Optical properties of size-resolved particles at a Hong Kong urban site during winter

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Abstract
Visibility degradation in Hong Kong is related to the city’s serious air pollution problems. To investigate the aerosols’ optical properties and their relationship with the chemical composition and size distribution of the particles, a monitoring campaign was conducted at an urban site in the early winter period (from October to December, 2010). The particle light scattering coefficient (Bsp) and absorption coefficient (Bap) were measured. Two collocated Micro-Orifice Uniform Deposit Impactor samplers (MOUDI110, MSP, USA) with nominal 50% cut-off aerodynamic diameters of 18, 10, 5.6, 3.2, 1.8, 1, 0.56, 0.32, 0.18, 0.1, and 0.056 μm were used to collect size-resolved particle samples. The average Bsp and Bap were 201.96 ± 105.82 Mm⁻¹ and 39.91 ± 19.16 Mm⁻¹, with an average single scattering albedo (ωo) of 0.82 ± 0.07. The theoretical method of light extinction calculation was used to determine the extinction of the size-resolved particulate matters (PM). The reconstructed light scattering coefficient correlated well with the measured scattering value in the Hong Kong urban area. Droplet mode (0.56–1.8 μm) particles contributed most to the particle light extinction (~69%). Organic matter, ammonium sulphate and elemental carbon were the key components causing visibility degradation in the droplet (0.56–1.8 μm) and condensation (0.1–0.56 μm) size ranges. Five sources contributing to particle light extinction have been identified using positive matrix factorisation (PMF). Traffic/engine exhausts and secondary aerosols accounted for ~36% and ~32% of particle light extinction, respectively, followed by sea salt (~15%). The remaining sources, soil/fugitive dust and tire dust, contributed by ~10% and 7%, respectively, to particle light extinction.

1. Introduction

Visibility impairment results from the scattering and absorption of incoming sunlight (Tao et al., 2009; Watson, 2002). The light extinction (Bext) can be used to describe its characteristics, providing a summation of light scattering and absorption from particulate and gaseous matter (Bohren and Huffman, 2008). Natural and pollution-derived particles disturb the Earth’s radiation balance and indirectly affect cloud formation and climate change (Bohren and Huffman, 2008; Ling et al., 2013; Rosenfeld, 1999; Yan et al., 2008). Particle optical properties are highly related to particle sizes, shapes and chemical components (Tsai et al., 2012; Yan et al., 2008; Yu et al., 2010).
The frequency of low visibility days in Hong Kong has increased over the last decade (HKO, 2013). Past studies (Chang and Koo, 1986; Cheung et al., 2005; Lai and Sequeira, 2001; Lee and Sequeira, 2002; Man and Shih, 2001; Sequeira and Lai, 1998; Wang et al., 2003) have shown that ammonium sulphate ([NH₄]₂SO₄) and elemental carbon (EC) are the most important factors causing this visibility impairment. Ammonium sulphate is a hydrophilic compound, and its resulting increase in relative humidity (RH) can enhance its light scattering effect. Many methods have been used to determine the scattering and absorption efficiency of chemical components, including the theoretical method, the partial scattering method, the measurement method and the multilinear regression (MLR) method (Hand and Malm, 2007). The theoretical and partial scattering methods have been used to determine the scattering and absorption efficiencies of chemical components in the USA. (Lowenthal and Kumar, 2004, 2006; Malm and Pitchford, 1997; Sloane, 1986). In Hong Kong, the MLR method and the US Interagency Monitoring of Protected Visual Environments (IMPROVE) equation have commonly been used to determine the contributions of different chemical components to visibility impairment in PM₂.₅ and PM₁₀ (Wang et al., 2003). A small number of studies have focused on determining the optical properties of size-resolved particles (Lowenthal et al. 1995; Sloane and Wolff, 1985).

In this study, optical parameters were measured and size-fractionated chemical components (i.e., elements, water soluble ions and carbon) were analysed hourly during the winter period at an urban site in Hong Kong. The study aims to 1) determine the characteristics and variations of the optical properties of size-segregated particles in an urban environment; 2) provide insight into size-resolved particles and their chemical extinction (the summation of (mass concentration × their mass extinction efficiency) for different chemical components) by using the theoretical method; and 3) identify potential sources contributing to particle light extinction.

2. Methods

2.1. Sampling site

Hong Kong occupies an area of 1104 square kilometres, with a population of seven million; it is one of the developed cities in the world (World Bank, 2011). The sampling site was located on the rooftop of an eight-floor building on the campus of the Hong Kong Polytechnic University (HKPU) (22.30°N, 114.17°E), as shown in Fig. 1. This site is close to the Cross Harbour Tunnel, subject to heavy traffic activity and regional pollutant transport.

