Correlation of atmospheric visibility with chemical composition of Kaohsiung aerosols

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Abstract

The objective of this study was to investigate the correlation of visibility with chemical composition of Kaohsiung aerosols. Daytime visibility was observed around noon at two observation sites in metropolitan Kaohsiung, Taiwan in the years of 1999 and 2000. Both seasonal and diurnal variation patterns of visibility were observed in the region. Ambient aerosols were sampled and analyzed for 11 constituents, including water-soluble ionic species (Cl−, NO3−, SO42−, NH4+, K+, Na+, Ca2+, and Mg2+) and carbonaceous contents (OC, EC, and TC), to characterize the chemical composition of Kaohsiung aerosols. Furthermore, a stepwise multiple linear regression model was developed to elucidate the influence of aerosol species on visibility impairments. The results showed that sulfate was the dominant species that affected both light scattering coefficient and visibility. On average, the percentage contributions of visibility degrading species to light scattering coefficient were 29% for sulfate, 28% for nitrate, 22% for total carbon, and 21% for PM2.5-remainder. An empirical regression model of visibility based on sulfate, nitrate, and relative humidity was also developed. The model showed that sulfate in PM2.5 was the most sensitive species to visibility variation, suggesting that the reduction of sulfate in PM2.5 could effectively improve the visibility of metropolitan Kaohsiung. During the investigation period, an event of Asian dusts intruded metropolitan Kaohsiung and dramatically increased the aerosol loadings, especially in the coarse particles. However, local visual air quality did not degrade accordingly during the Asian dust event because both visibility and light scattering coefficient are affected mainly by the fine particles. The results are discussed in detail in the paper.

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1. Introduction

Visibility degradation has become an environmental issue of public concern in most metropolitan areas in Taiwan recently. The impairment of visibility is not just an aesthetic problem; it could also be used as a visual indicator of ambient air quality in urban areas (Wark et al., 1998). Visibility is defined as the greatest distance in a given direction at which an object can be visually identified with unaided eyes. The object could be a dark object positioned prominently against the sky on the horizon in the daytime, or a known, preferably unfocused moderately intense light source at nighttime (Wark et al., 1998). The impairment of visibility is attributed primarily to the scattering and absorption of visible light by suspended particles, as well as by gaseous pollutants (e.g. NOx) in the atmosphere (Appel et al., 1985; Hodkinson, 1966; Groblicki et al., 1981; Latha and Badarinath, 2003). Among them, particulate light scattering has often been reported to be the dominant cause of light extinction in urban areas (Chan et al., 1999). Previous studies revealed that the size, chemical composition, and mass concentration of airborne particles substantially affect visibility (Conner et al., 1991; Malm and Pitchford, 1997). Fine particles, generally characterized as PM2.5, are believed to be mostly responsible for the scattering of visible light and to cause the degradation of visibility (Sloane et al., 1991). Although the extinction of visible light from gaseous species can also impair visibility, such species have a much weaker influence (Chan et al., 1999; Dzubay et al., 1982). Meteorological factors, especially humidity, could also contribute to the degradation of visibility (Tang et al., 1981; Tsai and Cheng, 1999). Nevertheless, meteorological conditions are hardly to be controlled and forecasted. Thus, this study focused mainly on the influence of chemical composition of Kaohsiung aerosols on the impairment of visibility and the light scattering and extinction coefficients.

Poor ambient air quality in the metropolitan Kaohsiung, Taiwan has become one of the major environmental concerns of general publics following rapid population growth and increasing industrialization over the past two decades. The ambient air quality in metropolitan Kaohsiung is the worst all over the Taiwan Island mainly because more than 60% of Taiwan’s heavy industries are situated in Kaohsiung City, or in its suburbs. Nowadays, the metropolitan Kaohsiung has more than 1,228,429 automobiles and motorcycles and a total of 1911 factories, including Taiwan’s largest oil refinery plant, 14 large-scale petrochemical plants, nine sizable iron and steel plants, two cement mills, and three fossil utility power plants. Consequently, the annual proportion of unhealthy days, defined as those days of which Pollutants Standard Index (PSI) exceeds 100, was 9.34% and 10.1% in 1999 and 2000, respectively (ROC EPA, 2000).

