Aerosol and Air Quality Research, 16: 1981–1990, 2016

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2016.02.0064

Reconstructed Light Extinction Coefficients of Fine Particulate Matter in Rural Guangzhou, Southern China

Xiaojia Chen[1], Senchao Lai[1,4*], Yuan Gao[2], Yingyi Zhang[1*], Yan Zhao[1], Duohong Chen[3], Junyu Zheng[1], Liuju Zhong[3], Shun-Cheng Lee[2], Bing Chen[1]

[1] *School of Environment and Energy, South China University of Technology, Guangzhou, China*
[2] *Department of Civil and Environmental Engineering, Research Center for Environmental Technology and Management, The Hong Kong Polytechnic University, Hung Hom, Hong Kong*
[3] *Guangdong Provincial Environmental Monitoring Center, Guangzhou, China*
[4] *Department of Multiphase Chemistry, Max Planck Institute for Chemistry, Mainz, Germany*

ABSTRACT

A one-year campaign was conducted to collected $PM_{2.5}$ samples in the rural area of Guangzhou, the largest megacity in South China, from March 2012 to February 2013. Mass concentration of $PM_{2.5}$, carbonaceous fractions (i.e., organic carbon (OC) and elemental carbon (EC)) and 6 water-soluble ions were analyzed. Light extinction coefficient (b_{ext}) of fine particulate matter was reconstructed using the revised IMPROVE formula at the site. The reconstructed b_{ext} was compared with the measured b_{ext} converted from visibility. A good correlation was obtained between the two sets of b_{ext} with a coefficient of determination (R^2) of 0.61 and a slope of 0.99. The average reconstructed b_{ext} in the study was 253.7 ± 162.9 Mm^{-1}. The seasonal reconstructed b_{ext} was in the order of autumn (319.4 ± 207.2 Mm^{-1}) > winter (269.6 ± 175.5 Mm^{-1}) > summer (219.0 ± 129.3 Mm^{-1}) > spring (193.3 ± 94.9 Mm^{-1}). $(NH_4)_2SO_4$ (AS) made a dominant contribution to the light extinction budget, accounting for 61.3% (155.6 ± 108.5 Mm^{-1}) annually, with highest in autumn (68.0%) and lowest in winter (55.2%). Organic matter (OM) was the second largest contributor accounting for 20.5% (52.2 ± 42.7 Mm^{-1}) with highest in winter (23.4%) and lowest in spring (18.0%). The relationship between reconstructed b_{ext} and measured b_{ext} was investigated under the influence of seasonality, visibility and $PM_{2.5}$ concentration. We found that b_{ext} could be reconstructed using revised IMPROVE formula in high $PM_{2.5}$ days (threshold value of ~60 μg m^{-3}). On other hand, the performance of formula was unsatisfactory for b_{ext} reconstruction of in low $PM_{2.5}$ days, when meteorological conditions could have significant impact on visibility.

Keywords: $PM_{2.5}$; Chemical composition; Reconstructed light extinction coefficient; Revised IMPROVE formula; Visibility.

INTRODUCTION

Visibility is an indicator of air quality in urban areas in the absence of special weather conditions (e.g., fog and rain) (Watson, 2002), and its deterioration has become one of the adverse effects of air pollution (Horvath and Noll, 1969). Generally speaking, visibility impairment is caused by scattering and absorption of light by aerosol particles and gases in the atmosphere (Ouimette and Flagan, 1982). It is a complex process with many factors involved including concentrations, size distributions, and composition of aerosol particles as well as meteorological conditions (Watson, 2002). Numbers of studies focused on the connection between visibility and air pollutants by statistical methods (White and Roberts, 1977; Barone *et al.*, 1978; Sloane *et al.*, 1991; Sequeira and Lai, 1998; Kuo *et al.*, 2013). Increasing evidence shows that elevated concentrations of fine particulate matter (aerodynamic diameter ≤ 2.5 μm, $PM_{2.5}$) are the main cause of visibility degradation in urban areas, because fine particles scatter visible light more efficiently than coarse particles (e.g., Ferman *et al.*, 1981; Pitchford, 1982; Malm, 1989; Yuan *et al.*, 2006; Deng *et al.*, 2008). Sulfate and carbonaceous species in $PM_{2.5}$ are usually the main chemical species contributing to visibility degradation in urban areas, whereas nitrates dominate at some locations (Leaderer *et al.*, 1979; Wolff *et al.*, 1982; Appel *et al.*, 1985; Kuo *et al.*, 2013).

