

## Composition, source, mass closure of PM<sub>2.5</sub> aerosols for four forests in eastern China

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### Abstract

PM<sub>2.5</sub> aerosols were collected in forests along north latitude in boreal-temperate, temperate, subtropical and tropical climatic zones in eastern China, i.e., Changbai Mountain Nature Reserve (CB), Dongping National Forest Park in Chongming Island (CM), Dinghu Mountain Nature Reserve (DH), Jianfengling Nature Reserve in Hainan Island (HN). The mass concentrations of PM<sub>2.5</sub>, organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC) as well as concentrations of ten inorganic ions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) were determined. Aerosol chemical mass closures were achieved. The 24-hr average concentrations of PM<sub>2.5</sub> were 38.8, 89.2, 30.4, 18 μg/m<sup>3</sup> at CB, CM, DH and HN, respectively. Organic matter and EC accounted for 21%–33% and 1.3%–2.3% of PM<sub>2.5</sub> mass, respectively. The sum of three dominant secondary ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) accounted for 44%, 50%, 45% and 16% of local PM<sub>2.5</sub> mass at CB, CM, DH and HN, respectively. WSOC comprised 35%–65% of OC. The sources of PM<sub>2.5</sub> include especially important regional anthropogenic pollutions at Chinese forest areas.

**Key words:** PM<sub>2.5</sub> aerosols; forests; OC/EC; WSOC; inorganic ions

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### Introduction

Aerosols (especially fine particulates with aerodynamic diameters less than 2.5 μm, PM<sub>2.5</sub>) are of central importance for atmospheric chemistry and physics. Aerosols can adversely affect visibility, scattering and absorbing solar radiation, change cloud nucleation process, influence global climate, and consequently affect human health (Pöschl et al., 2005; Kanakidou et al., 2005). Aerosols have a wide variety of natural and anthropogenic sources both derived from primary emissions and secondary processions. In all kinds of aerosols, aerosol at forest area is the subject of interest as its potential for emitting compounds that evidently influence aerosol formation in the forest atmosphere and its substantial biogenic components as well as unique aerosol characterization (Pio et al., 2001; Rissanen et al., 2006; Cheng et al., 2007). China has a vast land, 18% of the surface covered by forest, having almost all kinds of characteristic plant species of the northern hemisphere. The knowledge of Chinese forest aerosols is significant for the investigation of overall composition and transformation

processes of aerosols in China as well as in the world.

In recent years, studies on chemical compositions of Chinese aerosols are mainly focused on mega-cities, such as Beijing (He et al., 2001), Shanghai (Ye et al., 2003), Hongkong (Ho et al., 2006) as well as a series of capital cities (Wang et al., 2006a; Yang et al., 2005b); a few studies also investigated on dust-source region Aksu (Yabuki et al., 2005) and Horqin sand land in northeast China (Shen et al., 2007), however, detailed chemical composition studies on Chinese forest aerosols are still lacking.

This article focused on PM<sub>2.5</sub> aerosols at four typical forest areas along latitude in boreal, temperate, subtropical, tropical ecosystems in eastern China, i.e., Changbai Mountain Nature Reserve, Jilin Province (CB, 42°24'N, 128°28'E, boreal), Dongping National Forest Park, Chongming, Shanghai (CM, 30°50'N, 121°40'E, temperate), Dinghu Mountain Nature Reserve, Guangdong Province (DH, 23°10'N, 112°32'E, subtropical), Jianfengling Tropical Forests Nature Reserve, Hainan Province (HN, 18°40'N, 108°49'E, tropical). Concentrations of total PM<sub>2.5</sub>, organic carbon (OC), elemental carbon (EC), water soluble organic carbon (WSOC) and inorganic ions were determined. The purposes of the present study were to

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determine the sources and mass closures for four Chinese forest aerosols as well as make primary comparisons with other forest areas in the world to get a general profiles of Chinese forest aerosols.

Regarding to mass closure, it represents a unique tool to characterize different kinds of aerosols. i.e., the gravimetric mass of filter samples are divided into individually identified chemical species, while, measurement of total chemical species matches the gravimetric mass (Guinot et al., 2007). It is one frequently used method of quality assurance of PM measurement, and in general more than 60% of compositions in various aerosols can be identified (Rees et al., 2004; Tysro et al., 2005).

