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## Characterization and source apportionment of aerosol light extinction in Chengdu, southwest China



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## HIGHLIGHTS

• Aerosol optical and chemical properties in an urban environment were characterized.

• Aerosol hygroscopic curves were developed based on field measurements.

• Source apportionment of aerosol light extinction was estimated.

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## ABSTRACT

To investigate aerosol properties in the Sichuan Basin of China, field aerosol sampling was carried out in Chengdu, China during four one-month periods, each in a different season in 2011. Aerosol scattering coefficient ( $b_{sp}$ ) at dry (RH<40%) and wet (40% < RH<90%) conditions and aerosol absorption coefficient (bap) were measured. Additionally, daily PM<sub>2.5</sub> and PM<sub>10</sub> samples were also collected. PM<sub>2.5</sub> samples were subject to chemical analysis for various chemical components including major water-soluble ions, organic and elemental carbon (OC and EC), trace elements, as well as anhydrosugar Levoglucosan (LG) and Mannosan (MN). A multiple linear regression analysis was applied to the measured dry  $b_{\rm sp}$  against (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, organic mass (OM), fine soil (FS), and coarse mass (CM, PM<sub>2.5-10</sub>), and to the measured  $b_{ap}$  against EC in all the four seasons to evaluate the impact of individual chemical components of PM<sub>2.5</sub> and CM on aerosol light extinction ( $b_{ext} = b_{sp} + b_{ap}$ ). Mass scattering efficiency (MSE) and mass absorption efficiency (MAE) of the individual chemical components of PM2.5 were estimated based on seasonal regression equations and were then used for estimating  $b_{\text{ext}}$ . The annual  $b_{\text{sp}}$ ,  $b_{\text{ap}}$  and single scattering albedo (SSA) at dry conditions were 456  $\pm$  237 Mm<sup>-1</sup>, 96  $\pm$  48 Mm<sup>-1</sup> and 0.82  $\pm$  0.05, respectively. The annual average  $b_{sp}$  at ambient conditions estimated through hygroscopic curve of aerosol (f(RH)) was 763 ± 415 Mm<sup>-1</sup>, which was 1.7 times of the dry  $b_{sp}$ . The annual average SSA at ambient conditions also increased to 0.88  $\pm$  0.04. The estimated dry  $b_{\text{ext}}$  was only 2  $\pm$  9% higher than the measurements and the estimated ambient  $b_{ext}$  from individual chemical components was only 1  $\pm$  10% lower, on an annual basis, than that estimated from using f(RH). Secondary inorganic aerosols, coal combustion, biomass burning, iron and steel industry, Mo-related industry, soil dust, and CM to bext were estimated to account for  $41 \pm 19\%$ ,  $18 \pm 12\%$ ,  $14 \pm 13\%$ ,  $13 \pm 11\%$ ,  $5 \pm 4\%$ ,  $5 \pm 7\%$  and  $4 \pm 3\%$ , respectively, of the estimated ambient  $b_{\text{ext.}}$ 

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#### 1. Introduction

Atmospheric aerosols influence climate directly by scattering and absorbing solar radiation and indirectly by modifying clouds



microphysical properties. Due to the complexity of aerosol optical properties and aerosol-cloud interactions, large uncertainties remain in the quantification of the net impact of atmospheric aerosols on climate (Solomon, 2007). To reduce these uncertainties, a better understanding of aerosol physical, chemical and optical properties is needed at local, regional and global scales. Aerosol single scattering albedo, i.e., the ratio of aerosol scattering coefficient to extinction coefficient, is one of important aerosol optical properties that, to some extent, determines whether aerosols warm or cool the Earth system. A small variation of SSA could alter the estimated net impact of aerosol direct radiative forcing, e.g., from negative impact to positive or vice versa (Haywood and Boucher, 2000). It is well known that  $b_{sp}$  and thereby single scattering albedo changes dramatically with aerosol hydroscopic growth that is dependent on aerosol chemical components. Measurements of the aerosol hydroscopic growth are therefore required for better knowledge of SSA. Further understanding of these aerosol properties is helpful for chemical model simulations and satellite remote sensing of aerosols.

Comprehensive observations involving aerosol optical properties have been widely conducted around the world such as a series of Aerosol Characterization Experiments (ACE-1, ACE-2 and ACE-Asia) (Bates et al., 1998; Huebert et al., 2003; Raes et al., 2000) and Tropospheric Aerosol Radiative Forcing Observational Experiment (TARFOX) (Russell et al., 1999). Extensive studies focusing on aerosol optical properties in eastern Asian were only conducted during the most recent decade (Alam et al., 2012; Andreae et al., 2008; Cheng et al., 2008; Lee et al., 2009; Li et al., 2007, 2011; Marcq et al., 2010; Wang et al., 2010; Xu et al., 2002). There are evidences that aerosol chemical properties control their optical properties and thus affect climate via direct and indirect radiative forcing (Li et al., 1995; Menon et al., 2002; Xia, 2010). Studies have been conducted to quantify the relationship between aerosol optical properties and their chemical properties (Malm et al., 2003; Pitchford et al., 2007). In China these studies were based on the Mie theory (Cheng et al., 2008), IMPROVE formula (Cao et al., 2012; Yang et al., 2012), and multiple linear regression (Tao et al., 2014a). Using Mie theory method is challenging since this method requires long-term continuous measurements of particle size distributions. IMPROVE formula was originally developed for rural/remote areas and may not be directly applicable to urban environments (Tao et al., 2014a). Thus, multiple linear regression method might be a good alternative quantifying the relationship between aerosol optical and chemical properties in urban areas in China.

The Sichuan Basin is one of the heavily polluted regions in China or even in East Asia due to strong anthropogenic emissions and special terrains, as shown in Fig. 1. Annual mean aerosol optical depth of the Moderate Resolution Imaging Spectroradiometer (MODIS) in the Basin is close to unit which is even higher than observations in the North China Plain and Yangtze Delta region (Li



Fig. 1. The sampling location (30.65°N, 104.03°E) in Chengdu on a regional map superimposed with spatial distribution of annual mean fine aerosol optical depth (AOD) retrieved from MODIS satellite remote sensing in 2011.

et al., 2007). Chengdu is one of the biggest cities in the Sichuan Basin and is surrounded by Longquan Mountain and Qionglai Mountain (Fig. S1). The city suffered serious and frequent hazy weather due to the special topography (Chen and Xie, 2012; Tao et al., 2013). To date, few studies have systematically investigated the relationship between aerosol optical and chemical properties in this region. The present study aims to fill this gap through the quantification of aerosol optical properties in Chengdu using direct field measurements, identification of the relationship between aerosol optical mode and chemical properties of PM<sub>2.5</sub> and related sources to the total light scattering and absorption.