Atmospheric light extinction coefficient (b_{ext}) is a fundamental metric used to characterize air pollution impact on visibility. It can be allocated to the following four additive components: light scattering by particles (b_{sp}); light scattering by gases (b_{sg}), which is described by the Rayleigh scattering (RS) theory; light absorption by particles (b_{ap}), which is

* Corresponding author.
Tel.: +86 135 7097 4216
E-mail address: sclai@scut.edu.cn; zhyy@scut.edu.cn

dominated by soot, and light absorption by gases (b_{ag}) which is mainly by nitrogen dioxide (NO_2) (Watson, 2002; Pitchford *et al.*, 2007). While light extinction due to the gaseous components of the atmosphere is well understood and their contributions are relatively small, light extinction caused by particle is more complex than that by gaseous components. When particle size distribution and index of refraction are known, b_{sp} can be quite accurately estimated using Mie theory (Pitchford *et al.*, 2007). This method has been used in many intensive short-term studies (Tao *et al.*, 2014b; Gao *et al.*, 2015). When only aerosol composition data are available, the application of the IMPROVE formulas (including original and revised versions) is an easier and more widely used method than the Mie-theory method, which were established for the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network in Unite States (Hand *et al.*, 2011). The general expression is as follows:

$$b_{ext} = \sum_i MEE_i \times f_i(RH) \times [M]_i \quad (1)$$

where MEE_i is the dry mass extinction efficiency (MEE) of major aerosol species i; $[M]_i$ is the mass concentration of certain aerosol species; and $f_i(RH)$ is the water growth factor for hydrophilic aerosol species. According to the formula, contribution of each aerosol species and the total contribution by aerosol to light extinction can be calculated. Both the original and the revised formulas have been applied in the studies in China (Yang *et al.*, 2007; Tao *et al.*, 2009; Cao *et al.*, 2012; Zhang *et al.*, 2012; Xiao *et al.*, 2014). The major concern in applying the IMPROVE formulas is their universal applicability since the formulas were developed for rural/remote areas in United States (Sisler and Malm, 1994; Hand *et al.*, 2011). This is mainly due to the fact that the dry mass scattering efficiencies (MSEs) and mass absorption efficiencies (MAEs) as well as the humidification factor f(RH) may be variable at different sites under different conditions (Watson, 2002; Jung *et al.*, 2009; Tao *et al.*, 2014a). Some studies such as Jung *et al.* (2009) and Tao *et al.* (2014a) obtained the specific MSEs through multiple linear regression (MLR) method in urban Guangzhou to push the regression slope of estimated b_{ext} versus measured b_{ext} closer to unity. However, it is necessary to investigate the applicability of the formulas in different locations and the relationship with visibility data.

The Pearl River Delta (PRD) region, one of the most developed areas in China, has been suffering from air quality and visibility problems. Haze with simultaneous fine particle enhancement and severe visibility impairment has been frequently observed in the PRD region during the recent decades (Andreae *et al.*, 2008; Deng *et al.*, 2008; Tan *et al.*, 2009). The studies concerning haze and the related light extinction have been extensively carried out (e.g., Cheung *et al.*, 2005; Deng *et al.*, 2008; Jung *et al.*, 2009; Zhang *et al.*, 2013a, b; Tao *et al.*, 2014a; Gao *et al.*, 2015). In this study, we present the results of our measurement of $PM_{2.5}$ and its chemical composition as well as the application of the revised IMPROVE formula at a regional site in the PRD region in order to: (1) understand the relationship of public available visibility and chemical composition of $PM_{2.5}$; (2) evaluate the applicability of the revised IMPROVE formula to light extinction estimation; and (3) assess the contributions of individual components of $PM_{2.5}$ to the total light extinction.

METHODOLOGY

Sample Collection

$PM_{2.5}$ samples were collected in a regional site in the PRD region from March 2012 to February 2013. The sampling site, Tianhu (TH: 23.65°N, 113.63°E), was located in a recreational area ~60 km northeast of Guangzhou downtown. The site has no direct stationary source nearby and it is an ideal site for regional observation. Samples were taken at every 6 days with a duration of 24 h. A mini volume sampler (5 L min^{-1}, Airmetrics, US) equipped with PTFE filter (φ = 47 mm, Pall, US) and a median volume sampler (300 L min^{-1}, Mingye, China) equipped with quartz filter (25 × 20 cm, Pall, US) were used simultaneously for $PM_{2.5}$ sample collection. A total of 51 quartz filters and 52 PTFE samples were collected during the campaign.

Chemical Analysis

The chemical analysis has been described in detail previously by Lai *et al.* (2016). Briefly, the PTFE filters were analyzed for particle mass by gravimetry and for elements (including Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Br and Pb) by X-ray fluorescence (XRF). The quartz filters were used for the analyses of OC and EC, as well as water-soluble ions. Water extracts of the quartz-fiber filter were analyzed for water-soluble ions including Na^+, NH_4^+, K^+, Cl^-, NO_3^-, and SO_4^{2-}, by ion chromatography (DX90, Dionex, US). The OC and EC were determined using the thermo-optical transmittance (TOT) method (NIOSH protocol) by an aerosol OC/EC analyzer (Sunset Laboratory Inc., US).

Visibility and Other Meteorological Parameters

The meteorological data, including visibility (Vis), temperature (Temp), relative humidity (RH), and wind speed (WS) during the sampling period at Guangzhou Baiyun International Airport (BYA, 23.40°N, 113.30°E, ~44 km southwest of TH) were obtained from weather underground website (http://wunderground.com/) (Tan *et al.*, 2009; Zhang *et al.*, 2013a).