Visibility observed at Kaohsiung Meteorology Station for the past two decades shows that visibility has been significantly degraded in the metropolitan Kaohsiung. A monthly averaged visibility of 9.2 km with a range 2.3–23.1 km has been recorded from 1979 to 1998 (Yuan et al., 2002), which was much lower than most large cities in the world (Horvath, 1995). Increasing complaints on poor ambient air quality of metropolitan Kaohsiung, especially low visibility, has motivated researches to look into its main causes. At present, information concerning the contributions of chemical components of Kaohsiung aerosols to the light scattering and extinction coefficients and the impairment of visibility remains sparse. Very few literatures have quantitatively addressed the poor visibility of the metropolitan Kaohsiung (Yuan et al., 1998, 2002). Such data are, however, essential to establish limits on particulate matter in order to improve the visual air quality in the metropolitan region. Accordingly, this study aimed not only to investigate the temporal and spatial variations of visibility in metropolitan Kaohsiung, but also to identify the main causes of visibility impairment by means of measuring the chemical composition and optical properties of Kaohsiung aerosols.

2. Methodologies

2.1. Field observation of visibility

This study was based on both regular and intensive observations of visibility in metropolitan Kaohsiung. Regular observation was conducted to elucidate the temporal and spatial variation of visibility, while intensive observation was conducted to elucidate the diurnal variation of daytime visibility. Regular observation of visibility was performed each day at 11:00 am and 2:00 pm during November 1998 to December 2001. On the other hand, four intensive observation campaigns were carried out during 28 January–6 February, 21–30 May 1999, 8–16 January and 24–30 March 2000, which were conducted each hour from 7:00 am to 5:00 pm. Concurrently, Kaohsiung aerosols were sampled in situ and meteorological data were obtained from Kaohsiung Meteorology Station for further statistical analyses.

Visibility was observed visually at two observation sites, Kaohsiung Meteorology Station and Farshing
Temple, as shown in Fig. 1. At Kaohsiung Meteorology Station, the observations were made facing northward with an observation sector of 60°, while those at Farshing Temple were made facing eastward with an observation sector of 120°. Hence, the field observed visibility herein was also named as sector visibility. Objects were pre-identified prior to observation at each site for determining the visibility. The location of each pre-identified object was mapped with global positioning system (GPS) and the GPS data was then used to determine the distance from the observation site to each object with an error lower than 50 m. A series of landscape features at a variety of distances, most of them are tall buildings and stacks, are chosen as visual targets. The most distance feature that can be seen is recorded as visibility. In this study, 11 and 16 visual targets were positioned and observed from Kaohsiung Meteorology Station and Farshing Temple, respectively, as listed in Table 1.

2.2. Sampling and measurement of Kaohsiung aerosols

To realize the influence of aerosol characteristics on visibility impairment in metropolitan Kaohsiung, mass concentration and optical properties of Kaohsiung aerosols were simultaneously measured during the intensive observation periods. Atmospheric aerosols were collected in situ at Chentserng Air Quality Station (Fig. 1), which is one of the stations of Ambient Air Quality Monitoring Network (AAQMN), with 10-m height at the roof of a three-story building located at Central Kaohsiung. Both fine and coarse particles ($PM_{2.5}$ and $PM_{2.5-10}$) were sampled on quartz fiber filters by a dichotomous sampler (Anderson, Model 241) with a total flow rate of 16.7 l min$^{-1}$. Aerosol particles were collected for a 5-h period both in the morning (7:00 am–12:00 am) and in the afternoon.

![Location map showing study area at Kaohsiung City, Taiwan.](image)

Table 1

<table>
<thead>
<tr>
<th>Target code</th>
<th>Distance from the FT$^a$ observation site (m)</th>
<th>Target code</th>
<th>Distance from the KMS$^b$ observation site (m)</th>
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<tr>
<td>F16</td>
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</table>

FT$^a$: Farshing Temple.
KMS$^b$: Kaohsiung Meteorology Station.
(12:00 am–5:00 pm). Before and after field sampling, the quartz fiber filters (Pallflex 2500 QAT-UP, 37 mm) were weighed on an electrical balance (Sartorius WMC6014) with a reading precision of 10 μg to determine the mass concentration, after initially conditioning at 25±2 °C and 40±5% relative humidity for 24 h. After weighing, the filters were stored at 4 °C environment prior to chemical analysis to avoid the loss of semi-volatile species, particularly ammonium nitrate and organic carbon. During the intensive sampling periods, the size distribution of Kaohsiung aerosols was also measured with an integrating nephelometer (MOUDI), consisting of 10 stages with cut-off diameters ranging from 0.056 to 18.0 μm, respectively. The quartz fiber filters of 47 mm and 37 mm diameter (for the last stage only) were used as substrate material. The weighing and conditioning procedures were just the same as those used for the dichotomous sampler.