## 1 Experimental

### 1.1 Sample collection and site description

The geographic locations of Changbai Mountain Nature Reserve (CB), Chongming Island (CM), Dinghu Mountain Nature Reserve (DH), and Jingfengling Nature Reserve in Hainan Island (HN) are as the same as described by Wang et al. (2008). All sampling periods were selected taking into account the meteorological conditions and the maximum solar radiation, as well as high temperatures. The sampling periods were 23–28 July 2007 at CB, 13–15 June 2006 at CM, 2–10 August 2006 at DH, and 20–26 November 2006 during the dry season at HN. Total 24-hr PM<sub>2.5</sub> samples and six blank samples were collected with high-volume Graseby-Anderson PM<sub>2.5</sub> sampler (USA) at a flow rate of 1.13 m<sup>3</sup>/min. Meteorological parameters (i.e., temperature, wind speed, wind direction, relative humidity) were cited from <http://cdc.cma.gov.cn>. The detailed descriptions of sampling locations and sampling processions were illustrated by Wang et al. (2008).

### 1.2 Measurement of mass concentration of PM<sub>2.5</sub>

The field blanks and actual samples were weighed before and after sampling. Before weighing, the filters were conditioned at a relative humidity of (45 ± 2)% and a temperature of (25 ± 1)°C for 24 hr and the weighing was performed at the same conditions. Typical uncertainty for our gravimetric measurements is ± 20 µg, which represents less than ± 5% of total aerosol mass of field samples.

### 1.3 Measurement of OC, EC, WSOC concentration

Organic carbon and EC were determined from a 1.5-cm<sup>2</sup> portion of each quartz fiber filter with a Sunset Lab thermal-optical transmission instrument (Birch and Cary, 1996). Instrument blanks were tested everyday and one duplicate sample was tested in each ten samples. The method detection limit for OC was 0.2 µg C/cm<sup>2</sup>, uncertainty was less than ± 8% of OC for all field samples.

For WSOC measurement, six punches of quartz filters (1.5 cm<sup>2</sup> × 6) were cut into pieces, sonicated in 1 mL Mili-Q pure water for 30 min and then filtered. After filtration, 10 µL filtrates were added on a blank quartz filter, detected in the same manner as above OC/EC measurement. Triplicate analyses showed that precision of 10% could be

achieved.

## 1.4 Ion chromatography

Ion analysis was performed by a modular ion chromatography (Metrohm, Switzerland). A filter area of 2–6 punches was extracted in 10 mL Mili-Q water for 30 min in a sonic bath, then filtered through a syringe filter with 0.45 µm pore size. The anions were separated on a metrosep a supp 5-250 column (250 mm × 4 mm i.d., 5 µm particles) under room temperature, using a mixed solution of 3.2 mmol/L Na<sub>2</sub>CO<sub>3</sub> and 1.0 mmol/L NaHCO<sub>3</sub> as eluent at a flow rate of 0.7 mL/min. For cations, the column was metrosep C2-250 (250 mm × 4 mm i.d., 7 µm particles) operated at 35°C. The eluent was 4 mmol/L tartaric acid and the flow rate was 1.0 mL/min. One reproducibility and one blank test were performed every ten samples. Relative standard deviation was less than 5% in the reproducibility test. The detection limits (S/N = 3) for F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> are 0.02, 0.04, 0.01, 0.03, 0.01, 0.05, 0.04, 0.12, 0.06 and 0.07 mg/L, respectively. Average uncertainty on the major ions results is of the order of 10 µg/L, giving less than ± 2% of uncertainty in atmospheric ion concentration of our field samples.

## 2 Results and discussion

### 2.1 Mass concentration of PM<sub>2.5</sub>

The air mass back-trajectory plots during sampling periods are presented in Fig. 1 (NOAA/ARL, calculated by HYSPLIT 4 Model).

Changbai (CB) Mountain Nature Reserve is in the border between China and North Korea. The prevailing winds were in northwest and the southwest during sampling period. In 23–25 July, the wind was blown from the northwest, the air parcels were mainly transplanted from remote Mongolia Plateau, clean and dry; while, in 26–28 July, the prevailing wind veered round to the southwest, the air parcels were transferred from Chinese inland, polluted and moist. The PM<sub>2.5</sub> mass in the days with prevalent southeast wind were more than those days with prevailing northeast wind. During sampling period, the average temperature was 20.4°C, relative humidity ranged from 74% to 93%, and the 24-hr mass concentrations of PM<sub>2.5</sub> ranged between 20.7 and 70.2 µg/m<sup>3</sup> with an average of 38.8 µg/m<sup>3</sup>.