Reconstruction of $PM_{2.5}$ and Light Extinction

The dry $PM_{2.5}$ mass concentration was reconstructed mainly following the approach in fine PM reconstruction in IMPROVE (Hand *et al.*, 2011). Reconstructed $PM_{2.5}$ is calculated with the following algorithm:

$$PM_{2.5} = [AS] + [AN] + [OM] + [LAC] + [SS] + [FS] \quad (2)$$

where [AS], [AN], [OM], [LAC], [SS] and [FS] are the mass concentrations of ammonium sulfate ([AS] = 1.375 $[SO_4^{2-}]$), ammonium nitrate ([AN] = 1.29 $[NO_3^-]$), organic matter ([OM] = 1.6 [OC]), light absorbing carbon (LAC) (referred to as EC in this study, [LAC] = [EC]), sea salts ([SS] = 1.47

$[Na^+]$ + $[Cl^-]$ (Quinn *et al.*, 2000; Quinn *et al.*, 2001) and fine soil ([FS] = 2.2 [Al] + 2.49 [Si] + 1.63 [Ca] + 2.42 [Fe] + 1.94 [Ti]), respectively.

To investigate the contribution of each $PM_{2.5}$ chemical component to b_{ext} (in Mm^{-1}), a revised formula developed by the IMPROVE program is used (Pitchford *et al.*, 2007; Cao *et al.*, 2012; Wang *et al.*, 2013):

$$b_{ext} = 2.2 \times f_S(RH) \times [\text{Small AS}] + 4.8 \times f_L(RH) \times [\text{Large AS}] + 2.4 \times f_S(RH) \times [\text{Small AN}] + 5.1 \times f_L(RH) \times [\text{Large AN}] + 2.8 \times [\text{Small OM}] + 6.1 \times [\text{Large OM}] + 10 \times [\text{EC}] + 1.7 \times f_{SS}(RH) \times [\text{SS}] + 1 \times [\text{FS}] + 0.6 \times [\text{Coarse Mass}] + \text{Rayleigh Scattering (Site Specific)} + 0.33 \times NO_2\ (\text{ppb}) \quad (3)$$

The revised IMPROVE splits AS, AN and OM into small and large particle size modes. The large mode represents aged and/or cloud processed particles, whereas the small mode represents freshly formed particles. The apportionment of total concentration of sulfate into the small and large size fractions is accomplished using the following equations:

$$[\text{Large AS}] = [\text{Total AS}]^2/20; \text{ for } [\text{Total AS}] < 20\ \mu g\ m^{-3}$$
$$[\text{Large AS}] = [\text{Total AS}]; \text{ for } [\text{Total AS}] \geq 20\ \mu g\ m^{-3}$$
$$[\text{Small AS}] = [\text{Total AS}] - [\text{Large AS}]$$

If the total concentration of a component is less than 20 $\mu g\ m^{-3}$, the fraction of the fine particle component in the large mode is estimated by dividing the square of total concentration of the component by 20 $\mu g\ m^{-3}$. Otherwise, all of it is assumed to be in the large mode. The same method is used to separate total AN and OM concentrations into large and small size fractions. The numbers in the equation are the dry mass extinction efficiencies assigned to each species corresponding to 550 nm. The dry mass $PM_{2.5}$ scattering efficiencies for small- and large-mode AS (2.2 and 4.8 $m^2\ g^{-1}$), AN (2.4 and 5.1 $m^2\ g^{-1}$), OM (2.8 and 6.1 $m^2\ g^{-1}$) and the dry scattering efficiency for $PM_{2.5}$ sea salt of 1.7 $m^2\ g^{-1}$ were calculated using the Mie theory at a wavelength of 550 nm. f(RH) is the humidification factor ($f(RH) = b_{sp,RH}/b_{sp,dry}$) representing the enhancement of b_{sp} caused by hygroscopic growth. RH growth curves of $f_S(RH)$, $f_L(RH)$, and $f_{SS}(RH)$ of AS, AN, and SS refer to the work of Pitchford *et al.* (2007). We excluded the contribution of coarse mass and NO_2 due to their insignificant contribution to b_{ext} (Cheung *et al.*, 2005; Jung *et al.*, 2009; Gao *et al.*, 2015). A constant 10 Mm^{-1} is assigned to $b_{Rayleigh}$ (Sisler and Malm, 2000; Hand *et al.*, 2011).

In the calculation, sulfate is assumed to be fully neutralized ammonium sulfate, nitrate is assumed to be in the form of ammonium nitrate, and OM is calculated by OC concentrations multiplying by a factor of 1.6 (Turpin and Lim, 2001; Lai *et al.*, 2016). If there is inadequate ammonia in the atmosphere to fully neutralize sulfuric acid, ammoniated sulfate ion can be estimated from independent measurements of sulfate ion and ammonium ion as follows (Malm and Day, 2001; Tao *et al.*, 2009):

$$[\text{Sulfate}] = (0.944)\ [NH_4^+] + (1.02)\ [SO_4^{2-}] \quad (4)$$

where [Sulfate] is the mass concentration of the ammoniated sulfate; $[SO_4^{2-}]$ is the concentration of sulfate ion and $[NH_4^+]$ is the concentration of ammonium ion after adjusting for ammonium associated with ammonium nitrate. Examination of the scatter plot of 2 ($[SO_4^{2-}]$ + $[NO_3^-]$) and $[NH_4^+]$ (in moles) (Fig. S3) and a comparison of the calculated versus the measured NH_4^+ concentrations (Fig. S4) obtained in the present study indicated that SO_4^{2-}, NO_3^- and NH_4^+ predominantly existed as $(NH_4)_2SO_4$ and NH_4NO_3.