Additionally, the aerosol light-scattering coefficient was measured in situ with an integrating nephelometer (Radiance Research, Model M903) during two intensive sampling periods (January 8–16 and March 24–30) of 2000. The light source of the nephelometer had a peak wavelength of 530 nm. Freon-12 ($b_{sp} = 1.92 \times 10^{-4}$ m$^{-1}$) and particle-free air filtered through HEPA ($b_{sp} = 1.00 \times 10^{-5}$ m$^{-1}$, based on the Rayleigh scattering of gas molecules) were used for span and zero calibrations, respectively.

By the way, the hourly data of NO$_2$ obtained from the Chentserng Air Quality Station of AAQMN was used to estimate the light absorption coefficients by gases. All the hourly NO$_2$ concentrations were measured with a NO$_x$ gas analyzer (Thermo Electron Corp., Model 42 series), which uses a chemiluminescence-based technology. This chemiluminescence technology has been recognized worldwide as the standard high-performance NO$_x$ measurement method. Furthermore, all the NO$_2$ data had been officially validated by ROC EPA.

2.3. Chemical analysis of Kaohsiung aerosols

Kaohsiung aerosols collected on the quartz fiber filters were further analyzed for 11 chemical constituents. The quartz fiber filters were initially cut into three identical portions before chemical analysis. One part of the quartz filter was extracted for analyzing water-soluble ionic species, while the remaining two parts of the filter were analyzed to determine carbonaceous contents. Water-soluble ionic species, including major anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) and cations (Na$^+$, NH$_4^+$, K$^+$, Ca$^{2+}$, and Mg$^{2+}$), were determined with an ion chromatography (Dionex, Model DX100). Method detection limit (MDL) was estimated from the repeated analyses of predefined quality control solutions. The detection limits of those ion species of Cl$^-$, NO$_3^-$, SO$_4^{2-}$, Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, and Ca$^{2+}$ were 0.015, 0.006, 0.036, 0.021, 0.010, 0.030, 0.012, and 0.066 μg m$^{-3}$, respectively. The average recoveries ranged from a low of 90% for Na$^+$ to a high of 110% for Cl$^-$ with an overall average of 97%.

The carbonaceous contents (elemental, organic, and total carbons) of aerosol particles were measured with an elemental analyzer (Carlo Erba, Model 1108). Before the aerosol particles were collected, the quartz fiber filters had to be pre-heated at 900 °C for 1.5 h to expel the potential impurities. This preheating procedure minimized the background carbon in the quartz fiber filters and matrix, which would interfere with the analytical results, leading to an overestimate of the carbonaceous contents of aerosol particles. The elemental analyzer was operated using the procedure of oxidation at 1020 °C and that of reduction at 500 °C, with continuous heating of 15 min. Additionally, one-third of the quartz fiber filters were heated in advance by hot nitrogen gas (340–345 °C) for 30 min to expel organic carbon (OC) fraction, after which the amount of elemental carbon (EC) was determined. Another one-third of the quartz fiber filters were analyzed without heating and the carbon thus identified was characterized as total carbon (TC). The amount of organic carbon was then be estimated by subtracting elemental carbon from total carbon. Although the most widely used method, thermal analysis, was used to determine the carbon contents in ambient aerosols, a charring formation error from sample preheating was not taken into account for correction. This artifact might result in the overestimation of EC and the underestimation of OC (Yu et al., 2002; Chow et al., 2004). Thus, the EC and OC values obtained in this study can be considered as the conservative results. Even though commonly accepted standards and reference materials that can be used to quantify carbon materials as it appears in the atmosphere do not exist, an Organic Analytical Standard (OAS, Elemental Microanalysis Limited, B2038) consisting of purified urea was used as a routine working standard for the determination of carbon content in this study. The method detection limit of carbon content was observed to be 0.041 μg m$^{-3}$.

