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Long-term trend of haze pollution and impact of particulate matter in the Yangtze River Delta, China

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A B S T R A C T

Haze pollution caused by heavy particulate matter (PM) loading brings significant damage in eastern China. Long-term monitoring from 1980 to 2011 and 1-year field measurement in 2011–2012 are used for investigating visibility variation and the impact of PM pollution for the Yangtze River Delta (YRD). It was found that visual range in the YRD endured a sharp reduction from 13.2 km to 10.5 km during 1980–2000. Average mass extinction efficiency (MEE) for inhalable PM (PM_{10}) is 2.25 m^2/g in 2001–2011, and extinction coefficient due to PM_{10} is 207 Mm^{-1}, accounting for 36.2% of total extinction coefficient. MEE of $PM_{2.5}$ and $PM_{2.5-10}$ are 4.08 m^2/g and 0.58 m^2/g, respectively. Extinction coefficient due to $PM_{2.5}$ and $PM_{2.5-10}$ is 198 Mm^{-1} (39.6%) and 20 Mm^{-1} (4.0%) in 2011–2012. Maximum daily concentration of PM_{10} and $PM_{2.5}$ is estimated to be 63 $\mu g/m^3$ (RH: 73%) and 38 $\mu g/m^3$ (RH: 70%) to keep visual range above 10 km. Fine particulate matter is the key factor for haze pollution improvement in the YRD area.

1. Introduction

The phenomenon of haze refers to the reduction of visibility caused by the light extinction of particulate matter (PM) and is called “the pollution people see”(Hyslop, 2009). Haze not only has the direct depressive mental effect on human beings by the gray sky color (Hyslop, 2009), but also is an indicator of high concentration of particulate matter, with the potential to adversely impact public health (Tie et al., 2009), ecological systems (Chameides et al., 1999) and climate (Solomon et al., 2007). Particulate matter is the primary factor causing the reduction of visibility. Its major components, such as sulfate, nitrate and organic matter, have both high mass abundance and high extinction cross-section in the visible wavelength diameter range (Hand and Malm, 2007). Meanwhile, relative humidity is another important factor affecting the extinction effect, either by hydration of dry particles when relative humidity is higher than the deliquescence point, or by condensation of water vapor to droplets which occurs mainly in fog events (Elias et al., 2009; Winkler, 1988).

As the biggest developing country in the world, China undergoes severe haze pollution due to the intensive emission of air pollutants, especially in the city-clusters such as the Yangtze River Delta, Beijing–Tianjin Area and Pearl River Delta Area (van Donkelaar et al., 2010; Zhang et al., 2012). As one of the six largest city clusters in the world, the average visual range of the YRD observed by meteorological stations experienced a consistent decrease from ~25 km to <20 km with a trend of 2.4 km per decade from 1980s to 2010s (Che et al., 2009; Gao et al., 2011). Field observation studies conducted in megacities of the YRD such as Shanghai, Nanjing and Hangzhou have shown that the impaired visibility was mainly due to particulate matter pollution, especially fine particulate matter with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) (Fu et al., 2008; Huang et al., 2012; Xiao et al., 2011; Zhu, 2010). Furthermore, the statistical analysis of long-term datasets in the YRD also indicated that relative humidity of ambient air has significant correlation with visibility (Deng et al., 2011; Xiao et al., 2011; Xu et al., 2005; Zhang et al., 2011).

However, while the visibility trends of the YRD cities were investigated in the literature, the systematic analysis for the causes of the long-term visibility variation and its relationship with particulate matter have not been reported. Some scientific issues, such

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as the reduction of visibility is due to the fog or haze, and the quantitative contribution of particulate matter to the total extinction coefficient. Comprehensive in-situ experiments could answer these questions by measuring the extinction coefficient under dry and ambient relative humidity simultaneously and compare their differences (Liu et al., 2006; Xu et al., 2002). However, the measurement results could only represent a single site in the short term, and is difficult to be applied for long-term and regional haze assessment.

In this study, three different time-scale datasets: 30-year visibility monitoring, 10-year particulate matter monitoring and 1-year-continuous field measurement at six sites of the YRD, are collected and used to investigate the trends of haze pollution in the YRD and its relationship with particulate matter. Mass extinction efficiency (MEE) of particulate matter is estimated and applied for contribution assessment of particulate matter to total extinction coefficient and its hygroscopic growth factor.

2. Method

2.1. Experiment sites selection

The YRD region lies in the east of China and usually refers to the 16 core cities in Shanghai, southern Jiangsu province, eastern and northern Zhejiang province (Fig. 1). It includes China's biggest city of Shanghai and other important economic hubs like Nanjing, Suzhou, Hangzhou, and Ningbo.

Six core YRD cities, Nanjing, Suzhou, Nantong, Shanghai, Hangzhou and Ningbo, are chosen for the investigation of long-term monitoring dataset. One meteorological station and one environmental station are selected for each city (Fig. 1). All of them lie in the urban center of each city except for the meteorological site of Suzhou which is in the suburban area.

For 1-year field measurement, six sites are included and are located at the urban area of Nanjing, Suzhou, Shanghai, Hangzhou and Ningbo. Two of them are in Shanghai and lie in the west and east of Huangpu River in Shanghai, with the name of "Puxi" and "Pudong", respectively.

2.2. Data sources and measurement

Long-term monitoring datasets include both environmental and meteorological data. The indices from meteorological station include relative humidity (RH), visual range and ambient temperature from 1980-1-1 to 2012-12-31 (http://cdc.cma.gov.cn). The visual range, which is defined as the greatest distance at which a black object of suitable dimensions can be seen and recognized when observed against the horizon sky during daylight or could be seen and recognized during the night if the general illumination were raised to the normal daylight level (WMO, 2008), is observed by the naked-eye of a professional meteorologist four times (0:00, 6:00, 12:00, 18:00) per day. Daily RH and temperature are collected and checked by meteorological professionals. Daily concentration of inhalable particulate matter (PM_{10}) from 2001-1-1 to 2012-12-31 is converted from the daily API dataset for national key environmental cities (http://datacenter.mep.gov.cn), according to API definition when the primary pollutant is PM_{10} (http://datacenter.mep.gov.cn, Cheng et al., 2013; Qu et al., 2010). PM_{10} concentrations for these key cities are usually measured with the use of Tapered Element Oscillating Microbalance analyzers (Model RP1400a or RP1405)(Qu et al., 2010). The number of days with unavailable PM_{10} concentration when the primary pollutant is not PM_{10} is only 8 per year during 2001–2012 for the average of all cities.

1-year field observation was conducted at six sites from May 1st, 2011 to April 30th, 2012. The sites of Puxi, Pudong, Hangzhou and Nanjing have 1–3 months data absence due to the error of instruments. The results consist of hourly records of mass concentration of PM_{10}, $PM_{2.5}$ and black carbon, relative humidity and visual range for each site. The specific instruments used for each site are list in Table 1. The instruments for PM mass concentration are based on TEOM except for the beta attenuation principle at the Puxi site. BC mass concentration is determined by the 880 nm wavelength results of Aethalometer for all sites.