2.2. Continuous optical, gaseous and meteorological parameters measurements

The particle light scattering coefficients (Bsp) for fine suspended particles were measured hourly using an integrating nephelometer (wavelength, λ = 525 nm) with a heater (Aurora-1000 Ecotech, Melbourne, Australia) to maintain the RH of <60%. The heated nephelometer may have caused some evaporation of ammonium nitrate, (NH₄NO₃), which is one of chemical components leading to visibility impairment (Watson et al., 2008b). To restrict the nephelometer uncertainty to within ±10%, its sampling tube was designed based on Bergin et al. (1997). Calibration was performed by a daily zero check (to within ±1 Mm⁻¹) and a monthly span check (not more than 10% of the recommended value). The zero check was performed automatically by pumping in particle-free air. The span check was performed manually using carbon dioxide (CO₂), as recommended by the manufacturer (Aurora-1000 User Manual, 2008). Hourly black carbon (BC) concentrations (μg/m³) were measured using an aethalometer with a flow rate of 5 L/min (Magee Scientific Company, Berkeley, CA, USA, Model AE-31). The particles absorption coefficient (Bap) (Mm⁻¹) at λ = 532 nm was calculated from the BC
concentration in μg/m³ (λ = 880 nm), based on a mass absorption efficiency value of 8.28 m²/g, using the equation
\[ B_{\text{ap}}(532 \text{ nm}) = 8.28 \times \left[ \frac{BC \mu g/m^3}{(\text{Weingartner et al., 2003; Wu et al., 2009})} \right] \]
To maintain the same wavelength (λ = 532 nm) between B_{\text{sp}} and B_{\text{ap}}, the hourly B_{\text{ap}} at 525 nm was converted by applying an Angström exponent (α_s) of 1.3 in the Pearl River Delta (PRD) region (Jung et al., 2009; Xu et al., 2012) based on the following equation, as described in Ångström (1930) and Rocard and de Rothschild (1927):
\[ \text{B}_{\text{sp}}(532 \text{ nm}) = \frac{532 \text{ nm}}{525 \text{ nm}} \times (532 \text{ nm})^{0.056} \]

The single scattering albedo (SSA, \( \alpha_s \) at λ = 532 nm) is an important factor in estimating radiative forcing (Yan et al., 2008). It was calculated based on the ratio of \( B_{\text{sp}} \) to the sum of \( B_{\text{sp}} \) and \( B_{\text{ap}} \) at 532 nm.

The hourly-averaged concentrations of inorganic water-soluble ions—chloride (\( \text{Cl}^- \)), nitrate (\( \text{NO}_3^- \)), sulphate (\( \text{SO}_4^{2-} \)), sodium (\( \text{Na}^+ \)), ammonium (\( \text{NH}_4^+ \)), potassium (\( \text{K}^+ \)), calcium (\( \text{Ca}^{2+} \))—and magnesium (\( \text{Mg}^{2+} \))—were determined by Ambient ions monitoring (AIM) using a Dionex IC Model 90 (Sunnyvale, California, USA). The process for the measurement of ion species by AIM is described in the studies of Zhou et al. (2009, 2012). Hourly nitrogen dioxide (\( \text{NO}_2 \)) was measured using a chemiluminescence instrument (Model 42I Thermo Environmental instrument, Waltham, Massachusetts, USA; Xu et al., 2013). Concurrent meteorological parameters, such as wind direction (WD), wind speed (WS), relative humidity (RH), ambient temperature (T), and solar radiation, were measured using a portable automatic meteorological station (Model 05305VM and Model 41382 VC/VF, R.M. Young Company, Traverse City, Michigan, USA). Hourly gaseous, ionic, optical and meteorological measurements were taken from October 23, 2010 to December 31, 2010.

2.3. Integrated sample collection

Two collocated Micro-Orifice Uniform Deposit Impactor (MOUDI 100, MSP Corp., Shoreview, Minnesota, USA) samplers were operated at a 30 L/min flow rate. The MOUDI samplers had 10 stages with nominal 50% cut-offs at aerodynamic diameters of 18, 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32, 0.18, 0.1, and 0.056 μm. A total of 10 sets of 24-h samples (including one field blank to assess passive deposition), were collected in 2010, each from 10:00 am of one day to 10:00 am of the next (LST, Local standard time; samples taken October 23rd, November 1st, 4th, 7th, 13th, 25th, December 1st, 5th and 11th) using Teflon-membrane (φ = 47 mm, Pall Sciences, New York, USA) and quartz-fibre (47 mm QMA, Whatman, Maidstone, England) filters. The backup stage of the impactor used 37 mm Teflon-membrane and quartz-fibre filters.