Chongming (CB) Island is located in Changjiang River Delta, where congregated a large amount of population and numerous industries. The 24-hr concentrations of PM<sub>2.5</sub> at CM varied between 58 and 150 µg/m<sup>3</sup> with an average of 89.2 µg/m<sup>3</sup>, the maximum concentration, 150 µg/m<sup>3</sup>, was observed on 15 June. Wang et al. (2006b) had measured PM<sub>2.5</sub> concentration in Shanghai during September 2003 to January 2005. The 24-hr PM<sub>2.5</sub> concentrations ranged from 17.8 to 217.9 µg/m<sup>3</sup>, with an annual average of 94.6 µg/m<sup>3</sup>, which were comparable with the concentrations of PM<sub>2.5</sub> observed at CM, reflecting that CM was influenced by surrounding industrial pollution greatly.

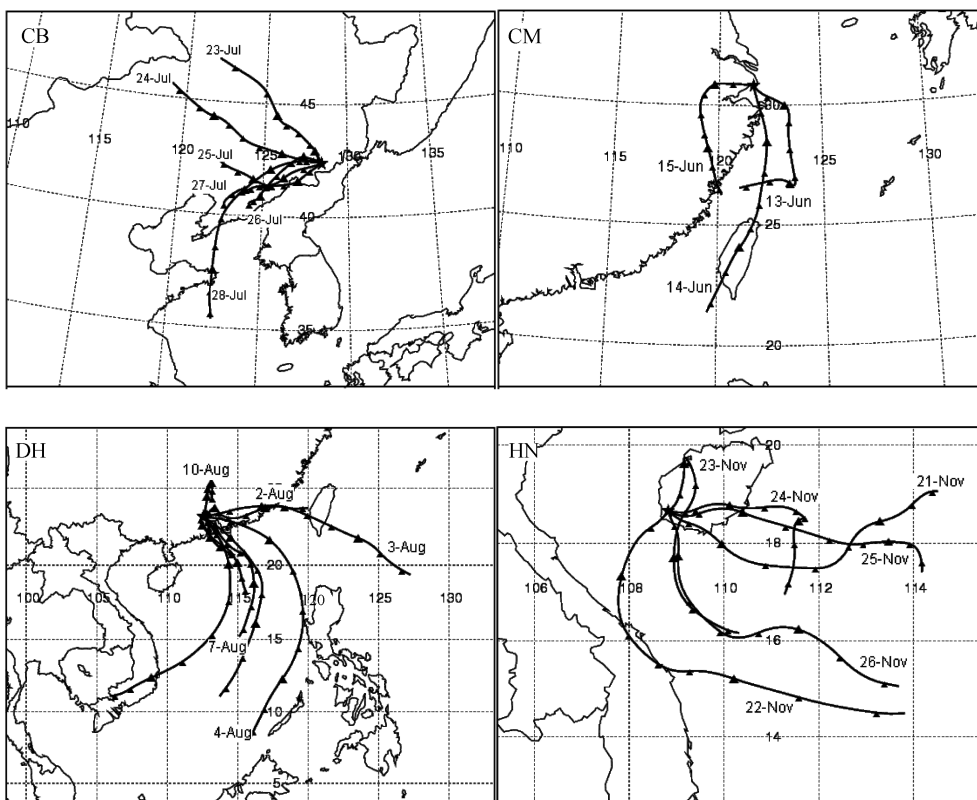


Fig. 1 Air mass back-trajectories (48 hr) plots during sampling period (AGL: 500 m, 12 UTC). Locations CB, CM, DH, and HN refer to Section 1.1.

Dinghu (DH) Mountain Nature Reserve is situated in the northwest edge of Zhujiang River Delta (ZRD), where lied Guangzhou and many moderate industrial cities in the northeast and the southeast and extensive mountain lands in west and north. During sampling period, local winds were mainly in southeast and northeast, pollutants were primarily come from Guangzhou and other ZRD cities. The 24-hr concentrations of PM<sub>2.5</sub> ranged between 15.5 and 40.8 μg/m<sup>3</sup> with an average of 30.8 μg/m<sup>3</sup>.

Jingfengling (HN) Nature Reserve is situated in tropical Hainan island. In the four forest areas, the PM<sub>2.5</sub> concentrations at HN were the lowest. The 24-hr mass

concentrations of PM<sub>2.5</sub> ranged from 12.7 to 26.7 μg/m<sup>3</sup> with an average of 18.0 μg/m<sup>3</sup>.