## 2. Methodology

## 2.1. Site description

The instruments used in this study were installed on the roof (21 m above ground) of an office building of the Chengdu Research Academy of Environmental Sciences (CRAES), located in the urban area of Chengdu (30.65°N, 104.03°E) (Fig. 1). This site was built with a clear vision of all the directions, around which there is a residential area and a park about 100 m to the east. There is no major air pollution source within a 5 km circumference of the site except mobile emissions, and thus the site represents the typical urban environment in Chengdu. According to the adverse dispersion conditions (e.g. lower wind speed, close topography) and the AOD data, the location of our observation site. While no doubt representing the Chengdu urban center, should also represent the Chengdu plain to some extent (Fig. 1 and Fig. S1).

# 2.2. Measurements of real time aerosol scattering and absorption coefficients and meteorological parameters

The  $b_{sp}$  was measured using two single wavelength integrating nephelometers (Ecotech Pty Ltd, Australia, Model Aurora1000G) at the wavelength of 520 nm. The scattering intensity over angles from 7° to 170° is measured and integrated to yield  $b_{sp}$ . One nephelometer controlled the relative humidity (RH) of inflow air to be less than 40% by the heated inlet to reduce the influence of water vapor on  $b_{sp}$  and obtain dry  $b_{sp}$ . On annual average, the aerosol sample was heated  $4 \pm 1$  °C. To some extent, the inner heater in nephelometer should affect the concentration of semi-volatile organic compounds or ammonium nitrate. However, the temperatures of aerosol sample were control under 26  $\pm$  6 °C airconditioned container. Thus, the loss of semi-volatile organic compounds or ammonium nitrate should be not significant. Another nephelometer shut down the heated inlet and conducted inside an air-conditioned container (25 °C). Thus, the RH in nephelometer did not equal to the RH in real ambient conditions and the measured  $b_{sp}$  should be defined as wet  $b_{sp}$  rather than ambient  $b_{sp}$ . These nephelometers were equipped with a conventional total suspended particulate (TSP) cyclone. The flow rate was set at 5 L min<sup>-1</sup>. Zero calibration was performed every day with particlefree air, and span check was done on a weekly basis using particlefree HFC-R134a gas. The result of total  $b_{sp}$  was corrected for Angular Nonidealities following the method described in a previous study (Anderson and Ogren, 1998). The nephelometer truncation error was expected to be around 5% considering that the majority (99%) of particles had an aerodynamic diameter ( $D_a$ ) smaller than 2.5  $\mu$ m at the CRAES site based on aerodynamic particle sizer (APS) model 3321 (TSI, Inc., St Paul, MN, USA) (Fig. 2) and a set of silica-gel diffusion driers (RH < 20%) was placed at the upstream of the

Fig. 2. Particle number size distributions (0.5  $\mu$ m-20  $\mu$ m) in the four seasons.

APS. The overall uncertainty of the nephelometers measurements should be of the order of  $\pm 10\%$  (Andreae et al., 2008).

The  $b_{ap}$  of 532 nm was converted by black carbon concentration of 880 nm measured by an aethalometer (Magee Scientific Company, Berkeley, CA, U.S.A., Model AE-31). The converted coefficient was 8.28 m<sup>2</sup> g<sup>-1</sup> (Wu et al., 2009; Yan et al., 2008) based on the comparison between the aethalometer and the photoacoustic spectrometer. The aethalometer was equipped with a conventional total suspended particulate (TSP) cyclone and a set of silica-gel diffusion driers (RH < 20%) was placed at the upstream of the aethalometer. The flow rate was set at 5 L min<sup>-1</sup>. The aethalometer was calibrated to zero by replacing the filter in the canister inlet with a clean filter every week. Overall, the uncertainty of  $b_{ap}$ measurements should be of the order of  $\pm$ 7% (Schnaiter et al., 2005; Lin et al., 2014).

Meteorological parameters, including wind direction (WD), wind speed (WS), relative humidity (RH), temperature (TEMP) and precipitation (PR) were measured every 10 min. Wind direction and wind speed were recorded by the wind monitor (Vaisala Company, Helsinki, Finland, Model QMW101). Ambient RH and temperature were measured by an RH/temperature probe (Vaisala Company, Helsinki, Finland, Model QMH101). Precipitation was measured by a rain gauge (Vaisala Company, Helsinki, Finland, Model QMR101). Both meteorological instruments were mounted at 3 m above the roof of the CRAES station (24 m above the ground).

## 2.3. PM sampling

 $PM_{2.5}$  and  $PM_{10}$  samples were synchronously collected using three low-flow air samplers (MiniVol TAC, AirMetrics Corp., Eugene, OR, USA).  $PM_{2.5}$  samples were collected at a flow rate of 5 L min<sup>-1</sup> on two types of filters: 47 mm quartz fiber filters (Whatman QM-A) and 47 mm Teflon filters (Whatman PTFE).  $PM_{10}$ samples were collected at a flow rate of 5 L min<sup>-1</sup> on 47 mm quartz fiber filters (Whatman QM-A). A total of 117 sets of  $PM_{2.5}$  samples (117 quartz fiber filters and 117 Teflon filters), 117  $PM_{10}$  samples (quartz fiber filters) and 12 sets field blanks samples (12 field quartz fiber filters and 12 Teflon filters) were collected during the periods of 6–30 January (representative of winter), 3 April to 3 May (spring), 1 - 31 July (summer), and 1 - 31 October (autumn) in 2011. The collection duration for each sample was 24 h (starting at 10:00 local time each day and ending at 10:00 the next day) (Tao et al., 2014b).



#### 2.4. Gravimetric weighing

 $PM_{2.5}$  Teflon filters and  $PM_{10}$  quartz filters were analyzed gravimetrically for particle mass concentration using a Sartorius MC5 electronic microbalance with a sensitivity of  $\pm 1 \ \mu g$  (Sartorius, Göttingen, Germany) after 24-h equilibration at a temperature between 20 °C and 23 °C and a relative humidity (RH) between 35% and 45% (Tao et al., 2014b).

## 2.5. Chemical analysis of PM<sub>2.5</sub> filter samples

Carbonaceous fraction of PM<sub>2.5</sub> samples (quartz filter) was analyzed for eight carbon fractions following the IMPROVE\_A thermal/optical reflectance (TOR) protocol on a DRI model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA, USA). Inorganic ions and elements of PM<sub>2.5</sub> samples (PTFE filter) were performed with ion chromatograph and inductively coupled plasma–mass spectrometry (ICP-MS), respectively. Moreover, silicon was quantified using X-ray fluorescence analysis (XRF, Epsilon5, PANalytical Company, Netherlands) on Teflon filters before acid digestion. Anhydrosugar LG and MN of PM<sub>2.5</sub> samples (quartz filter) were measured by a Dionex ICS-3000 system. The methods for chemical analysis of PM<sub>2.5</sub> filter samples can refer to Tao et al. (2014b).

