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Mass extinction efficiency and extinction hygroscopicity of ambient $PM_{2.5}$ in urban China

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ABSTRACT

The ambient $PM_{2.5}$ pollution problem in China has drawn substantial international attentions. The mass extinction efficiency (MEE) and hygroscopicity factor (f(RH)) of $PM_{2.5}$ can be readily applied to study the impacts on atmospheric visibility and climate. The few previous investigations in China only reported results from pilot studies and are lack of spatial representativeness. In this study, hourly average ambient $PM_{2.5}$ mass concentration, relative humidity, and atmospheric visibility data from China national air quality and meteorological monitoring networks were retrieved and analyzed. It includes 24 major Chinese cities from nine city-clusters with the period of October 2013 to September 2014. Annual average extinction coefficient in urban China was $759.3 \pm 258.3\ Mm^{-1}$, mainly caused by dry $PM_{2.5}$ ($305.8.2 \pm 131.0\ Mm^{-1}$) and its hygroscopicity ($414.6 \pm 188.1\ Mm^{-1}$). High extinction coefficient values were resulted from both high ambient $PM_{2.5}$ concentration ($68.5 \pm 21.7\ \mu g/m^3$) and high relative humidity ($69.7 \pm 8.6\%$). The $PM_{2.5}$ mass extinction efficiency varied from 2.87 to $6.64\ m^2/g$ with an average of $4.40 \pm 0.84\ m^2/g$. The average extinction hygroscopic factor $f(RH=80\%)$ was 2.63 ± 0.45. The levels of $PM_{2.5}$ mass extinction efficiency and hygroscopic factor in China were in comparable range with those found in developed countries in spite of the significant diversities among all 24 cities. Our findings help to establish quantitative relationship between ambient extinction coefficient (visual range) and $PM_{2.5}$ & relative humidity. It will reduce the uncertainty of extinction coefficient estimation of ambient $PM_{2.5}$ in urban China which is essential for the research of haze pollution and climate radiative forcing.

1. Introduction

Atmospheric visibility is a proven indicator of urban air quality (Watson, 2002). Haze is an apparent symptom of visibility degradation. Haze triggered by fine particulate matter ($PM_{2.5}$) has recently become one of the most active topics in atmospheric environment research (Zhang et al., 2012). Haze formation is closely related to meteorological conditions and high particulate matter (PM) mass loading (Wang et al., 2014). Its main contributors have attracted intensive interests due to its impact on cloud formation, public health, agriculture, and global climate change (Chen et al., 2003; Kang et al., 2004; Schichtel et al., 2001).

China is located in the eastern part of Asia, with large population, agriculture, production and consumption. Urban and regional visibility has been deteriorating in China with the rapid economic growth and increasing emissions during the past several decades (Chang et al., 2009; Che et al., 2009; Cheng et al., 2013), which has raised worldwide concerns and caused considerable health damage (Lelieveld et al., 2015). PM mass concentration, size distribution, chemical composition and especially optical properties under specific atmospheric conditions are key aspects for investigating its effect on visibility impairment in urban areas. In particular, the optical properties are highly dependent on the inherent PM properties and ambient relative humidity (RH) (Kotchenruther et al., 1999; Markowicz et al., 2003). Therefore, understanding the quantitative impacts of PM properties and RH on PM optical properties are important in obtaining reliable estimates not only of visibility impairment (IMPROVE, 2006; Malm et al., 1996; Pitchford et al., 2007), but also of the direct radiative forcing of

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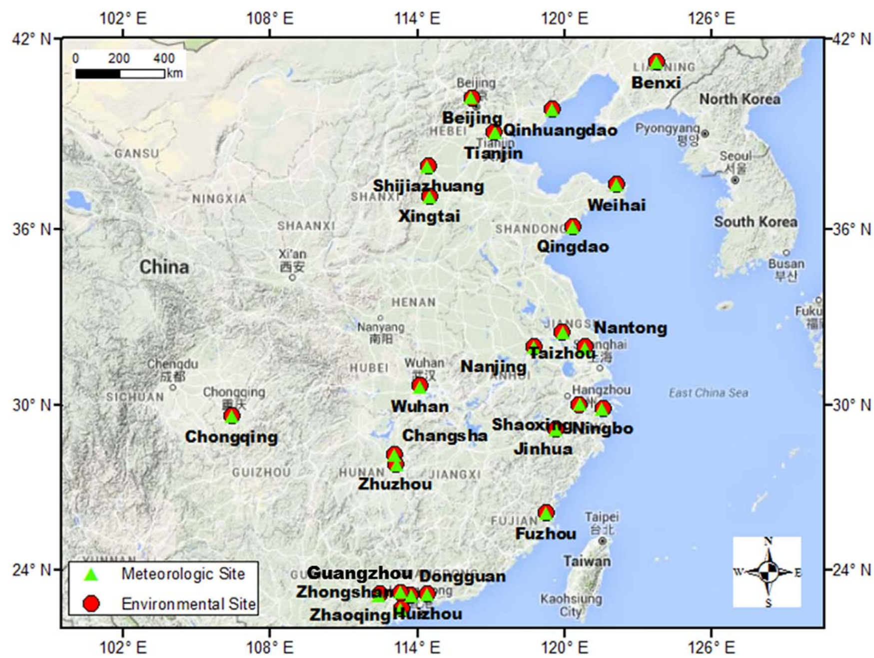

Fig. 1. Geographic location of stations in 24 key cities. Red circles represent air quality sites, and green triangles represent meteorological sites. City names are labeled with black bold characters. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

atmospheric aerosol (Carrico et al., 1998, 2000; Kotchenruther et al., 1998; Randles et al., 2004). The current literature mainly focuses on the mass concentration, chemical composition, and emission sources of $PM_{2.5}$ (Pui et al., 2014). The $PM_{2.5}$ mass extinction efficiency (MEE) and extinction hygroscopicity can be readily applied to study aerosol impacts on atmospheric visibility degradation and climate change, but they remain uncertain due to the sparseness of the field measurements and these studies are lack of the representativeness on the spatial and temporal scales (Jung et al., 2009; Liu et al., 2013; Pan et al., 2009; Xu et al., 2002).

