Chemical Composition of PM$_{2.5}$ and its Impact on Visibility in Guangzhou, Southern China

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ABSTRACT

A one-year field experiment was conducted in 2013 at an urban and suburban site in Guangzhou, Southern China to study the chemical compositions of PM$_{2.5}$ and reconstruct the IMPROVE Algorithm to investigate the impact of aerosol components on visibility. Annual average PM$_{2.5}$ mass concentration was 61.3 ± 27.6 and 54.2 ± 29.7 µg m$^{-3}$ at the urban and suburban site, with organic matter (OM), sulfate (SO$_4^{2-}$), and nitrate (NO$_3^-$) among the dominant components, accounting for 40.3%, 16.3%, and 8.0% of the PM$_{2.5}$ mass concentration respectively. Based on the modified IMPROVE Algorithm, the localized Mass Scattering Efficiencies (MSE) for sulfate and nitrate was obtained, with values of 2.16 ± 0.34 m$^2$ g$^{-1}$ and 2.63 ± 0.66 m$^2$ g$^{-1}$ at urban site and 2.22 ± 0.31 m$^2$ g$^{-1}$ and 2.76 ± 0.84 m$^2$ g$^{-1}$ at suburban site. Hygroscopic growth factors (Gf) for OM and EC were also taken into consideration with average values of 1.28 ± 0.13 m$^2$ g$^{-1}$ and 1.15 ± 0.11 m$^2$ g$^{-1}$ at the urban site and 1.18 ± 0.09 m$^2$ g$^{-1}$ and 1.10 ± 0.09 m$^2$ g$^{-1}$ at the suburban site. The estimated total light extinction coefficient was 294.7 ± 106.9 and 255.8 ± 119.0 Mm$^{-1}$ at the urban and suburban site, with OM, SO$_4^{2-}$ and NO$_3^-$ contributing 41.7%, 16.5% and 11.5% at the urban site, and 42.1%, 21.3% and 9.1% at the suburban site. Secondary water-soluble ions and OM as a whole was becoming increasingly vital under polluted conditions, with nitrate in particular being more important under heavily polluted conditions in Guangzhou.

Keywords: Chemical composition; Visibility; Light extinction coefficient; IMPROVE; Hygroscopic growth factor.

INTRODUCTION

Atmospheric aerosols impair visibility, negatively affect human health, and directly and indirectly impact regional and global climate (Chung and Seinfeld, 2005; Liu et al., 2011; Chen et al., 2013; Huang et al., 2014). Visibility is inversely proportional to the light extinction coefficient (Koschmieder, 1924), with particles contributing about 90% of the total column light extinction, and thus playing the critical role in visibility degradation. Given both the total loading values and their large extinction coefficients, the most important species include secondary water-soluble inorganic aerosol (e.g., ammonium sulfate and ammonium nitrate), organic carbon (OC), and elemental carbon (EC) (Cheung et al., 2005; Jung et al., 2009a; Tao et al., 2009). The IMPROVE Algorithms have been proposed to estimate the light extinction coefficient based on aerosol mass and chemical compositions (Sisler and Malm, 2000; Pitchford et al., 2007), and have been widely used to reconstruct light extinction coefficient and study contributions from individual aerosol chemical components (Cheung et al., 2005; Jung et al., 2009a; Tao et al., 2009; Cao et al., 2012; Han et al., 2012; Wang et al., 2015; Chen et al., 2016).

The IMPROVE Algorithms are empirical formulas developed from using long-term observations at remote sites (e.g., parks, mountains, and wilderness areas) in the U.S, meaning that direct application to other locations can introduce errors on the order of $-5.0\%$ to $+37\%$ due to the different physical, chemical, mixing, and optical properties of PM$_{2.5}$ at different locations (Bian, 2011; Jung et al., 2009a, b; Cao et al., 2012). To address this issue, a set of localized IMPROVE Algorithms has thus been developed for urban locations (Bian, 2011, Tao et al., 2014, 2015). Additionally, the IMPROVE Algorithms assumed that OC...
and EC were weakly or non-hygroscopic, and the respective hygroscopic growth factor for OC and EC, equal to one (Sisler and Malm, 2000; Pitchford et al., 2007). However, typically 20–80% of OC is water-soluble (Mader et al., 1994; Zappoli et al., 1999), and coating, aging, or chemical reactions occurring on the OC and EC particles would modify the hygroscopicity of aerosol and further affect the optical properties of the particles (Kanakidou et al., 2005; Andreae and Rosenfeld, 2008; Zhang et al., 2008; Cohen and Prinn, 2011; Cohen et al., 2011; Liu et al., 2013; Park et al., 2013; Cohen and Wang, 2014; Kirillova et al., 2014). Previous studies found that the hygroscopic growth factor \( G_f \) was small for fresh EC (refer to \( G_f,EC \) here) (< 1.1) (Pitchford et al., 1991; Hagen et al., 1992; Weingartner et al., 1997; Gysel et al., 2003) and increased to 1.2–1.3 due to the processes such as aging or coating by inorganic aerosols (Wyslouzil et al., 1994; Popovicheva et al., 2008; McMeeking et al., 2011; Cohen and Wang, 2014), or even could extend up to 1.4–1.6 (Khalizov et al., 2008; Liu et al., 2013). While \( G_f \) for OC (refer to \( G_f,OC \) here) showed a wide range of 1.0–1.6 (Carrico et al., 2005; McFiggans et al., 2005; Gysel et al., 2007; Kamilli et al., 2014), with the value possibly being as high as 1.6–2.0 for some organic acid mixed with water-soluble ions (Wise et al., 2003; Brooks et al., 2004). The overall conclusion is that \( G_f,OC \) is found to be larger than \( G_f,EC \) and that both \( G_f \) for carbonaceous aerosol is relatively lower than for inorganic water-soluble ions (Koehler et al., 2006; Kamilli et al., 2014). Unlike the \( G_f \) for sulfate and nitrate, which have been widely investigated and water growth curves as a function of relative humidity were built (Sisler and Malm, 2000; Pitchford et al., 2007), most of \( G_f,OC \) and \( G_f,EC \) mentioned above were conducted at a specific relative humidity (80–95%). Hence there are presently no available water growth curves for OC and EC. Xu et al. (2015) separated OC into hygroscopic and non-hygroscopic parts to study their effects on light extinction in Shanghai, China. However, this work fixed a fraction of these two parts of OC to the total OC, and then used the water curves for hygroscopic OC derived from the curves for sulfate and nitrate. For these reasons, we take the hygroscopic properties of OC and EC into consideration when we reconstruct the PM\(_{2.5}\) light extinction coefficient using long-term measurements.