The visibility data were converted to b_{ext} using Koschmeider equation (Horvath, 1971; Cheng *et al.*, 2013):

$$b_{ext} = 2.996/\text{Vis} \quad (5)$$

RESULTS AND DISCUSSION

Data Overview

The annual average concentration of $PM_{2.5}$ was 44.2 ± 25.8 $\mu g\ m^{-3}$, ranging from 16.3 to 140.0 $\mu g\ m^{-3}$. A seasonal variation in $PM_{2.5}$ mass concentrations was observed, with higher concentrations in autumn (67.1 ± 33.2 $\mu g\ m^{-3}$) and winter (40.8 ± 20.2 $\mu g\ m^{-3}$), and lower concentrations in spring (31.3 ± 12.4 $\mu g\ m^{-3}$) and summer (36.8 ± 18.6 $\mu g\ m^{-3}$). SO_4^{2-} was the largest contributor to $PM_{2.5}$ mass concentration (28.6%) followed by OC (13.8%) and NH_4^+ (12.0%). Good correlation of $R^2 = 0.80$ was found between the measured and reconstructed mass concentrations (see Fig. S1). It confirms the validity of the gravimetric and chemical components analyses. More details of the concentrations of $PM_{2.5}$ and the major chemical components at TH and the comparison with other previous studies in the region refer to our recent publication (Table 1 and Table 2 in Lai *et al.* (2016), respectively).

From March 18, 2012 to February 23, 2013, the daily averaged visibility varied from 2 to 24 km, with an average of 8.0 ± 2.8 km. The seasonal visibility ranked in the order of summer (8.7 km) > autumn (8.2 km) > winter (7.9 km) > spring (7.0 km). The seasonal pattern is consistent with the result observed in Guangzhou (Chang *et al.*, 2009). The percentage of days with daily averaged visibility less than 10 km was 92.0%, 62.0%, 75.8% and 55.2% in spring, summer, autumn and winter, respectively. If we adopt the definition of haze days characterized by visibility less than 10 km and RH < 90% without precipitation events (Deng *et al.*, 2008), then the frequency of haze days was 33.3%, 16.3%, 44.0% and 43.5%, respectively in four seasons. It can be seen that when considering the effect of RH, the relative changes of frequency of poor visibility (less than 10 km) were larger in spring and summer than those in autumn and winter. It suggests that larger fraction of low visibility occurred in spring and summer was due to the effect of high RH than in autumn and winter. Better visibility condition in summer could be mainly attributed to greater vertical mixing and horizontal dispersion than other seasons (Deng *et al.*, 2011; Tao *et al.*, 2014a).

Reconstructed b_{ext} Using IMPROVE Formula

Four samples with corresponding daily RH ≥ 90% were excluded to eliminate the effect of high RH (Doyle and

Dorling, 2002; Watson, 2002; Lee *et al.*, 2014). Totally, 47 samples were used for the light extinction analysis. The comparison of reconstructed b_{ext} and measured b_{ext} is shown in Fig. 1. The R^2 for the regression of reconstructed b_{ext} versus measured b_{ext} was 0.61 and the slope was 0.99. It shows that the revised IMPROVE formula can provide a reasonable estimate of light extinction in this study. Compared with the results reported using revised IMPROVE formula under ambient condition, the correlation was better than that in a study in urban Guangzhou (R^2 = 0.50) (Zhang *et al.*, 2013a) but worse than those in urban Guangzhou in winter (R^2 = 0.83) (Tao *et al.*, 2012) and Chengdu (R^2 = 0.77) (Wang *et al.*, 2013). Nevertheless, the negative intercept indicates the influence of other factors (see more discussion on the applicability of the revised IMPROVE formula). Sensitivity test shows that the slope and the R^2 are not sensitive to the selection of OM/OC ratio from 1.6 to 2.0 (Fig. S8).

Based on Eq. (3), the average reconstructed b_{ext} of 47 samples was 253.7 ± 162.9 Mm^{-1}. The value was smaller than those obtained in other studies in China, for example, 912 ± 882 Mm^{-1} in Xi'an (Cao *et al.*, 2012), 900 ± 623 Mm^{-1} in Chengdu (Wang *et al.*, 2013), 326 ± 248 Mm^{-1} in Guangzhou (Tao *et al.*, 2014a) and 292 Mm^{-1} in Jinan (Yang *et al.*, 2007). The seasonal median of reconstructed b_{ext} was in the order of autumn (257.3 ± 207.2 Mm^{-1}) > winter (180.7 ± 175.5 Mm^{-1}) > spring (171.6 ± 129.3 Mm^{-1}) > summer (164.5 ± 94.9 Mm^{-1}). The median value of reconstructed b_{ext} in spring was higher than that in summer. The average value of reconstructed b_{ext} was in the order of autumn (319.4 ± 207.2 Mm^{-1}) > winter (269.6 ± 175.5 Mm^{-1}) > summer (219.0 ± 129.3 Mm^{-1}) > spring (193.3 ± 94.9 Mm^{-1}). The seasonal pattern is similar with those observed in urban Guangzhou (Tao *et al.*, 2014a), Hong Kong (Zhang *et al.*, 2013b), Xiamen (Zhang *et al.*, 2012) and Chengdu (Wang *et al.*, 2013). This could be due to the samples collected in several high $PM_{2.5}$ days.