In this study, hourly average ambient $PM_{2.5}$ mass concentration, ambient RH and atmospheric visibility data for 24 major Chinese cities during October 2013 to September 2014 were retrieved and examined. The objective was to investigate the characteristics of $PM_{2.5}$ extinction property and its dependency on $PM_{2.5}$ mass & ambient RH in China urban areas. Results from this study will be helpful for establishing the quantitative relationship between ambient visual range and PM & RH, which will in turn benefit the government of China to draw up haze controlling strategies for improving visibility and public health.

2. Methodology

2.1. Measurement of visual range and PM mass concentration

Based on the current spatial distribution of meteorological and air quality monitoring sites, 24 major cities were selected in this study. The study area covered the core cities of nine major city-clusters in China, namely around-Beijing area (the cities of Beijing, Tianjin, Qinhuangdao, Shijiazhuang and Xingtai), the Yangtze River Delta (the cities of Nanjing, Ningbo, Shaoxing, Nantong, Taizhou and Jinhua), the Pearl River Delta (the cities of Guangzhou, Zhongshan, Zhaoqing, Huizhou and Dongguan), the west coast of Taiwan Strait (the city of Fuzhou), central Liaoning Province (the city of Benxi), Shandong Peninsula (the cities of Qingdao and Weihai), Changsha-Zhuzhou-Xiangtan metropolis (the cities of Changsha and Zhuzhou), Chengdu-Chongqing metropolis (the city of Chongqing) and around-Wuhan area (the city of Wuhan). These nine city-clusters held over half of China's population and gross domestic product, representing the most developed urban areas in China.

For each of the 24 cities, one site from national meteorological monitoring network and another nearby site from national air quality monitoring network were selected. Fig. 1 shows the geographic locations of the sites. The distance between the two sites were less than 3 km to keep the records representing the condition of the same location. The study period of all sites was from October 1st of 2013 to September 30th of 2014. Hourly average records of RH and visual range were obtained from the meteorological sites. Visual range was measured by two types of commercial visibility sensors automatically, i.e., Vaisala Transmissometer LT31 or Belfort Model 6000. Vaisala Transmissometer LT31 measures the transmission between the light source and receiver and thus provide the most accurate visual range. Belfort Model 6000 is based on the principle of forward scattering and shows good agreements with human eye observation in previous studies (Cheng et al., 2013). The datasets of visual range were collected with unique and stringent quality assurance and quality control (QA/QC) according to the specifications of national meteorological network, and has also been used in previous studies (He et al., 2016; Zhang et al., 2010). Hourly average mass concentrations of $PM_{2.5}$, PM_{10} and nitrogen dioxide (NO_2) were obtained from the national air quality network. $PM_{2.5}$ and PM_{10} concentrations were measured by either beta attenuation or tapered element oscillating microbalance (TEOM) attached with a filter dynamics measurement system (FDMS) (Cheng et al., 2016). NO_2 concentrations were measured by chemiluminescence according to national standard instruments and procedures (Ministry of Environmental Protection, 2013).

2.2. Estimation of dry mass extinction efficiency (MEE)

Dry mass extinction efficiency of ambient $PM_{2.5}$ is a key index for estimating the extinction coefficient of $PM_{2.5}$ and deriving the hygroscopic factor. The threshold RH was set to be under 40% for selecting records in the calculation of MEE. Under this RH, most $PM_{2.5}$ species will effloresce and lose bounded water (Martin, 2000).

The hourly visual range was first converted to total extinction coefficient ($b_{ext,}$ at 550 nm) according to Koschmieder's formula (Larson and Cass, 1989). Extinction coefficient due to $PM_{2.5}$ was estimated by subtracting extinction contribution from coarse particles ($PM_{2.5\text{–}10}$), Rayleigh scattering of air molecules and absorption of ambient NO_2

molecules from the total extinction coefficient (Eq. (1)). Rayleigh scattering was assumed to be 10 Mm^{-1} although it will vary with geographic and meteorological situations slightly (Bucholtz et al., 1995). NO_2 absorption was calculated by applying a factor of 0.33 to its mass concentration (ppb)(Pitchford et al., 2007). The extinction of coarse particles was estimated by an empirical value of mass extinction efficiency for $PM_{2.5-10}$ (i.e., 0.6 m^2/g) multiplying the corresponding mass concentration (Pitchford et al., 2007). Next, the hourly records with the RH < 40% were selected. Mass extinction efficiency of $PM_{2.5}$ was then derived from the linear regression results between extinction coefficient due to $PM_{2.5}$ and $PM_{2.5}$ mass concentration for each city (Eq. (2)). This method has also been used in several previous studies (Cheng et al., 2013; He et al., 2016; Zhang et al., 2010).

$$b_{ext}(PM_{2.5}) = 3912/[Visualrange] - 0.6*([PM_{10}] - [PM_{2.5}]) - 10 - [NO_2]*0.33 \tag{1}$$

where the unit of visual range is km and the unit of b_{ext} was Mm^{-1}. The factor of 3912 is used due to the contrast threshold of 0.02 set by the measurement instrument. The concentration unit of NO_2 is part per billion (ppb).

$$b_{ext}(PM_{2.5}) = MEE(PM_{2.5})*[PM_{2.5}], \quad whenRH<40\% \tag{2}$$

where the unit of $[PM_{2.5}]$ is $\mu g/m^3$ and the unit of b_{ext} is Mm^{-1}. The unit of MEE (slope of the regression line by Eq. 2) is m^2/g.

