Impacts of aerosol compositions on visibility impairment in Xi’an, China

Jun-ji Cao, Qi-yuan Wang, Judith C. Chow, John G. Watson, Xue-xi Tie, Zhen-xing Shen, Ping Wang, Zhi-sheng An

1. Introduction

Visibility is an indicator of urban air quality. Urban and regional visibility has been deteriorating in China in concert with economic growth and increasing emissions (Chang et al., 2009; Che et al., 2009). Intense “haze-fog” events in Beijing during late October of 2011 (e.g., http://news.yzdsb.com.cn/system/2011/11/10/011485620_01.shtml) raised public awareness of adverse effects associated with visibility impairment.

Xi’an, one of the largest cities in China, is situated on the Guanzhong Plain at the southern edge of the Loess Plateau with a resident population of eight million and two million visitors per year. Twenty-four hour average PM$_{2.5}$, which scatters and absorbs light (Chow et al., 2002a; Watson, 2002), ranged from 130 to 351 µg m$^{-3}$ in Xi’an (Cao et al., 2005; Han et al., 2010; Shen et al., 2009), exceeding the Chinese government’s recently issued 24-h PM$_{2.5}$ standard of 75 µg m$^{-3}$ by two- to five-fold (http://www.chinadaily.com.cn/china/2012-03/03/content_14745568.htm). From 1995 to 2005, visual range (VR; the farthest distance at which the human eye can distinguish a target against a background; Booker and Douglas, 1977) decreased ~5.71 km, with a VR of ~3.51 km. The threshold PM$_{2.5}$ mass concentration, corresponding to VR < 10 km, was ~88 µg m$^{-3}$. The revised IMPROVE equation was applied to estimate chemical extinction ($b_{ext}$), which on average was ~15% lower than measured $b_{ext}$. PM$_{2.5}$ ammonium sulfate was the largest contributor, accounting for ~40% of $b_{ext}$, followed by organic matter (~24%), ammonium nitrate (~23%), and elemental carbon (~9%), with minor contributions from soil dust (~3%), NO$_2$ (~1%), and NO$_3$ (~1%). High secondary inorganic aerosol contributions (i.e., SO$_4^{2-}$ and NO$_3$) were the main contributors for VR < 5 km. A Positive Matrix Factorization (PMF) solution to the Chemical Mass Balance (CMB) receptor model showed that coal combustion was the dominant factor, accounting for ~52% of the dry particle light scattering coefficient, followed by the engine exhaust factor (~31%). Other factors included biomass burning (~12%) and fugitive dust (~5%).
taken actions to reduce emissions such as: installing and operating sulfur dioxide (SO2) scrubbers on coal-fired power stations, using cleaner coals for large-scale boilers, substituting coal with cleaner fuels (e.g., liquefied petroleum gas, LPG) for domestic cooking and heating, and modernizing the urban vehicle fleet. These measures, however, have not improved air quality as anticipated. A good understanding of the causes of poor visibility is needed to implement effective emission reduction strategies. Improvements in visibility will also have co-benefits for public health, material and crop damage, and climate (Chow and Watson, 2011).

The objectives of this study are to: (1) examine the seasonal variations of VR and light extinction \(b_{\text{ext}}\); and (2) assess the causes of visibility impairment by relating \(b_{\text{ext}}\) to PM2.5 chemical composition.

## 2. Sampling and analysis

Sampling was conducted from February 15 to December 31, 2009, at an urban-scale (Chow et al., 2002b) site on the rooftop (~10 m above ground level) of the Institute of Earth Environment, Chinese Academy of Sciences (IEECAS; Cao et al., 2009). This site is located ~15 km southwest of downtown Xi’an in a residential/commercial neighborhood.

Twenty-four hour PM2.5 samples were collected daily from 1000 local standard time (LST) to 1000 LST the next day using a battery-powered mini-volume sampler (Airmetrics, Oregon, USA) with a flow rate of 5 L min\(^{-1}\). Quartz–fiber filters of 47 mm diameter (QMA; Whatman, Middlesex, UK) were used for mass, elements, water-soluble ions, and organic and elemental carbon (OC and EC, respectively) analyses. The quartz–fiber filters were preheated to 800 °C for 3 h before sampling and equilibrated using controlled temperature (20–23 °C) and relative humidity (RH: 35–45%) desiccators before and after sampling for 24 h prior to weighing on a Sartorius MC5 electronic microbalance with a ±1 μg sensitivity (Sartorius, Göttingen, Germany). Samples were stored air-tight in a refrigerator at about 4 °C before chemical analysis to prevent evaporation of volatilized components.