The two types of visibility sensors (Belfort Model 6000 and Vaisala PWD22) in field observation are both based on the forward scattering principle: the measuring ranges are 20 and 60 km, respectively. In order to make the measurement results comparable to manual observation results in the above long-term monitoring dataset, the results of Belfort Model 6000 with the measuring range of 0–60 km are corrected by a fitting equation which is derived after comparison with manual observation (Tan et al., 2010). The equation is a cubic polynomial fitting based on daily-averaged visibility sensor result (independent) and daily-averaged manual observation result (dependent). After the correction process, it is seen that the linear relationship coefficients between manual observation and visibility sensor are all above 0.7, and the absolute values is almost equal (Fig. 2).

2.3. Data processing

First of all, instantaneous visual range observation in long-term meteorological dataset and hourly visual range measurement in 1-year field observation dataset are both converted to extinction coefficient ($b_{ext,}$ 550 nm) according to Koschmieder's formula (Larson and Cass, 1989) (Equation (1)). Although Koschmieder's formula is only suitable for instantaneous condition, it could still be used for the conversion between hourly extinction coefficient and hourly visual range under acceptable bias. Previous studies (Che et al., 2009; Zhang et al., 2010) even use it directly on a daily scale. Considering the heavy aerosol loading in China, the extinction effect of air molecules could be neglected and the observed extinction coefficient could be regarded as decided by aerosol only.

$$b_{ext} = 2996/\text{Visual range} \quad (1)$$

where the unit of visual range is km and the unit of b_{ext} is Mm^{-1}. The coefficient of 2996 is used due to the contrast threshold selection of 0.05, which is recommended by the WMO observation handbook (WMO, 2008).

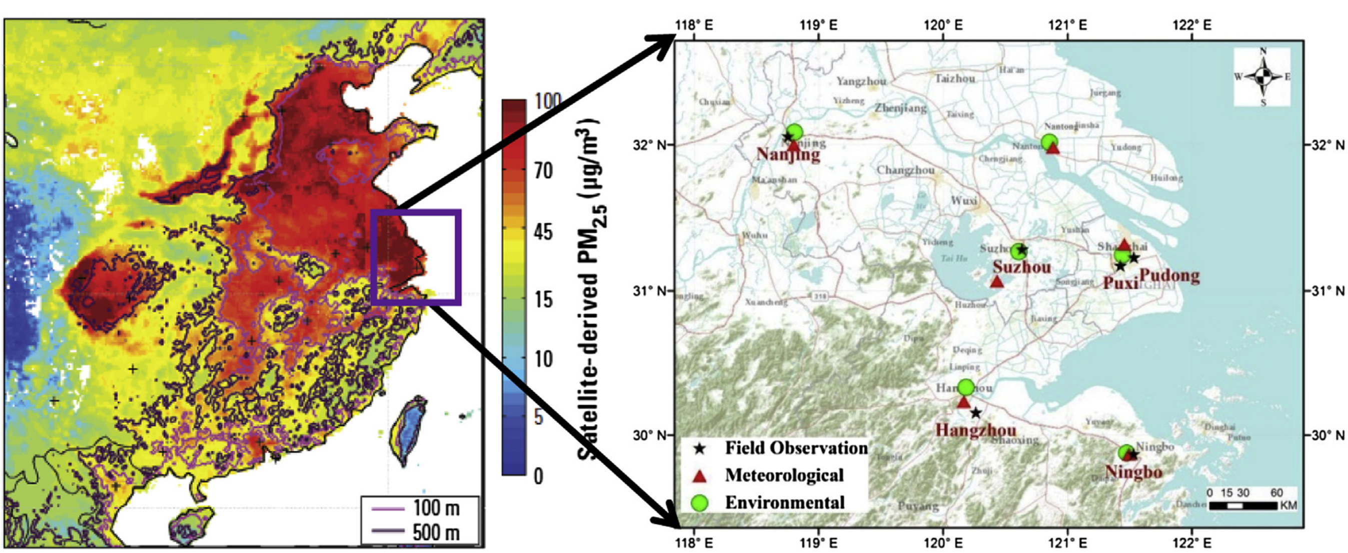

Fig. 1. Geographic location of stations in long-term monitoring dataset and sites of 1-year field measurement for the YRD cities. Green circle represents environmental stations, red triangle represents meteorological stations and black star stands for the field observation sites. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Instruments used for six 1-year field observation sites in the YRD.

Measured Index	Used instrument
$PM_{2.5}/PM_{10}$ mass concentration	TEOM1405 (Pudong, Nanjing, Suzhou, Hangzhou) Thermo Rp1400A (Ningbo) Thermo FH 62 C14 (Puxi)
Relative humidity	Met One (Puxi, Suzhou, Ningbo) VaisalaWXT520 (Pudong) TH-2009 (Nanjing) LUFFT (Hangzhou)
Visual range	Belfort Model 6000 (Suzhou, Hangzhou, Puxi) VaisalaPWD22 (Pudong, Nanjing)
Black carbon	880 nm of Aethalometer AE31 (Suzhou, Hangzhou, Ningbo, Pudong, Nanjing)

Meanwhile, the PM mass concentration in the long-term API dataset or the 1-year field measurement is based on TEOM principle under the heating temperature of 50 °C. The integrated comparison with the reference method of filter collecting/gravimetry, stabilized with sufficient time under the RH below 40–50%, is collected (Qu et al., 2010) and indicated that the results of the two methods agree pretty well ($Y = 1.10X$, $R^2 = 0.7$). Hence it is reasonable that the PM mass concentration in this study represents the dry condition of particulate matter with the removal of liquid water.

Mass extinction efficiency (MEE, 550 nm) for PM, which refers to the extinction effect per unit of mass concentration, is then calculated when relative humidity is not higher than 50%. The threshold value of 50% RH is decided as it is lower than the deliquescence point of major PM components and the hygroscopic effect could be neglected when RH is under this value (Zieger et al., 2011). It is noted that the MEE value in this study is referred to the dry condition with relative humidity no higher than 50%. For the long-term dataset of six cities from 2001 to 2011, daily MEE for PM_{10} is calculated as daily extinction coefficient divided by daily mass concentration of PM_{10} (Equation (2)) when daily average relative humidity is not higher than 50%, and the average MEE for each year and each city from 2001 to 2011 is decided by averaging those daily MEE values in the year for the city. For the 1-year observation dataset of six sites from 2011 to 2012, hourly MEE for $PM_{2.5}$ and $PM_{2.5-10}$ (coarse particles with the aerodynamic diameter between 2.5 μm and 10 μm) are calculated through the method of multiple linear regression between hourly extinction coefficient (dependent variable) and hourly mass concentration of $PM_{2.5}$ & $PM_{2.5-10}$ (independent variables) (Equation (3)) when hourly average relative humidity is not higher than 50%, and the average MEE for each city in 2011–2012 is decided by averaging those hourly MEE values for the city.

$$MEE_{PM_{10}} = b_{ext}/C_{PM_{10}} \quad \text{when RH} \le 50\% \qquad (2)$$

where the unit of $MEE_{PM_{10}}$ is "m^2/g" and the unit of b_{ext} and $C_{PM_{10}}$ is "Mm^{-1}" and "$\mu g/m^3$", respectively.

$$b_{ext} = MEE_{PM_{2.5}} * C_{PM_{2.5}} + MEE_{PM_{2.5-10}} * (C_{PM_{10}} - C_{PM_{2.5}}) \quad \text{when RH} \le 50\% \qquad (3)$$

where the unit of $MEE_{PM_{2.5}}$ and $MEE_{PM_{2.5-10}}$ is "m^2/g" and the unit of b_{ext} and $C_{PM_{2.5}}$ is "Mm^{-1}" and "$\mu g/m^3$", respectively.