## 2.6. Data analysis method

### 2.6.1. PM<sub>2.5</sub> mass reconstruction

To further evaluate whether the determined chemical components can represent the measured  $PM_{2.5}$ , the measured  $PM_{2.5}$  mass was reconstructed based on  $(NH_4)_2SO_4$  (1.375  $SO_4^{2-}$ ),  $NH_4NO_3$  (1.29  $NO_3^{-}$ ), OM, EC, FS and water. The thermodynamic equilibrium model-ISORROPIA II (reserve mode) (Fountoukis and Nenes, 2007) was applied to calculate water contents at a fixed relative humidity (40%) and temperature (23 °C). The converting factor between OC and OM should be varied with the dominant sources when reconstructing PM<sub>2.5</sub> mass. Considering that concentrations of the biomass burning tracer LG were much higher in autumn and winter than in spring and summer, the converting factor was chosen to be 1.6 in spring and summer and 1.8 in autumn and winter (Tao et al., 2014b). The FS component is often estimated through the following formula (Malm et al., 1994):

$$[FS] = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti]$$
(1)

Thus, the reconstructed PM<sub>2.5</sub> mass can be calculated through the following formula:

$$[PM_{2.5}] = [(NH_4)_2SO_4] + [NH_4NO_3] + [OM] + [EC] + [FS] + [Water]$$
(2)

The PM<sub>2.5</sub> mass in Chengdu was reconstructed on seasonal and annual basis using Eq. (1) and Eq. (2), as depicted in Fig. S2. The square of correlation coefficient ( $R^2$ ) between the reconstructed and measured PM<sub>2.5</sub> mass concentrations was higher than 0.94 in all the seasons and the slope ranged from 0.85 to 0.94. On average, the reconstructed masses explained 88 ± 10% of measured PM<sub>2.5</sub>. The results suggested the above dominant chemical species can mostly represent the measured PM<sub>2.5</sub>.

## 2.6.2. Estimation of dry MSE and MAE of aerosol chemical species

The MSE and MAE of aerosol chemical species in dry condition (RH < 40%) are key factors to estimate aerosol radiative forcing. Moreover, they are also the links between aerosol mass concentrations and aerosol  $b_{sp}$  and  $b_{ap}$ . In general, chemical species OM, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, and FS in PM<sub>2.5</sub> and CM are the dominant

contributors to  $b_{sp}$  (Pitchford et al., 2007). However, EC is the dominant absorption chemical component of aerosols and mainly distribute in PM<sub>2.5</sub> (Pitchford et al., 2007; Yu et al., 2010).

Due to the lack of information on the size distribution of these chemical species, multiple linear regressions of measured  $b_{sp}$  against the dominant species (OM, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> and FS) mass concentrations in PM<sub>2.5</sub> and CM were conducted to obtain their MSEs. Considering that EC in PM<sub>2.5</sub> was the dominant species absorbing light, EC MAE can be obtained by regression of  $b_{ap}$  against EC. An external mixing of individual species is assumed in the above analysis.

The amount of scattering and absorption associated with individual species can be estimated statistically using:

$$b_{sp} = a_1 f_L(RH) [(NH_4)_2 SO_4] + a_2 f_L(RH) [NH_4 NO_3] + a_3 [OM] + a_4 [FS] + a_5 [CM]$$
(3)

$$b_{\rm ap} = b_1 [\rm EC] \tag{4}$$

 $b_{\rm sp}$  and mass concentrations of chemical species are given in units of Mm<sup>-1</sup> and µg m<sup>-3</sup>, respectively. RH growth curves,  $f_L$ (RH), of sulfate and nitrate can be referred to the IMPROVE net results (Pitchford et al., 2007). Considering that most of the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> mass distributed in droplet mode (Yu et al., 2010), we used  $f_L$ (RH) rather than  $f_S$ (RH) in this study. Specially, the  $f_L$ (RH) should not be used to estimate MSEs because  $b_{\rm sp}$  was measured at dry condition. However, the  $f_L$ (RH) was the important parameter for verifying the estimated MSEs at wet condition.

## 3. Results and discussion

#### 3.1. Aerosol optical properties

The annual average  $b_{sp}$ ,  $b_{ap}$  and SSA were 456 ± 237 Mm<sup>-1</sup>, 96 ± 48 Mm<sup>-1</sup> and 0.82 ± 0.05, respectively, at dry conditions, in Chengdu. The low annual SSA value suggested the existence of strong light absorption in Chengdu. Evident seasonal variations of  $b_{sp}$ ,  $b_{ap}$  and SSA were observed (Table 1) and were discussed below in accordance with PM<sub>2.5</sub> and its components affecting these parameters.

The *b*<sub>sp</sub> decreased in the order of winter  $(619 \pm 208 Mm^{-1})$  > autumn (488 ± 216 Mm<sup>-1</sup>) > spring  $(431 \pm 269 \text{ Mm}^{-1})$  > summer  $(318 \pm 156 \text{ Mm}^{-1})$ . Earlier studies found that  $b_{sp}$  and PM<sub>2.5</sub> were closely related (Malm et al., 2003; Pitchford et al., 2007; Tao et al., 2014a). In this study,  $b_{sp}$  and PM<sub>2.5</sub> both had the highest values in winter and the lowest in summer (Table 1). Obviously, the PR in summer time was significantly higher than that in other seasons. PM2.5 average concentration in summer (89  $\mu$ g m<sup>-3</sup>) was significantly lower than that in spring (126  $\mu$ g m<sup>-3</sup>), autumn (111  $\mu$ g m<sup>-3</sup>) and winter (158  $\mu$ g m<sup>-3</sup>). The  $b_{sp}$  was also the lowest in summer. Besides, they also had high correlations in all the seasons with  $R^2 > 0.9$  (Fig. 3). These results suggested that  $b_{sp}$  had a close relationship with PM<sub>2.5</sub> in Chengdu. Wind speed (WD) can be a measure of horizontal diffusion, solar radiation (SR), a measure of mixing height or vertical diffusion, and precipitation intensity (PR), a measure of wet removal. These are the key metrological parameters affecting PM<sub>2.5</sub> concentrations. Although the impact of WS, SR and PR on PM<sub>2.5</sub> mass concentrations cannot be quantified here, higher WS, SR and PR generally decreased the  $PM_{2.5}$  concentrations and thus  $b_{sp}$  in Chengdu (Fig. S3). The relationship between WD and PM<sub>2.5</sub> is sometimes useful to understand the sources locations. However, the dominant wind directions were always N-NNE in all of the four seasons in this