The elemental concentrations were determined by Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (Epsilion 5 ED-XRF, PANalytical B.V., the Netherlands). The Epsilion 5 spectrometer uses a three-dimensional polarizing geometry with 11 secondary targets (i.e., CeO2, CsI, Ag, Mo, Zr, KBr, Ge, Zn, Fe, Ti, and Al) and one barkla target (Al2O3) that supplies a good signal–background ratio, and provides low detection limits (Watson et al., 1999). The X-ray source is a side window X-ray tube with a Gadolinium (Gd) anode, operated at an accelerating voltage of 25–100 kV and a current of 0.5–24 mA (maximum power: 600 W). The X-ray characteristic radiation is detected by a Germanium (Ge) detector (PAN 32). Each sample was analyzed for 30 min and laboratory quartz-fiber filter blanks were analyzed to evaluate analytical bias. The 10 elements determined by the ED-XRF method were Ca, Mg, S, K, Ti, Mn, Fe, As, Br, and Pb.

Water-soluble ions were determined by ion chromatography (Chow and Watson, 1999) [IC, Dionex 600, Dionex Corp, Sunnyvale, CA]. Cations, including Mg\(^{2+}\), K\(^+\), Ca\(^{2+}\), and Na\(^+\), were determined using a CS12A column (Dionex Company) with 20 mM methanesulfonic acid eluent. Anions, including F\(^-\), Cl\(^-\), NO\(_3\)\(^-\), and SO\(_4\)\(^{2-}\), were determined using an AS11-HC column (Dionex Company), with 20 mM potassium hydroxide (KOH) eluent. The detection limits were less than 0.05 mg L\(^{-1}\) for cations and anions. Standard Reference Materials produced by the National Research Center for Certified Reference Materials in China were analyzed for quality assurance (QA)/quality control (QC) purposes.

Carbonaceous species (OC, EC and carbon fractions) were analyzed using the thermal/optical reflectance (TOR) method (Chow et al., 1993, 2001, 2004, 2005, 2007, 2011) on a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). The IMPROVE_A protocol (Chow et al., 2007) produces four OC fractions (OC1, OC2, OC3, and OC4 in a 100% helium (He) atmosphere at 140 °C, 280 °C, 480 °C, and 580 °C, respectively); a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen (O2) was added to the analysis atmosphere); and three EC fractions (EC1, EC2, and EC3 in a 98% He/2% O2 atmosphere at 580 °C, 740 °C, and 840 °C, respectively). OC is defined as OC1 + OC2 + OC3 + OC4 + OP and EC as EC1 + EC2 + EC3 – OP. The analyzer was calibrated daily with known quantities of methane (CH4) (Chow et al., 2011).

Replicate analyses were performed on 10% of the samples. Average field blanks were subtracted and their associated uncertainties propagated to correct for passive deposition, especially the positive organic artifact due to adsorption of gas-phase organic components onto the filter during and/or after sampling (Chow et al., 2010a; Watson et al., 2009). More detailed descriptions of QA/QC procedures can be found in Cao et al. (2003) and Chow et al. (2011).

Five-minute averaged dry particle light scattering coefficient (\(b_{\text{scat, dry}}\)) was measured by Aurora–1000 single wavelength (\(\lambda = 520 \text{ nm} \)) integrating nephelometer equipped with a smart heater (Ecotech, Melbourne, Australia). Span calibration was carried out every month using R-134 gas, while zero calibration was performed every two days with particle-free air to subtract the Rayleigh scattering. The nephelometer draws the ambient air through a heated inlet at a flow rate of 5 L min\(^{-1}\) to retain RH < 60%.

Five-minute averaged nitrogen dioxide (NO2) gas was measured gas-phase chemiluminescence (Ecotech EC9841 Nitrogen Oxides Analyzer), with lower quantifiable limits of 0.5 ppb. Hourly wind speed (WS), temperature, RH, and atmospheric pressure were obtained from the Xi’an Meteorological Bureau, ~25 km north from the sampling site. Wind direction data was not available.