In the present study, measurements were carried out at one urban and one suburban site in Guangzhou, China from Nov. 2012 to Dec. 2013 to investigate the chemical components of PM\(_{2.5}\) and the relationship between aerosol composition and visibility. The IMPROVE Algorithm was modified so that it would be locally applicable for the geography, climate, and pollution levels unique to the urban and suburban sites in Guangzhou, using multiple linear regression (MLR) analysis. Mass Scattering Efficiencies (MSE) for sulfate and nitrate, and hygroscopic growth factors \( G_f \) for OC and EC were localized. The contributions of the individual chemical components of PM\(_{2.5}\) to visibility degradation were further quantified, and found to vary under different atmospheric pollution loadings. The chemical and physical reasons, including secondary aerosol formation are discussed and the impacts are explored.

METHODS

Sampling Sites

The field study was conducted at two sites in Guangzhou, the capital city of the Guangdong province of China (Fig. 1). Guangdong is located in a subtropical monsoon climate area with prevailing cold and dry air masses in winter (December–February) from the North and Northeast directions and warm and wet air masses in summer (May–August) from the ocean. The rainy season is from April to September while the rest of months belong to dry season.

At the urban site, instruments were set on the rooftop of a building, 15 m above the ground, in the Guangzhou Environmental Monitoring Center (23°07′59″N, 113°15′35″E) (EMC). The site is about 150 m away from the arterial roads and surrounded by residential and commercial buildings. No significant industrial emission sources are found surrounding the site. The station represents a typical urban environment.

At the suburban site, instruments were set on the rooftop of a building, 12 m above the ground, inside the Guangzhou Kangda Vocational Technical College (23°16′42″N, 113°
34°05′E) (VTC). The site is surrounded by residential buildings and without significant industrial emissions sources nearby. This station represents a typical suburban area.

**Aerosol Filter Sampling**

23-hour (10:00 am–09:00 am) samples were collected daily from Nov. 15, 2012, to Dec. 31, 2013. The samples were collected simultaneously on 47 mm Teflon filters (Whatman Inc., UK) and 20.3 cm × 24.5 cm quartz filters (Whatman Inc., UK) by a RP2300 four-channel low-volume sampler (16.7 L min⁻¹) and a US Thermo Andersen high-volume sampler (1130 L min⁻¹), respectively. Two Teflon filters were assembled to allow for parallel data collection every sampling day. Blank sampling was performed every sampling day, with a blank filter put on the free-sampling day. Blank sampling was performed every time as the other samples. A total of 169 and 160 sets of samples were collected at the urban and suburban site, respectively, including 115 and 94 sets during the dry season, and 54 and 66 sets during the wet season.

**Chemical Analysis**

The aerosol loaded filters were stored in a refrigerator at 4°C before chemical analysis to avoid the loss of volatile components. The quartz filters were prepared for the analysis of OC/EC and water-soluble ions. OC/EC was analyzed using thermo-optical transmittance (TOT) method (NOISH, 1999) by an OC/EC Analyzer (Sunset Laboratory Inc., USA). An external standard method was used to evaluate the accuracy and linearity of the results from the OC/EC Analyzer before chemical analysis every week. If the relative bias was less than ±5% and the correlation coefficient was greater than 0.99, the instrument could be used for chemical analysis.

Water-soluble ions including six cations (Na⁺, NH₄⁺, K⁺, Ca²⁺, Mg²⁺, and Al³⁺) and seven anions (F–, Cl–, NO₂⁻, NO₃⁻, Br⁻, SO₄²⁻, and PO₄³⁻) were measured by 883 Basic IC plus (Metrohm, Switzerland). Standard recovery experiments were conducted before ion and elemental analysis. The standard recovery rate was above 98% and the relative bias was less than 6% for ion analysis.