For the long-term dataset of six cities from 2001 to 2011, the contribution of extinction coefficient (550 nm) due to PM_{10} for each year and each city is calculated as the annual PM_{10} concentration multiplied by the average MEE for that year and that city (Equation (4)). For the 1-year observation dataset of six sites from 2011 to 2012, the contribution of extinction coefficient due to $PM_{2.5}$ and $PM_{2.5-10}$ for each month and each city is calculated as the monthly $PM_{2.5}$ mass concentration multiplied by the average MEE of $PM_{2.5}$ for that city and monthly $PM_{2.5-10}$ mass concentration multiplied by the average MEE of $PM_{2.5-10}$ for that city (Equations (5) and (6)). Meanwhile the hygroscopic growth factor of PM is calculated from the ratio of daily total extinction coefficient to the daily contribution of extinction coefficient due to $PM_{2.5}$ and $PM_{2.5-10}$ (Equation (7)).

$$b_{ext \to PM_{10}} = MEE_{PM_{10}} * C_{PM_{10}} \qquad (4)$$

$$b_{ext \to PM_{2.5}} = MEE_{PM_{2.5}} * C_{PM_{2.5}} \qquad (5)$$

$$b_{ext \to PM_{2.5-10}} = MEE_{PM_{2.5-10}} * C_{PM_{2.5-10}} \qquad (6)$$

$$f(RH) = b_{ext}/(b_{ext \to PM_{2.5}} + b_{ext \to PM_{2.5-10}}) \qquad (7)$$

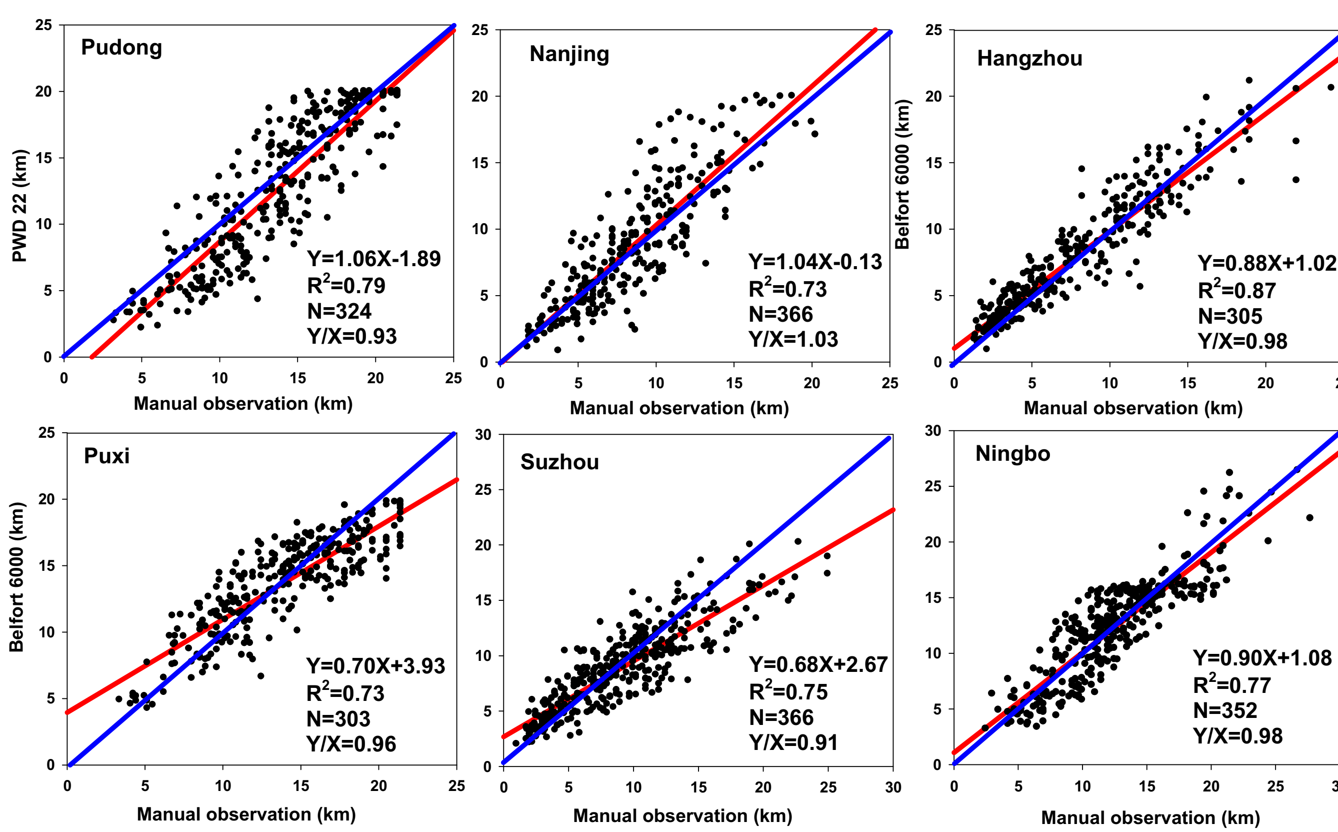

Fig. 2. Comparison of visual range results by manual observation and automatic sensor. The blue line represents 1:1 line while red line represents linear regression line. "*N*" represents the number of points used for regression. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Long-term trend of visual range and haze days

The annual average visual range for each city during 1980–2011 is plotted (Fig. 3). For all cities except for Shanghai, the visibility impairment increased significantly from 1980 to the year around 2000, and fluctuated near a constant value during 2000–2011. The city of Shanghai experience three phased slight increase of visibility. In detail, the annual average visual range of Suzhou, Nanjing and Hangzhou were 15.1 ± 9.0, 11.8 ± 6.7 and 9.8 ± 6.9 km in 1980, and then decreased sharply to 9.2 ± 6.6, 7.4 ± 5.5 and 6.4 ± 5.4 km in 1999, with decreases of 0.30, 0.22 and 0.17 km/year, respectively. During 2000–2011, the annual average visual range of Suzhou, Nanjing and Hangzhou varied around 10.0, 8.2 and 7.5 km, respectively. For Nantong and Ningbo, the annual visual range decreased from 19.6 ± 9.4 and 14.9 ± 8.6 km in 1980 to 12.7 ± 6.0 and 11.7 ± 3.8 km in 2003, with a decrease of 0.29 and 0.13 km/year, then fluctuated at 14.2 and 12.1 km from 2004 to 2011. The annual visual range of Shanghai was 9.4 km during 1980–1987, 11.0 km during 1988–2000 and 12.2 km during 2000–2011. Shi and Wu (2010) investigated the visibility of all the meteorological sites in Shanghai between 1981 and 2008 and found that the number of hazy days is increasing in the southwest region of Shanghai while it is decreasing in central urban region. The most likely reason for the inconsistent trend of visibility is due to the different development phase. The emission from the central urban area is reduced due to either source moving out or the complement of industrial process while its southwest region is still under the industrial development like other YRD cities.