## 3. Data analysis

The light extinction coefficient, \(b_{\text{ext}}\), is defined as the sum of the PM2.5 scattering (\(b_{\text{sp}}\), PM2.5 absorption (\(b_{\text{ag}}\), gas (NO2) absorption (\(b_{\text{ag}}\)), and Rayleigh scattering (\(b_{\text{ag}}\)) (Watson, 2002), where:

\[
b_{\text{ext}} = b_{\text{sp}} + b_{\text{ag}} + b_{\text{ag}} + b_{\text{ag}} \tag{1}
\]

\(b_{\text{ag}}\) values can approximate VR using the Koschmieder (1924a,b) equation:

\[
\text{VR} = 3.912 / b_{\text{ext}} \tag{2}
\]

Hygroscopic particles such as sulfates and nitrates grow into more efficient light-scattering sizes with increasing RH (Chow et al., 2002a). According to relationships described by Pitchford et al. (2007), this growth is approximated by:

\[
b_{\text{sp, wet}} = f(\text{RH}) \times b_{\text{sp, dry}} \tag{3}
\]

where \(b_{\text{sp, wet}}\) is the wet scattering coefficient, \(f(\text{RH})\) is the growth function, and \(b_{\text{sp, dry}}\) is the dry scattering coefficient measured by nephelometer at RH < 60%. The \(f(\text{RH})\) curve from Malm et al. (2003) was used for this study.

The absorption coefficient, \(b_{\text{ag}}\), is approximated by applying the IMPROVE mass extinction efficiency of 10 m\(^2\) g\(^{-1}\) to the EC concentration (Chow et al., 2010b; Pitchford et al., 2007; Watson, 2002):

\[
b_{\text{ag}} \left( \text{Mm}^{-1} \right) = 10 \left( \text{m}^2 \text{g}^{-1} \right) \times [\text{EC}] \left( \mu \text{g m}^{-3} \right) \tag{4}
\]
Gaseous NO2 absorption is estimated by using the absorption efficiency of Hodkinson (1966):
\[ b_{ag} \text{ (Mm}^{-1} \text{)} = 0.33 \times [\text{NO2}] \text{(ppb)}. \]  
(5)

The Rayleigh scattering coefficient \( b_{ag} \) was assumed to be a constant value of 10 Mm\(^{-1}\) at sea level (Watson, 2002).

The revised IMPROVE chemical extinction equation (Pitchford et al., 2007) is:
\[
\begin{align*}
\text{Large Sulfate} & = [\text{Total Sulfate}]^2/20, \text{for}[\text{Total Sulfate}] < 20 \mu g \text{ m}^{-3} \\
\text{Large Sulfate} & = [\text{Total Sulfate}] \text{, for}[\text{Total Sulfate}] \geq 20 \mu g \text{ m}^{-3} \\
\text{Small Sulfate} & = [\text{Total Sulfate}] - [\text{Large Sulfate}]
\end{align*}
\]

The Large and Small sulfate indicate formation through dry and aqueous mechanisms (John et al., 1990) and are defined by the IMPROVE equation as:
\[
\begin{align*}
\text{Large Sulfate} = [\text{Total Sulfate}]^2/20, \text{for}[\text{Total Sulfate}] < 20 \mu g \text{ m}^{-3} \\
\text{Large Sulfate} = [\text{Total Sulfate}] \text{, for}[\text{Total Sulfate}] \geq 20 \mu g \text{ m}^{-3} \\
\text{Small Sulfate} = [\text{Total Sulfate}] - [\text{Large Sulfate}]
\end{align*}
\]

The same method is used to separate total nitrate and organic mass (OM) concentrations into the Large and Small size fractions. OM was estimated by multiplying the OC by 1.6, which is suitable for urban aerosol (Turpin and Lim, 2001; Cao et al., 2005). The soil fraction was estimated from the Fe level according to the global crustal abundance of 3.3% (Taylor and McLenna, 1985):
\[
\text{Soil dust} = (1/0.035) \times [\text{Fe}] = 28.57 \times [\text{Fe}]
\]

The positive matrix factorization (PMF) solution to the Chemical Mass Balance (CMB) receptor model (Paatero and Tapper, 1994; Watson et al., 2008) was used to assess potential sources of visibility degradation. The PMF model was run multiple times, extracting three to six factors. Each run was initialized with random starting points, and the most physically interpretable profiles were found with a four factor solution. The frequency distribution of scaled residuals was taken into account, most of which were between -2 and +2, ensuring a good agreement between the PMF model results and the input data. As with most PMF-CMB solutions, there are indications of some mixing of sources within each factor (Watson and Chow, 2012). Linear regression analysis was used to estimate source contribution to \( b_{ag, dry} \). The regression coefficients were then multiplied by the normalized source contributions to calculate the contribution of each source factor to the respective aerosol property for each sample.