#### Table 1

| Site      | Country           | Period          | $b_{ m sp}/{ m Mm^{-1}}$ | $b_{\rm ap}/{ m Mm^{-1}}$ | SSA             | Reference            |
|-----------|-------------------|-----------------|--------------------------|---------------------------|-----------------|----------------------|
| Chengdu   | Southwest, China  | 2011            | 456 ± 237                | 96 ± 48                   | 0.82 ± 0.05     | This study           |
|           |                   | 2011.4-2011.5   | $431 \pm 269$            | $120 \pm 68$              | $0.80 \pm 0.03$ |                      |
|           |                   | 2011.7          | 318 ± 156                | 79 ± 34                   | $0.79 \pm 0.04$ |                      |
|           |                   | 2011.10         | $488 \pm 216$            | $98 \pm 42$               | $0.83 \pm 0.05$ |                      |
|           |                   | 2011.1          | $619 \pm 208$            | 89 ± 36                   | $0.88 \pm 0.02$ |                      |
| Xi'an     | North west, China | 2009            | 525 ± 339                | $83 \pm 52$               |                 | Cao et al., 2012     |
|           |                   | 2009.3-2009.5   | $434 \pm 247$            | 73 ± 35                   |                 |                      |
|           |                   | 2009.6-2009.8   | $455 \pm 267$            | $58 \pm 21$               |                 |                      |
|           |                   | 2009.9-2009.11  | $606 \pm 310$            | 107 ± 55                  |                 |                      |
|           |                   | 2009.2, 2009.12 | $657 \pm 437$            | $104 \pm 70$              |                 |                      |
| Beijing   | North, China      | 1999.6          | $488 \pm 370$            | $83 \pm 40$               | $0.81 \pm 0.08$ | Bergin et al., 2001  |
| Shanghai  | East, China       | 2010.12-2011.3  | $293 \pm 206$            | $66 \pm 47$               | $0.81 \pm 0.04$ | Xu et al., 2012      |
| Lin'an    | East, China       | 1999.11         | $353 \pm 202$            | $23 \pm 14$               | $0.93 \pm 0.04$ | Xu et al., 2002      |
| Guangzhou | South, China      | 2004.10-2004.11 | $418 \pm 159$            | $91 \pm 60$               | $0.83 \pm 0.05$ | Andreae et al., 2008 |
| Granada   | Spain             | 2005.12-2006.2  | $84 \pm 62$              | $28 \pm 20$               | $0.66 \pm 0.11$ | Lyamani et al., 2008 |
| Atlanta   | U.S.A.            | 1999.7-1999.9   | 121 ± 48                 | 16 ± 12                   | $0.87 \pm 0.08$ | Carrico et al., 2003 |



**Fig. 3.** Correlations between  $b_{sp}$  and  $PM_{2.5}$  in the four seasons.

study (Fig. S4), and the highest concentrations of chemical species in PM<sub>2.5</sub> were mostly linked with the N-NNE wind direction where a large number of industrial factories situated (20 km away from the urban Chengdu) (Fig. S5). This forbids us to further investigate the impact of WD on PM<sub>2.5</sub> distribution.

The regression slope between  $b_{sp}$  and PM<sub>2.5</sub> is a good approximation of PM<sub>2.5</sub> mass scattering efficiency (MSE), which reflects the scattering ability of one unit mass of PM<sub>2.5</sub> since nearly 99% of particle numbers ( $dN/d\log(D_a)$ ) was distributed in <2.5 µm based on synchronous APS results (Fig. 2). PM<sub>2.5</sub> MSE decreased in the order of autumn (4.4 m<sup>2</sup> g<sup>-1</sup>) > winter (3.9 m<sup>2</sup> g<sup>-1</sup>) > summer (3.7 m<sup>2</sup> g<sup>-1</sup>) > spring (3.5 m<sup>2</sup> g<sup>-1</sup>). The refractive indexes and densities of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, OM, water, FS, EC and other fraction from literature (Cheng et al., 2008; Watson, 2002) are summarized in Table 2. The particle mass scattering efficiencies ( $E_{scat}$ ) of these chemical species were calculated according to Bohren and Huffman (2008):

$$E_{\text{scat}}(\text{or } E_{\text{abs}}) = \frac{3}{2\rho D_g} Q_{\text{scat}}(\text{or } Q_{\text{abs}})$$
(5)

#### Table 2

The refractive indexes and densities of the chemical species.

| Chemical species  | Refractive index  | Density  |  |
|---|---|--|--|
| (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub><br>NH <sub>4</sub> NO <sub>3</sub><br>OM<br>Water<br>FS<br>EC | 1.54-10 <sup>-7</sup> i<br>1.54-10 <sup>-7</sup> i<br>1.55-0.001i<br>1.33-0i<br>1.56-0.006i<br>1.80-0.54i | $\begin{array}{c} 1.748 \text{ g cm}^{-3} \\ 1.725 \text{ g cm}^{-3} \\ 1.4 \text{ g cm}^{-3} \\ 1.00 \text{ g cm}^{-3} \\ 2.66 \text{ g cm}^{-3} \\ 1.5 \text{ g cm}^{-3} \\ \end{array}$ |  |
| Other   | 1.58-0.0051   | 2.00 g cm <sup>3</sup>   |  |

Where  $\rho$  is the density of a chemical species,  $D_g$  is the particle's Stokes diameter,  $Q_{\text{scat}}$  is the single particle scattering efficiency, and  $Q_{\text{abs}}$  is the single particle absorption efficiency.

Fig. 4a shows that  $Q_{scat}$  was similar for most dominant chemical species except for EC and water. Additionally, the size distributions (0.5–2.5 µm) of these chemical species were somewhat similar in the four seasons (Fig. 2). Therefore, the mass scattering efficiencies of PM<sub>2.5</sub> should be determined by its average density. The average density of PM<sub>2.5</sub> was obtained from the densities of the dominant chemical species, which were identified using Eq. (2) (Table 3) with their respective densities listed in Table 2, weighted by their mass fractions in PM<sub>2.5</sub>. The average density of PM<sub>2.5</sub> decreased in the order of spring (1.72 g cm<sup>-3</sup>) > summer (1.66 g cm<sup>-3</sup>) > winter (1.61 g cm<sup>-3</sup>) > autumn (1.59 g cm<sup>-3</sup>). As can be seen from Eq. (5), the seasonal variations of the density of PM<sub>2.5</sub> were opposite to those of PM<sub>2.5</sub> MSE.