Figure 2 shows the relationship between concentrations of PM<sub>2.5</sub> and the meteorological data at CB, CM, DH and HN during sampling periods. Average temperature and relative humidity were approximately close in four forest areas; wind direction and wind speed were major factors that influence the PM<sub>2.5</sub> mass. When the air parcels come from polluted districts (e.g., the southwest of CB, the southeast of DH and the southeast of HN), the local concentrations of PM<sub>2.5</sub> were increased with the rising in wind speed as wind favored for the transport of pollutants,

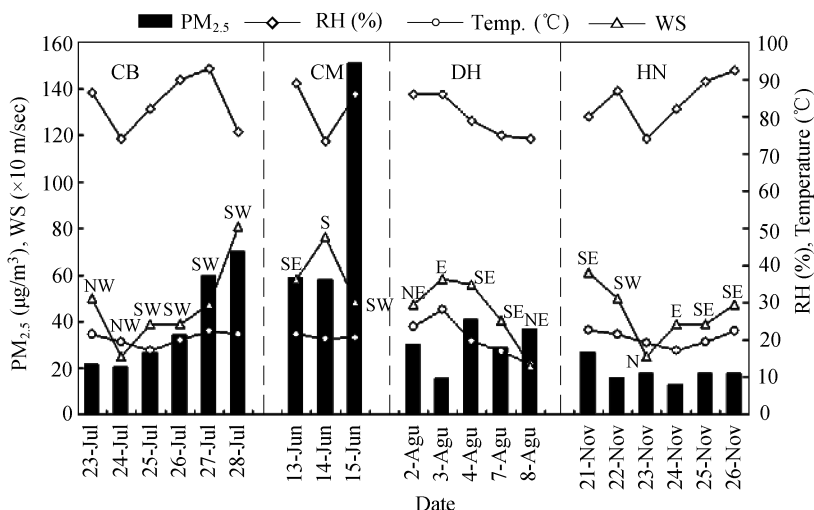


Fig. 2 Concentrations of PM<sub>2.5</sub> and the meteorological data (wind direction, wind speed, temperature and relative humidity (RH)) at CB, CM, DH and HN during sampling periods.

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while the PM<sub>2.5</sub> levels were much higher than that with air parcels come from other relatively clean regions. The close association between PM<sub>2.5</sub> mass and wind direction as well as wind speed indicated that the air quality at four forest areas was dominated by regional transport, it was typical regional pollution.

Tables 1 and 2 list the recent studies regarding PM<sub>2.5</sub> at forest areas over the world. The concentrations of PM<sub>2.5</sub> in other studies were ranged from 10.6 to 26.7 µg/m<sup>3</sup>. As we known, the discrepancies of gravimetric mass are ± 15% of mass within different sampling methods (Rees et al., 2004). There only found a median PM<sub>2.5</sub> concentration at HN, the concentrations of PM<sub>2.5</sub> at CB, CM and DH were all high in studied forest areas comparing with other areas in the world.

## 2.2 Concentration of OC, EC, WSOC

The average concentrations of OC and EC at CB, CM, DH and HN were 4.9, 9.9, 5.3, 2.4 µg/m<sup>3</sup> and 0.5, 1.6, 0.7, 0.2 µg/m<sup>3</sup>, respectively (Table 1). Turpin and Lim (2001) had argued for multiple factors OC-to-POM (particle organic matter) of 1.6 ± 0.2 for urban and 2.1 ± 0.2 for non urban aerosols. Moreover, Sciare et al. (2005) had defined POM at Crete, an island in the Eastern Mediterranean Sea, as 2.1× OC. In addition, 1.8

was usually used as multiplier OC-to-POM for summer aerosols in Chinese urban sites (Wang et al., 2006a; Guinot et al., 2007). In view of the above, we supposed a relatively high OC-to-POM conversion factor as 1.9 for CB, CM and DH, and a factor of 2.1 for HN, since the objects we studied were aged forest aerosols in warm climate. Hence, organic matter contributed 24%, 21%, 33%, 28% and EC accounted for 1.4%, 1.8%, 2.3%, 1.3% of PM<sub>2.5</sub> mass at CB, CM, DH, HN, respectively. It is well known that NIOSH (National Institute of Occupational Safety and Health) method and IMPROVE (Interagency Monitoring Protected Visual Environments) method are two thermal-optical methods can be applied in OC/EC determination. All studies illustrated in Table 1 were used NIOSH except that by Tanner et al. (2004) used IMPROVE. Therefore, the OC/EC values measured in Tanner's study are not used in further discussion since a lower OC value and a higher EC value usually got by IMPROVE than by NIOSH (Chow et al., 2001).