2.3. Estimation of hygroscopic factor

Hourly average hygroscopic growth factor was calculated from the ratio of $PM_{2.5}$ extinction coefficient at ambient RH to that under dry conditions (shown in Eq. (3)). The former was given by Eq. (1), while the latter is given by multiplying $PM_{2.5}$ mass extinction efficiency and mass concentration. The relationship between hourly hygroscopic growth factor and relative humidity was further fit to an empirical convex function to describe the monotonic growth of f(RH) with RH (Eq. (4)). The mathematic model of Eq. (4) has been frequently used in previous studies (Liu et al., 2008; Pan et al., 2009; L. Zhang et al., 2015). The values of parameters “a” and “b” were derived from fitting for each city.

$$f(RH) = b_{ext}(PM_{2.5}) / (MEE(PM_{2.5})*[PM_{2.5}]) \tag{3}$$

$$f(RH) = 1 + a\left(\frac{RH}{100}\right)^b \tag{4}$$

3. Results and discussion

3.1. Annual extinction coefficient and other related factors

Annual extinction coefficient, visual range, $PM_{2.5}$ mass concentration and relative humidity for each city are listed in Table 1. The average extinction coefficient and visual range of all 24 cities were 759.3 ± 258.3 Mm^{-1} and 10.5 ± 3.9 km, respectively. There were 13 cities with the annual average visual range lower than 10 km, which was the current threshold value of haze definition. The five cities with the lowest visual range were Wuhan (5.5 km), Changsha (5.6 km), Chongqing (6.1 km), Nanjing (6.2 km) and Shaoxing (6.3 km). Meanwhile, the five cities with the highest extinction coefficient were Changsha (1153 Mm^{-1}), Wuhan (1117 Mm^{-1}), Chongqing (1073 Mm^{-1}), Taizhou (1070 Mm^{-1}) and Shaoxing (1033 Mm^{-1}). Minor difference between the two lists of cities of the lowest visual range and the highest extinction coefficient was detected. Changsha had the highest annual extinction coefficient while it ranked the second for the annual visual range. Taizhou ranked the fourth of the highest extinction coefficient while it only ranked the sixth of lowest visual range. It is mainly due to that the annual extinction coefficient was averaged based on the hourly extinction coefficient converted from hourly visual range by Koschmieder's formula. As a result, the annual extinction coefficient and annual visual range no longer strictly followed Koschmieder's formula.

Table 1
Annual average of total extinction coefficient, visual range, $PM_{2.5}$ mass and relative humidity for each city (average ± standard deviation).

city name	visual range (km)	total extinction coefficient (550 nm, Mm^{-1})	$PM_{2.5}$ mass ($\mu g/m^3$)	relative humidity (%)
Changsha	5.6 ± 4.1	1153.1 ± 823.0	74.3 ± 57.5	79.3 ± 17.0
Wuhan	5.5 ± 3.6	1116.7 ± 781.9	96.6 ± 64.7	76.3 ± 18.8
Chongqing	6.1 ± 4.9	1072.9 ± 781.7	81.4 ± 51.9	78.5 ± 14.9
Taizhou	6.5 ± 5.0	1070.2 ± 843.4	72.1 ± 51.9	75.1 ± 18.4
Shaoxing	6.3 ± 4.4	1032.8 ± 754.6	61.3 ± 40.5	74.6 ± 16.0
Nanjing	6.2 ± 3.9	1001.8 ± 755.9	73.9 ± 50.8	71.4 ± 19.4
Xingtai	9.1 ± 7.7	924.6 ± 839.9	127.2 ± 93.8	58.5 ± 20.6
Shijiazhuang	8.7 ± 7.3	915.3 ± 808.5	111.8 ± 86.5	56.6 ± 21.3
Zhuzhou	6.1 ± 4.2	914.9 ± 560.2	76.3 ± 55.5	79.6 ± 19.5
Nantong	8.6 ± 7.1	897.2 ± 793.6	64.4 ± 49.7	75.8 ± 18.0
Qinhuangdao	10.4 ± 9.2	859.0 ± 811.1	58.2 ± 45.6	70.7 ± 20.5
Beijing	10.3 ± 8.7	843.6 ± 798.9	92.5 ± 68.6	50.1 ± 21.7
Jinhua	7.7 ± 4.7	808.5 ± 633.5	68.8 ± 45.8	74.3 ± 16.9
Tianjin	9.7 ± 7.2	780.4 ± 701.7	83.5 ± 59.9	49.3 ± 21.3
Guangzhou	9.2 ± 5.4	667.0 ± 563.8	52.7 ± 30.3	75.2 ± 18.7
Ningbo	11.4 ± 8.0	623.8 ± 570.0	42.5 ± 34.3	76.9 ± 15.9
Qingdao	14.3 ± 10.3	564.2 ± 588.4	55.5 ± 47.1	70.2 ± 17.6
Zhaoqing	14.0 ± 11.7	562.5 ± 584.6	61.5 ± 40.4	67.3 ± 17.2
Zhongshan	15.7 ± 11.3	458.6 ± 479.2	45.2 ± 35.9	73.2 ± 17.9
Fuzhou	15.2 ± 8.6	427.6 ± 438.9	38.1 ± 24.5	70.6 ± 15.2
Benxi	15.4 ± 8.4	410.9 ± 425.0	61.8 ± 43.8	58.0 ± 21.4
Weihai	16.4 ± 9.3	401.5 ± 409.0	52.6 ± 37.3	67.6 ± 18.2
Huizhou	16.4 ± 10.3	377.9 ± 387.0	42.7 ± 23.9	72.9 ± 17.1
Dongguan	17.1 ± 9.8	339.0 ± 319.8	48.9 ± 31.3	70.1 ± 19.1
Average[a]	10.5 ± 3.9	759.3 ± 258.3	68.5 ± 21.7	69.7 ± 8.6

[a] The standard deviation is calculated from the deviation of the results of 24 cities.