Before sampling, the quartz-fibre filters were preheated at 900 °C for 3 h to minimise organic artifacts (Ho et al., 2006). Both the Teflon-membrane and quartz-fibre filters were weighed before and after sampling using a microbalance (Model MCS, Satorius, Goettingen, Germany) with a sensitivity of ±1 μg in the 0–250 mg range. Before weighing, the filters were equilibrated in a desiccator (DRY-100, WEIFO, TAIWAN) for 24 h in a temperature (25 ± 5 °C) and RH (35 ± 10%) controlled environment. After weighing, the filters were stored in air-tight containers in a refrigerator at 4 °C to prevent the evaporation of volatile components. Sample flow rates within ±10% of the specification were verified at the beginning and end of each sampling period.

Some uncertainty in the MOUDI sampler measurements resulted from the effects of temperature, relative humidity and particle bounce (Chow et al., 2005; Huang et al., 2004; Milford and Davidson, 1987). To eliminate these uncertainties, artifacts in the size-resolved particle concentration data were corrected using the method provided by Wang et al. (2013b); Nie et al. (2010). The MOUDI samples were categorised into two to three groups based on the degree of sampling loss. An averaged integrated loss degree, which was later used to constrain sampling losses, was estimated from a regression analysis between MOUDI and AIM for each group of samples determined earlier. The value resulting from subtraction of the MOUDI samples with and without sampling losses was used to derive a loss function for each size bin below a certain degree of integrated loss. The constrained loss percentages in each individual size range were used to correct the size-resolved MOUDI data.

2.4. Chemical analysis

After gravimetric analysis, Teflon-membrane filters were analysed for the presence of NaCl (from Na to U) at the Institute of Earth and Environment, Chinese Academy of Science, China, using energy-dispersive X-ray fluorescence (XRF) analyses (Epsilon 5 ED-XRF, PANalytical B.V., the Netherlands; Watson et al., 1999). The quartz-fibre filters were analysed for organic carbon (OC), elemental carbon (EC) and water-soluble ions in the Air Laboratory of HKPU. A portion of the quartz-fibre filter samples (0.526 cm²) were used for OC and EC analysis by the DRI Model 2001 Thermal/Optical Carbon Analyser (Atmoslytic Inc., Calabasas, CA, USA), following the IMPROVE-A/Thermal-Optical reference (TOR; Chow et al., 2007, 2011; Ho et al., 2002). For ion analysis, half of quartz-fibre filters were extracted with 10 ml of ultra-pure water (specific resistance ≥18.1 MΩ, Millipore). The extraction solutions were filtered and stored in plastic vials in the refrigerator at 4 °C until analysis. Water soluble ions including \( \text{Cl}^- \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), \( \text{Na}^+ \), \( \text{K}^+ \), \( \text{Ca}^{2+} \) and \( \text{NH}_4^+ \) were analysed using ion chromatography (ICS3000, DIONEX, Sunnyvale, CA, USA; Chow and Watson, 1999).

Teflon-membrane filters were used to determine measured mass concentrations for different particle sizes. The reconstructed mass was calculated based on the mass reconstruction of the soil dust (2.2 × Al + 2.49 × Si + 1.63 × Ca + 2.42 × Fe + 1.94 × Ti), organic matters (OC × 1.8), soot (EC), ammonium sulphate (1.375 × SO₄²⁻), ammonium nitrate (1.29 × NO₃⁻) and non-crustal trace elements (the sum of non-geological trace elements). A reasonable correlation of \( R^2 = 0.90 \) was found between the measured and reconstructed mass concentrations. This result confirmed the validity of the gravimetric and chemical measurements. Supplemental Figures S1–S3 provide more detailed information on the validity of the chemical measurements, including reconstructed and measured mass, anion vs. cation balance, and internal consistency (i.e., sulphate vs. sulphur, chloride vs. chlorine).
2.5. Estimation of particle light scattering and absorption

The size-resolved particle scattering and absorption coefficient was calculated using Mie theory (Mie, 1908; Sloane, 1983, 1984, 1986; Sloane and Wolff, 1985):

\[ B_{sp} = \int \sigma_{sp} n(D) dD, \]  