2.4. Correlation of light scattering coefficient and visibility with chemical compositions of Kaohsiung aerosols

The correlation of field measured light scattering coefficient and observed visibility with the chemical
composition of the aerosol particles was determined to identify the chemical species of aerosol particles that strongly scatter visible light in the atmosphere. A stepwise multiple linear regression (MLR) model developed for the correlation of light scattering coefficient with chemical composition ((NH₄)₂SO₄, NH₄NO₃, and carbonaceous contents) of aerosol particles was established and validated. Moreover, another multiple linear regression (MLR) model was also developed to correlate visibility with chemical composition ((NH₄)₂SO₄ and NH₄NO₃) of aerosol particles and relative humidity. The derived multiple regression models were further applied to determine the contributions of major chemical species of Kaohsiung aerosols to the visual air quality of metropolitan Kaohsiung.

3. Results and discussion

3.1. Chemical composition of Kaohsiung aerosols

The chemical composition of the fine (PM₂.₅) and coarse (PM₂.₅−10) particles collected in the metropolitan Kaohsiung during the intensive sampling periods of 1999–2000 is summarized in Table 2 and Fig. 2. The mass concentrations of the fine and coarse particles over this period ranged from 11 to 115 µg m⁻³ and from 11 to 160 µg m⁻³, respectively. The average concentrations of the fine and coarse particles were around 66 and 60 µg m⁻³, respectively. It showed that the PM₂.₅ concentrations in the metropolitan Kaohsiung commonly violated the proposed 24-h PM₂.₅ regulation (65 µg m⁻³) of National Ambient Air Quality Standard (NAAQS) in USA. As shown in Fig. 2, the PM₁₀ concentrations in three winter periods (146±42, 143±44, and 146±43 µg m⁻³) were markedly higher than those in the early summer period (55±30 µg m⁻³). Results obtained from the chemical analysis of Kaohsiung aerosols indicated that the most abundant chemical components in the Kaohsiung aerosols were SO₄²⁻, NO₃, NH₄, and carbonaceous contents. The concentrations of sulfate in PM₂.₅ and PM₂.₅−10 was 0.8–25.6 and 0.8–10.6 µg m⁻³, respectively. The concentrations of nitrate in PM₂.₅ and PM₂.₅−10 was 0.5–26.5 and 0.1–22.0 µg m⁻³, respectively. The concentration of ammonium in PM₂.₅ and PM₂.₅−10 was 0.2–32.5 and 0.1–17.4 µg m⁻³, respectively. Although organic carbon (OC) and elemental carbon (EC) appeared to be the most significant contributors to the fine particles, they were also present in the coarse particles. The total carbon (TC) in PM₂.₅ and PM₂.₅−10 ranged from 2.0 to 42.2 µg m⁻³ and from 2.1 to 31.5 µg m⁻³, respectively.

Overall, the carbonaceous contents, including OC and EC, accounted for approximately 25% of the fine particles (PM₂.₅) and 17% of the coarse particles (PM₂.₅−10), while water-soluble ionic species accounted for about half of the fine particles and 37% of the coarse particles. Additionally, compared to the amount in the fine particles, metallic ions, including sodium, calcium, magnesium, and potassium, were relatively abundant in the coarse particles. The unidentified

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Mean chemical composition and ratios of PM₂.₅ to PM₁₀ in Kaohsiung aerosols during the sampling periods of 1999–2000</th>
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</thead>
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<tr>
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<td>PM₂.₅</td>
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<tr>
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</tr>
<tr>
<td>SO₄²⁻</td>
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</tr>
<tr>
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</tr>
<tr>
<td>NH₄⁺</td>
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</tr>
<tr>
<td>K⁺–Mg²⁺–Ca²⁺</td>
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</tr>
<tr>
<td>EC</td>
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</tr>
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<td>OC</td>
<td>14.37</td>
</tr>
<tr>
<td>Remainders</td>
<td>16.61</td>
</tr>
</tbody>
</table>

n: number of measurements from which the means are determined in each season.
EC: elemental carbon.
OC: organic carbon.
Remainders: unidentified fractions in aerosol particles.
Ratio: PM₂.₅/PM₁₀.
Units for PM₂.₅ and PM₂.₅−10: µg m⁻³.
fractions in the fine and coarse particles, recorded as “remainders”, refer to chemical components that were not analyzed, including water content, non-soluble species and so on. In this study, on average, approximately one fifth of the fine aerosols and almost one-third of the coarse aerosols collected at the metropolitan Kaohsiung during the sampling periods of 1999–2000, were unidentified.