The list of cities with the highest $PM_{2.5}$ mass and relative humidity were not the same as those with poorest visibility. The average $PM_{2.5}$ mass loading of all 24 cities was 68.5 ± 21.7 $\mu g/m^3$. Xingtai (127 $\mu g/m^3$), Shijiazhuang (112 $\mu g/m^3$), Wuhan (97 $\mu g/m^3$), Beijing (93 $\mu g/m^3$) and Tianjin (84 $\mu g/m^3$) had the highest annual $PM_{2.5}$ mass concentration. Four of these top five cities are located in the around-Beijing area, indicating this area was the most $PM_{2.5}$ polluted region in urban China. Previous source apportionment studies of these cities found that anthropogenic sources, i.e., vehicles, industrial emissions and energy-generating sectors were the major $PM_{2.5}$ contributors (Cheng et al., 2016; Karagulian et al., 2015). Meanwhile, the average RH of all 24 cities was 69.7 ± 8.6%. The cities with the highest RH included Zhuzhou (80%), Changsha (79%), Chongqing (79%), Ningbo (77%) and Wuhan (76%). They are all located at the southern China and near the Yangtze River or large lakes. The water-continent location and the precipitation of monsoon climate brought abundant precipitation and moisture for these cities (Lin et al., 2007; Lu and Ming, 2012).

The inconsistency between the city list of highest extinction coefficient and highest $PM_{2.5}$ or RH illustrates the complexity causes for extinction coefficient. Among the five cities of the highest extinction coefficient, only Wuhan was among the five cities with the highest $PM_{2.5}$ mass concentration. Changsha, Wuhan and Chongqing were among the top five cities of the highest RH. Taizhou and Shaoxing were not in the top five list of $PM_{2.5}$ mass or RH. Hence, ambient extinction coefficient was not only related to the absolute value of $PM_{2.5}$ mass concentration and RH, but also effected by the mass extinction efficiency and extinction hygroscopic factor. The latter two factors were mainly governed by the size distribution and chemical composition of $PM_{2.5}$. The following two sections provide detailed discussion of these two factors.

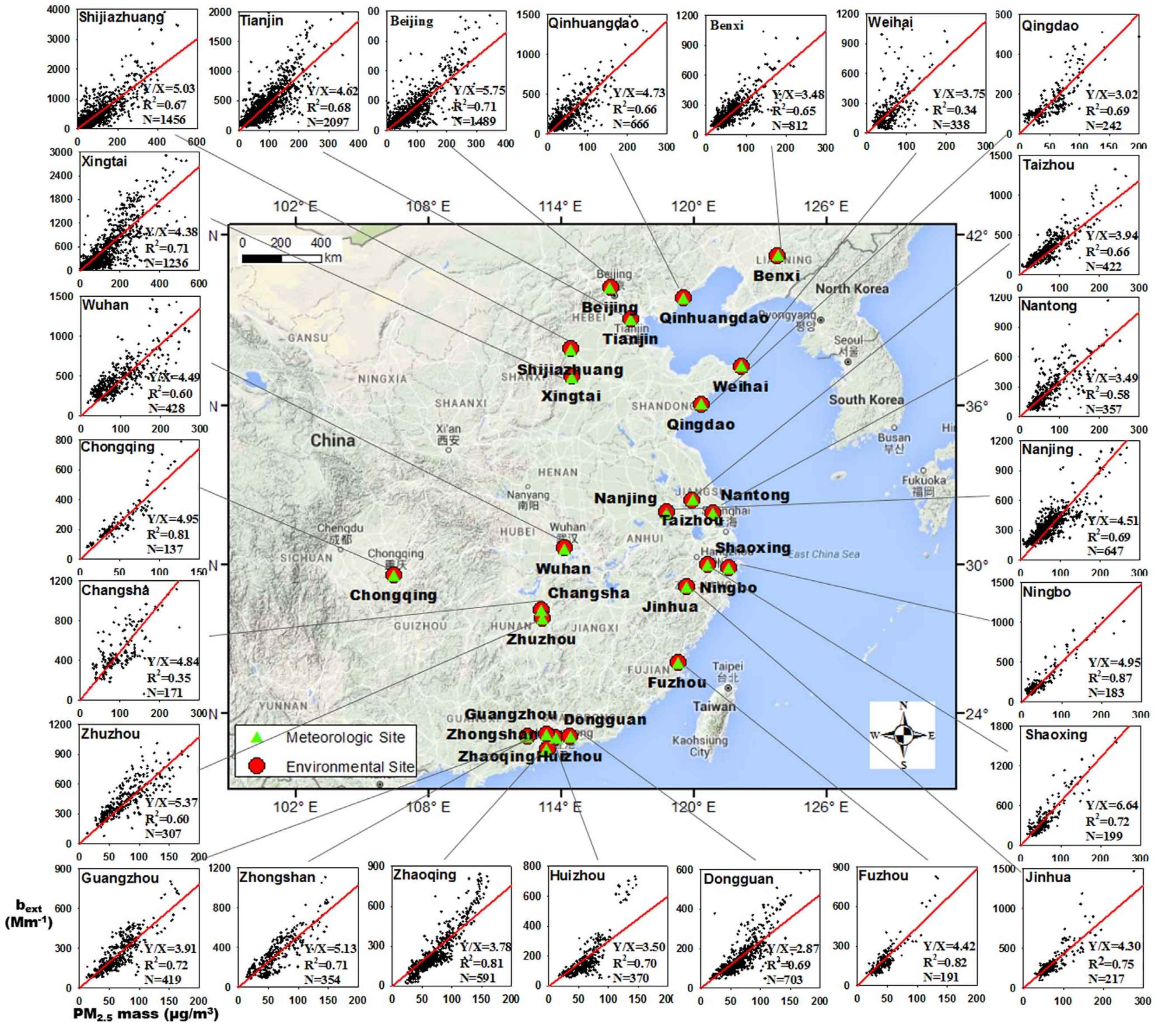

Fig. 2. Regression result between dry extinction coefficient (550 nm) and $PM_{2.5}$ mass concentration. The gray dots represent observation data points with RH < 40% and the red line represents linear regression line. “N” represents the number of records used for regression. “Y/X” represents the slope of regression line, namely the value of mass extinction efficiency (MEE).