(2)

where \( \sigma_{sp} \) is the scattering cross section, which depends on the incident light wavelength (\( \lambda \)), the stokes diameter (\( D \); Cheng et al., 2008), and the complex index of refraction (m), which can be calculated using Mie theory for spherical particles (Bohren and Huffman, 2008; Rosenberg et al., 2012; Wiscombe, 1980). The MOUDI stage concentrations were converted to continuous size distributions using a log-normal distribution (Dong et al., 2004; Twomey, 1975; Winklmayr et al., 1990). The number concentration \( n(D) dD \) was then determined from the mass concentrations of the different species (Sloane, 1984), using the following equation:

\[ n(D) dD = \frac{M(D)}{\rho \times \left( \frac{D}{10} \right)^3 \times \pi \times D^3} \]  

(3)

The ELSIE program is configured for five chemical components (USA IMPROVE; Sisler et al., 1996): soil dust (Eq. (5)), organic matter (Eq. (6)), ammonium sulphate (Eq. (7)), ammonium nitrate (Eq. (8)), and sea salt (Eq. (9)). Water content was estimated using the ZSR (Zdanovski–Stokes–Robinson) method (Clegg et al., 1998; Clegg and Seinfeld, 2004; Stokes and Robinson, 1966). The densities (\( \rho \)) and complex indices of refraction (m) obtained are shown in Table 1.

The particle light extinction (\( B_{ext} \)) was calculated as a summation of particle light scattering (\( B_{sp} \)) and particle light absorption (\( B_{ap} \)):

\[ B_{ext} = B_{sp} + B_{ap} = \int \sigma_{sp} n(D) dD + \int \sigma_{ap} n(D) dD \]  

(4)

where only the followed chemical species were considered and each species or element was multiplied by a molar correction factor (mcf), as in Malm et al. (1994):

\begin{align*}
\text{Soil dust} & = 2.2 \times Al + 2.49 \times Si + 1.63 \times Ca + 2.42 \times Fe + 1.94 \times Ti \\
\text{Organic matters} & = OC \times 1.8 \\
\text{Ammonium nitrate} & = 1.29 \times NO_3^{-}
\end{align*}

Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>Density (g/cm³)</th>
<th>Refractive index</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium sulfate</td>
<td>1.76</td>
<td>1.53, i0.0</td>
<td>(Watson et al., 2008b)</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>1.73</td>
<td>1.55, i0.0</td>
<td>(Watson et al., 2008b)</td>
</tr>
<tr>
<td>Organic matters</td>
<td>1.2</td>
<td>1.55, i0.0</td>
<td>(Watson et al., 2008b)</td>
</tr>
<tr>
<td>Elemental carbon</td>
<td>1.7</td>
<td>1.9, i0.6</td>
<td>(Watson et al., 2008b)</td>
</tr>
<tr>
<td>Soil</td>
<td>2.3</td>
<td>1.56, i0.005</td>
<td>(Watson et al., 2008b)</td>
</tr>
<tr>
<td>Sea salt</td>
<td>2.17</td>
<td>1.54, i0.0</td>
<td>(Tang, 1996)</td>
</tr>
<tr>
<td>Water content</td>
<td>1.00</td>
<td>1.33, i0.0</td>
<td>(Watson et al., 2008b)</td>
</tr>
</tbody>
</table>

Fig. 2. a. Time series on hourly particle scattering coefficient (\( B_{sp} \)), absorption coefficient (\( B_{ap} \)) and single scattering albedo (\( \omega_o \)). b. Frequency distribution of hourly particle scattering coefficient (\( B_{sp} \)), absorption coefficient (\( B_{ap} \)) and single scattering albedo (\( \omega_o \)).
Ammonium sulphate = 1.375 × SO$_4^{2-}$  \hspace{1cm} (8)

Sea salt = 1.8 × Cl$^-$  \hspace{1cm} (9)

It should be noted that only fine nitrate particles were considered as ammonium nitrate in the equation. The reasons for not considering coarse nitrate particles were 1) that coarse particles are not important for particle light extinction (Jung et al., 2009; Li et al., 2013); and 2) that the mass concentration of coarse nitrate particles in the study was less than 10% of the mass concentration of coarse particles.

In the study, particle light absorption was estimated using the following equations: $B_{ap} = \int \sigma_{ap} n(D) dD$ and $n(D) dD = \frac{(M(D))}{\rho_{EC} \pi D^3}$. The EC concentration was used to calculate particle light absorption. The density and refractive index of EC are given in Table 1.