Average uncertainties of OC and EC within different instruments and different sampling methods are ± 15% and ± 35%, respectively (Rees et al., 2004; Subramanian et al., 2004). Also, the high levels of OC and EC were found at all study areas except HN. Specifically, OC was slightly higher at CB than at K-pusta, Hungary (46°58'N, 19°35'E,

**Table 1** Concentrations of PM<sub>2.5</sub>, OC, EC and WSOC at forest areas over the world

Locations	Sampling time	Mass conc. (µg/m <sup>3</sup> )			Reference
		PM <sub>2.5</sub>	OC	EC	
K-pusta, Hungary	24 May–29 Jan 2006	12.7 <sup>a</sup>	3.3 <sup>a</sup>	0.3 <sup>a</sup>	Maenhaut et al., 2008
K-pusta, Hungary	4–10 Jul 2003	14.1	4.2	0.2	Ion et al., 2005
Hyytiälä, Finland	24 Jul–6 Aug 2004	–	4.0	0.2	Kourtchev et al., 2005 <sup>b</sup>
Hyytiälä, Finland	28 Jul–12 Aug 2005	–	2.9	0.05	Kourtchev et al., 2008 <sup>ab</sup>
Julich, Germany	16–22 Jan 2003	–	4.6	0.4	Kourtchev et al., 2008 <sup>b</sup>
Hohenpeissenberg, Germany	16–30 May 2002	10.6	–	–	Hock et al., 2008
Research Triangle Park, USA	Summer 2003	18.5	4.6	0.3	Lewandowski et al., 2007
Research Triangle Park, USA	Summer 2000	20.1	4.0	0.4	Edney et al., 2003
Lock Rock, USA	30 Jun–14 Aug 2001	19.0	4.0	0.7	Tanner et al., 2004
Duke forest, USA	10–23 Jul 2003	–	3.2	0.2	Bhat and Fraser, 2007
Balbina, Brazil	25–28 Jul 2001	–	1.2	0.06	Clayes et al., 2004
CB, China	23–28 Jul 2007	38.8	4.9	0.5	This study
CM, China	13–15 Jun 2006	89.2	9.9	1.6	This study
DH, China	2–10 Aug 2006	30.8	5.3	0.7	This study
HN, China	20–26 Nov 2007	18.0	2.4	0.2	This study

<sup>a</sup> Calculated from OC<sub>10</sub>, EC<sub>10</sub> and ratios of OC<sub>2.5</sub>/OC<sub>10</sub>, EC<sub>2.5</sub>/EC<sub>10</sub>; <sup>b</sup> calculated by OC<sub>1</sub>/OC<sub>2.5</sub> = 0.75, EC<sub>1</sub>/EC<sub>2.5</sub> = 0.75 from PM<sub>1</sub> data.

**Table 2** Concentrations of secondary ions (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) at forest areas over the world

Locations	Sampling time	Mass conc. (µg/m <sup>3</sup> )			Reference	
		PM <sub>2.5</sub>	SO <sub>4</sub> <sup>2-</sup>	NO <sub>3</sub> <sup>-</sup>		NH <sub>4</sub> <sup>+</sup>
Ren-ai township, Taiwan	18–31 Oct 2002	26.7	6.9	1.5	3.2	Cheng et al., 2007
Yosemite NP, USA	13 Jul–4 Sep 2002	–	1.19	0.33	0.41	Lee et al., 2008
San Gorgonio, USA	1–30 Jul 2003	–	1.71	1.58	1.31	Lee et al., 2008
Great Smoky Mnt NP, USA	26 Jul–18 Aug 2004	–	7.66	0.17	1.94	Lee et al., 2008
Grand Canyon NP, USA	1–30 May 2003	–	1.01	0.30	0.42	Lee et al., 2008
Research Triangle Park, USA	Summer 2003	–	6.85	0.19	2.22	Lewandowski et al., 2007
Lock Rock, USA	30 Jun–14 Aug 2001	–	7.7	0.01	1.7	Tanner et al., 2004
K-pusta, Hungary	24 May–29 Jun 2006	–	2.87	0.57	1.34	Maenhaut et al., 2008
K-pusta, Hungary	Summer 2000	26.4	6.5	0.2	2.2	Temesi et al., 2003 <sup>a</sup>
CB, China	23–28 Jul 2007	38.8	12.97	0.33	3.94	This study
CM, China	13–15 Jun 2006	89.2	23.14	10.89	10.28	This study
DH, China	2–10 Aug 2006	30.8	10.24	0.47	3.04	This study
HN, China	20–26 Nov 2007	18.0	2.17	0.13	0.56	This study

<sup>a</sup> data of PM<sub>1.7</sub>.