The average contributions of AS, AN, OM, EC, SS, FS and RS to the light extinction budget were 61.3% (155.6 ± 108.5 Mm^{-1}), 7.8% (19.7 ± 27.7 Mm^{-1}), 20.5% (52.2 ± 42.7 Mm^{-1}), 3.3% (8.4 ± 4.0 Mm^{-1}), 2.3% (5.8 ± 2.7 Mm^{-1}), 0.9% (2.2 ± 1.5 Mm^{-1}) and 3.9% (10.0 Mm^{-1}), respectively (Fig. 2). The predominant contribution of sulfate to aerosol light extinction budget is consistent with the results from many other studies, such as in Xi'an (39.8%) (Cao *et al.*, 2012), Jinan (41%) (Yang *et al.*, 2007) and Guangzhou (50 ± 11%) (Tao *et al.*, 2014a). The contribution of OM was comparable to those in mentioned studies, i.e., 23.8% in Xi'an, 22% in Jinan and 19% in Guangzhou, while the contribution of AN was much lower than those in these studies. The small contribution of AN was mainly due to its relatively low abundance in $PM_{2.5}$ (accounting for 7.6% on annual basis), while large contribution of AS was attributed to its dominant abundance as well as the influence of hygroscopic growth effect. Seasonally, the highest contribution of AS was found in autumn (68.0%) but the lowest was in winter (55.2%). The highest contribution of OM was found in winter (23.4%) and the lowest was in spring (18.0%). AN had the highest contribution to b_{ext} in winter (11.2%) but the lowest in autumn (3.8%). The contribution of EC, FS and RS to light extinction were relatively constant in different seasons.

Applicability of IMPROVE Formula

As mentioned in introduction section, the attempts have been made to localize the IMPROVE formulas in China. They focused on the regression slope of the reconstructed b_{sp} or/and b_{ext} versus measured b_{sp} or/and b_{ext}. The variation of the slope is attributed to the MSEs for scattering species such as AS and AN, and MAEs for absorption species (i.e., EC). Furthermore, the assumption that OM is not hygroscopic is subject to the increasing evidence that organics may

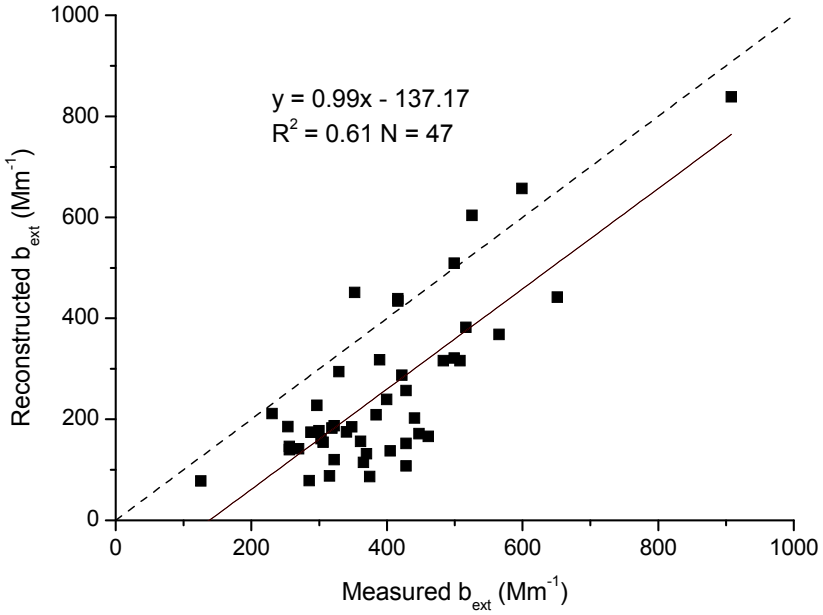

Fig. 1. Scatter plot of reconstructed b_{ext} based on the IMPROVE formula versus measured b_{ext}.