Evident different seasonal patterns were found for dry  $b_{ap}$  than for  $b_{sp}$  (Table 1). The  $b_{ap}$  decreased in the order of spring (120  $\pm$  68 Mm<sup>-1</sup>) > autumn (98  $\pm$  42 Mm<sup>-1</sup>) > winter (89  $\pm$  36 Mm<sup>-1</sup>) > summer (79  $\pm$  34 Mm<sup>-1</sup>). In general, EC is the dominant contributor to  $b_{\rm ap}$ . However, EC had different seasonal patterns from those of  $b_{ap}$  and decreased in the order of winter  $(8.2 \ \mu g \ m^{-3}) > spring \ (6.8 \ \mu g \ m^{-3}) > autumn \ (6.7 \ \mu g \ m^{-3}) > summer (5.5 \ \mu g \ m^{-3}).$  Apparently, the MAE of EC was very low in winter although EC concentration was very high. Generally, the single particle absorption efficiency  $(Q_{abs})$  of EC is also determined by its diameter, besides the mixing state, based on Mie theory. This relationship is shown in Fig. 4b. In fact, the estimated MAE of EC should not be larger than 6.8 m<sup>2</sup> g<sup>-1</sup> based on Eq. (5) if assuming an external mixing state and a Stokes diameter of 0.5  $\mu$ m. However, the MAEs of EC were higher than 14 m<sup>2</sup> g<sup>-1</sup> in spring, summer and autumn, which were almost double of the theoretical value of 6.8 m<sup>2</sup> g<sup>-1</sup>. Therefore, the MAE of EC should be mainly determined by its mixing state rather than its diameter. The lower MAE of EC in winter should be related with the more external mixing state (Yu et al., 2010). This is likely the reason and is further discussed in Section 3.3. Although the seasonal patterns of  $b_{sp}$  and  $b_{\rm ap}$  were different, the seasonal patterns of SSA were consistent with those of  $b_{sp}$  (Table 1), which showed winter  $(0.88 \pm 0.02) > autumn (0.83 \pm 0.05) > spring (0.80 \pm 0.03) > sum$ mer  $(0.79 \pm 0.04)$ .

The  $b_{sp}$ ,  $b_{ap}$  and SSA values obtained in the present study agreed well with the range of the values in literature (Table 1). For example,  $b_{sp}$  in Chengdu was higher than those in Shanghai

 $(293 \text{ Mm}^{-1} \text{ in winter})$  (Xu et al., 2012), Guangzhou (418 Mm<sup>-1</sup> in autumn) (Andreae et al., 2008), Lin'an (353 Mm<sup>-1</sup> in autumn) (Xu et al., 2002), Granada (84  $Mm^{-1}$  in winter) (Lyamani et al., 2008) and Atlanta (121 Mm<sup>-1</sup> in summer) (Carrico et al., 2003), and lower than those measured in Xi'an (in four seasons) (Cao et al., 2012) and Beijing (488  $Mm^{-1}$  in summer) (Bergin et al., 2001). Obviously,  $b_{sp}$ in Chengdu was higher than that in the coastal cities where PM<sub>2.5</sub> concentrations were low and the diffusion conditions were better. Although Xi'an, Beijing as well as Chengdu were all inland cities, the PM<sub>2.5</sub> concentrations in Xi'an and Beijing were much higher than that in Chengdu. Regarding  $b_{ap}$ , it was higher than those in Xi'an (73  $Mm^{-1}$  in spring and 58  $Mm^{-1}$  in summer), Shanghai (66  $Mm^{-1}$  in winter), Guangzhou (91  $Mm^{-1}$  in autumn), Lin'an (23  $Mm^{-1}$  in autumn), Granada (28 Mm<sup>-1</sup> in winter) and Atlanta (16 Mm<sup>-1</sup> in summer), and lower than those measured in Xi'an (107 Mm<sup>-1</sup> in autumn and 104 Mm<sup>-1</sup> winter) and Beijing (83 Mm<sup>-1</sup> in summer). Noticeably, the average EC concentration (6.7  $\mu$ g m<sup>-3</sup>) in autumn in Chengdu was lower than that in Guangzhou (7.1  $\mu$ g m<sup>-3</sup>) (Andreae et al., 2008), but  $b_{ap}$  in Chengdu was higher than that in Guangzhou. The reason was that MAE of EC (14.3  $m^2 g^{-1}$ , discussed in Section 3.3) in Chengdu was higher than that in Guangzhou (8.5  $m^2 g^{-1}$ ). These results suggested higher levels of  $b_{sp}$  and  $b_{ap}$  in Chengdu compared to many other cities. SSA in Chengdu (0.82) was close to those in Beijing (0.81), Shanghai (0.81) and Guangzhou (0.83), but was higher than that in Granada (0.66) and lower than the average value in China (0.89) (Li et al., 2007) and values in Lin'an (0.93) and Atlanta (0.87). These results indicated that the higher SSA accompanied the lower EC concentration. For example, SSA was high in the relatively clean cities such as Lin'an and Atlanta, where EC concentrations were relatively low.

#### 3.2. Aerosol hygroscopic properties

Knowledge of aerosol hygroscopic properties is important for accurately calculating aerosol radiative forcing and estimating  $b_{sp}$ under ambient conditions from that under dry conditions. The impact of humidity on  $b_{sp}$  was commonly described by a parameter referred to as hygroscopic curve f(RH) which was defined as the ratio of the instantaneous  $b_{sp}$  with variable-RH to the  $b_{sp}$  at some minimum RH ( $f(RH) = b_{sp}(RH)/b_{sp}(RH_{min})$ ) (Malm et al., 2003). To estimate f(RH) curves, one nephelometer was operated continuously in a dry mode (RH < 40%) while another one was scanned through RHs < 90%. The average measured f(RH) values based on 1 h and 24 h average data are summarized in Table 4. The f(RH)



Fig. 4. Size-resolved single particle scattering (a) and absorption (b) efficiencies of dominant chemical components.

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| DM chomica        | l componente a | and CM and   | coloctod | motoorological  | paramotors in four | coscope in Chopedu  |
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|                                       | Annual ( <i>n</i> = 117) | Spring $(n = 31)$ | Summer ( $n = 30$ ) | Autumn ( $n = 31$ ) | Winter $(n = 25)$ |
|---------------------------------------|--------------------------|-------------------|---------------------|---------------------|-------------------|
| $PM_{2.5}/\mu g m^{-3}$               | 119.2 ± 56.3             | 126.1 ± 65.5      | 88.7 ± 35.1         | 110.6 ± 48.8        | 157.9 ± 51.1      |
| Reconstructed $PM_{2.5}/\mu g m^{-3}$ | 105.4 ± 50.8             | 105.6 ± 60.3      | 79.5 ± 35.4         | 104.4 ± 45.9        | 137.5 ± 43.1      |
| $(NH_4)_2SO_4/\mu g m^{-3}$           | 34.0 ± 19.5              | 36.4 ± 24.9       | 31.5 ± 19.1         | 26.4 ± 13.2         | 43.8 ± 14.7       |
| $NH_4NO_3/\mu g m^{-3}$               | 13.8 ± 12.4              | 13.2 ± 11.2       | 6.6 ± 4.3           | 16.7 ± 10.9         | $20.0 \pm 7.0$    |
| $OM/\mu g m^{-3}$                     | 28.8 ± 15.4              | 23.8 ± 11.6       | $16.8 \pm 6.6$      | 36.1 ± 16.5         | 40.2 ± 12.7       |
| $EC/\mu g m^{-3}$                     | $6.8 \pm 3.6$            | $6.8 \pm 4.5$     | $5.5 \pm 2.5$       | 6.7 ± 3.3           | 8.2 ± 3.7         |
| $FS/\mu g m^{-3}$                     | $6.7 \pm 4.4$            | $10.1 \pm 5.9$    | 5.4 ± 3.7           | $5.5 \pm 2.3$       | $5.4 \pm 2.2$     |
| Water/µg m <sup>-3</sup>              | $15.0 \pm 8.4$           | 15.3 ± 10.6       | $12.4 \pm 6.9$      | $13.1 \pm 6.8$      | $19.8 \pm 6.9$    |
| Others/µg m <sup>-3</sup>             | 13.8 ± 12.4              | 20.5 ± 10.2       | 9.2 ± 5.7           | 6.2 ± 11.8          | $20.4 \pm 13.9$   |
| $CM/\mu g m^{-3}$                     | 53.7 ± 29.3              | 78.0 ± 38.5       | 39.9 ± 13.7         | 39.2 ± 19.7         | 58.2 ± 16.9       |
| WS/m s <sup><math>-1</math></sup>     | $1.0 \pm 0.4$            | $1.1 \pm 0.5$     | $1.1 \pm 0.4$       | $0.9 \pm 0.4$       | $1.0 \pm 0.3$     |
| WD/°                                  | 19                       | 351               | 20                  | 11                  | 37                |
| TEMP/°C                               | $18.1 \pm 8.5$           | $20.3 \pm 4.8$    | 26.6 ± 2.9          | $18.5 \pm 2.3$      | $4.0 \pm 1.1$     |
| RH/%                                  | 71 ± 11                  | 68 ± 11           | 72 ± 13             | 72 ± 10             | 72 ± 11           |
| PR/mm                                 | 318.4                    | 23.0              | 263.2               | 21.4                | 10.8              |