2.6. Source apportionment of visibility degradation

The PMF model is a multivariate factor analysis method that functions by dividing speciated data into two matrices: factor contribution ($g$) and factor profile ($\hat{f}$). It can be illustrated by the
3.1. Aerosol optical property

Fig. 2a presents the hourly time series of $B_{sp}$, $B_{ap}$ and single scattering albedo ($\omega$), Large variations were found in the hourly optical measurements, which ranged from 2.4 to 789 Mm$^{-1}$ for $B_{sp}$, from 4.8 to 157 Mm$^{-1}$ for $B_{ap}$ and from 0.33 to 0.94 for $\omega$ (Table 2). The monthly $B_{sp}$ and $B_{ap}$ frequently reached 100–200 Mm$^{-1}$ and 20–40 Mm$^{-1}$, respectively. Scattering accounted for a majority of particle light extinction; $\omega$ was mostly in the range of 0.8–0.9 (Fig. 2b).

In general, average $B_{sp}$ and $B_{ap}$ values in this study were 45–100 lower than those measured in Chinese mega cities such as Guangzhou, Shanghai and Beijing during the winter period (Andreae et al., 2008; He et al., 2009; Xu et al., 2012). However, the average $B_{sp}$ (202 ± 106 Mm$^{-1}$) was ~50% to 70% higher than the values of 60 Mm$^{-1}$, 84 Mm$^{-1}$ and 93 Mm$^{-1}$, measured at Valencia (Spain), Granada (Spain), and Southern Mexico city (Mexico), respectively, while the average $B_{ap}$ of 40 ± 19 Mm$^{-1}$ was ~30% to 40% higher (Garcia et al., 2010; Lyamani et al., 2008; Titos et al., 2012; Xu et al., 2012). The mean and median $\omega$ of 0.83 and 0.82 were similar to the $\omega$ values measured in Shanghai and Guangzhou (0.81–0.82) (Yan et al., 2008) but lower than the 0.85–0.9 measured in rural China, 0.85–0.95 in the Northern hemisphere (obtained by AERONET) and 0.92 in a Hong Kong rural area during the winter period (Table 3).

In general, light extinction ($B_{ext}$) includes particle light scattering ($B_{sp}$), particle light absorption ($B_{ap}$), gaseous light absorption and Rayleigh scattering.

3. Results and discussion

### 3.1. Aerosol optical property

Table 2

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Particle light scattering ($B_{sp}$ at 532 nm) (Mm$^{-1}$)</th>
<th>Particle light absorption ($B_{ap}$ at 532 nm) (Mm$^{-1}$)</th>
<th>Single scattering albedo (SSA, $\omega_o$) *</th>
</tr>
</thead>
<tbody>
<tr>
<td>The HK Polytechnic University (PU)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>201.96</td>
<td>39.91</td>
<td>0.82</td>
</tr>
<tr>
<td>Standard deviation (SD)</td>
<td>105.82</td>
<td>19.16</td>
<td>0.07</td>
</tr>
<tr>
<td>Maximum</td>
<td>788.91</td>
<td>156.95</td>
<td>0.94</td>
</tr>
<tr>
<td>Minimum</td>
<td>2.43</td>
<td>4.77</td>
<td>0.33</td>
</tr>
<tr>
<td>Median</td>
<td>183.04</td>
<td>36.99</td>
<td>0.83</td>
</tr>
<tr>
<td>Hours</td>
<td>1679</td>
<td>1600</td>
<td>1600</td>
</tr>
</tbody>
</table>

* $\omega_o = \frac{B_{ap}}{B_{sp}+B_{ap}}$.