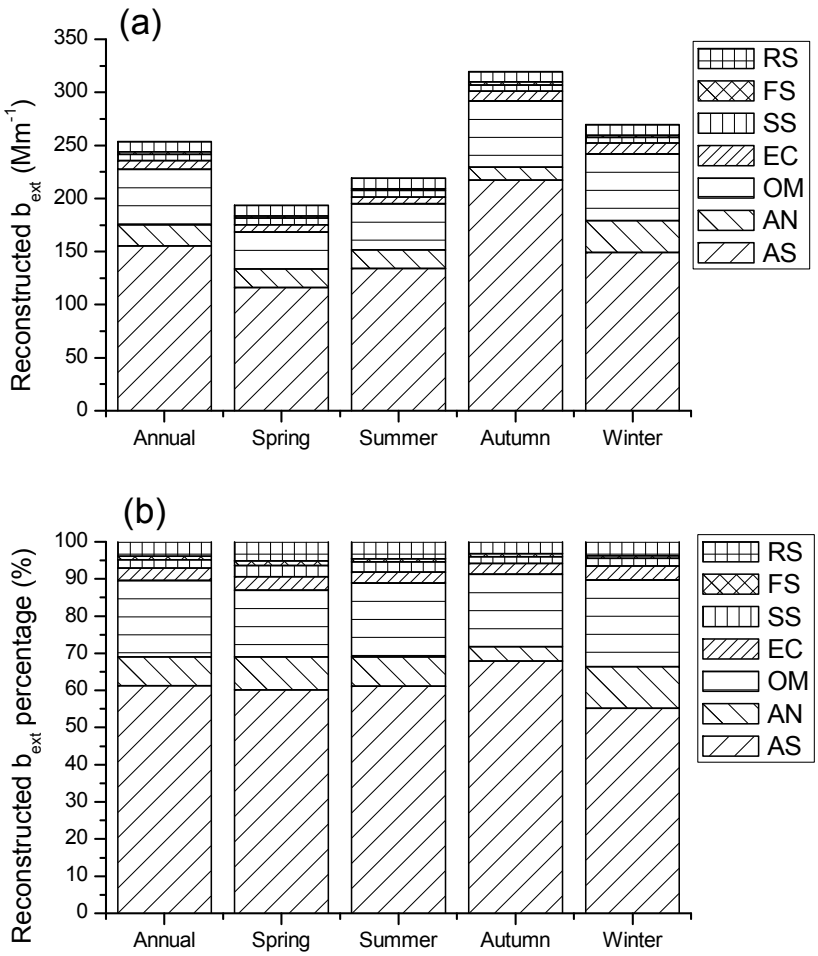

Fig. 2. Light extinction budget for four seasons.

Table 1. Statistics of $PM_{2.5}$ concentrations and light extinction.

	$PM_{2.5\text{-rec}}$ ($\mu g\ m^{-3}$)	$PM_{2.5\text{-mea}}$ ($\mu g\ m^{-3}$)	$b_{ext\text{-rec}}$ (Mm^{-1})	$b_{ext\text{-mea}}$ (Mm^{-1})	ME[a] (Mm^{-1})	MAE[b] (Mm^{-1})	MRE[c]	MARE[d]
Spring-Summer	30.1	36.8	205.5	382.4	–176.91	180.80	–0.47	0.48
Autumn-Winter	42.8	53.4	292.6	403.0	–110.41	129.25	–0.30	0.34
Best25% Visibility[e]	25.3	36.1	156.3	264.1	–107.80	107.80	–0.40	0.40
Worst25% Visibility[e]	56.8	65.2	424.3	555.3	–131.01	155.35	–0.26	0.30
Lowest25% $PM_{2.5}$[f]	19.2	21.0	130.9	321.8	–187.78	187.78	–0.57	0.57
Highest25% $PM_{2.5}$[f]	63.9	67.4	446.6	464.3	–17.68	65.29	–0.04	0.15

[a] ME: mean error of reconstructed and measured b_{ext}; [b] MAE: mean absolute error of reconstructed and measured b_{ext}; [c] MRE: mean relative error of reconstructed and measured b_{ext}; [d] MARE: mean absolute relative error of reconstructed and measured b_{ext}.
[e] Best25%/Worst25% visibility days.
[f] Lowest25%/Highest25% measured $PM_{2.5}$.

account for an important fraction of aerosol hygroscopic growth (Watson *et al.*, 2008). Here we present our assessment on the applicability of IMPROVE formula under the influence of seasonality, visibility and PM mass concentration. The statistics of measured and reconstructed $PM_{2.5}$ concentrations and b_{ext} in different groups are summarized in Table 1. Statistical measures, i.e., mean error (ME), mean absolute error (MAE), mean relative error (MRE) and mean absolute relative error (MARE), are shown.

To evaluate the seasonal effect, we categorized the samples into two groups, i.e., Spring-Summer and Autumn-Winter, due to the higher b_{ext} reconstructed in autumn and winter periods. The correlation between reconstructed and measured b_{ext} in Autumn-Winter samples (R^2 = 0.70, $p < 0.01$) (Fig. 3(b)) is better than that in Spring-Summer (R^2 = 0.40, $p < 0.01$) (Fig. 3(a)). Lower error measures including ME, MAE, MRE and MARE were observed in Autumn-Winter samples than those in Spring-Summer samples. Nevertheless,

seasonality does not appear to be an important factor to affect the agreement between measured and reconstructed b_{ext}.

Comparison was further made between the Best25% and Worst25% visibility days based on daily visibility. The correlation between measured and reconstructed b_{ext} in the Worst25% visibility days ($R^2 = 0.64$, $p < 0.01$) (Fig. 3(d)) was much better than that in the Best25% visibility days ($R^2 = 0.19$, $p = 0.16$) (Fig. 3(c)). The MRE and MARE were lower in the Worst25% visibility days than those in the Best25% days even though ME and MAE displayed contrary result. It shows that the revised IMPROVE formula is more suitable for b_{ext} estimation in hazy days.