The standard of China Meteorological Administration defines haze when the visual range is less than 10 km and relative humidity is lower than 80% (China Meteorological Administration, 2010). For the day when visual range is less than 10 km and relative humidity is higher than 95%, the standard attributes it to a fog day. For the day when visual range is less than 10 km and relative humidity is between 80% and 95%, additional measurements like $PM_{2.5}$, PM_1 and extinction coefficient is required to identify whether it is haze or not, which is called "unidentified" in this study for short. The counting of three different types of days is plotted according to the above-stated standard (Fig. 4). In general, six cities can be divided into three types according to haze days variation patterns. For the cities of Nanjing, Hangzhou and Suzhou, the haze days increase continually from about 40, 50, 20 in 1980s to 140, 160 and 70 after 2001; For the cities of Nantong and Ningbo, there are less than 15 haze days per year before 2000, however, the number increases to 50 days per year after 2001. The city of Shanghai remained at about 66 days in 1980–2011 in spite of fluctuation during 1985–1995. In contrast, the number of fog days and unidentified days have no obvious variation for all cities from 1980 to 2011. Correspondingly, the number of days with visibility less than 10 km also increases significantly due to the increase of haze days.

The variation of temperature and relative humidity is also investigated from six meteorological stations in the past thirty years. The annual relative humidity dropped continuously from 79.0 ± 12.5% in 1980 to 71.7 ± 13.6% in 2011. Meanwhile, the average atmospheric temperature of these cities increases from 15.2 ± 8.9 °C in 1980 to 16.5 ± 9.5 °C in 2011. The decreasing relative humidity, which might be caused by the rising atmospheric temperature, will benefit the visibility, as it will weaken the

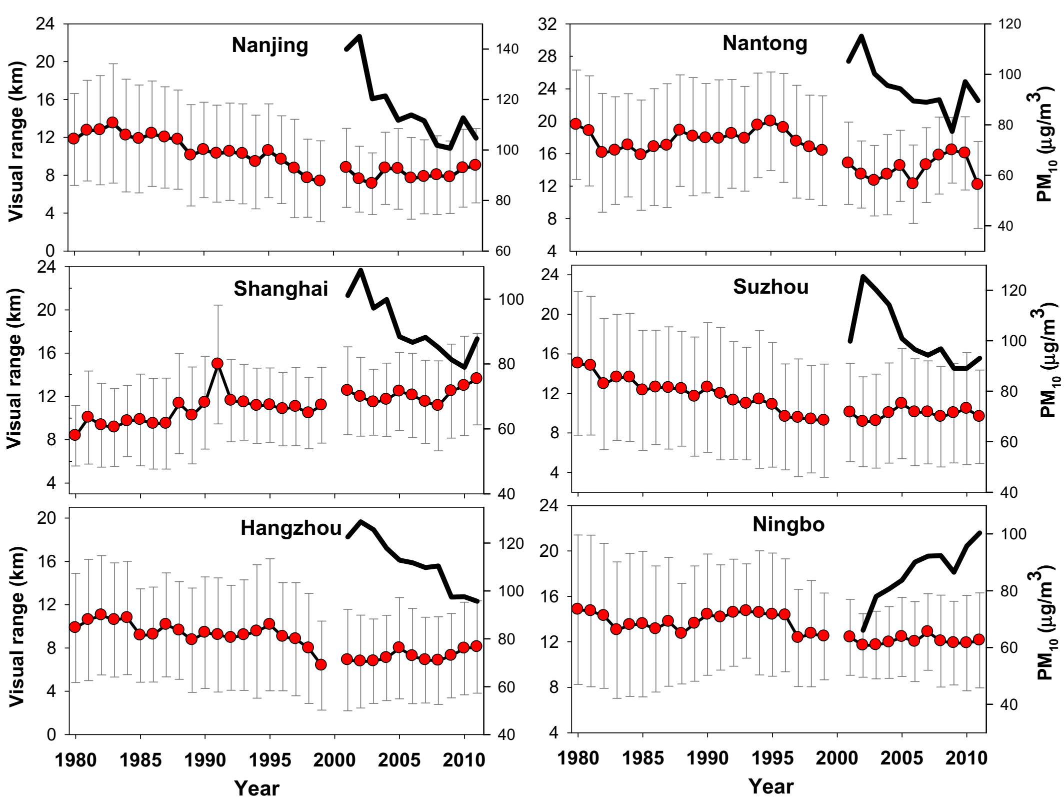

Fig. 3. Long-term trends of the annual visual range and PM_{10} concentration in the YRD cities. The red dots represent the annual visual range and the ends of the whiskers represents one standard deviation of visual range, the solid black line represents annual PM_{10} concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

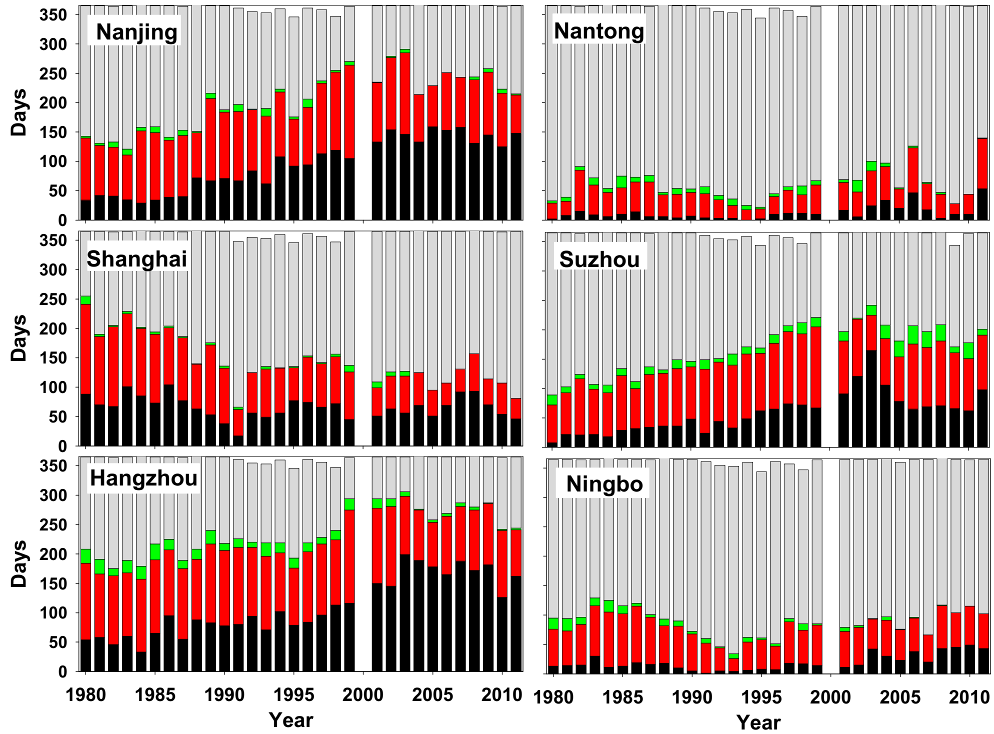

Fig. 4. Time evolution of haze days for the YRD cities under current haze standard. Black bar represents haze days; Red bar represents unidentified days, which means decided by further measurement; Green bar represents fog days; Gray bar represents good days with the daily visual range higher than 10 km. The absence of data for year of 2000 is due to the absence of visual range record in this year. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

hygroscopic effect of PM and reduce the occurrence of fog. Therefore the decreasing relative humidity could not increase the number of total days with visual range lower than 10 km. The increase of fine particulate matter concentration might be responsible for the increase of haze days, although there is no $PM_{2.5}$ monitoring data during this period.