Elemental compositions of the PM₂.₅ samples, including V, Cd, Mn, Co, Ni, Cu, Zn, As, Se, Cr, Sn, Sb, Ba, Hg, Ti, Pb, and Bi, were determined by ICP-MS instrument. Detailed information about chemical analysis can be referred to Wang et al. (2012). Blank filters were also analyzed and the sample results were corrected by the average of the blank concentrations in the text.

**Observation of Meteorological and Aerosol Optical Parameters**

Hourly meteorological data including temperature, relative humidity, wind direction, wind speed and precipitation were measured using a Weather Measurement Instrument (WXT520, Vaisala, Finland) at the two sites from 2011 to 2013. Hourly aerosol optical data, including visibility and light extinction coefficient, were measured using a forward-scattering visibility sensor (Belfort Model 6000, USA) at the two sites from 2011 to 2013. The hourly light-scattering and light-absorption coefficients for dry particles were measured using an Aurora-1000 Nephelometer (Ecotech, Victoria, Australia) and an AE31 Aethalometer (Magee Scientific, USA) at the urban site from October to December in 2013. Daily manual observation of visibility data was obtained from the China Meteorological Data Sharing Service System (http://cdc.cma.gov.cn/home.do).

**Real-Time Online Measurement of PM₄₅ Chemical Components**

Hourly real-time online monitoring of PM₂.₅ chemical components was also conducted at the urban site in 2013. Water soluble ions were monitored using an Ambient Ion Monitor IC (URG9000D, USA) and carbonaceous materials were monitored using an Online Sunset Laboratory OCEC Carbon Aerosol Analyzer (RT4, Sunset Lab, USA). The online measurements were used to evaluate the localized IMPROVE algorithm.

**RESULTS AND DISCUSSION**

**Characteristics of PM₂.₅ Chemical Composition**

**Overview of PM₂.₅ Chemical Composition**

The average mass concentration of PM₂.₅ and its chemical components in the wet season, the dry season, and annual average at the urban and suburban sites are given in Table 1. The annual average PM₂.₅ mass concentration at the urban site was 61.3 ± 27.6 µg m⁻³ with 1.3 times higher in the dry season than that in wet season. As for the suburban site, the annual average PM₂.₅ mass concentration was 54.2 ± 29.7 µg m⁻³ with 1.6 times higher in the dry season than that in the wet season.

To determine the spatial similarity between the two sites, a Coefficient of Divergence (CD), a self-normalizing parameter, was calculated based on the data at the two sites, for each of the chemical components, according to Eq. (1):

\[
CD_{ik} = \frac{1}{p} \sum_{j=1}^{p} \frac{(x_{ij} - x_{ik})}{(x_{ij} + x_{ik})}^2
\]

where \(x_{ij}\) and \(x_{ik}\) represent the annual average concentration for chemical i at site j and k, respectively, and p is the total number of chemical components (Wongphatarakul et al., 1998). The value of CD ranges from 0 to 1 with smaller values representing higher similarities. In previous works, a CD of 0.2 was used as the threshold separating homogenous and heterogeneous spatial difference (Massoud et al., 2011).
Table 1. Average concentration ± standard deviation of PM$_{2.5}$ and its chemical components at the two sites during wet and dry seasons and during the whole year period (Unit: µg m$^{-3}$).

<table>
<thead>
<tr>
<th>Site</th>
<th>Season</th>
<th>PM$_{2.5}$</th>
<th>SO$_4^{2–}$</th>
<th>NO$_3^{–}$</th>
<th>NH$_4^+$</th>
<th>OC</th>
<th>EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban</td>
<td>Wet</td>
<td>50.8 ± 21.2</td>
<td>9.1 ± 4.5</td>
<td>4.9 ± 4.3</td>
<td>4.0 ± 3.8</td>
<td>11.1 ± 3.6</td>
<td>2.6 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
<td>66.2 ± 28.9</td>
<td>9.4 ± 5.0</td>
<td>6.0 ± 4.8</td>
<td>4.3 ± 2.2</td>
<td>16.6 ± 8.1</td>
<td>2.9 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>Annual</td>
<td>61.3 ± 27.6</td>
<td>9.3 ± 4.9</td>
<td>5.7 ± 4.7</td>
<td>4.2 ± 4.2</td>
<td>14.9 ± 7.5</td>
<td>2.8 ± 1.2</td>
</tr>
<tr>
<td>Suburban</td>
<td>Wet</td>
<td>40.4 ± 23.2</td>
<td>7.4 ± 4.0</td>
<td>2.5 ± 2.4</td>
<td>2.9 ± 1.9</td>
<td>9.1 ± 4.1</td>
<td>2.1 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
<td>63.2 ± 30.2</td>
<td>10.8 ± 6.2</td>
<td>4.5 ± 3.2</td>
<td>5.0 ± 2.7</td>
<td>17.7 ± 8.4</td>
<td>3.2 ± 1.7</td>
</tr>
<tr>
<td></td>
<td>Annual</td>
<td>54.2 ± 29.7</td>
<td>9.4 ± 5.7</td>
<td>3.7 ± 3.0</td>
<td>4.1 ± 2.6</td>
<td>14.2 ± 8.1</td>
<td>2.7 ± 1.6</td>
</tr>
</tbody>
</table>

The CD value was found to be 0.37 during the wet season and 0.14 during the dry season, respectively, with an annual average 0.19. This indicates a relatively homogeneous spatial distribution between the two sites on an annual basis or during the dry season, but a heterogeneous distribution during the wet season. This makes physical sense, given that during the wet season, the removal rate is higher, which in turn results in less transport and secondary production.