OC: 3.3–4.2  $\mu\text{g}/\text{m}^3$ ), also slightly higher at DH than at Research Triangle Park, North Carolina, USA (35°89'N, 78°88'W, OC: 4.0–4.6  $\mu\text{g}/\text{m}^3$ ), and much higher at CM than at the other forest areas at a similar latitude. The zones at similar latitude are considered to have similar plant type and similar vegetable emissions as well as closer environmental temperature, more organic matter at Chinese forest areas could not be accounted for by more local vegetation emissions but by heavier regional anthropogenic influences. In addition, EC is emitted from combustion source and its chemical transformation in atmosphere is limited (Wang et al., 2006a). Considering a minor EC was from biomass burning in summer aerosol, the relatively high EC values at CB, CM and DH were also ascribed to more regional industrial emissions.

WSOC was reported to contribute 20%–90% of OC in aerosols around the world (Alves et al., 2008). The average WSOC concentrations at CB, CM and DH were 2.3, 4.4, 3.4  $\mu\text{g}/\text{m}^3$ , accounted for 46.9%, 44.4% to 64.1% of OC respectively (Table 3). The WSOC value for HN was absent due to the deficiency of filters. Comparing with WSOC/OC ratios for Beijing (31.8%), Shanghai (41.7%), and Guangzhou (43.3%) in the summer of 2002 and 2003 reported by Feng et al. (2006, NIOSH method), WSOC/OC ratios at CB, CM and DH were more than those in nearby urban cities: Beijing (situated at the similar latitude as CB and near to CB), Shanghai (adjacent to CM), Guangzhou (adjacent to DH), it was common with ratios for other rural/urban aerosols in the world, reflecting that the aerosols become aged during transport.

As we known, WSOC/OC ratios were reported for several forest areas in the world, i.e., K-pusta, Hungary (62%, Ion et al., 2005, NIOSH method), Hyytiälä, Finland (35%–45%, Alves et al., 2002), Balbina, Brazil (45%–75%, Mayol-Bracero et al., 2002). Recently, Ding et al. (2008, NIOSH method) had reported that the WSOC/OC ratio in Centreville, Alabama, a rural site in southeast America, was 80% in summer, 2004, general WSOC/OC ratio was evaluated to be 55%–60% at rural background sites (Yu et al., 2005). The WSOC/OC ratios for Chinese forest aerosols were slightly lower than or comparable with average ratios for forest aerosols over the world.

### 2.3 Concentration of inorganic ions

Table 3 illustrates the concentrations of F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> at four forest areas. Total concentrations of inorganic ions were 18.1, 48.0, 15.3, 4.4  $\mu\text{g}/\text{m}^3$  at CB, CM, DH and HN, contributing 47%, 54%, 50% and 24% of local PM<sub>2.5</sub> mass, respectively. About 65%–95% of total inorganic ions were sulfate, nitrate, ammonium. Average uncertainties of major ions between different sampling methods are assessed to be  $\pm 15\%$  (Rees et al., 2004; Tanner et al., 2004). It was found that the sum of three major secondary ions at the study sites were all higher than that at other forest areas in the world, except HN which was comparable with the level in forest areas in eastern America, such as Yosemite NP, San Gorgonio, Grand Canyon NP (Table 2).

Atmospheric Cl<sup>-</sup> is derived from sea salt and coal combustion while sea salt is dominant source of Cl<sup>-</sup> in summer. The higher concentration of Cl<sup>-</sup> found at CM and HN (two island sites) than that at CB and DH (two terrestrial sites) reflects the marine contribution in coastal areas (Table 3). Meanwhile, sea salt is also the major source of atmospheric Na<sup>+</sup> in summer. The fact that the higher concentrations of Na<sup>+</sup> at CM, DH, HN (0.51–0.78  $\mu\text{g}/\text{m}^3$ ) than at CB (0.07  $\mu\text{g}/\text{m}^3$ ) is consistent with the geographical locations for four forests: CM and HN are located at seaside, and DH is about 100 km from seashore, only CB is inland which would not be affected by ocean. In this study, contributions of sea salt were calculated according to aerosol abundances of Na<sup>+</sup> and Cl<sup>-</sup> at CM, DH and HN.

Calcium is important crustal element, atmospheric Ca<sup>2+</sup> is a trace marker for crustal matter. Recently, some methods have been suggested to estimate the concentration of crustal matter in the atmosphere according to Ca<sup>2+</sup>. Typically, the abundances of Ca<sup>2+</sup> in crustal matter were 5.6% during non-Saharan dust periods and 15% during Saharan dust periods (Guinot et al., 2007). Moreover, Sciars et al. (2005) also supposed a relatively high abundance of Ca<sup>2+</sup> in crustals of 9.1% for aerosols at Crete island. As we known, dust is more uniformly distributed in regional scale and the average abundance of Ca<sup>2+</sup> in crustal matter is decided depending on dust origin. In the most part of

