72	1.77	2.99
K^+	2.00	6.43	6.58	0.89	5.41
Ca^{2+}	2.41	7.64	6.94	1.86	6.06
Mg^{2+}	0.17	0.41	0.59	0.89	0.48
WSII	23.44	80.69	138.33	33.89	105.79
OC	15.35	30.23	47.67	17.48	38.14
EC	4.73	6.21	8.97	5.78	7.78
POM	21.49	42.32	66.74	24.47	53.40
SOC	2.15	12.9	22.6	1.4	16.4
SOC/OC(%)	14.0	41.8	45.0	6.3	36.6
OC/EC	3.25	4.87	5.31	3.02	4.90
NO_3^-/SO_4^{2-}	0.57	0.72	1.01	0.45	0.92
$WSII/PM_{2.5}$ (%)	24.7	42.8	47.3	30.5	44.9

OC: organic carbon; EC: elemental carbon; POM: particulate organic matter; SOC: secondary organic carbon.

direction (NH), southeasterly direction (SEH) and under stagnation condition (SH) and was in the sequence of: SH > NH > SEH. Lower concentration of WSII species in SEH suggested a higher temperature and relative clean air would be against the accumulation of pollutants.

All WSII exhibited similar trend with $PM_{2.5}$ (Fig. 3). The concentrations increased before Jan 7 and decreased after that, occurred an approximate symmetric peak shape. The effect of haze episode on WSII ions was different. F^-, Cl^-, and K^+ in haze episode were 1.8, 7.0, and 2.7 times higher than those in normal days. The ratio of Cl^-/F^- ranged from 1.59–6.67 in normal days and 8.54–17.30 in