On average, the concentrations of individual chemical component were generally comparable between the two sites, with only a few exceptions, such as NO$_3^{–}$ was found at the urban site to be about double the suburban site during the wet season. This could in part be caused by rapid conversion from traffic NO$_x$ to nitrate at the urban site (Wang et al., 2016), coupled by more rapid loss of nitrate to wet deposition en-route to the suburban location. Secondly, at the suburban site, the concentration of OC was about two times higher during the dry season than the wet season, which could be caused by a combination of different air mass origins in different seasons (Peng et al., 2011), more efficient precipitation scavenging during wet season, and differences in secondary OC formation between the wet and dry seasons.

SO$_4^{2–}$ concentrations were comparable at the urban site during the wet and dry seasons while higher concentration was found during the dry season at the suburban site, which will be discussed in the next section in the paper.

The fractions of major chemical components in PM$_{2.5}$ during the wet season, the dry season, and annual average are shown in Fig. 2. Organic Matter (OM = 1.6 [OC]) (Turpin and Lim, 2001), SO$_4^{2–}$, and NO$_3^{–}$ were among the dominant chemical components in PM$_{2.5}$, accounting for 40.3%, 16.3%, and 8.0%, respectively, with the other optically important species, such as EC, accounting for 4.8% due to more emissions emitted near the urban area. Unidentified materials were about 16.7% among the total PM$_{2.5}$ mass. The possible compositions of the unidentified mass are fine soil, sea salt, water, and possibly POM that is not accounted for by the conversion factor (here is 1.6).

Analysis of Chemical Components in PM$_{2.5}$

a) Water Soluble Ions

The Sulfur Oxidation Ratio (SOR) and Nitrogen Oxidation Ratio (NOR) are ways to quantify oxidation of SO$_2$ and NO$_2$, and thus are indicators of secondary transformation processes (Wang et al., 2005). The equations for SOR and NOR are calculated using Eqs. (2)–(3), where $n$-SO$_4^{2–}$ and $n$-NO$_3^{–}$ are the molar concentrations of particulate SO$_4^{2–}$ and NO$_3^{–}$; and $n$-SO$_2$ and $n$-NO$_2$ are the molar concentrations of the precursor gases SO$_2$ and NO$_2$.

$$\text{SOR} = n$-SO$_4^{2–}$/($n$-SO$_4^{2–}$ + $n$-SO$_2$) (2)$$

$$\text{NOR} = n$-NO$_3^{–}$/($n$-NO$_3^{–}$ + $n$-NO$_2$) (3)$$

The SOR and NOR values during the wet and dry seasons at the two sites are shown in Table 2, with slightly higher values of SOR and NOR found at the suburban site. This is consistent with the fact that higher values of SOR and NOR are expected under conditions of greater atmospheric oxidation capacity and of longer residence time in the atmosphere to undergo oxidation in the atmosphere.

A similar trend was observed for SO$_4^{2–}$, with concentrations at the suburban site during the dry season considerably higher than during the wet season, and the suburban site having considerably higher overall levels than the urban site, as also noted by Cohen et al. (2011). The average mass concentration of SO$_2$ was 20.6 ± 8.4 and 25.4 ± 11.8 µg m$^{-3}$ at the urban site during wet and dry season. The similar level of precursors and oxidation capacity led to non-significant difference for SO$_4^{2–}$ at the urban site during wet and dry season. Although the average mass concentration of SO$_2$ was lower, about 19 µg m$^{-3}$ at the suburban site, the stronger oxidation capacity during dry season resulted in higher SO$_4^{2–}$ concentration. The oxidation capacity can be revealed by O$_3$ concentration which was 1.32 times higher than that at the wet season at the suburban site.

b) Carbonaceous Materials

The OC/EC minimum ratio method was used to estimate the concentration of secondary organic carbon (SOC) (Castro et al., 1999). SOC can be estimated as a linear function of the minimum of the OC to EC ratio, as represented by the factor (OC/EC)$_{\text{min}}$ in (Eq. (4)).

$$\text{SOC} = \text{OC} - \left(\frac{\text{OC}}{\text{EC}}\right)_{\text{min}} \times \text{EC} \quad (4)$$

However, since the abundance of OC and EC varies among sources, the minimum ratio of OC to EC was location- and season-dependent (Cao et al., 2007). So assumptions inherent to this method would introduce uncertainties in the estimation of SOC (Yu, 2011).

Using this method, (OC/EC)$_{\text{min}}$ was computed to be 1.73 and 2.10 at the urban site, and 2.55 and 2.82 at the suburban site during the wet and dry seasons respectively.
Fig. 2. Fractions (in percentage) of chemical components in PM$_{2.5}$ at the two site during wet, dry and annual periods (*Elements included 17 elements; OM = 1.6 × OC; Sea Salt = 1.8 × Cl$^-$; Other ions consisted of Na$^+$, K$^+$, Ca$^{2+}$, Mg$^{2+}$, F$^-$, NO$_2^-$, Br$^-$ and PO$_4^{3-}$).