4. Results and discussion

4.1. Seasonal variations of visibility

Daily averaged VR (Supplemental Fig. S1) varied from 0.6 to 28.5 km, with an average of 6.4 ± 4.5 km. Table 1 shows that average VR was 35–45% higher in spring (8.0 km) and summer (7.4 km) than during autumn (4.8 km) and winter (4.5 km). Although average VR in 2009 was ~23% higher than 2007 (Chang et al., 2009), it was lower than those reported from other large Chinese cities such as Beijing, Tianjin, Nanjing, Guangzhou, and Shanghai (Chang et al., 2009; Deng et al., 2011; Zhao et al., 2011).

As shown in Supplemental Fig. S2, wind speeds (1.8 m s\(^{-1}\)) and temperature (20.0 °C) during spring and summer indicate greater vertical mixing and horizontal dispersion than during winter, resulting in lower PM\(_{2.5}\) mass. Higher precipitation during spring and summer (465.4 mm or 70.4% of the 2009 precipitation; China Statistical Yearbook, 2010) could also scavenges pollutants. Average PM\(_{2.5}\) concentrations during autumn and winter were 171.4 and 203.4 μg m\(^{-3}\), respectively, 1.2–2.0 times higher than during the other seasons. Reduced visibility during autumn and winter was associated with higher secondary inorganic aerosols and organic carbon, with RH in the range of 67–78%. This differs from Beijing, where the lowest VR is found in summer and also associated with high RH (Zhang et al., 2010).

PM\(_{10}\) concentrations were translated to an air pollution index (API; see Table S1) in the “Blue Sky Project” (Zhang et al., 2010). Air quality is considered good when PM\(_{10}\) is below 150 μg m\(^{-3}\) with API < 100. This criterion resulted in 304 “Blue Sky” days during

### Table 1

<table>
<thead>
<tr>
<th>Parameter*</th>
<th>( b_{ag, dry} ) (Mm(^{-1}))</th>
<th>( b_{ag, wet} ) (Mm(^{-1}))</th>
<th>( b_{ag} ) (Mm(^{-1}))</th>
<th>( b_{ag} ) (Mm(^{-1}))</th>
<th>( b_{ag} ) (Mm(^{-1}))</th>
<th>( b_{ag} ) (Mm(^{-1}))</th>
<th>VR (km)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>434.3 ± 247.0</td>
<td>632.2 ± 488.7</td>
<td>72.7 ± 34.7</td>
<td>8.0 ± 2.5</td>
<td>10</td>
<td>711 ± 499</td>
<td>8.0 ± 4.9</td>
</tr>
<tr>
<td>% of best</td>
<td>67 %</td>
<td>83 %</td>
<td>12 %</td>
<td>1.5</td>
<td>2.0</td>
<td>867 ± 697</td>
<td>7.4 ± 4.3</td>
</tr>
<tr>
<td>Summer</td>
<td>454.5 ± 267.4</td>
<td>798.0 ± 694.4</td>
<td>57.5 ± 21.2</td>
<td>6.3 ± 2.2</td>
<td>10</td>
<td>1434 ± 1114</td>
<td>4.8 ± 3.6</td>
</tr>
<tr>
<td>% of best</td>
<td>62 %</td>
<td>86 %</td>
<td>10 %</td>
<td>1.2</td>
<td>1.9</td>
<td>1607 ± 1361</td>
<td>4.5 ± 3.7</td>
</tr>
<tr>
<td>Autumn</td>
<td>606.3 ± 310.4</td>
<td>1307.1 ± 1080.4</td>
<td>106.7 ± 55.4</td>
<td>8.6 ± 2.2</td>
<td>10</td>
<td>1102 ± 1020</td>
<td>6.4 ± 4.5</td>
</tr>
<tr>
<td>% of best</td>
<td>46.8</td>
<td>88.3</td>
<td>9.6</td>
<td>0.9</td>
<td>1.2</td>
<td>863 ± 697</td>
<td>7.4 ± 4.3</td>
</tr>
<tr>
<td>Winter</td>
<td>657.4 ± 436.9</td>
<td>1488.0 ± 1332.2</td>
<td>104.0 ± 69.6</td>
<td>8.3 ± 2.8</td>
<td>10</td>
<td>1607 ± 1361</td>
<td>4.5 ± 3.7</td>
</tr>
<tr>
<td>% of best</td>
<td>52.8</td>
<td>86.8</td>
<td>10.9</td>
<td>1.1</td>
<td>1.2</td>
<td>1067 ± 1361</td>
<td>4.5 ± 3.7</td>
</tr>
<tr>
<td>Annual</td>
<td>525.3 ± 338.7</td>
<td>1009.2 ± 994.6</td>
<td>82.6 ± 52.3</td>
<td>7.7 ± 2.6</td>
<td>10</td>
<td>1102 ± 1020</td>
<td>6.4 ± 4.5</td>
</tr>
<tr>
<td>% of best</td>
<td>58.2</td>
<td>86.3</td>
<td>10.9</td>
<td>1.2</td>
<td>1.6</td>
<td>1067 ± 1361</td>
<td>4.5 ± 3.7</td>
</tr>
</tbody>
</table>