The correlations between measured and reconstructed b_{ext} in Lowest25% and Highest25% $PM_{2.5}$ groups were further investigated. Strong and significant correlation was found in the Highest25% $PM_{2.5}$ samples ($R^2 = 0.82$, $p < 0.01$) with the slope of 0.97 (Fig. 3(f)). Moreover, ME, MAE, MRE and MARE were much lower in the Highest25% $PM_{2.5}$ samples than those in the Lowest25% $PM_{2.5}$ group. On the other hand, very poor correlation was observed between

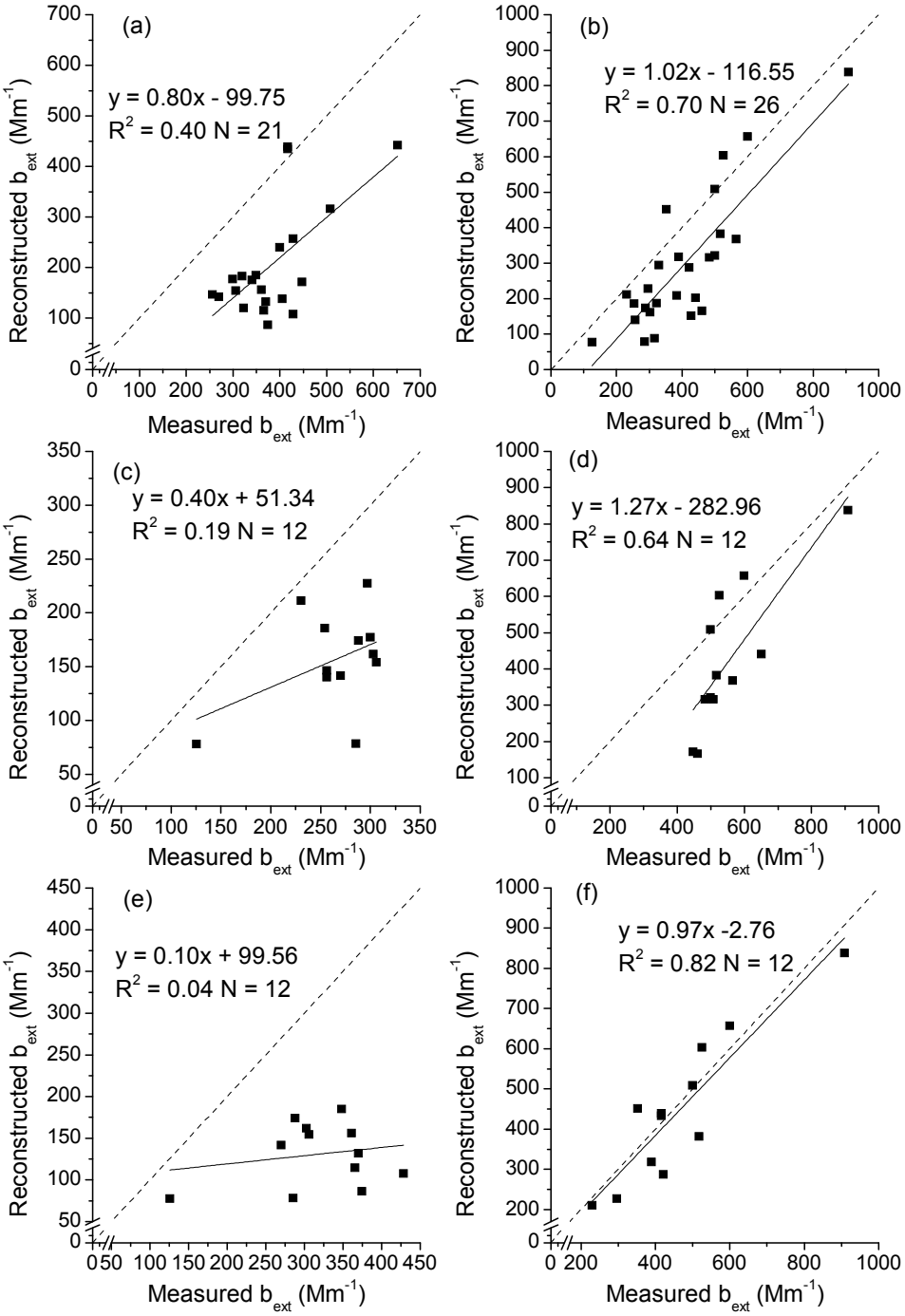

Fig. 3. Scatter plots of reconstructed b_{ext} versus measured b_{ext}: (a) Spring–Summer; (b) Autumn–Winter; (c) Best25% visibility days; (d) Worst25% visibility days; (e) Lowest25% measured $PM_{2.5}$; (f) Highest25% measured $PM_{2.5}$.

measured and reconstructed b_{ext} in Lowest25% $PM_{2.5}$ group ($R^2 = 0.04$, $p = 0.53$) (Fig. 3(e)), suggesting that the formula could not reconstruct the b_{ext} using PM chemical components during low $PM_{2.5}$ days.

Therefore, the range of mass concentration of $PM_{2.5}$ should be taken into account when the revised IMPROVE formula is applied to estimate b_{ext}. We investigated the measured and reconstructed b_{ext} in different mass concentration range (larger than 50%, 75%, 80% and 90% percentiles of measured $PM_{2.5}$). It was found that R^2 increased from 0.65 to 0.90, and the slope increased from 0.94 to 0.97 as the threshold value varied from 50% to 90% percentiles (the slope for the 80% percentiles was 0.95). However, given the good correlation for the Highest25% $PM_{2.5}$ samples, i.e. $PM_{2.5}$ samples larger than 75% percentiles ($R^2 = 0.82$, slope = 0.97), it is reasonable to choose the 75% percentiles (57.6 μg m^{-3}) as the threshold value. Then we arbitrarily suggest that the $PM_{2.5}$ concentration of 60 μg m^{-3} could be a possible threshold for b_{ext} estimation using the revised IMPROVE formula. Nevertheless, this threshold value is really crude and should be tested in more future studies.