Table 2. The value of SOR and NOR, ratio of OC to EC, SOC concentration and its proportion to OC during the wet and dry season at the two sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Season</th>
<th>SOR</th>
<th>NOR</th>
<th>OC/EC</th>
<th>SOC$_{OC}$ (µg m$^{-3}$)</th>
<th>SOC/OC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban</td>
<td>Wet</td>
<td>0.22</td>
<td>0.04</td>
<td>4.4</td>
<td>6.6</td>
<td>58.2</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
<td>0.22</td>
<td>0.05</td>
<td>5.7</td>
<td>10.5</td>
<td>60.3</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.22</td>
<td>0.05</td>
<td>5.4</td>
<td>8.6</td>
<td>59.3</td>
</tr>
<tr>
<td>Suburban</td>
<td>Wet</td>
<td>0.22</td>
<td>0.06</td>
<td>4.6</td>
<td>4.2</td>
<td>40.1</td>
</tr>
<tr>
<td></td>
<td>Dry</td>
<td>0.29</td>
<td>0.10</td>
<td>6.0</td>
<td>8.6</td>
<td>47.3</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.26</td>
<td>0.08</td>
<td>5.5</td>
<td>6.4</td>
<td>43.7</td>
</tr>
</tbody>
</table>

These values are comparable with previous studies conducted in the PRD, with values between 1.1 and 2.4 (Cao et al., 2003, 2004, 2007; Huang et al., 2012). On the other hand, the annual average ratio of OC to EC was about 5.5 in Guangzhou, which is similar to or higher than the values at urban areas in the Southeastern USA and Europe (Lim and Turpin, 2002; Weber et al., 2007; Blanchard et al., 2011; Yubero et al., 2014). It was noticed that the annual average contribution of SOC to OC was higher at the urban site (59%) than the suburban site (44%) (Table 2). Cao et al. (2003, 2004) also found that the percentage of SOC in OC was 56% and 62% respectively in winter and summer in the urban areas of Guangzhou, while it was 53% and 54% respectively in the suburban area around Guangzhou during 2002. Under relative high temperature and oxidizing environment, the abundance of reactive components of VOCs (i.e., Propane, Toluene, Ethyne) from fresh vehicular exhausts favor the formation of SOC through the fast photo-oxidation in urban areas (Huang et al., 2011; Nordin et al., 2013; Deng et al., 2016; Zhou et al., 2016). Therefore, the reasons that SOC to OC ratios were lower in the suburban site probably due to the less emissions and lower reactivity of VOCs species in the suburban site.

The Contribution of PM$_{2.5}$ to Visibility Impairment

Since errors would be introduced in visibility measurements, especially when the visibility is higher than 15 km. Manual observation of visibility from 2011 and 2012 was used to correct automatically collected visibility data. Additionally, visibility data in 2013 were used to validate the best fit curves at the two sites. The bias before and after visibility correction was 12 and −3 km at the urban site, and 9 and −4 km at the suburban site where the visibility is greater than 15 km. A significant reduction in the bias was found after visibility correction. We use the corrected visibility as a surrogate from this point forward.

Relative humidity has a known effect on visibility impairment, where water is uptake by aerosols, causing them to swell and change their extinction cross sections. However, this is not done uniformly for all particles, such as the unaged and uncoated EC not uptake water, and only certain types of unaged and uncoated OC uptake water. Furthermore, different hydrophilic aerosols as well as aerosols of different sizes uptake water at different amounts. To approximate all of these processes, hourly measured PM$_{2.5}$, corrected visibility, and relative humidity were mixed at the two sites. The relationship between PM$_{2.5}$ and visibility
under different RH conditions from 2011 to 2013 is shown in Fig. 3. An exponential relationship was assumed to exist between PM$_{2.5}$ and visibility, with higher PM$_{2.5}$ concentrations, corresponding to lower visibility, as has been found in many studies (Deng et al., 2008; Zhang et al., 2015). We have found that the visibility degradation is very sensitive to PM$_{2.5}$ under relatively clean conditions (concentration less than 50 µg m$^{-3}$), leading to visibility being considered impacted (i.e., lower than 10 km) at the urban site when RH < 80% and at the suburban site when RH < 70%. In the cases of higher RH conditions (RH > 80% and RH > 70% at urban and suburban site), visibility can be lower than 10 km even when the PM$_{2.5}$ mass concentration was less than 50 µg m$^{-3}$, which was affected by the precipitation. A value of 50 µg m$^{-3}$ for PM$_{2.5}$ mass concentration was thus chosen as the threshold value above which visibility would be lower than 10 km at the urban site when RH < 80% and at the suburban site when RH < 70%. Zhang et al. (2015) also found the threshold concentration of 50 µg m$^{-3}$ in Beijing (2012.11–2013.1). However, much higher values (88 and 100 µg m$^{-3}$ in Xi’an (2009) and Guangzhou (2006), respectively) were proposed in earlier studies (Deng et al., 2008; Cao et al., 2012). The threshold concentration has reduced in recent years, illustrating the atmospheric environment is more susceptible to pollution.