* The four seasons were designated as December and mid-February for winter, March to May for spring, June–August for summer, and September–November for autumn.

b Dry scattering coefficient measured by nephelometer at RH < 60%.

c Wet scattering coefficient modified by ambient RH.

d Absorption by aerosols calculated from \( 10 \text{ (m}^2 \text{ g}^{-1}\) \times [EC] \text{(μg m}^{-3}\)\).

e Absorption by gas calculated from \( 0.33 \times [\text{NO2}] \text{(ppb)}\).

f Rayleigh scattering.

g Light extinction estimated by sum of daily \( b_{ag, dry}, b_{ag}, b_{ag}, \) and \( b_{ag} \), then averaged over each season.

h Visual range (VR) calculated from 3.912/\( b_{ag} \times 1000 \text{ km}\).
2009 (China Statistical Yearbook, 2010), ~80% of which occurred during the study period (see Supplemental Fig. S1). Optical measurements from this study, however, show ~65% of “Blue Sky” days were hazy (VR < 10 km and RH < 80%, China Meteorological Administration, 2010).

As shown in Table 1, the wet light scattering coefficient ($b_{sp,wet}$) had the highest contribution to $b_{ext}$, in the range of 632–1488 Mm$^{-1}$, accounting for ~84–88% of $b_{ext}$. Light scattering by dry particles ($b_{sp,dry}$) was correlated with PM$_{2.5}$ mass ($r = 0.7$), and ranged from 434 to 657 Mm$^{-1}$, accounting for 83–87% of dry $b_{ext}$. Similar single scattering albedos (i.e. $w_0 = b_{sp,dry}/b_{ext}$) were also found in the Pearl River and Yangtze River Delta regions of China (Cheng et al., 2008; Deng et al., 2008; Xu et al., 2002). The particle absorption coefficient ($b_{ap}$) contributed to 10–13% of $b_{ext}$, with the remaining 2–4% attributed to gases.

Table 2 presents the diurnal variations of $b_{sp,dry}$ and meteorological conditions. It shows elevated morning (0800–1000 LST) and evening (2300 LST) $b_{sp,dry}$ with minimum during afternoon (1400–1700 LST). Evening highs and afternoon lows in $b_{sp,dry}$ corresponded to the diurnal RH measurements. Elevated RH at night enhances the growth of hygroscopic particles (i.e. sulfates and nitrates) to sizes that scatter more light. These diurnal variations are similar to those found in other urban areas (Lyamani et al., 2008; Pereira et al., 2011); mainly driven by variations of emission sources and meteorological conditions (Pereira et al., 2008). Morning peaks in $b_{sp,dry}$ coincide with lower dispersion (i.e., low wind speed) and high emissions from traffic during rush hours (Cao et al., 2009). The decrease after the morning peak is associated with coupling of the surface inversion layer to layers aloft, low RH, and high wind speeds. The increase in $b_{sp,dry}$ during the evening hours

![Fig. 1. Diurnal variations of hourly averaged dry light scattering coefficient ($b_{sp,dry}$), wind speed, relative humidity (RH), and temperature changes during spring (March to May), summer (June to August), autumn (September to November), and winter (December to mid-February) in 2009.](image-url)
is attributed to the evening rush hour, increased domestic cooking and heating emissions, and formation of the nighttime surface inversion.