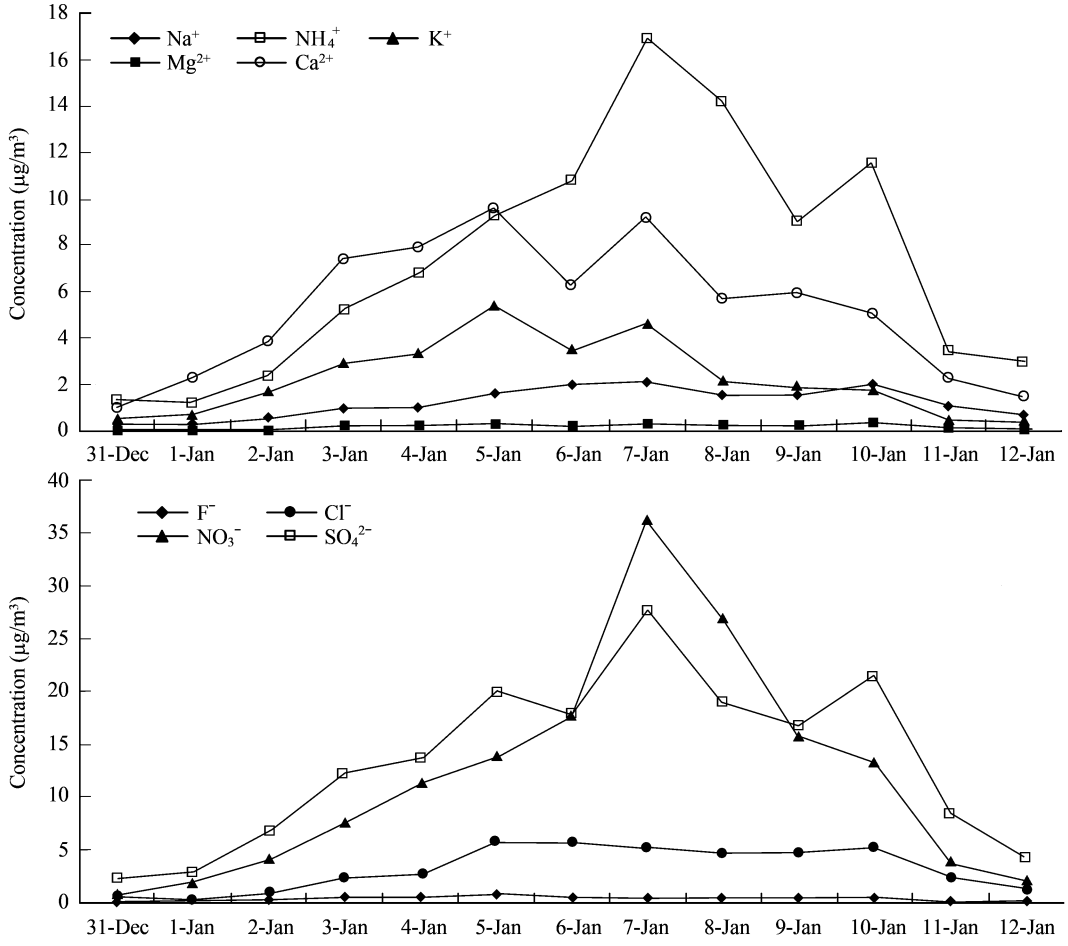

Fig. 3 Concentrations of the water soluble inorganic ions in $PM_{2.5}$ during sampling period.

haze days. Cl^- is usually considered from coal combustion (He *et al*., 2001). Guangzhou is an important industrial city in South China with coal as main energy, therefore, a large amount of Cl^- would be accumulated during haze episode. Average concentrations of crustal WSII ions (Na^+, Mg^{2+} and Ca^{2+}) in haze episode were 1.2–4.3 times higher than those in normal days, while the ratios of Ca^{2+}/Mg^{2+} in haze episode under stagnation conditions (15.5) were much higher than those in haze episode from southerly direction (7.1), indicating that resuspension of road dust, and construction dust will increase the accumulation of Ca^{2+} at stagnation condition.

NO_3^- and SO_4^{2-} represent the secondary aerosol from the transformation of their precursors of SO_2 and NO*x* (Wang *et al*., 2005). Average concentrations of SO_4^{2-} and NO_3^- were 33.02 and 30.38 μg/m^3, respectively, in $PM_{2.5}$ in haze days, were 6.5 and 3.4 times, respectively, higher than those in normal days. NO_3^- experienced the largest variation in WSII ions through sampling period. The highest daily concentration of NO_3^- was 65 times higher than the lowest. The ratio of NO_3^-/SO_4^{2-} was 1.02 under stagnation and 0.55 in normal days, and tended to be larger when air pollution became more serious. The ratio of NO_3^-/SO_4^{2-} is contrary to the result in Beijing (Wang *et al*., 2006), where the ratio in haze days (0.64) was lower than in normal days (0.83). Previous studies have indicated when NO*x* emission rate higher than the sources of radicals, the formation of HNO_3 constitutes main radical sink (Stein and Dennis, 2003). During haze period, the concentration of NO*x* greatly surpassed that of SO_2. Under high NO*x* condition the concentrations of OH and H_2O_2 were reduced (Poppe *et al*., 1993), and further decreased the possibility of SO_4^{2-} formation. Thus, nitrate was the highest single compound under stagnation and its highly evaluation had great effect on the reduction of visibility. In addition, the ratio of NO_3^-/SO_4^{2-} has been used as an indicator of the relative importance of mobile vs. stationary sources of sulfur and nitrogen in atmosphere (Arimoto *et al*., 1996). The ratio of NO_3^-/SO_4^{2-} during haze episode was higher than that in normal days and relatively higher than those reported in other places, such as 0.43 in Shanghai (Yao *et al*., 2002), 0.35 in Qingdao (Hu *et al*., 2002), and 0.13 in Guiyang (Xiao and Liu, 2004), indicating haze pollution were mainly controlled by vehicle emission.

Nitrogen oxidation ratio (NOR = $n\mathrm{NO_3^-}/(n\mathrm{NO_3^-} + n\mathrm{NO_2})$) and sulfur oxidation ratio (SOR = $n\mathrm{SO_4^{2-}}/(n\mathrm{SO_4^{2-}} + n\mathrm{SO_2})$) can be used to estimate the transformation degree of nitrogen and sulfur (Sun *et al*., 2006). Higher contribution of sulfate and nitrate in haze episode could be related to higher oxidation rates of SO_2 and NO_2. Average NOR value was much higher in haze days (0.24) than normal days (0.09), which indicated that the NO_2 transformation in haze days was more significant than that in normal days. On the other hand, average SOR in haze days (0.29) was slightly higher than that in normal days (0.22).