values based on 1 h data and 24 h average data are very close to each other at the same RH intervals. The 1 h average f(RH) and the 24 h average f(RH) are strongly correlated with  $R^2$  larger than 0.99 and the slopes of the regression lines are all close to unity. This indicates good reproducibility and accuracy of the f(RH) values on different time scales. Thus, it can be used to estimate the  $b_{sp}$  under ambient RH conditions. According to the f(RH) values, the estimated annual average  $b_{sp}$  at ambient conditions was 763 ± 415 Mm<sup>-1</sup>, which was 1.7 times of dry  $b_{sp}$ . The estimated annual average SSA at ambient conditions also increased to 0.88 ± 0.04, which was evidently higher than that at dry conditions (0.82 ± 0.05). These values suggest that the hygroscopic chemical species had posed significant impact on aerosol scattering properties.

The  $b_{sp}$  at ambient condition ( $b_{sp}$ -ambient) and at dry condition ( $b_{sp}$ -dry) were calculated based on Eq. (3). Thus, f(RH) can be also calculated by the ratio of  $b_{sp}$ -ambient/ $b_{sp}$ -dry. The calculated f(RH) and the measured f(RH) are summarized in Table 4. Generally, the measured f(RH) was slightly higher, e.g., 6%, than the calculated one. The most likely cause should be the exclusion of the impact of some ware-soluble organic species in the calculated f(RH). In fact, the higher biomass burning tracer LG in Chengdu meant the higher water soluble organic carbon, which had slightly hygroscopic behavior (Mochida and Kawamura, 2004; Rissler et al., 2006). Overall, the measured and the calculated f(RH) were in reasonable agreement.

In general, the measured f(RH) for real-world aerosols were always significantly lower than those laboratory-generated values for pure chemical species, e.g.  $(NH_4)_2SO_4$  and  $NH_4NO_3$  (Pitchford et al.,

#### Table 4

Statistical summary of measured and calculated f(RH) in 5% relative humidity increments.

| RH/%    | Mean<br>(24 h) | Standard<br>deviation | Mean<br>(1 h) | Standard<br>deviation | Calculated (24 h) | Mean<br>(Malm et al., 2003) |
|---------|----------------|-----------------------|---------------|-----------------------|-------------------|-----------------------------|
| 25-30   |                |                       | 1.16          | 0.03                  |                   | 0.99                        |
| 31-35   | 1.19           | 0.02                  | 1.22          | 0.08                  | 1.00              | 1.02                        |
| 36-40   | 1.24           | 0.04                  | 1.25          | 0.08                  | 1.14              | 1.07                        |
| 41-45   | 1.28           | 0.07                  | 1.28          | 0.09                  | 1.20              | 1.11                        |
| 46-50   | 1.30           | 0.05                  | 1.31          | 0.09                  | 1.21              | 1.15                        |
| 51-55   | 1.37           | 0.07                  | 1.37          | 0.12                  | 1.29              | 1.21                        |
| 56-60   | 1.47           | 0.14                  | 1.45          | 0.18                  | 1.35              | 1.28                        |
| 61-65   | 1.58           | 0.18                  | 1.61          | 0.21                  | 1.40              | 1.38                        |
| 66 - 70 | 1.61           | 0.06                  | 1.63          | 0.13                  | 1.53              | 1.48                        |
| 71-75   | 1.68           | 0.12                  | 1.66          | 0.13                  | 1.62              | 1.67                        |
| 76-80   | 1.74           |                       | 1.82          | 0.14                  | 1.69              | 1.76                        |
| 81-85   | 1.92           |                       | 1.88          | 0.09                  | 1.99              | 2.06                        |
| 85-90   | 2.12           |                       | 2.16          | 0.15                  | 2.10              | 2.64                        |

2007). This is because non-hygroscopic species (e.g. EC, mineral dust) also contributed to  $b_{sp}$ . Compared with f(RH) obtained from the Big Bend experiment (Malm et al., 2003), values from the present study were slightly higher at RH < 70%, but similar at 70% < RH < 80%, and evidently lower at 80% < RH<90%. Compared with Lin'an (a rural site in the Yangtze River delta) experiment (Xu et al., 2002), the average f(RH) value was slightly higher at RH = 60% and similar at RH > 80%. In theory, f(RH) values of aerosols should be determined by f(RH) values of individual pure species and their number (or mass) concentration fractions assuming all species were externally mixed. Thus, the f(RH) curves in Chengdu, Big Bend and Lin'an were mostly similar because (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> were the dominant hygroscopic species at all the three sites. Other non-hygroscopic species had little impact on f(RH) (Lin et al., 2014).

# 3.3. Estimation and verification of MSE and MAE of aerosol chemical species

The MSE and MAE of aerosol chemical species are the important parameters in global circulation and chemical transport models for computing radiative forcing of aerosols and chemical extinction budgets used for visibility regulatory purposes (Hand and Malm, 2007). Considering that the MSEs of chemical species might vary with their mass concentrations, multiple linear regression of the measured dry  $b_{sp}$  against the mass concentration of each chemical species was performed in the four seasons (Tao et al., 2014a). The MSEs were estimated by the stepwise multiple linear regression through self-compiled Matlab program. The constraints of the multiple linear regression results were as follows: the calculated MSEs and  $R^2$  must be larger than zero and 0.90, respectively; the slopes between the estimated and the measured  $b_{sp}$  must be in the range of 0.95 and 1.05. The calculation step of MSE is 0.1 (Tao et al., 2014a).