The monitoring of PM_{10} concentration is started from June of 2000 in China. As shown in Fig. 3, the annual PM_{10} concentrations of the six cities varied at the range of 66–145 μg/m^3 during 2001–2011. Ningbo is the only city with the increasing rate by 52% from 2002 to 2011 (no data available for Ningbo in 2001), while annual concentration in the other five cities decreased by 7%–35% from 2001 to 2011. However, the annual visual range trend and haze days were not explained by the trend of PM_{10} concentration for each city in 2001–2011. The substantial reason is that the particle size distribution of PM_{10} has changed after the removal of coarse particles during the period (Cheng et al., 2013). The concentration of fine PM that decides the extinction effect has no notable reduction (Lin et al., 2010).

3.2. *Mass extinction efficiency of dry particulate matter*

Mass extinction efficiency is a critical parameter that links the aerosol concentration with aerosol optical property. According to the equation given in Section 2.3, the average value of MEE for PM_{10} is estimated to be 2.25 ± 1.02 m^2/g from 2001 to 2011, with the range of 1.64–2.95 m^2/g (Table 2). Zhang et al. (2010) estimated the PM_{10} MEE value of 3.14 m^2/g for Beijing using the similar method. Most other studies calculate mass scattering efficiency (MSE) through the scattering coefficient measurement of nephelometer. If the single scattering albedo (SSA) is assumed to be 0.8 (Xu et al., 2012), the related MSE in this study is 1.8 m^2/g. Bergin et al. (2001) and Jung et al. (2009) reported the PM_{10} MSE value in Beijing of 2.3 ± 1.6 and 2.5 ± 1.1 m^2/g, respectively. Hand and Malm (2007) reviewed the measurement studies from 1990 to 2007 and estimated the average MSE value of 1.7 ± 1.0 m^2/g for urban areas. Concerning the MEE value variation with aerosol physical and chemical properties, the results of this study is comparative with and close to the MSE values from other studies.

For the differences between cities, Hangzhou holds the highest PM_{10} MEE value of 2.95 ± 1.23 m^2/g, two other cities of Nanjing and Shanghai have that of 2.23 ± 0.90 and 2.14 ± 0.85 m^2/g. Ningbo, Suzhou and Nantong have the values of 1.88 ± 0.65, 1.85 ± 0.73 and 1.64 ± 0.65 m^2/g, respectively. It is known that the extinction effect is decided by fine PM due to the combining effect of their extinction cross-section and dominated number concentration (Hand and Malm, 2007), hence the MEE value of PM_{10} is mainly decided by the MEE value of fine PM and the mass ratio of fine PM. From the 1-year field measurement results (Table 2), the rank of $PM_{2.5}$ MEE values agrees well with the rank of PM_{10} MEE for different cities.

The temporal trend of annual MEE value from 2001 to 2011 for each city is investigated (Fig. 5). A general increasing trend of MEE value is observed for all cities except for Ningbo. Compared to the

Table 2
Mass extinction efficiency values of dry PM (Mean ± Standard deviation[a], m^2/g, 550 nm).

City	PM_{10} (2001–2011)	$PM_{2.5}$ (2011–2012)	$PM_{2.5-10}$ (2011–2012)
Nanjing	2.23 ± 0.90	4.23 ± 0.13	0.76 ± 0.09
Nantong	1.64 ± 0.65	–	–
Shanghai	2.14 ± 0.85	Pudong: 4.10 ± 0.06 Puxi: 4.58 ± 0.14	Pudong: 0.46 ± 0.04 Puxi: 0.66 ± 0.20
Suzhou	1.85 ± 0.73	3.93 ± 0.10	0.60 ± 0.09
Hangzhou	2.95 ± 1.23	5.27 ± 0.17	0.23 ± 0.14
Ningbo	1.88 ± 0.65	3.78 ± 0.12	0.66 ± 0.12
Average	2.25 ± 1.02	4.08 ± 0.03	0.58 ± 0.02

[a] Standard deviation in MEE represents the variation of daily value for PM_{10} or given by the multiple regression results for $PM_{2.5}$ and $PM_{2.5-10}$.

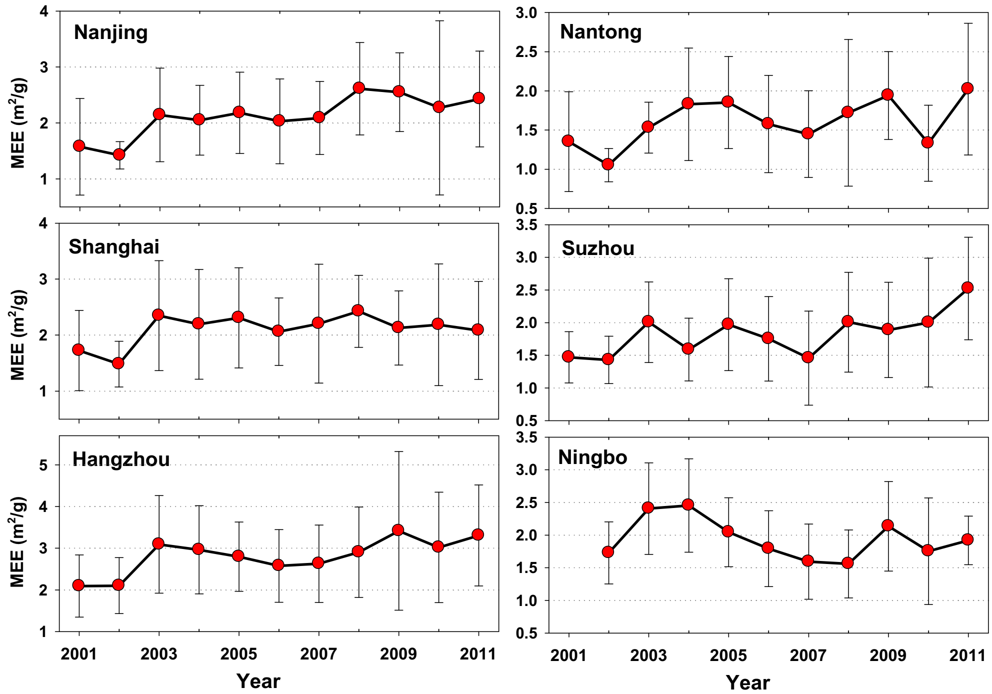

Fig. 5. Variation of MEE value (550 nm) for the YRD cities (2001–2011). The red circle represents the mean value, and the ends of the whiskers represent one standard deviation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

value in 2001, MEE value increases by 21–71% in 2011 for cities except for Ningbo. MEE value increases in 2002–2004, then drops to the level in 2001 by 2011 for the city of Ningbo. As the value of MEE depends on the size distribution and chemical components of particles, the change of MEE could be an indicator for the properties change of aerosol in the YRD. As shown in Fig. 3, PM_{10} mass concentration is decreasing year by year in the past decade for all cities except for Ningbo. The main control efforts include a strengthened PM emission standard for power plants issued in 2003, the installation of electrostatic precipitators (ESP) for 92% of the pulverized coal units, etc. (Wang and Hao, 2012). It is inferred that the reduction of PM_{10} is mainly due to the removal of primary coarse particulate matter. Meanwhile, increasing trend of AOD in eastern China from satellites indicated that the secondary fine aerosol is rising in the YRD region (Guo et al., 2011; Lin et al., 2010). The removal of coarse particles and rising of fine particles both increase the value of MEE for PM_{10}. The increasing of MEE could also account for the inconsistent trend of PM_{10} concentration and visual range in 2001–2011. For the case of Ningbo, the dropping trend of MEE might be caused by the increasing fraction of coarse particles, as the PM_{10} concentration rises.