2.2 Concentrations and sources of carbonaceous

The concentration of organic carbon (OC) and elemental carbon (EC) was significantly higher in $PM_{2.5}$ in haze days than those in normal days (Fig. 4). The daily concentrations for haze episode and normal days were 38.14 and 15.35 μg/m^3 for OC and 7.78 and 4.73 μg/m^3 for EC, respectively. During haze episode, the concentration of carbonaceous species showed similar trend with WSII species and was in the sequence of: SH > NH > SEH. The daily concentrations of OC in haze days were significantly higher than those in other cities, such as Helsinki, Seoul (Kim *et al*., 1999; Park *et al*., 2002), Beijing (21.5 μg/m^3, Duan *et al*., 2005). During this period, the level of EC remained relatively stable.

During haze episode, with the decrease of wind speed and increase of the temperature and RH, the concentrations of OC and EC started to increase, reaching the maximum daily concentration of 61.56 μg/m^3 for OC and 10.8 μg/m^3 for EC on 7 Jan, respectively. These high concentrations could have been due to the stagnation condition with a combination of very low wind speed, high RH, and low mixing boundary layer.

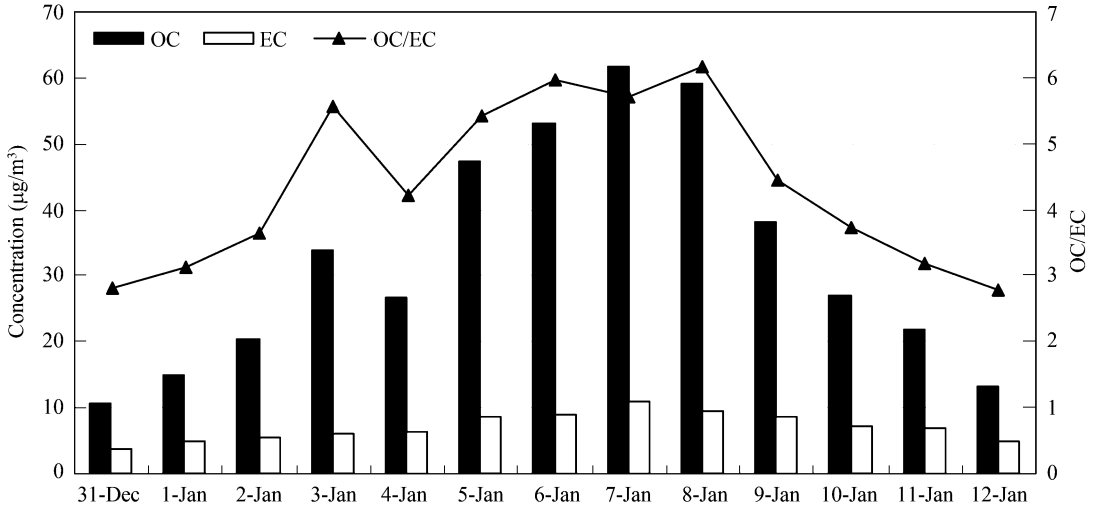

Fig. 4 Concentration of OC, EC (μg/m^3) and ratio of OC/EC during sampling.