The estimated seasonal average MSEs of  $(NH_4)_2SO_4$ ,  $NH_4NO_3$ , OM, FS and CM and MAE of EC are summarized in Table 5. The estimated MSEs of  $(NH_4)_2SO_4$  and  $NH_4NO_3$  seemed irrelevant to or even opposite to their mass concentrations, which was different from the results observed in Big Bend and Guangzhou (Malm et al., 2003; Tao et al., 2014a). The rationale might be that MSEs of pure species were related to their size distributions according to Mie theory, i.e., their Stokes diameter is approximately the green wavelength (550 nm) whereas their MSEs should be higher.

Moreover, the estimated MSEs and MAE of individual species were just the optimum numerical solutions of the multiple linear regressions. The concentrations of dominant chemical species (e.g. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, OM and EC) in PM<sub>2.5</sub> should have inherent connections caused by the same sources. In fact, the contributions

 Table 5

 Estimated MSEs and MAE of individual species by stepwise multiple linear regression.

| Species                         | Spring (Apr-11)  |        | Summer (Jul-11)  | Summer (Jul-11) |                  | Autumn (Oct-11) |                  | Winter (Jan-11) |  |
|---------------------------------|------------------|--------|------------------|-----------------|------------------|-----------------|------------------|-----------------|--|
|                                 | $AVG/m^2 g^{-1}$ | RSTD/% | $AVG/m^2 g^{-1}$ | RSTD/%          | $AVG/m^2 g^{-1}$ | RSTD/%          | $AVG/m^2 g^{-1}$ | RSTD/%          |  |
| $(NH_4)_2SO_4$                  | 5.1 ± 0.3        | 6      | 5.7 ± 0.2        | 4               | $6.0 \pm 0.7$    | 12              | $4.4 \pm 0.7$    | 16              |  |
| NH <sub>4</sub> NO <sub>3</sub> | $6.1 \pm 0.4$    | 7      | $1.7 \pm 0.8$    | 47              | $4.2 \pm 0.9$    | 21              | 6.7 ± 1.8        | 27              |  |
| OM                              | $3.0 \pm 0.5$    | 17     | $4.8 \pm 0.8$    | 17              | $6.9 \pm 0.3$    | 4               | $6.5 \pm 0.5$    | 8               |  |
| FS                              | $1.3 \pm 0.3$    | 23     | $1.0 \pm 0.5$    | 50              | $0.9 \pm 0.2$    | 22              | $0.8 \pm 0.3$    | 38              |  |
| CM                              | $0.8 \pm 0.2$    | 25     | $1.4 \pm 0.3$    | 21              | $0.6 \pm 0.1$    | 17              | $0.5 \pm 0.2$    | 40              |  |
| EC                              | $15.6 \pm 0.2$   | 1      | $14.4\pm0.2$     | 1               | $14.3 \pm 0.3$   | 2               | $10.5 \pm 0.1$   | 1               |  |

of the main sources to the dominant species changed with time (Tao et al., 2014b). Thus, their MSEs and MAE should also change with time (Malm et al., 2003). However, their MSEs and MAE were determined by the multiple linear regressions based on one seasonal data, causing under- or overestimation on daily time scale. To investigate this type of error, the relative standard deviation (RSTD = standard-deviation/average) of MSEs and MAE of chemical species were calculated using daily data for each season (Table 5). As shown in Table 5, RSTD of MSEs varied significant with the season. Generally, MSEs were lower while RSTD of MSEs were higher for FS and CM than for other chemical species (e.g. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> and OM). The RSTD of MSE for NH<sub>4</sub>NO<sub>3</sub> was much higher than for other dominant chemical species (e.g. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> and OM), especially in summer, likely due to the strong dependence of NH<sub>4</sub>NO<sub>3</sub> formation and volatility on the temperature.

The estimated and the measured  $b_{sp}$  correlated very well under both dry and wet conditions with  $R^2$  larger than 0.92 throughout the year (Fig. 5a, b). The slopes of the regression lines ranged from 0.96 to 1.00. Regarding the ambient  $b_{sp}$ , good correlations ( $R^2 > 0.92$ ) were also found in all the four seasons between those estimated based on f(RH) curve and those based on chemical species MSEs (Fig. 5c), although with a slightly larger regression slope (1.04) in summer. This demonstrates the reasonable accuracy of both the observed f(RH) using dry and wet nephelometers and the estimated MSE of the chemical components using the stepwise multiple linear regression.

EC was the dominant absorption species in aerosols and EC MAE can be directly obtained from linear regression between the measured  $b_{\rm ap}$  and EC (Table 5). The RSTD of MAE for EC was relatively lower compared with the RSTD of MSE for other species. Good correlations ( $R^2 > 0.93$ ) between the measured  $b_{\rm ap}$  and EC

were found in all the seasons (Fig. 6). The slope of  $b_{ap}$  against EC, which is the EC MAE, ranged from 10.5 to 15.6. EC MAE (10.5 m<sup>2</sup> g<sup>-1</sup>) was evidently lower in winter than in the other seasons. As shown in Fig. 4b, it is believed that the seasonal differences in EC MAE were mainly caused by the different mixing states of EC with other chemical species in different seasons. The lower EC MAE in winter suggests that more EC mass fractions were externally mixed with other chemical components in this season.

Element carbon was mainly produced by coal combustion and biomass burning as supported by the results from Positive Matrix Factorization (PMF) model (Tao et al., 2014b). When EC was from coal combustion outside the city and was transported to the city, it was likely to be internally mixed with sulfate and other chemical components. However, if EC was locally produced from biomass burning, the possibility of externally mixing increased. It was a common practice to use waste wood as energy source to generate heat in the cold and wet winter in urban Chengdu. EC produced from local wood combustion was likely to be externally mixed with other particles. The excellent correlation between LG and MN  $(R^2 = 0.96)$  and the lowest regression slope (7.8) in winter as compared to other seasons (Fig. 6) suggest that wood combustion might be the dominant biomass burning source in winter (Oliveira et al., 2007; Pio et al., 2008; Tao et al., 2014b). The good correlation between LG and EC ( $R^2 = 0.86$ ) in winter (Fig. 6) further supported this hypothesis.

## 3.4. Contributions of PM<sub>2.5</sub> sources to aerosol light extinction

The light extinction coefficients ( $b_{ext} = b_{sp} + b_{ap}$ ) in dry and ambient conditions were calculated from MSEs and MAE of all the identified chemical species. The  $b_{ext}$  was not measured directly, and the measured  $b_{ext}$  was obtained from the sum of the measured  $b_{sp}$ 



Fig. 5. Estimated versus measured  $b_{sp}$  in dry, wet and ambient conditions in the four seasons.



Fig. 6. Measured b<sub>ap</sub> versus EC, LG versus MN, and LG versus EC in the four seasons.