Localization and Verification of the IMPROVE Algorithm

Calculation and Verification of Light Extinction Coefficient

Corrected light extinction coefficient could be estimated based on the Koschmieder formula (Eq. (5)) and the corrected visibility above.

$$\text{Vis} = \frac{3.912}{B_{\text{ext}}}$$

(5)

where, $B_{\text{ext}}$ is the light extinction coefficient (km$^{-1}$) and Vis denotes visibility (km).

The hourly light-scattering coefficient and light-absorption coefficient, which were measured by Nephelometer and Aethalometer at the urban site from October to December in 2013, were used to evaluate the light extinction coefficient. The light extinction from Nephelometer and Aethalometer (refer to Bext1 here), the pre-corrected light extinction (refer to Bext2 here) and the post-corrected light extinction (refer to Bext3 here) were 325.9 ± 169.3, 248.3 ± 194.1, and 317.1 ± 97.8 Mm$^{-1}$, respectively. The bias and the correlation coefficient between Bext1 and Bext2 were 77.5 Mm$^{-1}$ and 0.50 (P < 0.05), while the bias and the correlation coefficient between Bext1 and Bext3 were 8.8 Mm$^{-1}$ and 0.67 (P < 0.05). In general, the corrected light extinction coefficient showed a better performance, indicating the corrected light extinction is reliable for further analysis. The corrected light extinction coefficient was used to localize the IMPROVE Algorithm below.

Localization and Variation of the IMPROVE Algorithm

According to the Original IMPROVE Algorithm (Eq. (6), Sisler and Malm, 2000), we have modified the Algorithm as Eq. (7).

$$B_{\text{ext}_{\text{Original}}} = 3 \times f(RH) \times [(NH_4)_2SO_4 + NH_4NO_3] + 4 \times [OM] + 10 \times [EC] + 1 \times [Fine Soil] + 0.6 \times [Coarse Mass]$$

(6)

$$B_{\text{ext}_{\text{local}}} = a \times f_{L}(RH) \times [(NH_4)_2SO_4] + b \times f_{L}(RH) \times [NH_4NO_3] + 4 \times G_{f,OC} \times [OM] + 10 \times G_{f,EC} \times [EC] + 1.7 \times f_{SS}(RH) \times [Sea Salt] + 0.6 \times [Coarse Mass] + Rayleigh scattering + 0.33 \times [NO_2]$$

(7)

$$\text{where, } [(NH_4)_2SO_4] = 1.375 \times [SO_4^{2-}]; \ [NH_4NO_3] = 1.29 \times [NO_3^{-}]; \ [OM] = 1.6 \times [OC]; \ [Sea salt] = 1.8 \times [Cl^{-}]; \ [Coarse Mass] = [PM_{10}] – [PM_{2.5}]; \ [Fine Soil] = 2.2 \times [Al] + 2.49 \times [Si] + 1.63 \times [Ca] + 2.42 \times [Fe] + 1.94 \times [Ti].$$

Fig. 3. The relationship between visibility and PM$_{2.5}$ mass concentration under the different RH conditions.
The contribution of fine soil to the light extinction was roughly estimated by making the best of the elements data of our study and other reference (Ke, 2013) and the result showed that, the fine soil contributed 2%–3% of light extinction. Furthermore, referred to the work of Jung et al. (2009a) and considered the entire unidentified fraction as fine soil, the roughly estimated light extinction coefficient of fine soil accounted for less than 5% of the total light extinction. Previous studies conducted in the PRD region also found that fine soil had a minor contribution to aerosol mass and the total light extinction (Cheung et al., 2005; Andreea et al., 2008; Tao et al., 2009; Wang et al., 2012). Therefore, the light extinction of fine soil was ignored in this study. The absorption of NO2 and the scattering of sea salt were also taken into consideration in this study (Pitchford et al., 2007). Hygroscopic growth factors for large mode sulfate and nitrate (fL(RH)) and sea salt aerosol (fss(RH)) referred to the work of Pitchford et al. (2007). Though sulfate and nitrate mainly peak in droplet mode (0.5–1.0 µm), nitrate would be bi-modal distribution in coastal and remote areas due to the effect of chloride depletion of sea salt aerosols (Meng and Seinfeld, 1994). Rayleigh scattering of 12 Mm−1 was used for each monitoring site, regardless of site elevation and meteorological condition in this study (Sisler and Malm, 2000). In Eq. (7), a and b were the localized Mass Scattering Efficiencies (MSE) for sulfate and nitrate, and 4 and 10 m2 g−1 were the MSE for OM and EC. Coefficients Gf,OC and Gf,EC were the localized Gf for OM and EC and used to preliminarily examine the impact of water uptake by carbonaceous aerosol on the optical properties in this study, which was an average and fixed value since the absence of water curves for OM and EC.

A total of 120 samples was randomly selected from the entire samples to localize the IMPROVE Algorithm using multiple linear regression (MLR). Based on previous studies, Gf,OC and Gf,EC was predefined within a certain range (1.0–2.6 for OM and 1.0–2.0 for EC). A fixed Gf,OC and Gf,EC was set during each MLR process with a step length of 0.05. So each run of MLR exported 693 results. A certain number of best runs tended to be stable. So the specific result with the minimum bias between estimated and measured light extinction was considered as the best run. The process was performed for hundreds and thousands time until the average values (a, b, Gf,OC and Gf,EC) based on a certain number of best runs tended to be stable. So the average values based on the best 300 runs were chosen as the localized coefficient in this study.