The ratio of OC/EC exceeding 2 was used to identify the presence of secondary organic carbon (SOC). In this study, the OC/EC ratios were 4.90 ± 0.98 and 3.26 ± 0.18 for the haze and normal days, respectively. Thus, the ratios may show SOC formation during haze period. Due to the lack of an analytical technique for directly quantifying the atmospheric concentrations of primary OC and SOC, OC/EC minimum ratio method, which relies mainly on ambient measurement of OC and EC, received widespread application (Turpin and Huntzicker, 1995; Castro *et al*., 1999). The approach can only be employed when the ratio of $(OC/EC)_{min}$ can be assumed to remain reasonably constant during the sampling campaign (Turpin *et al*., 1991). The meteorology remained constant from Jan 2 to Jan 12. Hence, the following Eq. (1) can be obtained for the semi-quantitative estimation of SOC.

$$OC_{sec} = OC_{tot} - EC \times (\frac{OC}{EC})_{min} \quad (1)$$

where, OC_{sec} is secondary organic carbon, OC_{min} is the total measured ambient organic carbon, and $(OC/EC)_{min}$ is the minimum OC/EC ratio of the ambient aerosol. The $(OC/EC)_{min}$ used in this study are 2.79. High level SOC was found in haze days (Table 1). SOC concentrations during haze episode were in the range of 2.73–31.43 μg/m^3 accounting for 12.6%–54.7% of OC. SOC and SOC/OC showed strong positive correlation with $PM_{2.5}$ (r = 0.94 and 0.84, respectively).

Gas-phase photochemical reactions followed by gas-to-particle condensation have been suggested to be one of important routes for the formation of secondary species in Pear River Delta (Ho *et al*., 2006). Yao *et al*. (2002) suggested that in-cloud processes also play an important role in the formation of secondary species. Under high NOx conditions the concentrations of oxidants (OH, H_2O_2, and O_3) are reduced (Poppe *et al*., 1993; Kang *et al*., 2004). Thus low O_3 concentrations were found on haze episode and such phenomena had also occurred in Seoul (Kang *et al*., 2004) and central England (Harrison and Yin, 2008). Since Guangzhou is the largest city in Pear River Delta, and with the highest level of $PM_{2.5}$, OC and EC (Cao *et al*., 2004; Duan *et al*., 2007), it is reasonable to consider that the sources are local and the impact by long-range transport are minor. Thus, relatively higher value of SOC and SOC/OC in haze episode can be attributed to the stable atmospheric condition and the prolonged residence time would strengthen in-cloud processes. On the other hand, relative low temperature and high RH in haze episode would enhance the condensation of volatile secondary organic compounds on pre-exist aerosol. The precursors and formation mechanisms of SOC are poorly