Table 3

<table>
<thead>
<tr>
<th>Site (urban site)</th>
<th>Period (month, year)</th>
<th>$B_{sp}$ (Mm$^{-1}$)</th>
<th>$B_{ap}$ (Mm$^{-1}$)</th>
<th>SSA $\omega_o$</th>
<th>Instrumentation References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKPU, HK</td>
<td>Oct.–Dec., 2010</td>
<td>202</td>
<td>40</td>
<td>0.82</td>
<td>M9003 Nephelometer EcoTech</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Winter, 2004</td>
<td>259</td>
<td>58</td>
<td>0.82</td>
<td>AE-31, Magee scientific</td>
</tr>
<tr>
<td>Guangzhou, China</td>
<td>Oct.–Nov., 2004</td>
<td>418</td>
<td>91</td>
<td>0.80</td>
<td>Nephelometer, Radiance research, PASP, Radiance Research, M903</td>
</tr>
<tr>
<td>Shanghai, China</td>
<td>Dec., 2010–Mar., 2011</td>
<td>293</td>
<td>66</td>
<td>0.81</td>
<td>M9003 PAS</td>
</tr>
<tr>
<td>Valencia, Spain</td>
<td>Winter, 2006–2010(average)</td>
<td>60</td>
<td>N.A.</td>
<td>N.A.</td>
<td>3563 Nephelometer, TSL Inc.</td>
</tr>
<tr>
<td>Granada, Spain</td>
<td>Winter, 2005</td>
<td>84</td>
<td>28</td>
<td>0.75</td>
<td>3563 Nephelometer, TSL Inc.</td>
</tr>
<tr>
<td>Southern Mexico City</td>
<td>Feb. 2005</td>
<td>93</td>
<td>20</td>
<td>0.82</td>
<td>5012 MAAP, Thermo, Inc.</td>
</tr>
</tbody>
</table>

N.A. = not available.
Fig. 4. Diurnal variation of: a) hourly dry particle light scattering coefficient ($B_{sp}$); b) hourly particle absorption coefficient ($B_{ap}$); c) single scattering albedo ($\omega_o$); d) wind speeds; e) NO$_2$; f) nitrate; and g) gasoline-typed vehicle counts (#).
3.2. Temporal variation of aerosol optical properties

The value of the optical components was averaged for each hour of the day during the October to December 2010 period, to obtain the average measurements as a function of local standard time (LST). The \( B_{sp} \) and \( B_{ap} \) showed clear diurnal variation with small standard errors (Fig. 4). Their respective values were found to be 22% and 24% higher on weekdays than on weekends. A similar morning peak in \( B_{sp} \) was observed around 08:00 LST on weekdays and weekends (Fig. 4a). A slight increase in \( B_{sp} \) in the afternoon (14:00–16:00 LST) is related to secondary aerosol formation by the photochemical reaction of gaseous precursors (Yan et al., 2008). But a sharp increase was only found during the late afternoon period (18:00–20:00 LST) on weekends, with weekdays instead showing a decrease over this period. In addition, similar patterns were observed over this period in \( NO_3^- \) (Fig. 4f) and vehicle count (Fig. 4g), which could reflect the increase in local traffic activity. For the particle light absorption (\( B_{ap} \)), an elevated value (53–54 Mm\(^{-1}\)) occurred during the morning (08:00–9:00 LST) and afternoon (17:00–18:00 LST) rush hours on weekdays (Fig. 4b). Weekends exhibited a more prolonged morning (08:00–11:00 LST) and afternoon (17:00–20:00 LST) peak with lower values of 37.4 Mm\(^{-1}\) and 44.4 Mm\(^{-1}\), respectively. The decrease of \( B_{ap} \) at noon (12:00 LST) suggests that the increase in the planetary boundary layer (PBL) and higher wind speeds cause more efficient dispersion (Fig. 4d). Lower \( B_{ap} \) values in the early morning were observed, potentially due to dry deposition causing particle removal. Previous studies (Titos et al., 2012; Xu et al., 2012; Yan et al., 2008) have shown that BC, as a primary pollutant, is the main contributor to \( B_{ap} \), and similar diurnal pattern of \( B_{ap} \) has been found at urban sites in Spain and Shanghai and a Beijing rural site. The evening peak (20:00–21:00 LST) found during the weekend coincides with the increase in hourly-averaged \( NO_2 \) (Fig. 4e), \( NO_3^- \) (Fig. 4f) and traffic counts (Fig. 4g) (Hong Kong Transportation Department). For this reason, the diurnal variation of single scattering albedo (SSA, \( \omega_o \); Fig. 4c) showed a maximum value during the early morning hours (02:00–04:00 LST) and decreased to a minimum in the early traffic hours and late afternoon. The diurnal pattern of single scattering albedo indicated a reduction of light absorption loading in the early morning due to dry deposition particle removal.

3.3. Chemical and optical characteristics of size-resolved particles

The particle size modes were defined as follows: a coarse mode (1.8–10 \( \mu \)m), droplet mode (0.56–1.8 \( \mu \)m), condensation mode (0.1–0.56 \( \mu \)m) and nucleation mode (\(<0.1 \mu \)m). Particle light scattering and absorption varied with particle size (Chow et al., 2002; Kleefeld et al., 2002; Watson, 2002; Yu et al., 2010). Fig. 5a shows a bimodal size distribution, which dominated in coarse mode with a mass median aerodynamic diameter (MDAD) of 10 \( \mu \)m.