3.2. Dry $PM_{2.5}$ mass extinction efficiency

The regression result of mass extinction efficiency for each city is illustrated in Fig. 2. The MEE values varied from 2.87 to 6.64 m^2/g, with an average value of 4.40 ± 0.84 m^2/g. No distinct regional characteristics were observed from the spatial distribution of MEE values. The cities with the three highest MEE values were Shaoxing (6.64 m^2/g), Beijing (5.75 m^2/g), Zhuzhou (5.37 m^2/g), while the cities with the three lowest MEE values were Dongguan (2.87 m^2/g), Qingdao (3.02 m^2/g), Benxi (3.48 m^2/g). Significant diversity was observed between the cities in the same city-cluster. For instance, the MEE range of the three largest city-clusters were from 4.38 to 5.75 m^2/g for around-Beijing area, from 3.49 to 6.64 m^2/g for the Yangtze River Delta and from 2.87 to 5.13 m^2/g for the Pearl River Delta. The values of MEE for each city were mainly affected by the relative mass ratio between $PM_{2.5}$ major components, i.e., inorganic, organic and crustal (Pitchford et al., 2007). Shaoxing (6.64 m^2/g), Chongqing (4.95 m^2/g), Wuhan (4.49 m^2/g) and Guangzhou (3.91 m^2/g) were selected for further illustration. $PM_{2.5}$ chemical composition data near to the observation sites were collected from the prior literature. The mass percentages of organic matter and elemental carbon were 39% and 12% for Shaoxing, 33% and 5% for Chongqing, 25% and 2% for Wuhan and 16% and 8% for Guangzhou, respectively (Hong et al., 2010; Tao et al., 2014; Zhang et al., 2015b). Meanwhile, the summarized ratio of secondary inorganic species (sulfate, nitrate and ammonia) was 41% for Shaoxing, 45% for Chongqing, 38% for Wuhan and 41% for Guangzhou, respectively. The MEE is estimated as 4 m^2/g for organic matter, 10 m^2/g for elemental carbon, and 3 m^2/g for secondary inorganic species, much higher than that of soil composition (1 m^2/g) and sea salt (1.8 m^2/g) in the original IMPROVE equation (Pitchford et al., 2007). It indicates the larger mass percentages of carbonaceous substances and secondary inorganic species in $PM_{2.5}$, the larger integrated $PM_{2.5}$ MEE value. There is a consistency between the MEE order and corresponding $PM_{2.5}$ species abundances of the above mentioned four cities. However, chemical speciation results from literatures differed by measurement periods, instruments, and QA/QC procedures, which makes comparisons of all 24 cities difficult. Hence, a national $PM_{2.5}$ chemical observation network, whose results could be of great use for substantial explaining data for the diversity of MEE among cities, is in urgent need.

The regression MEE results had high statistical indicators and were

Table 2
Mass extinction efficiency of ambient $PM_{2.5}$ in China (550 nm, unit: m^2/g).

Location	Year	MEE value	Reference
24 cities of China	2013–2014	4.4 ± 0.84	This study
YRD	2011–2012	4.1	Cheng et al. (2013)
Eastern China	2014	5.0	He et al. (2016)
Review	1990–2007	4.5[a]	Hand and Malm (2007)
Beijing	2006	4.3[a]	Jung et al. (2009)
Lin'an	1999	5.0[a]	Xu et al. (2002)
Beijing(China)	2003–2008	4.7[b]	Zhang et al. (2010)

[a] Estimated by single scattering albedo(SSA) of 0.8 according to the literature.
[b] The mass ratio of $PM_{2.5}$ to PM_{10} is set to be 0.56, and relative humidity is set to be 40% according to the literature.

comparable to that of other studies. The regression coefficient of R^2 varied from 0.34 to 0.87, with the average of 0.67 ± 0.12, indicating high regression linearity and credible regressed MEE results. The number of sampling included in the regression varied from 137 to 2097, with an average of 585 hourly records. This relatively wide range was mainly caused by the different number of hours with RH < 40%. Table 2 compares the average MEE value with those from previous studies in China. As many studies only measured mass scattering efficiency (MSE) with nephelometers, the empirical single scattering albedo(SSA) value of 0.8 was used to covert MSE to MEE (Xu et al., 2012). Although these studies differed in research groups, instrumentation, location, and time, the retrieved MEE values varied in a narrow range of 4.1–5.0 m^2/g. Note that the MEE value of 4.4 m^2/g in urban China is statistically similar to the 4.5 m^2/g value found in in developed countries where the $PM_{2.5}$ mass concentrations were relatively lower (Hand and Malm, 2007). The MEE value from this study could represent the nationwide level of extinction efficiency in current urban China and be used for estimating the $PM_{2.5}$ extinction contributions.

3.3. Hygroscopic extinction factor

The regression results of hygroscopic growth factor (f(RH)) according to Eq. (4) for each city is presented in Fig. 3. In general, the hygroscopicity among the 24 cities showed notable variations but no regional pattern was observed, similar to that of MEE. The value of f (RH = 80%) is usually used for evaluating the hygroscopicity of $PM_{2.5}$ (Liu et al., 2008, 2013; Pan et al., 2009). The average f(RH = 80%) of all 24 cities was 2.63 ± 0.45. The two strongest-hygroscopicity cities were Tianjin (f(RH = 80%):3.72, a:6.2, b:3.7) and Qingdao (f (RH = 80%):3.60, a:6.2, b:3.9). In contrast, the three weakest-hygroscopicity cities were Zhuzhou (f(RH = 80%):1.95, a:1.7, b:2.6), Weihai (f(RH = 80%):2.20, a:2.0, b:2.3) and Chongqing (f(RH = 80%):2.20, a:3.2, b:4.4). Qingdao and Weihai belong to the same city-clusters. However, the f(RH = 80%) of Qingdao was 1.6 times as that of Weihai. The dominant factors influencing hygroscopicity are the abundances of hydrophilic species in ambient $PM_{2.5}$, i.e., sulfate, nitrate, ammonia and seal salt. This is somewhat different from the factors influencing mass extinction efficiency. The hygroscopic effect of carbonaceous substances is assumed to be much weaker than inorganic ions, although