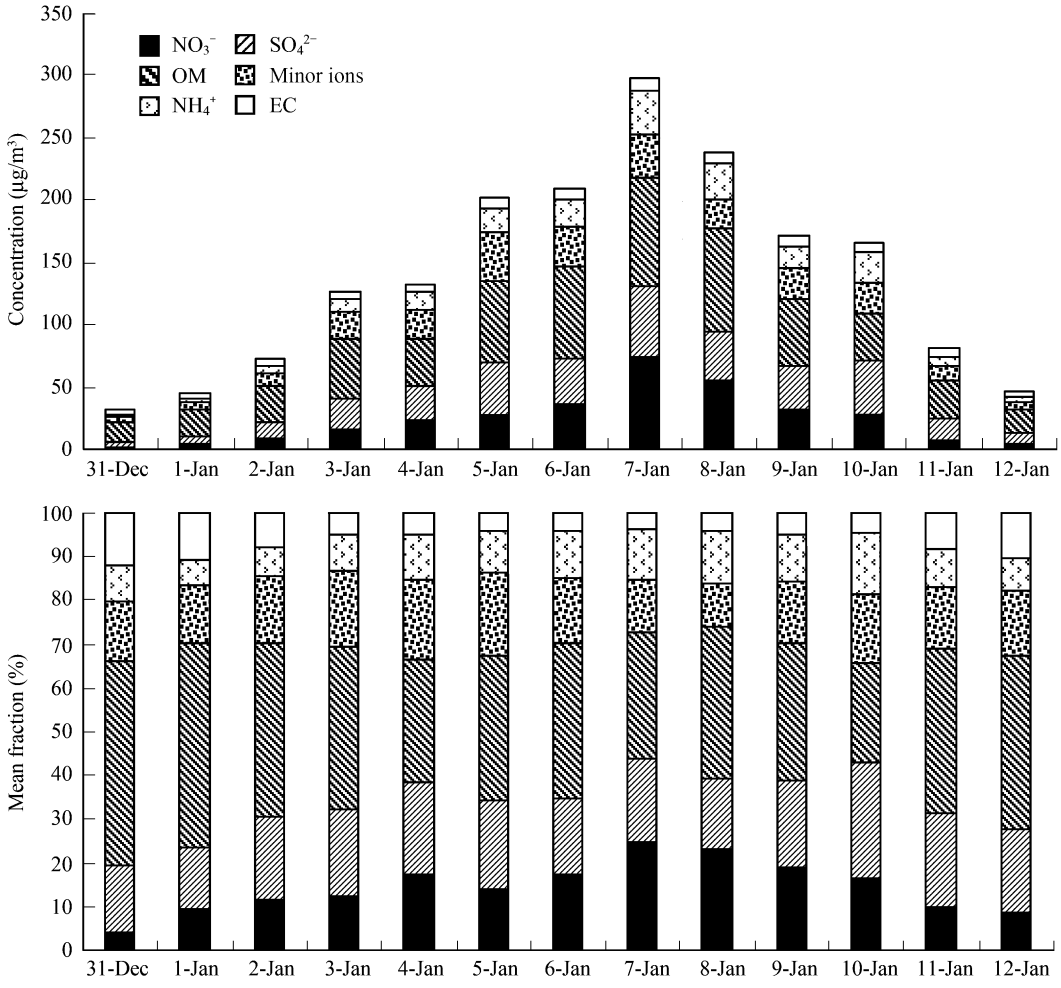

Fig. 5 Mass balances of the chemical species in $PM_{2.5}$ during sampling days.

defined (Pun and Seigneur, 2007) and the impact of NO*x* on the formation of SOC needs further investigation.

2.3 Chemical composition of $PM_{2.5}$

Daily variations of the mass balance for major ionic species (NO_3^-, SO_4^{2-}, and NH_4^+), minor ions (Cl^-, F^-, Na^+, K^+, Ca^{2+}, and Mg^{2+}), OM (organic materials), and EC are shown in Fig. 5. POM has been calculated using the factor of 1.4 to account for unmeasured hydrogen and oxygen in organic materials (Chow *et al*., 1994). In this study, the chemical species presented in the sequence of OM > SO_4^{2-} > minor ions > EC > NO_3^- in normal days, of OM > SO_4^{2-} > NO_3^- > minor ions > EC in haze days for NH and SEH, and OM > NO_3^- > SO_4^{2-}> other ions > EC in haze days under stagnation condition. The ratio of major ionic species to the total $PM_{2.5}$ was low (17.27%) during normal days and increased to 34.64% during haze episode. The secondary species (SOC, NO_3^-, SO_4^{2-}, and NH_4^+) accounted for about 69% of the total mass of $PM_{2.5}$ in haze days and 45% in normal days and the great increase of their concentration played an important role in the visibility deterioration in Guangzhou.

3 Conclusions

The chemical compositions of the water-soluble inorganic ions were determined and the carbonaceous species in $PM_{2.5}$ samples were collected during a typical haze episode to study the characteristics and possible sources of haze episode. The concentration of all chemical species measured during haze episode was much higher than those in normal days, especially for secondary organic carbon, nitrate, sulfate and ammonia. Organic material was the most abundant chemical species during the sampling period. Nitrate and sulfate were the two most abundant water-soluble inorganic species. High OC/EC ratios and SOC level indicate the formation of SOC was occurred during haze episodes.

This haze episode lasted for 10 d and was characterized by symmetric peak shape, which revealed the cooperative effect of anthropogenic activities and meteorological conditions. During sampling period, the weather system was characterized by the stagnation condition dominated under the alternation of northerly and southerly winds. Air pollution and visibility has a good relationship with the air mass transport distance and secondary species were mainly controlled by local processes. High concentration of nitrate and sulfate in haze days was likely due to the high sulfur and nitrogen oxidation and the formation of nitrate and sulfate was accelerated during haze days under stagnation condition. Higher concentration of SOC might due to the condensation on high level particles and in-cloud process.

Acknowledgments

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