4.2. Correlation of visual range with \( \text{PM}_{2.5} \) and meteorological parameters

The correlation matrix in Table 2 illustrates that VR was negatively correlated with RH \( (r = -0.71) \), \( \text{PM}_{2.5} \) \( (r = -0.57) \), and NO\(_2\) \( (r = -0.33) \). This is consistent with Fig. 2, which shows that most of the days with low VR (<5 km) were associated with high RH (~90%) without precipitation.

VRs in Fig. 2 are exponentially associated with \( \text{PM}_{2.5} \) mass, consistent with the linear relationship between \( \text{PM}_{2.5} \) and VR was negatively related to secondary inorganic ions (SO\(_4^{2-}\) and NO\(_3^-\)) with correlations in the range of 0.71 to 0.62, consistent with previous studies (Tao et al., 2009; Yang et al., 2007; Yuan et al., 2006). High correlations \((0.81 < r < 0.88)\) were found between \( \text{PM}_{2.5} \) mass and major constituents: anions (SO\(_4^{2-}\) and NO\(_3^-\)), cation (NH\(_4^+\)), and carbon (OC and EC). Water-soluble potassium (K\(^+\)) was correlated with \( \text{PM}_{2.5} \) mass \((r = 0.88)\), carbon (OC and EC, \( r = 0.86 \)), and Cl\(^-\) \((r = 0.78)\), consistent with biomass burning contributions.

4.3. Effect of \( \text{PM}_{2.5} \) chemical composition on light extinction

Chemical \( b_{\text{ext}} \) (based on the revised IMPROVE equation), was highest during winter \((1328 \text{ Mm}^{-1})\), followed by autumn \((1316 \text{ Mm}^{-1})\), spring \((659 \text{ Mm}^{-1})\), and summer \((602 \text{ Mm}^{-1})\), with an annual average of 912 ± 882 Mm\(^{-1}\). Average chemical \( b_{\text{ext}} \) in Xi’an was 1.3–3.1 times higher than that measured in Jinan, China \((292 \text{ Mm}^{-1}, \text{Yang et al., 2007})\), Guangzhou, China \((367 \text{ Mm}^{-1}, \text{Jung et al., 2006})\), and Seoul, Korea \((704 \text{ Mm}^{-1}, \text{Kim et al., 2006})\). As shown in Fig. 3, \((\text{NH}_4\text{H}_2\text{SO}_4)\) was the largest contributor accounting for 39.8% of \( b_{\text{ext}} \), consistent with previous studies (Tao et al., 2009; Yang et al., 2007). OM \((23.8\%)\) and NH\(_4\)NO\(_3\) \((23.1\%)\) contributions were also important. Higher NH\(_4\)NO\(_3\) contributions were apparent during autumn, while OM contributions were important for all seasons (Fig. 3). Particle light absorption \( (b_{\text{ap}}) \) from EC contributed 9.1% of \( b_{\text{ext}} \).

For non-urban IMPROVE sites, Malm and Day (2000) found sulfates contributed ~60–70% of \( b_{\text{ext}} \) in the eastern United States, while OM contributed ~35% of \( b_{\text{ext}} \) in the western United States. Chan et al. (1999) found that poor visibility in Brisbane, Australia was associated with traffic emissions, followed by secondary...
sulfates and biomass burning. For urban sites, Yang et al. (2007) and Jung et al. (2009) found that (NH$_4$)$_2$SO$_4$ was the largest contributor (41%–47%) to $b_{ext}$ in Jinan and Guangzhou, followed by OM (∼22%).

According to the Xi'an Statistical Yearbook (2010), coal burning (a major source of energy generation) was over 7.85 × 10$^{10}$ tons in 2009, with ∼93% used to generate electricity and heating. Annual SO$_2$ emissions were estimated to be 8.3 × 10$^{5}$ tons. More coal combustion in the winter heating season (middle of November to the middle of March) is consistent with elevated light scattering by (NH$_4$)$_2$SO$_4$ (534 Mm$^{-1}$), and lower VR.