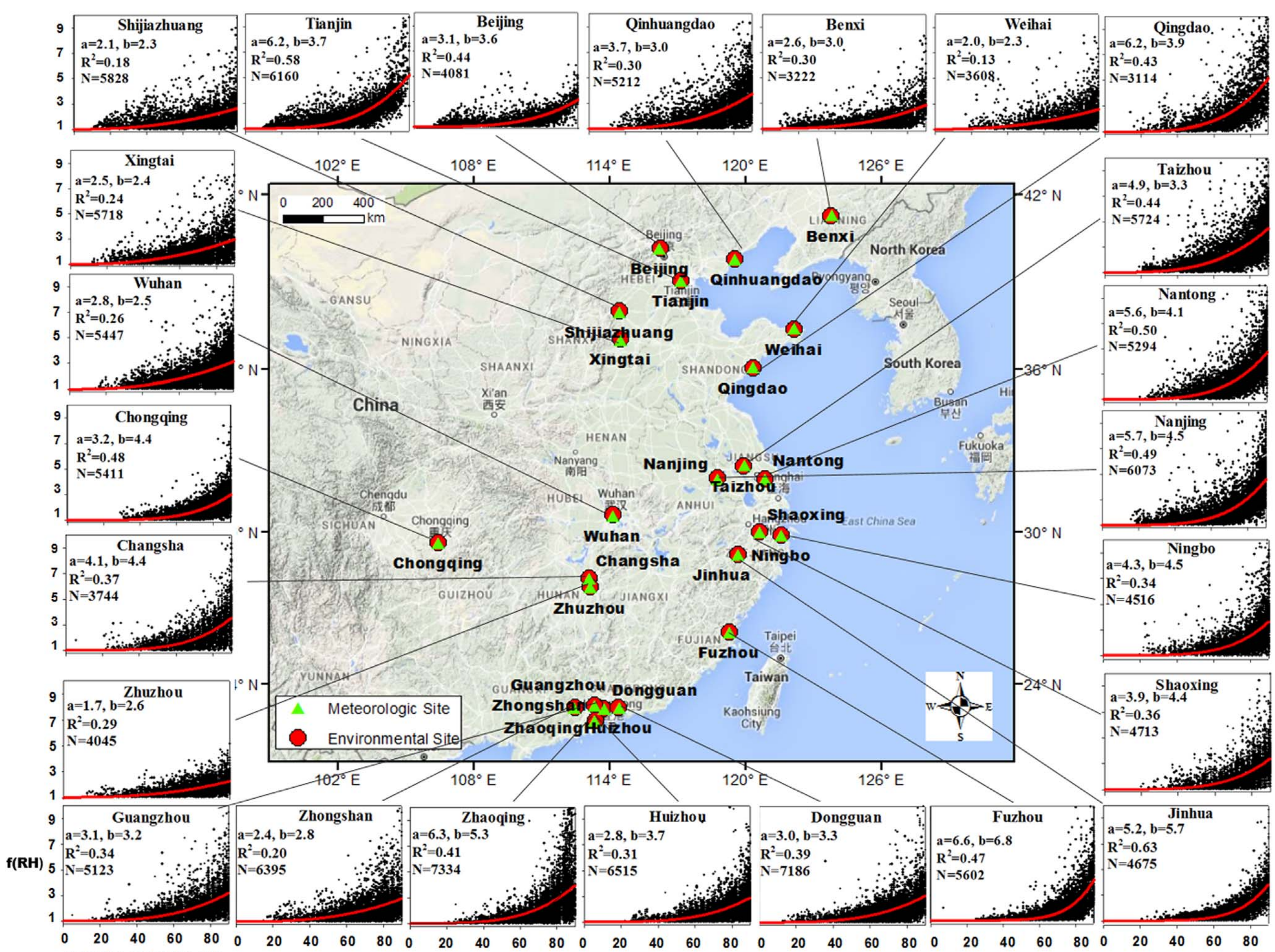

Fig. 3. Regression result between hygroscopic growth factor of extinction coefficient (550 nm) and relative humidity. The gray dots represent observation data points and the red line represents regression line. "N" represents the number of points used for regression.

Table 3
Parameter values of "a" and "b" in extinction hygroscopic factor (Eq. (4)) of ambient $PM_{2.5}$.

Location	Year	Classification	a	b	Reference
24 cities of China	2013–2014	Urban	3.9 ± 1.5	3.7 ± 1.1	This study
Lin'an, China	2013	Locally polluted	1.2	5.5	Zhang et al. (2015)
		Northerly polluted	1.2	3.9	
		Dust-influenced	1.0	4.5	
Beijing, China	2007	Urban	8.8	9.7	Liu et al. (2013)
Rural area near Beijing (China)	2006	Dust	0.6	5.2	Pan et al. (2009)
		Clean	1.2	6.1	
		Pollutant	2.3	6.3	
Guangzhou, China	2006	Urban	2.1	3.6	Liu et al. (2008)
		Mixed	3.3	3.9	
		Marine	4.9	5.0	
South Africa	2000	Regional air	2.5	3.6	Magi and Hobbs (2003)
		Aged heavy smoke	1.3	4.9	

the part of water-soluble organic carbon has some hygroscopicity. Taking Tianjin and Zhongshan for example, their f(RH = 80%) were 3.72 and 2.28, respectively. The mass percentage of inorganic ions was 45.5% for Tianjin, 9% higher than that of Zhongshan, while the abundance of carbonaceous substances was 23.5% for Tianjin, much lower than the value of 40.0% for Zhongshan (Hagler et al., 2006; Zhao et al., 2013). An accurate and nationwide explanation of hygroscopicity differences requires long-term national $PM_{2.5}$ chemical speciation network, which is not available in urban China yet.