**Table 3** Concentrations of PM<sub>2.5</sub>, OC, EC, WSOC and ten inorganic ions at four forest areas ( $\mu\text{g}/\text{m}^3$ )

Species	CB (n = 6)		CM (n = 3)		DH (n = 5)		HN (n = 6)	
	Average	Concentration range	Average	Concentration range	Average	Concentration range	Average	Concentration range
PM <sub>2.5</sub>	38.8	20.7–70.2	89.2	58–151	30.4	15.5–40.8	18	12.7–26.7
OC	4.9	3.6–6.2	9.9	5.3–16.4	5.3	1.6–8.2	2.4	1.4–4
EC	0.5	0.2–1.1	1.6	1.4–1.7	0.7	0.4–0.8	0.2	0.1–0.8
WSOC	2.3	1.51–2.74	4.4	2.55–7.04	3.4	3–4.3	–	–
F <sup>-</sup>	0.01	n.d.–0.04	n.d.	n.d.	n.d.	n.d.	0.09	0.04–0.14
Cl <sup>-</sup>	0.02	n.d.–0.10	0.54	n.d.–0.89	0.02	n.d.–0.10	0.34	0.13–0.58
NO <sub>3</sub> <sup>-</sup>	0.33	0.21–0.53	10.89	1.66–25.28	0.47	0.12–0.67	0.13	0.06–0.19
SO <sub>4</sub> <sup>2-</sup>	12.97	1.72–32.47	23.14	10.54–46.26	10.24	1.64–18.15	2.17	1.35–2.73
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	0.21	0.09–0.32	0.45	0.16–0.83	0.29	0.06–0.53	0.01	n.d.–0.05
Na <sup>+</sup>	0.07	0.01–0.19	0.78	0.70–0.89	0.51	n.d.–0.71	0.61	0.22–1.24
NH <sub>4</sub> <sup>+</sup>	3.94	0.58–10.30	10.28	4.29–21.39	3.04	0.27–5.20	0.56	n.d.–0.84
K <sup>+</sup>	0.39	0.06–0.87	1.52	0.59–3.13	0.37	n.d.–0.74	0.25	0.17–0.32
Ca <sup>2+</sup>	0.15	0.10–0.18	0.38	0.24–0.50	0.28	n.d.–0.46	0.21	n.d.–0.50
Mg <sup>2+</sup>	0.03	n.d.–0.09	0.06	0.05–0.07	0.05	n.d.–0.09	0.05	0.02–0.08

China, especially in the north part,  $\text{Ca}^{2+}$  was primarily come from soil dust, road dust and construction dust, and contribution ratios of  $\text{Ca}^{2+}$  to crustal matter are close to 5.6% (He et al., 2001; Yao et al., 2002; Ye et al., 2003; Yang et al., 2005a; Duan et al., 2006). However, in subtropical and tropical climatic zones in South China, due to more resuspended dusts in the air, contribution ratios of  $\text{Ca}^{2+}$  to crustal matter are more close to 9.1% (Ho et al., 2006; Wang et al., 2006a). In this study, for closing  $\text{PM}_{2.5}$  mass, 5.6% and 9.1% were both used as dividend conversion factors to calculate the contributions of crustal matter in the atmosphere from  $\text{Ca}^{2+}$  at four forest areas (Table 3).

Total concentrations of trace inorganic ions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) at CB, CM, DH and HN were 0.88, 3.72, 1.52, 1.56  $\mu\text{g}/\text{m}^3$ , contributed 2.3%, 4.2%, 5.0%, 8.7% of local  $\text{PM}_{2.5}$  mass, respectively (Table 3). Maenhaut et al. (2008) had reported that the sum concentration of trace ions ( $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) and trace elements (K, Ca) at K-pusta was 0.25  $\mu\text{g}/\text{m}^3$ , accounting for 1.8% of  $\text{PM}_{2.5}$  mass in the summer of 2006. These reported data were lower than that obtained in the present study. Since studies on entire inorganic ions for forest aerosols are too limited, it is hard to make comparison on trace inorganic ions between Chinese forests and other forest areas in the world.