![Fig. 5](image)

**Table 4**

<table>
<thead>
<tr>
<th>Sampling date (2010)</th>
<th>Measured (optical) particle light scattering ( (Mm^{-1})^a )</th>
<th>Measured ( NO_2 ) light scattering ( (Mm^{-1})^b ) ( 0–10 \mu )m</th>
<th>Measured ( PM_{10} ) light scattering ( (Mm^{-1})^b ) ( 0–1.8 \mu )m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct. 23–24</td>
<td>171.7</td>
<td>196.3</td>
<td>184.0</td>
</tr>
<tr>
<td>Nov. 1–2</td>
<td>253.4</td>
<td>282.4</td>
<td>265.1</td>
</tr>
<tr>
<td>Nov. 4–5</td>
<td>394.4</td>
<td>418.4</td>
<td>407.3</td>
</tr>
<tr>
<td>Nov. 7–8</td>
<td>202.2</td>
<td>237.3</td>
<td>229.9</td>
</tr>
<tr>
<td>Nov. 13–14</td>
<td>163.8</td>
<td>222.6</td>
<td>191.5</td>
</tr>
<tr>
<td>Nov. 25–26</td>
<td>219.8</td>
<td>247.9</td>
<td>234.0</td>
</tr>
<tr>
<td>Dec. 1–2</td>
<td>227.4</td>
<td>272.1</td>
<td>260.5</td>
</tr>
<tr>
<td>Dec. 5–6</td>
<td>253.3</td>
<td>287.4</td>
<td>263.6</td>
</tr>
<tr>
<td>Dec. 11–12</td>
<td>210.2</td>
<td>203.7</td>
<td>191.5</td>
</tr>
<tr>
<td>Average</td>
<td>232.9</td>
<td>263.1</td>
<td>247.5</td>
</tr>
</tbody>
</table>

\( ^a \) Measured by Nephelometer at \( \lambda \) of 532 nm.

\( ^b \) Calculation based on Eq. (2).
(MMAD, D\text{pp1}) of 3 μm and a standard deviation (\sigma_g1) of 2.87, and condensation mode, with an MMAD (D\text{pp2}) of 0.4 μm and a standard deviation (\sigma_g2) of 2.98. The mass concentration for each mode constituted ~26% of the total PM18 mass.

The US IMPROVE equation is not suitable for determining the optical properties of size-resolved particles. For this reason, Mie theory was also used in this study. Fig. 5b shows a good correlation (R^2 = 0.9) between the nephelometer-measured and chemical-reconstructed fine particle Bsp, with a regression slope of ~0.92 based on Eq. (2) and the sum of MOUDI stages excluding EC, NO2 and Rayleigh scattering.

Fig. 5c show the single mode particle Bsp distribution with a peak in the droplet mode (0.56–1.8 μm). Coarse particles accounted for only ~5% of the particle Bsp. The average PM10 light scattering was primarily due to fine particles, PM1.8 (~94%) (Table 4), indicating that fine particles are the main contributor to visibility impairment. As shown in Table 5, the droplet mode accounted for 74% of the total particle Bext, further confirming the importance of small particles (0.56–1.0 μm) in visibility degradation (Table 5).

To better understand their chemical and optical characteristics, particles have been divided into four size groups, the nucleation mode (<0.1 μm), condensation mode (0.1–0.56 μm), droplet mode (0.56–1.8 μm) and coarse mode (1.8–10 μm). Table 5 shows that soil dust contributes the most in the coarse mode and that contributions from EC are low and predominately in the condensation mode. Organic matter was the largest contributor to Bext in the droplet mode (~43%) and condensation mode (~8%), suggesting the influence of nearby vehicle exhaust. Ammonium sulphate was the second largest contributor, at around 20% in droplet mode, but different result have been found in other urban area studies (Cao et al., 2012; Cheung et al., 2005; Jung et al., 2009; Tao et al., 2009; Wang et al., 2013a). Ammonium nitrate was the largest contributor to visibility impairment in Xi’an (~23%) and Guangzhou (~16%) (Cao et al., 2012; Tao et al., 2009). However, only 4% of Bext in droplet mode and 1% in condensation mode was attributed to this component in this study.