Based on the field measurement results of 2011–2012, the average MEE values of 2011–2012 in six field observation sites is 4.08 m^2/g for $PM_{2.5}$ with the range of 3.78–5.27 m^2/g for different sites and 0.58 m^2/g for $PM_{2.5-10}$ with the range of 0.23–0.76 m^2/g for different sites (Table 2). The MEE value of fine PM is 7 times coarse PM, which means the extinction effect of coarse PM is so low that it could be neglected as the coarse PM mass concentration is similar to that of fine PM. Only the studies of mass scattering efficiency of $PM_{2.5}$ are found from literatures. Xu et al. (2002) conducted a measurement in Linan, a site in the YRD region, and got the MSE value of 4.0 m^2/g for $PM_{2.5}$, Bergin et al. (2001) and Jung et al. (2009) measured the $PM_{2.5}$ MSE value of Beijing in different year and got the values of 2.6 and 3.4 m^2/g. Hand and Malm (2007) gave the average review value of $PM_{2.5}$ MSE for 3.2 ± 1.3 m^2/g from 32 studies, and $PM_{2.5-10}$ MSE for 0.6 ± 0.3 m^2/g from 6 studies in urban area. The MEE values given in this study includes both the absorption function and scattering function, if the SSA is assumed to be 0.8 (Xu et al., 2012), the related MSE value is to be 3.26 m^2/g, which is very close to that of other studies.

It is noticed that Hangzhou has the largest MEE value of $PM_{2.5}$ with 5.27 m^2/g which is much higher than that of other cities. One major reason might be the high mass concentration ratio of absorption components such as black carbon. The MEE value will grow with the ratio of BC to $PM_{2.5}$ as the individual MEE value of BC is 7.5 ± 1.2 m^2/g (Bond and Bergstrom, 2006), much higher than that of any other components like sulfate, nitrate and organic. From the field measurement results of 2011–2012, the average mass ratio of BC to $PM_{2.5}$ in Hangzhou is 10.8%, much higher than that of other sites in the range of 5.3%–7.5%. Further measurement beyond this study, however, is still necessary to verify the above-stated reason.

3.3. Contribution of particulate matter on extinction coefficient and its hygroscopic growth factor

Based on the results of MEE value under dry conditions, extinction coefficient contribution due to PM_{10} and other factors like relative humidity are estimated from 2001 to 2011 (Fig. 6). The average extinction coefficient due to PM_{10} for all cities is 207 Mm^{-1}(36.2% of the total extinction coefficient) in the past decade in the YRD, with the average RH value of 73%. However, the extinction coefficient contribution by PM_{10} varies significantly in different cities. Hangzhou and Nanjing holds the highest 310 Mm^{-1} (37.5% of total) and 242 Mm^{-1} (32.5% of total) by dry PM_{10}, respectively, while that of Shanghai, Suzhou and Ningbo is 191 Mm^{-1} (52.7%), 184 Mm^{-1} (27.1%) and 164 Mm^{-1} (43.7%), respectively. Nantong has the lowest at 148 Mm^{-1} (33.4%). The absolute contribution of PM_{10} is related to PM_{10} concentration and component, while the contribution of relative humidity is more complicated, which is related to local ambient meteorological conditions and hydrophilic properties of PM. There is no notable

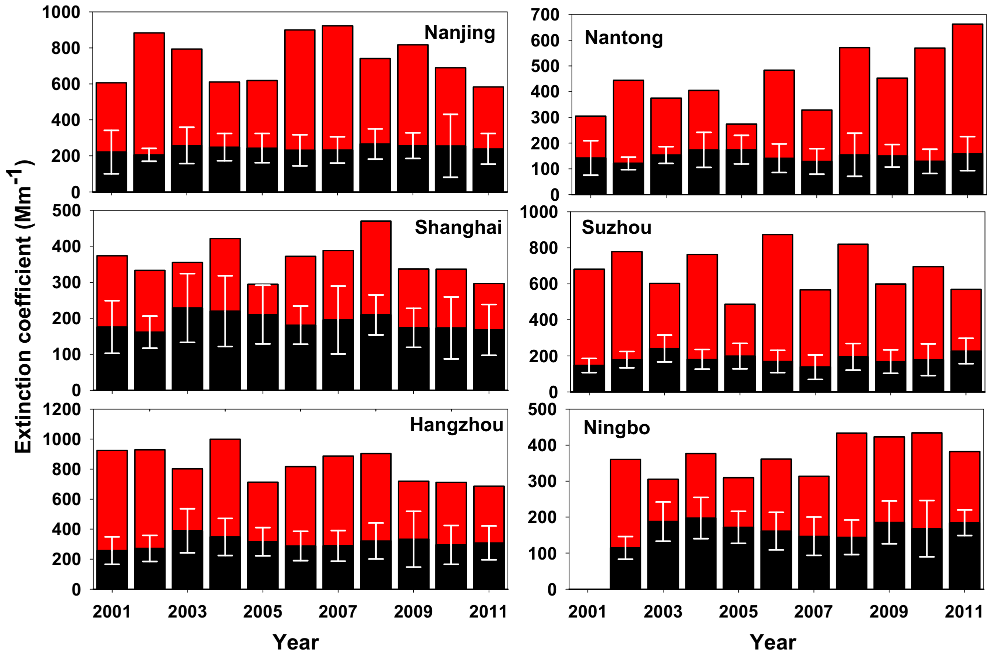

Fig. 6. Annual extinction coefficient (550 nm) due to PM_{10} and remainder for the YRD cities (2001–2011). Black bar represents the contribution due to PM_{10} and the ends of whiskers stand for its one standard deviation, the red bar represents the remainder extinction coefficient by the difference between total extinction coefficient and extinction coefficient due to PM_{10}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