The localized MSE for sulfate and nitrate was 2.16 ± 0.34 and 2.63 ± 0.66 m2 g−1 at the urban site and 2.22 ± 0.31 and 2.76 ± 0.84 m2 g−1 at the suburban site, respectively. While the localized Gf,OC and Gf,EC was 1.28 ± 0.13 and 1.15 ± 0.11 at the urban site, 1.18 ± 0.09 and 1.10 ± 0.09 at the suburban site. Hand and Malm (2007) reviewed that MSE for sulfate and nitrate was 3.34 ± 1.68 (ranged from 0.83 to 8.30) and 2.83 ± 0.76 (varied between 1.77 and 6.20) m2 g−1 using the MLR method. Overall, the localized MSE and GF were acceptable and reasonable which could be used for following analysis in this study.

Hourly real-time online monitoring of PM2.5 chemical components conducted at the urban site was used to validate the Local IMPROVE Algorithm. Overall, the correlation coefficient was both 0.72 for the Localized and Original IMPROVE Algorithm, but with lower bias of −5.7 Mm−1 for localized IMPROVE Algorithm compared with the bias of −70.1 Mm−1 estimated by Original IMPROVE Algorithm.

**Contributions of Chemical Components to Visibility Variation**

The Local IMPROVE Algorithm was applied to analyze the contribution of each chemical component to light extinction coefficient during the wet and dry seasons at the two sites (Fig. 4). The annual average light extinction coefficient was 294.7 ± 106.9 and 255.8 ± 119.0 Mm−1 at the urban and suburban site without significant difference between the two sites. The particle light extinction accounted for more than 90% of the total light extinction coefficient. The annual average value was 18.7% and 10.4% for (NH4)2SO4 and NH4NO3, 41.9% and 11.7% for OM and EC at the two sites. (NH4)2SO4, NH4NO3 and OM contributed 16.5%, 11.5% and 41.7%, respectively, at the urban site, 21.3%, 9.1% and 42.1%, respectively, at the suburban site. Sea salt, coarse mass, NO2 and Rayleigh scattering contributed about 3–6%, 5%, 2–4% and 4% at the two sites, respectively.

The total light extinction was higher during dry season with a value of 321.0 ± 113.1 and 288.1 ± 114.5 than that of wet season with a value of 247.8 ± 75.4 and 186.8 ± 74.6 at the urban and suburban site. (NH4)2SO4 contributed relatively higher during the wet than dry season, which is related to the impact of relative humidity. The hygroscopicity of (NH4)2SO4 made these chemical components growing faster under the higher relative humidity and further enhanced light extinction and scattering coefficients (Jung et al., 2009a).

The light extinction coefficient estimated using the IMPROVE Algorithm and the contribution of chemical components to visibility impairment in China was summarized in Fig. 5. The estimated light extinction in this study was comparable with other studies conducted in Guangzhou with a variation between 326 and 428 Mm−1 during 2006–2010 (Jung et al., 2009a; Tao et al., 2009; Wang et al., 2012 Tao et al., 2014), while higher than that conducted in rural and coastal cities (Cheung et al., 2005).

The extinction was at similar levels in Guangzhou compared with Eastern China, for example, Yangtze River Delta, which is also an economic zone (Lin et al., 2014; Shen et al., 2014). The light extinction coefficient was the highest in Northern China – the most polluted region in China, ranging from 600 to 900 Mm−1 (Cao et al., 2012; Zhu et al., 2012; Xiao et al., 2014; Tao et al., 2015b). OM and (NH4)2SO4 were always the most important components contributing to visibility degradation (up to 50%) in China regardless of the location. The load percentage of NH4NO3 was the highest in Northern China owing to larger vehicle populations (more than 5 million in 2014 in Beijing while the population was about 2.7 million in Guangzhou).

PM2.5 mass concentration was divided into four intervals (<35, 35–75, 75–115, >115 µg m−3, representing non-, light-,
Fig. 4. (a) The chemical components light extinction coefficient and (b) their load percentage during wet and dry season, and under the different PM$_{2.5}$ concentration intervals at the two sites.

Fig. 5. The estimated light extinction coefficient based on IMPROVE Algorithm and chemical components load percentage in China.
high-, and extreme-polluted conditions, respectively) to investigate the relative contributions of individual chemical components to visibility impairment under different polluted conditions (Fig. 4). Samples with precipitation happened were excluded from the analysis. The contribution of (NH$_4$)$_2$SO$_4$ and OM fluctuated with the increased of PM$_{2.5}$ mass concentration. In general, secondary water-soluble ions and OM was becoming increasingly vital under polluted conditions, while the contribution of EC and coarse mass, as mainly came from primary sources, showed an overall decrease trend. The average extinction coefficient of NH$_4$NO$_3$ increased markedly from non-polluted (11.7 Mm$^{-1}$) or light-polluted (24.9 Mm$^{-1}$) conditions to heavy- (40.9 Mm$^{-1}$) and extreme-polluted (68.9 Mm$^{-1}$) conditions at the two sites. The average contributions also increased from 6.9% to as high as 14.6%, illustrating the significant effect of NH$_4$NO$_3$ on light extinction under seriously polluted conditions in Guangzhou.