Chemical $b_{ext}$ slightly underestimated optical $b_{opt}$ as shown in Fig. 4, with a regression slope of 0.85 ± 0.02 and $r$ = 0.91. The revised IMPROVE equation (see Eq. (6)) is a reasonable starting point for $b_{ext}$ in Xi’an, but more locally-derived dry scattering and absorption coefficients and f(RH) might improve the agreement. These would require more specific measurements of particle size as a function of RH (Pitchford and McMurry, 1994).

VR is sorted into four categories in Table 3 to compare variations in chemical components under good to poor visibility: Type I (VR > 10 km), Type II (5 < VR ≤ 10 km), Type III (1 < VR ≤ 5 km), and Type IV (VR ≤ 1 km). For Type I, OM (38.5%) was the largest $b_{ext}$ contributor, followed by (NH$_4$)$_2$SO$_4$ (30.2%) and NH$_4$NO$_3$ (8.4%). For Type IV, (NH$_4$)$_2$SO$_4$ (49.9%) and NH$_3$NO$_3$ (27.9%) accounted for nearly 80% of $b_{ext}$, similar to Type III, with >70% of $b_{ext}$ from (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. Although OM increased with lower VR, its relative contributions varied from 16.2% to 31.4% of $b_{ext}$.

Table 4 shows increases in most of the chemical species concentrations (except for Ca$^{2+}$ and Mg$^{2+}$) corresponding with lower VR. For Types III and IV visibility conditions, SO$_4$ and NO$_3$ concentrations were 2.9 and 14.1 times higher than for Type I good visibility, respectively.

### 4.4. Source apportionment of visibility degradation

The PMF–CMB used PM$_{2.5}$ OC, EC, Ca, Mg, S, K, Ti, Mn, Fe, As, Br, and Pb to apportion $b_{sp,dry}$ to source factors. Derived source factors and contribution estimates are shown in Supplemental Fig. S3 and Fig. 5. The largest source factor, contributing 52.2% to $b_{sp,dry}$, was loaded on S, As, and Pb and was assigned to coal combustion. This factor contributed 60.7% in winter, 53.6% in autumn, 47.2% in spring, and 45.2% in summer, consistent with variations for PM$_{2.5}$ mass and energy consumption (Cao et al., 2009).

Factor 2 was enriched in EC, Br, and Pb, and was assigned to engine exhaust (Xu et al., 2012), accounting for 30.8% of $b_{sp,dry}$ with the highest during summer (39.3%). The total number of motor vehicles in Xi’an increased from ∼5.4 × 10$^5$ in 2005 to ∼10.1 × 10$^5$ in 2009 (Xi’an Statistical Yearbook, 2010). Engine NO$_x$ emissions are related to NO$_x$ levels. Gasoline and diesel engine exhaust contain light-absorbing EC, indicative of incomplete combustion (Cao et al., 2006; Watson et al., 1994).

Factor 3 had high loadings on K and OC, and was assigned to biomass burning (Duan et al., 2004; Xie et al., 2008). In nearby non-urban areas, wheat straw and maize stalks are burned for cooking year round, and burned for heating during winter. This source accounted for 12.3% of $b_{sp,dry}$.

Factor 4 had high loadings on Ca, Mg, Ti, Fe, and Mn, and was assigned to fugitive dust (Cao et al., 2008; Xie et al., 2008). An estimated ∼283 km$^2$ (∼27% of total area of Xi’an) was under construction during the study period (Xi’an Statistical Yearbook, 2010). Construction dust as well as vehicle-related resuspended road dust contributed 4.7% of $b_{sp,dry}$ with the highest during spring.

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### Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Type I $b_{ext}$</th>
<th>Type II $b_{ext}$</th>
<th>Type III $b_{ext}$</th>
<th>Type IV $b_{ext}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average S.D.</td>
<td>Average S.D.</td>
<td>Average S.D.</td>
<td>Average S.D.</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SO$_4$</td>
<td>115.2 103.9</td>
<td>187.5 103.9</td>
<td>607.8 412.1</td>
<td>2663.5 311.5</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>32.1 28.9</td>
<td>92.5 68.2</td>
<td>379.4 256.8</td>
<td>1490.1 334.3</td>
</tr>
<tr>
<td>OM</td>
<td>146.5 68.4</td>
<td>180.3 86.2</td>
<td>266.8 204.8</td>
<td>866.1 379.9</td>
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<tr>
<td>EC</td>
<td>49.2 16.5</td>
<td>73.7 34.5</td>
<td>101.9 59.6</td>
<td>246.4 29.5</td>
</tr>
<tr>
<td>Soil dust</td>
<td>31.6 24.8</td>
<td>33.1 29.6</td>
<td>25.4 18.1</td>
<td>62.2 4.9</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>6.3 1.6</td>
<td>7.2 2.4</td>
<td>8.7 2.7</td>
<td>13.7 1.1</td>
</tr>
</tbody>
</table>

$b_{ext}$: Light extinction coefficient; OM: Organic mass = 1.6 × OC; EC: Elemental carbon. Soil dust: Estimated by Fe/0.035; and S.D.: Standard deviation.