#### 2.4 Mass closure of $\text{PM}_{2.5}$ aerosols in eastern Chinese forests

Chemical mass closures of  $\text{PM}_{2.5}$  aerosols at four forest areas were calculated in Fig. 3. For mass reconstruction, eight aerosol components were considered, i.e., (1) organic matter (OM), which was evaluated as in Section 2.2. In addition, oxalate was also involved in organic matter; (2) EC; (3) non-sea-salt sulphate (nss- $\text{SO}_4^{2-}$ ), calculated as  $\text{SO}_4^{2-} - 0.231 \times \text{Na}^+$  (Cheng et al., 2007); (4) nitrate; (5) ammonium; (6) sea salt, estimated as  $\text{Cl} + 1.4486 \text{Na}$ , whereby, 1.4486 is the ratio of the sum concentration of all elements except Cl in sea water to the concentration of Na. Sea salt was evaluated to account for 0–6% of  $\text{PM}_{2.5}$  mass at four forest areas; (7) crustal matter. According to the discussion presented in Section 2.3, contributions of crustal matter at CB and CM were assessed to be non-sea-

salt calcium ( $\text{nss-Ca}^{2+} = \text{Ca}^{2+} - 0.038 \times \text{Na}^+$  (Sciare et al., 2005)) divided by 5.6%, at the same time, contributions of crustal matter at CB and CM were assessed to be nss- $\text{Ca}^{2+}$  divided by 9.1%. In this way, crustal matters were evaluated to be 2.1–6.3  $\mu\text{g}/\text{m}^3$ , account for 7%–11% of  $\text{PM}_{2.5}$  mass at four forest areas; (8) other ions referred to the non-crustal matter-non-sea salt ions, i.e.,  $\text{K}^+$ ,  $\text{F}^-$ ,  $\text{Na}^+$  and  $\text{Cl}^-$  for DH, and  $\text{K}^+$  and  $\text{F}^-$  for CM, DH and HN.

About 64%–95% of  $\text{PM}_{2.5}$  mass at four forest areas were identified. The unresolved mass was regarded to be retained water, volatilization losses, undetermined components such as trace minerals, and also due to measurement artifacts as well as the uncertainty resulted from rough conversion factor calculation.

The ionic balance calculations ( $\Sigma^+/\Sigma^-$ , neq/ $\text{m}^3$ ) for four forest aerosols suggested that aerosols at CB and CM were prone to be acidic, acid aerosols involving important bound water in gravimetric mass (Rees et al., 2004). Harrison et al. (2003) had applied hydration multiplication factor of 1.29 to convert their inorganic species (ammonium sulfate, nitrate and sea salt) into hydrated species. If assuming similar factor to assess hydrated species in CB and CM aerosols, approximate 13%–15% of  $\text{PM}_{2.5}$  mass were retained water for CB and CM. Adding this fraction of bound water, more than 90% of aerosols were identified. In addition, the evaporation loss of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and other semi-volatile organics during post-sampling filter handling and conditioning might be one reason of important discrepancy between determined chemical compositions and total  $\text{PM}_{2.5}$  mass for HN, which assessed to account for more than 10% of  $\text{PM}_{2.5}$  mass.

### 3 Conclusions

Twenty-four-hour samples of airborne  $\text{PM}_{2.5}$  particulate matter have been collected at typical four Chinese forest areas (CB, CM, DH, HN), the concentrations of  $\text{PM}_{2.5}$  mass, OC, EC, WSOC and ten inorganic ions were determined. Aerosol chemical mass closure calculations were performed. Average 24-hr  $\text{PM}_{2.5}$  concentrations were 38.8, 89.2, 30.4, 18  $\mu\text{g}/\text{m}^3$  at CB, CM, DH and HN, respectively. Organic matter, EC and three dominant inorganic ions (sulfate, nitrate, ammonium) contributed 21%–33%, 1.3%–2.3% and 16%–50% of  $\text{PM}_{2.5}$  mass, respectively. Major components of  $\text{PM}_{2.5}$  also included crustal matter, sea salt and bound water.

Relatively high concentrations of  $\text{PM}_{2.5}$ , organic matter, sulfate, ammonium were observed at CB, CM and DH. The air quality at four Chinese forest areas was dominated by regional transport, attributed to a typical regional pollution.

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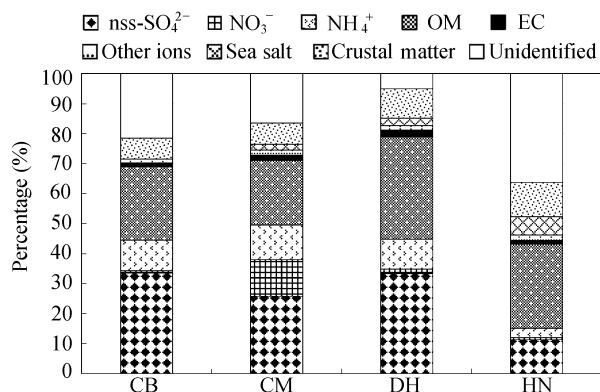


Fig. 3 Percentage of chemical components attributable to the  $\text{PM}_{2.5}$  mass at four Chinese forest areas (CB, CM, DH, HN).

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