Fig. 7. Estimated versus measured  $b_{\text{ext}}$  in dry and ambient conditions in the four seasons.

and measured  $b_{ap}$  in this study. Excellent correlation ( $R^2 > 0.94$ ) between the measured and estimated  $b_{ext}$  was found in both dry and ambient conditions (Fig. 7). On annual average, the estimated dry  $b_{\text{ext}}$  was slightly overestimated by 2  $\pm$  9% compared to the measurements. (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, OM, FS, CM and EC accounted for 30  $\pm$  11%, 13  $\pm$  6%, 30  $\pm$  14%, 1  $\pm$  2%, 9  $\pm$  7% and 17  $\pm$  5%, respectively, of the estimated dry  $b_{\text{ext}}$ . However, on annual average, the estimated ambient  $b_{\text{ext}}$  using major chemical components was lower by  $1 \pm 10\%$  compared to that using *f*(RH). These components,  $(NH_4)_2SO_4$ ,  $NH_4NO_3$ , OM, FS, CM, and EC, accounted for 46 ± 16%, 15  $\pm$  10%, 19  $\pm$  10%, 1  $\pm$  1%, 6  $\pm$  5% and 11  $\pm$  4%, respectively, of the estimated ambient  $b_{\text{ext}}$ . The contributions of hygroscopic species,  $(NH_4)_2SO_4$  and  $NH_4NO_3$ , to the ambient  $b_{ext}$  remarkably increased compared with their contributions to the dry  $b_{\text{ext.}}$ 

Detailed PM<sub>2.5</sub> source-apportionment analysis was conducted in a separate study using PMF method (Tao et al., 2014b). Six source profiles were identified for PM2.5 which included secondary inorganic aerosols, coal combustion, biomass burning, iron and steel industry, Mo-related industry, and soil dust. The fractions of major chemical components (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, OC, Al and EC) in each source profile were also obtained (Table 6). From the information presented in Tables 5 and 6, the contributions of individual PM<sub>2.5</sub> source profile to the total aerosol light extinction  $(b_{ext})$  can be estimated. Note that the estimated contribution from CM was first deducted from the total  $b_{\text{ext}}$  before applying the raining portion to PM<sub>2.5</sub> source profile apportionment analysis. Seasonal contributions averaged from daily values at ambient and dry conditions are shown in Fig. 8.

It was found that secondary inorganic aerosols, coal combustion, biomass burning, iron and steel industry, Mo-related industry, soil dust and CM accounted for  $34 \pm 17\%$ ,  $19 \pm 12\%$ ,  $16 \pm 14\%$ ,  $13 \pm 11\%$ ,  $6 \pm 5\%$ ,  $6 \pm 7\%$  and  $6 \pm 3\%$ , respectively, of the estimated dry  $b_{\text{ext.}}$ However, they accounted for  $41 \pm 19\%$ ,  $18 \pm 12\%$ ,  $14 \pm 13\%$ ,  $13 \pm 11\%$ ,  $5 \pm 4\%$ ,  $5 \pm 7\%$  and  $4 \pm 3\%$ , respectively, of the estimated ambient  $b_{\text{ext}}$ . The secondary inorganic aerosols were the largest contributor among all the source profiles in all the seasons. Due to the hygroscopic behavior of the chemical compounds dominated in this source profile, a significant increase in its contribution at ambient condition is also identified when compared to that at dry condition. The percentage contributions to the estimated ambient  $b_{\text{ext}}$  varied significantly with season for all the PM<sub>2.5</sub> source profiles as well as for CM. The sum of all the industrial related sources (secondary inorganic aerosols, coal combustion, iron and steel industry and Mo-related industry) accounted for 77% of the estimated ambient

| Table 6   |
|---|
| Relative contributions of dominant chemical components in the six source profiles |

|                                |                                    |                    | -                  |                               |                        | -            |
|--------------------------------|------------------------------------|--------------------|--------------------|-------------------------------|------------------------|--------------|
|                                | Secondary<br>inorganic<br>aerosols | Coal<br>combustion | Biomass<br>burning | Iron and<br>steel<br>industry | Mo-related<br>industry | Soil<br>dust |
| $SO_4^{2-}/\mu g \ \mu g^{-1}$ | 0.319                              | 0.198              | 0.000              | 0.292                         | 0.000                  | 0.090        |
| $NO_3^-/\mu g \ \mu g^{-1}$    | 0.099                              | 0.000              | 0.264              | 0.000                         | 0.106                  | 0.000        |
| $OC/\mu g \ \mu g^{-1}$        | 0.068                              | 0.153              | 0.320              | 0.129                         | 0.168                  | 0.099        |
| Al/μg μg <sup>-1</sup>         | 0.001                              | 0.004              | 0.001              | 0.000                         | 0.007                  | 0.034        |
| $EC/\mu g \ \mu g^{-1}$        | 0.029                              | 0.091              | 0.098              | 0.111                         | 0.000                  | 0.036        |
|                                |                                    |                    |                    |                               |                        |              |



**Fig. 8.** Contributions from CM and the six sources of  $PM_{2.5}$  to the estimated  $b_{ext}$  at ambient and dry conditions in the four seasons.

 $b_{\text{ext.}}$  These results suggested that industrial coal consumption need to be controlled.

## 4. Conclusions

Chemically-resolved PM<sub>2.5</sub>, PM<sub>10</sub> and aerosol optical properties were measured for four-months, with one month in each season in 2011 at an urban environment in southwest China. Strong light absorbing was identified in Chengdu as implied by the low value of SSA. An *f*(RH) curve was generated from nephelometer measurements under dry and humid conditions and was used to estimate  $b_{sp}$  and SSA at ambient conditions. The estimated annual average ambient  $b_{sp}$  was 763 ± 415 Mm<sup>-1</sup>, 70% higher than the dry  $b_{sp}$ , and the estimated annual average ambient SSA was 0.88 ± 0.04, 7% higher than the dry SSA. These results suggest that the hygroscopic chemical components had great impact on the scattering properties of atmospheric aerosols.

The MSE and MAE of individual chemical components were generated from the linear regression between their mass concentrations and the measured  $b_{\text{ext}}$ , and were used to estimate  $b_{\text{ext}}$  at dry and ambient conditions and contributions from individual components. Using mass fractions of SO<sub>4</sub><sup>2–</sup>, NO<sub>3</sub><sup>-</sup>, OC, Al and EC in the six PM<sub>2.5</sub> source profiles and daily PM<sub>2.5</sub> source apportionment generated from a previous study and their MSEs/MAE obtained in this study, the contributions of each PM<sub>2.5</sub> source profile as well as CM to the estimated ambient  $b_{\text{ext}}$  were calculated. The industrial related sources (secondary inorganic aerosols, coal combustion, iron and steel industry and Mo-related industry) accounted for 77% of the estimated ambient  $b_{\text{ext}}$ . Thus, more rigorous air pollutant control measures from these industries should be implemented in Chengdu to reduce hazy weather occurrence frequency.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.07.017.

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