### Table 4

<table>
<thead>
<tr>
<th>Observable$^a$</th>
<th>Type I</th>
<th>Type II</th>
<th>Type III</th>
<th>Type IV</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Average S.D.$^b$</td>
<td>Average S.D.</td>
<td>Average S.D.</td>
<td>Average S.D.</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>96.0 51.1</td>
<td>118.2 43.9</td>
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<td>511.8 100.6</td>
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<td>16.0 6.8</td>
<td>35.2 17.5</td>
<td>109.9 8.6</td>
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<tr>
<td>NO$_2$</td>
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<td>22.3 13.1</td>
<td>62.0 2.2</td>
</tr>
<tr>
<td>Cl$^-$</td>
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<td>5.8 5.4</td>
<td>14.7 3.5</td>
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<tr>
<td>NH$_3$</td>
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<td>6.3 6.3</td>
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<td>K$^+$</td>
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<tr>
<td>Mg$^{2+}$</td>
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<td>0.4 0.3</td>
<td>0.2</td>
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<tr>
<td>Ca$^{2+}$</td>
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<td>1.3 1.1</td>
<td>4.9</td>
</tr>
<tr>
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<td>29.9 13.7</td>
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<tr>
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<td>10.2 6.0</td>
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</tr>
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<td>51.7 16</td>
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<td>WS</td>
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<td>1.7 0.7</td>
<td>1.4 0.6</td>
<td>0.8 0.4</td>
</tr>
</tbody>
</table>

$^a$ Units: PM$_{2.5}$ and chemical species, mg m$^{-3}$; Relative humidity (RH), %; Wind speed (WS), m s$^{-1}$; 
$^b$ S.D.: Standard deviation.

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**Fig. 5.** Average source contribution (in percent) of each PMF–CMB source factor to dry particle light scattering coefficient ($b_{sp,dry}$) for each season from February 15 to December 31, 2009 in Xi’an, China.
(10.4%) when wind speed was faster than other seasons (see Supplemental Fig. S2).

5. Conclusions

Daily dry particle light scattering coefficients, PM2.5, NO2 were collected in Xi’an from February 15 to December 31, 2009 to investigate the causes of visibility degradation and its temporal variability. Average VR was 6.4 ± 4.5 km, with the largest seasonal variations found in spring (1.5–28.5 km), followed by summer (1.2–18.9 km). The lowest VR was found in winter (0.8–10.7 km), mainly due to the elevated PM2.5 mass, sulfates, and nitrates. Diurnal particle light scattering coefficients (b_{D, dry}) showed early morning and late evening peaks with a low in the afternoon hours. This diurnal cycle was likely due to variations of emission sources and meteorological conditions. Elevated PM2.5 mass was associated with VR < 10 km, and a PM2.5 threshold value of 88 μg m⁻³ (i.e., low visibility occurs when PM2.5 > 88 μg m⁻³).

Based on the revised IMPROVE equation, (NH4)2SO4 was the largest contributor, accounting for 39.8% of light extinction coefficient, followed by OM (23.8%), NH4NO3 (23.1%), and EC (9.1%), with minor contribution from soil dust (3.4%) and NO2 (0.8%). Chemical extinction was ~15% lower than optical extinction, but they were highly correlated. Elevated concentrations of secondary aerosol species (e.g., SO4²⁻ and NO3⁻) were the main causes of VR.

The PMF solution to the CMB receptor model indicated that coal combustion (52.2%) was the largest contributor to b_{PM2.5} followed by engine exhaust (30.8%), biomass burning (12.3%), and fugitive dust (4.7%). Approximately 65% of “Blue Sky” days reported by the provincial government corresponded to VR < 10 km.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.atmosenv.2012.05.036.

References