Using correlation analysis, we found that the visibility correlated significantly with the three meteorological parameters, that is r of –0.85 with RH ($p < 0.01$), of –0.59 with temperature ($p < 0.05$) and of –0.58 with wind speed ($p < 0.05$) in the Lowest25% measured $PM_{2.5}$ samples. In the Highest25% measured $PM_{2.5}$ samples, significant correlation was only observed between visibility and RH ($r = –0.63$, $p < 0.05$) among the meteorological parameters (Table 2). It suggests that meteorological parameters exerted a stronger influence on light extinction for the Lowest25% measured $PM_{2.5}$ days than those for Highest25%. It may partly explain why the correlations of reconstructed and measured b_{ext} in low concentration samples were poorer than those in high ones.

Although the revised IMPROVE formula has been proved to be applicable for b_{ext} estimation, uncertainty still needs to be considered. Our visibility data was obtained from a public resource and they were recorded in a site about 40 km from the sampling site. Although the data were obtained from two sites and time resolution is on daily basis, the revised IMPROVE formula still works quite well for the b_{ext} estimation. Therefore, the uncertainty caused by the difference of visibility data seems minor and acceptable. A previous study (Horvath and Noll, 1969) has also pointed out that no statistical difference between the visibility data measured at two sites with about 20 km distance. It suggests that the revised IMPROVE formula can be applied in a broad region rather than limited in a small spot.

Nowadays, the observation of $PM_{2.5}$ has been conducted in many sampling sites and it is more widespread than the optical property observation (e.g., measurements of visibility, b_{sp}, b_{ap} etc.). Estimation using revised IMPROVE formula could be a simple and applicable method to estimate visibility and understand its adverse effects locally and regionally. From the above discussion, it should be notice that the revised IMPROVE formula can be successfully applied for b_{ext} estimation in high $PM_{2.5}$/visibility events. However, it may not be suitable to apply the formula during the periods with low $PM_{2.5}$/visibility or high RH.

CONCLUSION

The relationship between visibility and revised IMPROVE formula was used to evaluate the contribution of $PM_{2.5}$ to reduced visibility at a regional site in the PRD region from March 2012 to February 2013. The revised IMPROVE formula was used to reconstruct b_{ext} based on the data of chemical components of $PM_{2.5}$. The reconstructed b_{ext} had a significant correlation with the measured b_{ext} converted from visibility data ($R^2 = 0.61$ and slope = 0.99). It shows that the revised IMPROVE formula can be well applied in the PRD region. From our reconstruction of b_{ext}, AS was the dominant contributor (61.3%) to the light extinction budget while OM was the second largest contributor that accounted for 20.5%. AN accounted for 7.8% and other chemical species together with RS contributed only about 10%. Relationship between the reconstructed and measured b_{ext} was investigated regarding the influence of seasonality, visibility and fine particle concentration. We found that better correlations between reconstructed and measured b_{ext} was observed in the days with relatively high $PM_{2.5}$ and a threshold value of 60 μg m^{-3} was suggested. It indicates that the application of the revised IMPROVE formula is conditional on the pollution of fine particulate matter as well as the meteorological conditions. Chemical components related to light extinction in $PM_{2.5}$ are the major constraints for visibility impairment in polluted days. However, when $PM_{2.5}$ concentration decreases, meteorological conditions become more important factors to influence the visibility. In order to obtain a reasonable evaluation of reconstructed b_{ext}, some unusual events that can deteriorate visibility such as precipitation, high RH (90% or less) need to be excluded. Measured $PM_{2.5}$ concentration needs to be high enough so that the effect of the $PM_{2.5}$ on visibility would not be overwhelmed by the meteorological parameters. In the future work, in order to avoid the systematic uncertainty from the data of different sites, simultaneous measurements of PM and optical parameters as well as meteorological parameters are recommended. Besides, to obtain reliable statistical results, the sampling frequency can also be adjusted to increase the number of samples.

Table 2. Correlation coefficients of visibility with meteorological parameters and reconstructed species for the Lowest25% and the Highest25% of measured $PM_{2.5}$.

	RH	Temp	WS	AS	AN	OM	EC	SS	FS
Lowest25% measured $PM_{2.5}$	–0.85**	–0.59*	0.58*	–0.26	0.64*	0.12	0.35	0.31	0.82**
Highest25% measured $PM_{2.5}$	–0.63*	0.14	0.55	–0.64*	–0.33	–0.83**	–0.84**	–0.57*	–0.27

* Correlation is significant at the 0.05 level (2-tailed test). ** Correlation is significant at the 0.01 level (2-tailed test).

ACKNOWLEDGMENTS

This work is supported by the joint project of Guangdong-National Natural Science Foundation of China (Grant No. U1033301) and the National Natural Science Foundation of China (Grant No. 41105083, 41275130 and 41105084). Senchao Lai would like to thank the support of the China Scholarship Council.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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Received for review, February 9, 2016
Revised, May 9, 2016
Accepted, May 31, 2016