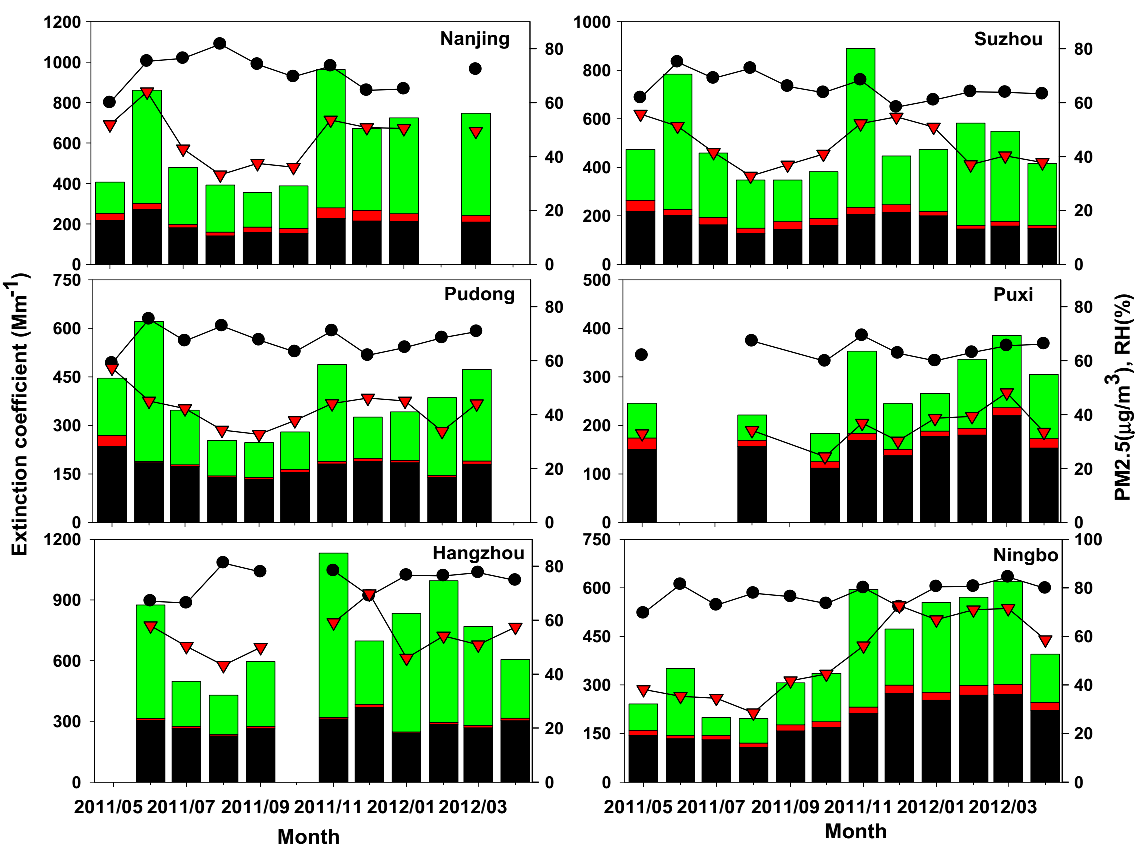

Fig. 7. Monthly extinction coefficient (550 nm) due to $PM_{2.5}$, $PM_{2.5-10}$ and remainder for the YRD cities (2011–2012). Black bar and red bar represents extinction coefficient due to $PM_{2.5}$ and $PM_{2.5\text{-}10}$, while green bar represents the remainder extinction coefficient by the difference between total extinction coefficient and the summary of extinction coefficient due to $PM_{2.5}$ and $PM_{2.5\text{-}10}$. The black circle represents monthly relative humidity while the red triangle represents monthly $PM_{2.5}$ concentration. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

change of absolute contribution or percentage due to PM_{10} between 2001 and 2011 for all cites. The reason for that has been stated previously: fine PM concentration and its chemical constitution have no significant variation, although coarse PM has been reduced considerably in the decade. If the contribution ratio of PM_{10} is assumed at 36.2% (the average RH of 73%) and with MEE value of 2.25 m^2/g in the YRD, it is estimated that daily PM_{10} concentration should be lower than 63 $\mu g/m^3$ in order to keep the daily visual range above 10 km using the threshold selection of 0.05.

From the results based on 1-year field measurement in 2011–2012 (Fig. 7), the average extinction coefficient due to $PM_{2.5}$, $PM_{2.5-10}$ are 198 Mm^{-1} and 20 Mm^{-1} for all sites, and their average contribution ratios to total extinction coefficient are 39.6%, 4.0%. It is comparative with the contribution ratio of relative humidity of 40% to total scattering coefficient from another measurement study in the YRD region (Xu et al., 2002). However, the contribution ratio of $PM_{2.5}$ varies with different sites. Hangzhou has the highest of 285 Mm^{-1} (35.6%) by dry $PM_{2.5}$, while that of Nanjing and Ningbo is 199 Mm^{-1} (33.2%) and 195 Mm^{-1} (48.4%). Suzhou, Pudong and Puxi have the values of 174 Mm^{-1} (34.0%), 172 Mm^{-1} (45.1%) and 162 Mm^{-1} (57.3%). The contribution of coarse particles is in the range of 9–32 Mm^{-1} for different sites. It is so low that it could be neglected when compared with the contribution of fine particles and relative humidity. Furthermore, the seasonal variation of extinction coefficient is notable in Fig. 7. The pollution loading in the months of summer and autumn (July, August, September and October) is much lower than other seasons, either the extinction contribution of PM or that of relative humidity, especially compared with the pollution level of winter months. The meteorological conditions differences in different seasons are the dominant factors for the above seasonal variation (Cheng et al., 2013). Meanwhile there are two peaks in June and November which is possibly caused by the impact of open biomass burning, usually occurred in the two months (Zhu et al., 2012).