Table 1 summarizes the ratios of PM$_{2.5}$ to PM$_{10}$ based on the mass and chemical concentrations of Kaohsiung aerosols. The mean mass ratios of PM$_{2.5}$ to PM$_{10}$ were approximately 0.51–0.62, with an exception of lower ratio of 0.41 in March of 2000, when an Asian dust event intruded metropolitan Kaohsiung. In general, the majority of PM$_{10}$ was in the fine particles in urban areas. The fractions of sea salts (denoted by Cl$^-$ and Na$^+$) in the coarse particles were about twice higher than those in the fine particles (in Fig. 2). These data, combined with the average ratios of PM$_{2.5}$ to PM$_{10}$ less than 0.5 for both Na$^+$ and Cl$^-$, showed that sea salts were present mainly in the coarse particles. The average ratios of PM$_{2.5}$ to PM$_{10}$ sulfate exceeded 0.7 during the intensive sampling periods, implying that most of PM$_{10}$ sulfates were in the fine particles since sulfates are the major component of secondary photochemical products in the fine particles (Sweet and Gatz, 1998).

However, the average ratios of PM$_{2.5}$ to PM$_{10}$ nitrates were around 0.5 during the intensive sampling periods, with an exception of lower average of 0.33 in March of 2000. Accordingly, the majority of PM$_{10}$ nitrates appeared equally in both the fine and coarse particles. The average ratios of PM$_{2.5}$ to PM$_{10}$ ammonium ranged from 0.64 to 0.81, implying that ammonium was abundant in the fine particles.

Elemental and organic carbons (EC and OC) in PM$_{2.5}$ constituted over 60% of the carbonaceous contents in PM$_{10}$ during the intensive sampling periods (Table 1). Moreover, the ratios of organic to elemental carbons (OC/EC) in the fine particles ranged from 1.05 to 4.39 with an average of 2.26. A primary OC/EC ratio of 2.2 was assumed to indicate the general direction for forming secondary aerosols (Turpin et al., 1991; Turpin and Huntzicker, 1995). Another investigation applied an OC/EC ratio of 2.0 to identify the potential formation of secondary aerosols (Chow et al., 1994). However, the average OC/EC ratios obtained from this study were higher than the criteria reported in previous literature. The results presented herein for the fine particles suggested that secondary aerosols could be commonly formed in the region. This study also revealed that the carbonaceous materials were present mostly in the fine particles, resulting from the emission of volatile organic compounds (VOCs) from both industrial and mobile sources in the metropolitan Kaohsiung.

### 3.2. Temporal and spatial variation of visibility

Regular observation of daytime visibility was performed at 11:00 am and 2:00 pm at two observation sites in metropolitan Kaohsiung. Fig. 3 plots the cumulative distribution of visibility observed from November 1998 to December 2001. It showed that the field observed visibilities in metropolitan Kaohsiung were always lower than 21 km, ranging from 0.7 to 20.6 km. According to the levels of visibility (i.e. 2 and 8 km) regulated by the Environmental Protection Department of Kaohsiung City, the cumulative percentage of visibility less than 2 and 8 km were 7.8 and 76.2%, respectively. Approximately 50% of the field observed visibilities were lower than 5 km, indicating that the visibility in metropolitan Kaohsiung has been seriously impaired. Moreover, regular observation of daytime visibility at Kaohsiung Meteorology Station yielded an average visibility of 5.8 and 6.5 km at 11:00 am and 2:00 pm, respectively. The results were lower than the previously reported monthly average visibility of 7.2 km (1975–1994) with a range of 3.3–13.10 km (Yuan et al., 2002).

Fig. 4 illustrates the monthly variation of daytime visibility during the investigation period from November 1998 to December 2001. A significant seasonal variation of visibility was observed in metropolitan Kaohsiung. The visibility was generally higher in summer and lower in late autumn and winter. Moreover, the mean seasonal visibilities in spring, summer, fall, and winter were 5.4, 9.1, 8.2, and 3.4 km, respectively. Low visibility observed in late autumn and winter was mainly due to the high frequency of fog formation, resulting from the radiation inversion occurred in the early morning.