### 3.4. Source light extinction apportionment

Eighty-one samples (9 stages × 9 samples) were used to identify potential sources and quantify particle source contributions to light extinction in the PMF model using methods similar to Huang et al. (2006) and Cao et al. (2012). A total of 20 base runs and five factors were identified (Fig. 6). The five factors, which were selected based on previous studies in HKPU roadside areas (Cheng, 2007), were soil/fugitive dust, secondary aerosols, sea salt, tire dust, and traffic/vehicle engine exhaust. Detailed source profiles are shown in Figure S4. Factor 1 was identified as soil/fugitive dust (Cheng, 2007), which was dominated by chemical components, Mn, Al, Si, Ca, Ti and Fe. Because there were construction areas around the sampling site, the soil/fugitive dust contribution to particle light extinction was 10%. Factor 2 was the second largest contributor to

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**Table 5**

<table>
<thead>
<tr>
<th>Size Group</th>
<th>Total mass</th>
<th>Ammonium sulfate</th>
<th>Ammonium nitrate</th>
<th>Organic matters</th>
<th>Elemental carbon</th>
<th>Soil dust</th>
<th>Sea salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse mode (1.8–10 μm)</td>
<td>4%</td>
<td>1%</td>
<td>Nil(^a)</td>
<td>1%</td>
<td>&lt;1%</td>
<td>1%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Droplet mode (0.56–1.8 μm)</td>
<td>74%</td>
<td>20%</td>
<td>4%</td>
<td>43%</td>
<td>2%</td>
<td>5%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Condensation mode (0.1–0.56 μm)</td>
<td>22%</td>
<td>7%</td>
<td>1.1%</td>
<td>8%</td>
<td>5%</td>
<td>1%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Nucleation mode (&lt;0.1 μm)</td>
<td>0.4%</td>
<td>N.A(^b)</td>
<td>N.A(^b)</td>
<td>N.A(^b)</td>
<td>0.4%</td>
<td>N.A(^b)</td>
<td>N.A(^b)</td>
</tr>
</tbody>
</table>

\(^a\) The particle Bext data calculated based on the Eq. (4).
\(^b\) The data is below 0.1%.
\(^c\) The data is not available.
B_{sp} (~32%) and was abundant in NH_{4}^{+}, SO_{4}^{2−}, NO_{3}^{−} and OC (Huang et al., 2006a), identifying it as the secondary aerosol component. The prevailing northerly wind in the cold season is likely to enhance the transport of these secondary aerosol pollutants. Factor 3 was enriched in Na, Cl^{−} and nitrate, and was identified as sea salt (Huang et al., 2006). It accounted for ~15% of the total B_{ext}. Factor 4 was identified as tire dust (Cheng, 2007), being dominated by Zn, Mn and Pb. The contribution of tire dust was ~7% of the B_{ext} due to high traffic volumes close to the sampling site. Factor 5 was dominated by EC and OC and identified as the traffic or vehicle engine exhaust (Cao et al., 2012; Huang et al., 2006). This is the largest contributor to the B_{ext}, accounting for 36% of the total. This large contribution was due to the busy traffic flow near the site at the Cross Harbour Tunnel. Therefore, the local visibility impairment was primarily due to the traffic emissions and the regional secondary aerosol pollution.

4. Conclusion

Hourly particle light scattering and absorption coefficients, gaseous NO_{2}, meteorological parameters (i.e. RH, wind speed, temperature) and 24-h size-resolved particle measurements were collected in a Hong Kong urban area from October 23rd to December 31st, 2010 to investigate the temporal variability of optical properties and the contributing chemical components. The average particle light scattering (B_{ps}) and absorption coefficients (B_{ap}) were 201.96 ± 105.82 Mm^{-1} and 39.1 ± 19.16 Mm^{-1}, respectively. The majority of particle light extinction (B_{ext}) was due to particle scattering, with an SSA (ω_{sp}) of 0.82 ± 0.07. The diurnal variation pattern for particle B_{ps} differed between weekdays and weekends, and when elevated particle B_{ps} values were found during the late evening hours.

Based on Eq. (2), it is clear that particle size rather than mass directly affects particle B_{ext}. Droplet mode (0.56–1.8 μm) particles contributed the most to particle B_{ext} compared to other four size groups. Within this mode, organic matter had the highest contribution (~41%) to particle B_{ext}. Organic matter and ammonium sulphate were the highest contributors to the condensation mode (0.1–0.56 μm), accounting for ~8% and 7% of B_{ap}, respectively, followed by elemental carbon (~5%).

By using the PMF model, five source factors were determined. Traffic/engine exhaust was the largest source, accounting for ~36% of B_{ext}, followed by secondary aerosols (~32%), sea salt (~15%), soil dust (~10%) and tire dust (~7%).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.atmosres.2014.10.020.

References