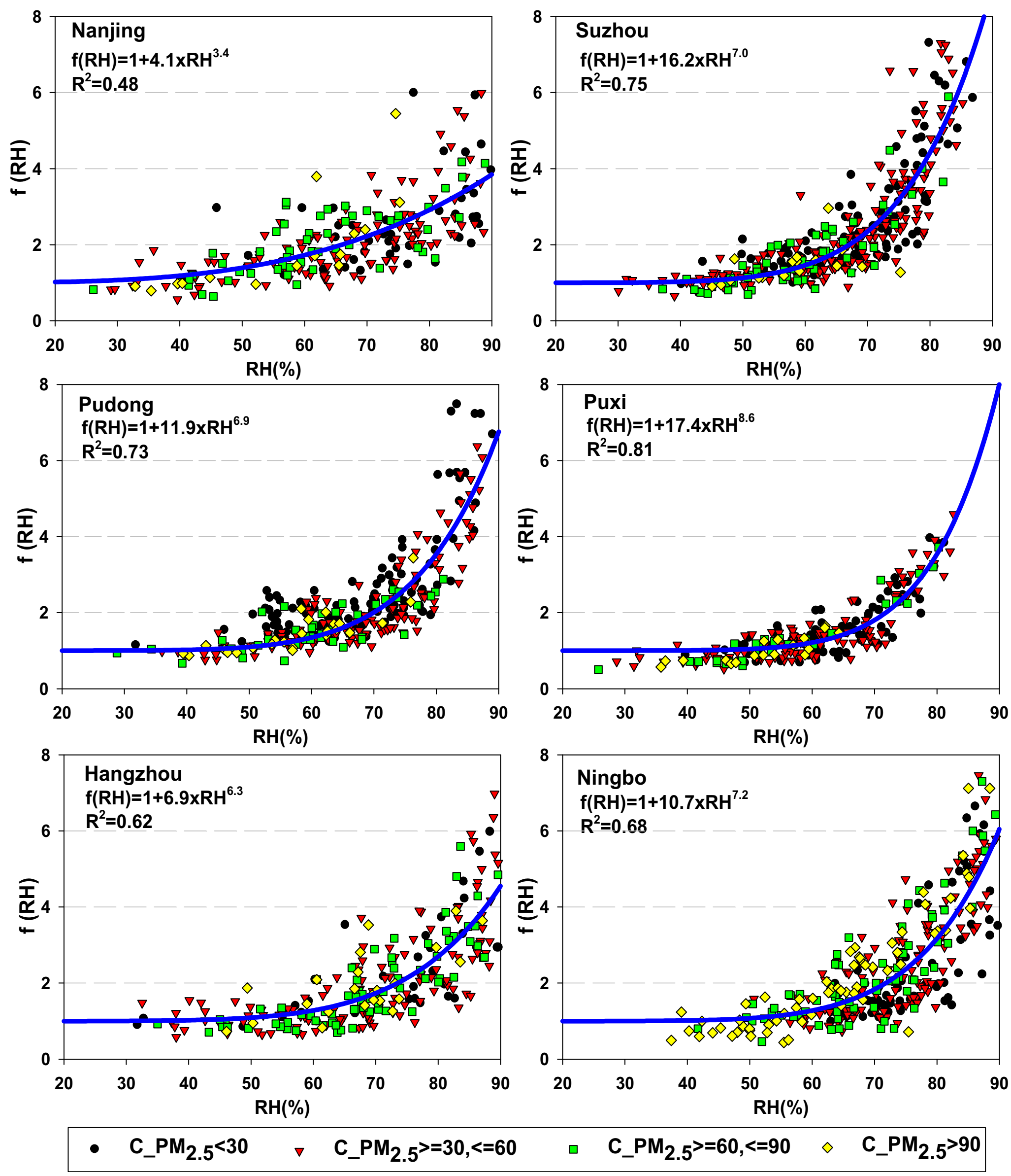

Fig. 8. Hygroscopic growth factor of particulate matter for the YRD cities (2011–2012). The power regression formula and *R* square value are labeled in each graph. The dots with different symbols represent the days with different class of daily $PM_{2.5}$ concentration, i.e., black circle means less than 30 $\mu g/m^3$, red triangle means 30–60 $\mu g/m^3$, greed square means 60–90 $\mu g/m^3$ and yellow diamond means higher than 90 $\mu g/m^3$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

It can also be seen that the extinction coefficient due to PM is closely related to $PM_{2.5}$ concentration, while the extinction coefficient due to RH is related to both relative humidity and $PM_{2.5}$ concentration. The statistical analysis results indicate that the contribution of relative humidity correlated with both relative humidity and $PM_{2.5}$ concentration for all sites, with the Pearson correlation coefficients of 0.50–0.56 and 0.20–0.33, respectively. It is reasonable as with more fine particles, especially soluble components like sulfate and nitrate, they can absorb much more water through the hygroscopic effect, which results in a large extinction coefficient. Hence when the concentration of fine particles is reduced, the absolute extinction coefficient contribution due to relative humidity will also decrease. If the contribution ratio of $PM_{2.5}$ is assumed at 39.6% (the average RH of 70%) and with MEE value of 4.08 m^2/g, it is estimated that daily $PM_{2.5}$ concentration should be lower than 38 $\mu g/m^3$ in order to keep the daily visual range above 10 km in the YRD using the threshold selection of 0.05.

The hygroscopic growth factor of PM is investigated for each site based on the daily scale and is plotted versus relative humidity in Fig. 8. The upper limit of RH is set to 90% in order to exclude the impact of fog and rain events. The power regression with the constant term of "1" (Liu et al., 2008) is conducted to fit the date points. It is seen that the value of *R* square is 0.6–0.8 except for the value of 0.48 for Nanjing site. The regression formula of *f*(RH) for each site is $1 + 4.1 \times RH^{3.4}$ for Nanjing, $1 + 16.2 \times RH^{7.0}$ for Suzhou, $1 + 11.9 \times RH^{6.9}$ for Pudong, $1 + 17.4 \times RH^{8.6}$ for Puxi, $1 + 6.9 \times RH^{6.3}$ for Hangzhou and $1 + 10.7 \times RH^{7.2}$ for Ningbo. Concerning of the annual relative humidity in 2011–2012 for each site (71% of Nanjing, 66% of Suzhou, 68% of Pudong, 64% of Puxi, 73% of Hangzhou, 77% of Ningbo), their according hygroscopic growth factors are 2.28 for Nanjing, 1.88 for Suzhou, 1.83 for Pudong, 1.37 for Puxi, 1.95 for Hangzhou and 2.63 for Ningbo. Although the method in this study is based on the constant value of PM mass extinction efficiency, the *f*(RH) value range of six sites are still close to the results of direct field measurement from other studies summarized by Pan et al. (2009). It is also seen that the *f*(RH)–RH curve is well mixed by the points of different $PM_{2.5}$ mass concentration class, indicated that *f*(RH) value has no direct relationship with $PM_{2.5}$ mass concentration. Actually the value of *f*(RH) is mainly decided by both the RH value and the chemical and physical properties of particulate matter (Pan et al., 2009).

4. Conclusions

In this study, long-term monitoring records and 1-year field measurement datasets are used to investigate haze in the YRD region, an important economic zone in China. In the past thirty years, the visual range in most YRD cities endured a sharp reduction, especially in the period of 1980–2000. From 2001 to 2011, the visual range of all cities exhibited a fluctuating variation around a stable low value. Concentration of fine particulate matter is the dominant factor that determines the change of visual range, although the slight decrease of relative humidity could benefit visibility to some extent.

Mass extinction efficiency is estimated based on different datasets. For the average of all the YRD cities, MEE for PM_{10} is 2.25 m^2/g for the last decade and increases year by year, indicating the control of coarse particles makes PM_{10} more efficient for light extinction. MEE for fine PM and coarse PM are 4.08 m^2/g and 0.58 m^2/g respectively, based on field observation in 2011–2012. The extinction effect of coarse PM could be ignored compared to that of fine PM.

Average extinction coefficient due to PM_{10} for all cities is 207 Mm^{-1} (36.2% of total extinction coefficient) in the past decade. The average extinction coefficient due to $PM_{2.5}$, $PM_{2.5-10}$ and relative humidity is 198 Mm^{-1} (39.6%), 20 Mm^{-1} (4.0%) and 282 Mm^{-1} (56.4%) in 2011–2012. According to the MEE value and contribution of particulate matter, maximum daily concentration of PM_{10} and $PM_{2.5}$ are estimated to be 63 $\mu g/m^3$ (the average RH of 73%) and 38 $\mu g/m^3$ (the average RH of 70%) to keep visual range above 10 km for the YRD. The hygroscopic growth factor is in the range of 1.37–2.63 for all sites with average of 1.99 under their annual average RH value.

The results of this study imply that fine PM is the key to improve visibility in the YRD, as the concentration reduction of fine PM not only lowers the absolute extinction contribution from PM itself, but also reduces the extinction contribution from relative humidity simultaneously.

Acknowledgments

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