During the intensive observation periods, daytime visibility was observed at two observation sites each hour from 7:00 am to 5:00 pm. Fig. 5 illustrates the diurnal variation of daytime visibility and compares the visibility observed at two sites. The visibilities observed at Kaohsiung Meteorology Station (northward) were slightly higher than those at Farshing Temple (eastward). Visibility tended to increase in the morning and then leveled off at 2:00–3:00 pm in the afternoon. During four intensive observation periods, the visibilities in three winter periods were markedly higher than those in the early summer period. On
average, the lowest mean visibilities at 7:00 am were 5.7 and 4.8 km at Kaohsiung Meteorology Station and Farshing Temple, respectively. While, the highest mean visibilities at 3:00–5:00 pm were 7.9 km and 7.5 km at Kaohsiung Meteorology Station and Farshing Temple, respectively. It is quite consistent with previously reported diurnal variation of visibility observed for the past two decades (Yuan et al., 1998). In that study, the lowest visibility observed at 7:00 am were around 5 km at Kaohsiung Meteorology Station, while the highest visibility observed at 3:00–5:00 pm were around 8 km. The phenomenon was attributed to
the following two reasons. First of all, relative humidity was usually higher in the early morning, causing fog formation, which scattered visible light and hence impaired visibility. Secondly, the primary fine particles emitted from motor vehicles in rush hours would enhance the effects of light scattering and absorption, and thus reduced the visibility due to the condensation and nucleation of moisture onto the fine particles in the early morning.

3.3. Light scattering coefficients

Results from the measurements of nephelometry indicated that, during the third intensive measuring period (January 8–16, 2000), an hourly average $b_{sp}$ (dried) of 330 Mm$^{-1}$ with a range of 93–574 Mm$^{-1}$ was recorded. During the fourth intensive measuring period (March 24–30, 2000), the hourly average $b_{sp}$ (dried) was 290 Mm$^{-1}$ with a range of 85–673 Mm$^{-1}$. For comparison, they are of similar magnitude to values recorded in metropolitan areas in the Yangtze delta region of South China (Xu et al., 2002).

Fig. 6 illustrates the time-series of visibility ($L_v$), light scattering coefficient ($b_{sp}$), and particle mass concentration ($\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$). An inverse correlation was found between visibility and light scattering coefficient from their entirely opposite trends. Furthermore, the time-matched sets of data showed that the light scattering coefficient varied closely with $\text{PM}_{2.5}$ concentration.

The mass light scattering efficiency (i.e. the scattering of visible light by unit concentration of aerosols or particle components) was estimated by a linear regression method. The regression formula derived in this study is expressed by the following equation.

$$b_{sp} = 3.6\text{PM}_{2.5} + 0.3\text{PM}_{2.5-10} \quad (R^2 = 0.87)$$

where $b_{sp}$ denotes the scattering coefficient (in Mm$^{-1}$), and the unit used for PM concentration was in μg m$^{-3}$. This equation corresponds to a $\text{PM}_{2.5}$ mass light scattering efficiency of 3.6 m$^2$ g$^{-1}$ and a much lower value (0.3 m$^2$ g$^{-1}$) for $\text{PM}_{2.5-10}$ with an $R^2$ (fraction of variance explained) of 0.87. The results indicated that the scattering of visible light in metropolitan Kaohsiung was dominated by the fine particles, as has been revealed in previous studies (Waggoner and Weiss, 1980; Richards et al., 1999; Chan et al., 2002). The influence of the coarse particle fraction of $\text{PM}_{10}$ on scattering coefficient is smaller for two reasons: (1) according to Mie theory, the maximum scattering efficiency for green light is at the small particle size range, and (2) since the angular truncation error grows with particle size, the nephelometer does not fully respond to light scattering by coarse particles (White et al., 1994).
Based on the fact that $b_{sp}$ values are highly correlated not only with the mass concentration, but also with the chemical composition of the fine particles (Meszaros et al., 1998; Richards et al., 1999), a statistical approach of multiple linear regression (MLR) was used to elucidate the correlation of light scattering coefficient with the chemical composition of the fine particles. The correlation matrix of visibility, light scattering coefficient, air pollutant concentrations (PM$_{2.5}$ and NO$_2$), chemical species in PM$_{2.5}$, and meteorological parameters (temperature, relative humidity, and wind speed) is summarized in Table 3. The correlation coefficients showed that visibility increased with temperature and wind speed, while decreased with relative humidity and the concentration of PM$_{2.5}$ and NO$_2$. Among the chemical composition of PM$_{2.5}$, sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), and carbonaceous contents (TC) were strongly correlated
with light scattering coefficient, while with a strong inverse correlation to visibility. According to the correlation matrix, ammonium sulfate ((NH₄)₂SO₄), ammonium nitrate (NH₄NO₃), total carbon (TC), and PM₂.₅-remainders were selected as independent variables, while light scattering coefficient was considered as dependent variable in a stepwise multiple linear regression method. The multiple linear regression model of light scattering coefficient is described in the following form,