The number of samples for each city included in Fig. 3 varied from 3114 in Qingdao to 7334 in Zhaoqing, over four times as that of mass extinction efficiency shown in Fig. 2. This difference is caused by only including hourly records with RH < 40% in Fig. 2 and including all records in Fig. 3. As a result, the regression coefficient R^2 for hygroscopicity varied from 0.13 to 0.63, lower than that of MEE. The lower R^2 values in Fig. 3 were also probably due to the complexity of the $PM_{2.5}$ hygroscopicity. As the bulk $PM_{2.5}$ contains numerous hydrophilic and hydrophobic species, the integrated extinction hygroscopicity is difficult to be perfectly described by a single mathematic model.

The parameters "a" and "b" in Eq. (4) from this study were comparable and falling in the similar range of previous studies. Theoretically, the parameter "a" means the maximum value of hygroscopicity when RH equals 100%, while the parameter "b" determines the curvature of hygroscopicity curve (Zhang et al., 2015). The average value of "a" and "b" in this study were 3.92 ± 1.52 and 3.74 ± 1.11, respectively, both were in the ranges of 0.64–8.77 and 3.60–9.74 from previous studies shown in Table 3. Different ambient air pollution type exhibits significant variation of "a" and "b" values. The average values of "a" and "b" in this study were similar to the results from mixed and marine locations in Guangzhou (Liu et al., 2008). It is reasonable as most cities in this study are located in the vicinity of the coastal area. The values of parameter "a" and "b" from our one-year records better represent the long-term value over urban China compared to those conducted at one single site in a short period (Table 3).

3.4. Apportionment of extinction coefficient

Fig. 4 shows apportionment of ambient total extinction coefficient budget to contributions from dry $PM_{2.5}$, hygroscopicity enhancement, Raleigh scattering, and NO_2 for each city. Annual extinction coefficient due to dry $PM_{2.5}$ was estimated by annual ambient $PM_{2.5}$ mass concentration multiplying mass extinction efficiency. Annual extinction coefficient due to coarse particles ($PM_{2.5-10}$), Rayleigh scattering of air molecules and absorption extinction of NO_2 was calculated according to Eq. (1). Then the remaining of annual extinction coefficient was regarded as annual extinction coefficient due to hygroscopicity of ambient $PM_{2.5}$. Dry $PM_{2.5}$ and its hygroscopicity dominated the total extinction coefficient overwhelmingly, whether for the average of all 24 cities or the top highest cities (shown in Fig. 4a). Dry $PM_{2.5}$ and its related hygroscopicity contributed 305.8 ± 131.0 Mm^{-1} (40.3%) and 414.6 ± 188.1 Mm^{-1} (54.6%), respectively of the total extinction coefficient. The remaining extinction coefficient due to coarse particles, Rayleigh scattering and NO_2 absorption were only 21.4, 10 and 7.5 Mm^{-1}, respectively. The sum contribution of these three items was 5.1%. As to the top five cities with the highest extinction coefficient (i.e., Changsha, Wuhan, Chongqing, Taizhou and Shaoxing), $PM_{2.5}$ hygroscopicity contributions were 1.49–2.23 times of dry $PM_{2.5}$. The extinction coefficient due to hygroscopicity for these five cities ranked the 1st, 3rd, 4th, 2nd and 7th among all cities, similar to the order of total extinction coefficient. Meanwhile, the extinction coefficient due to dry $PM_{2.5}$ for these five cities only ranked the 11th, 5th, 6th, 10th and 8th among all cities.

Ambient $PM_{2.5}$ mass concentration and the level of mass extinction efficiency are the two dominant factors of the extinction coefficient due to dry $PM_{2.5}$. As shown in Fig. 4b, the top five cities with the highest dry $PM_{2.5}$ extinction coefficient were Shijiazhuang (620.5 Mm^{-1}), Xingtai (588.2 Mm^{-1}), Beijing (537.3 Mm^{-1}), Zhuzhou (445.4 Mm^{-1}) and Wuhan (424.0 Mm^{-1}). Note that Shijiazhuang exceeded Xingtai by 32.3 Mm^{-1} although its $PM_{2.5}$ mass concentration was 15 μg/m^3 lower than Xingtai (Table 1). Furthermore, Beijing ranked in front of Wuhan while the order of $PM_{2.5}$ mass was the opposite. Zhuzhou ranked to the 4th although its $PM_{2.5}$ mass only ranked the 7th. The key factor caused this discrepancy was the different level of $PM_{2.5}$ mass extinction efficiency for these cities, which has been discussed earlier in the Section 3.2.

The extinction coefficient due to hygroscopicity is compared in Fig. 4c. Multiple factors, including ambient RH, $PM_{2.5}$ hygroscopic factor, and dry $PM_{2.5}$ extinction coefficient, were regarded to determine the hygroscopicity extinction enhancement. The five cities with the highest extinction coefficient due to hygroscopicity were Changsha (786.0 Mm^{-1}), Taizhou (701.8 Mm^{-1}), Wuhan (674.1 Mm^{-1}), Chongqing (637.9 Mm^{-1}) and Nantong (615.1 Mm^{-1}). Their corresponding annual average RH were 79.3%, 75.1%, 76.3%, 78.5% and 75.8%, and the corresponding f(RH = 80%) values were 2.54, 3.35, 2.60, 2.20 and 3.24. Changsha ranked the first mainly due to its high RH. Taizhou and Nantong ranked the second and fifth mainly because their f(RH = 80%) were higher than other cities. Wuhan and Chongqing ranked the third and fourth because of their elevated extinction coefficient due to dry $PM_{2.5}$. In summary, the extinction coefficient due to hygroscopicity is affected by the nonlinear effects of ambient RH, hygroscopic curve and initial extinction coefficient due to dry $PM_{2.5}$, as indicated by Eqs. (3) and (4).