Under the condition that the PM$_{2.5}$ concentration exceeded 115 µg m$^{-3}$, the total light extinction coefficient was higher at the suburban than the urban site. The wind direction data showed that the wind at the suburban site mainly came from southwest under the extremely polluted condition. The downwind area-suburban site, was greatly affected by the upwind area (urban area Guangzhou and industrial city Foshan). Furthermore, the wind speed was around 1.0 m s$^{-1}$ at the suburban site, which was in favor of the accumulation of productions under such meteorological condition over the downwind areas. So under such condition, the average mass concentration of SO$_4^{2-}$, NH$_4^+$, OC and EC was much higher at the suburban site with an average value of 20.7, 10.1, 30.0 and 4.8 µg m$^{-3}$ than that of at the urban site with a mean concentration of 13.7, 7.1, 23.8 and 3.9 µg m$^{-3}$. However, the concentration of NO$_3^-$ was relatively lower at the suburban site (10.4 µg m$^{-3}$) than that at the urban site (12.7 µg m$^{-3}$). Nitrate can be produced locally or transported from upwind areas. The NOR value was 0.14 at the suburban site under the extremely-polluted condition, which was about 2 folds higher than that at the urban site, indicating the significant local formation of nitrate at the suburban site. But due to the limitation of precursors (the concentration of NO$_3^-$ was 47.3 and 126.3 µg m$^{-3}$ at the suburban and urban site) and evaporation during the transportation process (Seinfeld and Pandis, 1998), the nitrate concentration was lower at the suburban site but was still much higher than that under the non- or light-polluted conditions. Overall, pollutants transported from upwind areas or formed locally resulted in the relatively higher loading of chemical components and further led to a higher light extinction coefficient at the suburban sites under the extremely-polluted condition.

Though strict quality controls on sampling and chemical analysis were adopted, one should keep in mind that some drawbacks of this manual sampling method may exist, such as the loss of the volatile compounds (e.g., ammonium nitrate, etc.), due to the long time of the sampling periods and high temperature (Nie et al., 2012). The estimated average aerosol nitrate loss was 12.9% at both of the sites based on the empirical formula (Squizzato et al., 2013), which was compatible with or less than previous studies conducted in the USA with a loss range of 10–28% and in Europe with a loss range of 20–26% (Yu et al., 2006; Squizzato et al., 2013). Further efforts to decrease the loss of nitrate during sampling and chemical analysis and improve understanding of nitrate aerosol evaporation on light extinction are needed.

CONCLUSIONS

Annual average PM$_{2.5}$ mass concentration during Nov. 2012 to Dec. 2013 was 61.3 ± 27.6 and 54.2 ± 29.7 µg m$^{-3}$ at the urban and suburban site, respectively, in Guangzhou. Annual average concentration of secondary water soluble inorganic ions (SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$) and carbonaceous aerosol (OC and EC) was 17.2 and 22.6 µg m$^{-3}$, accounting for 32% and 42%, respectively, of the total PM$_{2.5}$ mass concentration in Guangzhou. The predominant chemical components in PM$_{2.5}$ were OM and SO$_4^{2-}$ with the concentration of 23.2 and 9.4 µg m$^{-3}$, respectively, during the sampling period. PM$_{2.5}$ chemical components and visibility were sensitive to relative humidity conditions. Visibility decreased dramatically with increasing PM$_{2.5}$ mass concentration when the relative humidity was lower than 70%. The visibility was less than 10 km once the PM$_{2.5}$ concentration surpassed 50 µg m$^{-3}$ in Guangzhou.

The localized MSE for sulfate and nitrate was 2.16 ± 0.34 and 2.63 ± 0.66 m$^2$ g$^{-1}$ with the hygroscopic growth factor for OM and EC was 1.28 ± 0.13 and 1.15 ± 0.11 at the urban site, while the value was 2.22 ± 0.31 and 2.76 ± 0.84 m$^2$ g$^{-1}$ and 1.18 ± 0.09 and 1.10 ± 0.09 at the suburban site, respectively. The estimated total light extinction coefficient was 294.7 ± 106.9 and 255.8 ± 119.0 Mm$^{-1}$ at the urban and suburban site without significant difference between the two sites and was comparable with those obtained in earlier years (326–428 Mm$^{-1}$ in 2006–2010). (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, OM and EC accounted for 18.7%, 10.3%, 41.9% and 11.7%, respectively, of the total light extinction. NH$_4$NO$_3$ played a much more important role on visibility degradation under severe polluted conditions, suggesting the importance of controlling future vehicle emissions to curb the increasing of NO$_3^-$ and its precursors.

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REFERENCES

Andreae, M.O., Schmid, O., Yang, H., Chand, D.L., Yu,

Bian, Q.J. (2011). *Study of Visibility Degradation over the Pearl River Delta Region: Source Apportionment and Impact of Chemical Characteristics*. Hong Kong University of Science and Technology.


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