4. Conclusions

Annual total extinction coefficient in urban China was 759.3 ± 258.4 Mm^{-1}, mainly contributed by dry $PM_{2.5}$ (305.8 ± 131.0 Mm^{-1}) and its hygroscopicity (414.6 ± 188.1 Mm^{-1}). The top five cities with the highest extinction coefficient were Changsha (1153 Mm^{-1}), Wuhan (1117 Mm^{-1}), Chongqing (1073 Mm^{-1}), Taizhou (1070 Mm^{-1}) and Shaoxing (1033 Mm^{-1}). Elevated extinction coefficient values were resulted from increased mass concentrations of ambient $PM_{2.5}$ and ambient relative humidity. The $PM_{2.5}$ mass extinction efficiency ranged from 2.87 to 6.64 m^2/g with an average value of 4.40 ± 0.84 m^2/g. The average value of "a" and "b" in this study were 3.92 ± 1.52 and 3.74 ± 1.11, respectively, and the specific hygroscopic factor with the RH of 80% was 2.63 ± 0.45. The values of $PM_{2.5}$ mass extinction efficiency and hygroscopic factor were similar to those found in developed countries, in spite of the significant

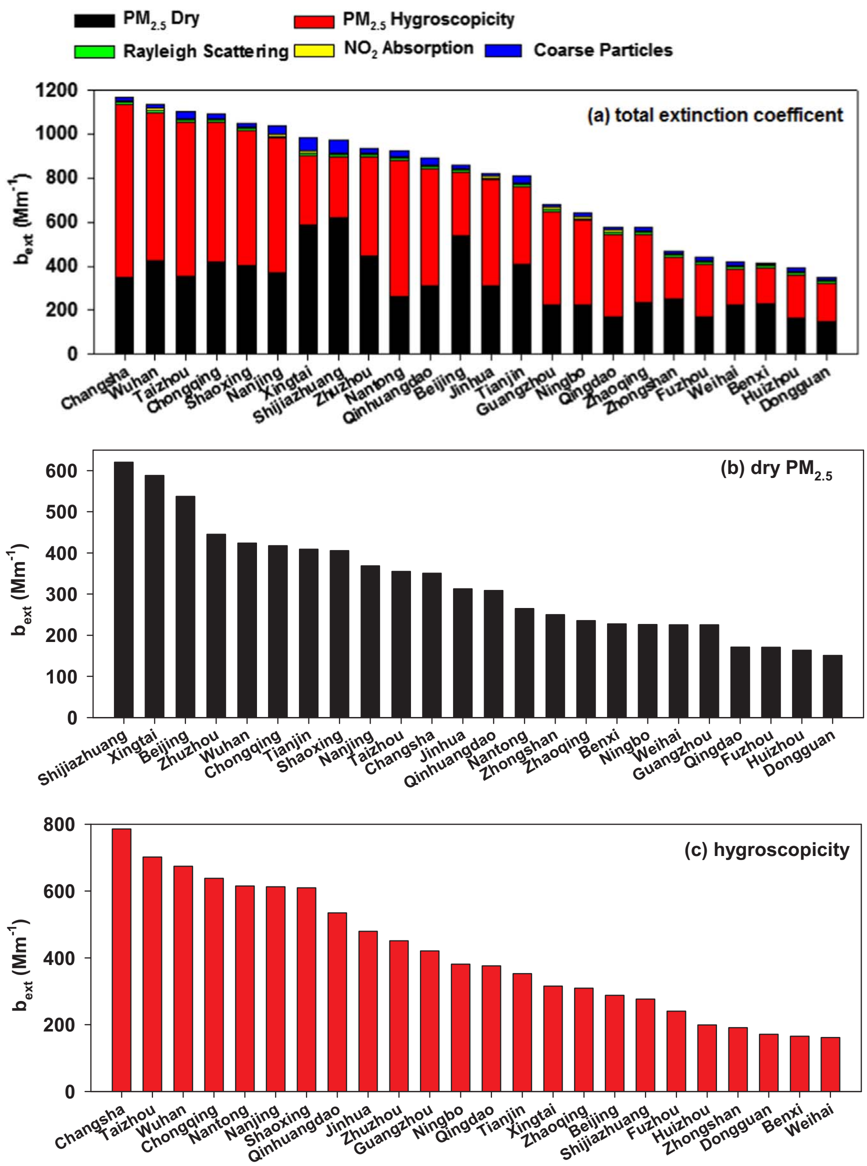

Fig. 4. Annual extinction coefficient (550 nm) due to dry $PM_{2.5}$ and its hygroscopicity, Rayleigh scattering and ambient NO_2 absorption for 24 key cities. The order index is as: (a) total extinction coefficient; (b) dry $PM_{2.5}$; (c) hygroscopicity.

diversities among different cities in China, mainly related to $PM_{2.5}$ species abundances of each city. Ambient RH, $PM_{2.5}$ mass concentration, $PM_{2.5}$ mass extinction efficiency and hygroscopic factor jointly dominate the extinction coefficient.

Results from this study will provide strong basis for establishing quantitative relationship between ambient extinction coefficient (visibility) and $PM_{2.5}$ & RH, and reduce the uncertainty in estimating extinction coefficient of ambient $PM_{2.5}$ in urban China. Furthermore, this study is crucial for the research of haze pollution and radiative forcing. A national $PM_{2.5}$ chemical monitoring network in urban China is needed to provide quantitative explanation of diversity of MEE and hygroscopicity enhancement. Such a network is also in urgent need to develop pollution reduction strategies and evaluate the effectiveness of pollution control policies.

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