\[ b_{sp} = \sum_{i=1}^{n} a_i M_i \]  

where \( b_{sp} \) is the light scattering coefficient (km⁻¹), \( n \) is the number of chemical species, \( a_i \) is the mass light scattering efficiency of the \( i \)th chemical species (m² g⁻¹), and \( M_i \) is the mass concentration of the \( i \)th chemical species (µg m⁻³). Among them, the concentrations of (NH₄)₂SO₄ and NH₄NO₃ can be estimated by multiplying [SO₄²⁻] and [NO₃⁻] by a factor of 1.40 and 1.29, respectively (Cass, 1979). The empirical MLR model of light scattering coefficient as a function of chemical species of PM₂.₅ is shown herein,

\[ b_{sp} = 0.0046[(\text{NH}_4)_2\text{SO}_4] + 0.0067[\text{NH}_4\text{NO}_3] + 0.0033[\text{TC}] + 0.0032[\text{PM}_2.5-\text{remainder}] \]

\( (R^2 = 0.97) \).

Table 4 lists the statistical results concerning the estimated regression coefficients in the MLR model. The regression coefficients \((a_i)\) derived from Eq. (3) revealed mass scattering efficiencies of 4.6 m² g⁻¹ for (NH₄)₂SO₄, 6.7 m² g⁻¹ for NH₄NO₃, 3.3 m² g⁻¹ for
TC, and 3.2 m² g⁻¹ for PM₂.⁵-remainder with an R² of 0.97. These values are compared with those in other cities in Table 5. The mass scattering efficiency of (NH₄)₂SO₄ at Kaohsiung was higher than that obtained at Kwangju, Korea (Kim et al., 2001), but lower than those obtained at Brisbane, Australia (Chan et al., 1999), Taichung, Taiwan (Tsai and Cheng, 1999), Denver (Groblicki et al., 1981) and Los Angeles, USA (Appel et al., 1985). The mass scattering efficiency of NH₄NO₃ at Kaohsiung was higher than those obtained at Taichung, Taiwan (Tsai and Cheng, 1999), Denver (Groblicki et al., 1981) and Los Angeles, USA (Appel et al., 1985), whereas the mass scattering efficiency of TC at Kaohsiung was below the averaged value of those obtained in the aforementioned studies. Moreover, the relative contributions of the chemical species to bₛₚ were estimated based on both their measured concentrations during the sampling days and their derived mass scattering efficiencies. Although the mass scattering efficiency of (NH₄)₂SO₄ was lower than that of NH₄NO₃, chemical composition data showed that sulfate was still the most effective species in PM₂.⁵ on the variation of light scattering coefficient. It explained the fact that (NH₄)₂SO₄ was the most important contributor to the light scattering coefficients. Fig. 7 shows the mean relative contributions of chemical species in the fine particles to the overall light scattering coefficients. Clearly, (NH₄)₂SO₄ and NH₄NO₃ were the major scattering species, accounting for 29% and 28% of the overall light scattering coefficient, respectively, while TC and PM₂.⁵-remainder accounted for 22% and 21%, respectively.

### 3.4. Analysis of light extinction budget

In this study, light extinction coefficient (bₑₓₜ) was further reconstructed assuming that it is the sum of the coefficients of light scattered by particles (bₛₚ) and clean

#### Table 3

Correlation matrix of atmospheric visibility and light scattering coefficient verse chemical species in the fine particles, meteorological parameters, and NO₂ gas in January and March of 2000

<table>
<thead>
<tr>
<th></th>
<th>Lᵥ</th>
<th>bₛₚ</th>
<th>PM₂.⁵</th>
<th>TC</th>
<th>CI</th>
<th>NO₃</th>
<th>SO₄²</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>NO₂</th>
<th>Temp</th>
<th>RH</th>
<th>WS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lᵥ</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bₛₚ</td>
<td>-0.90</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM₂.⁵</td>
<td>-0.91</td>
<td>0.89</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Lᵥ: atmospheric visibility; bₛₚ: scattering coefficient; TC: total carbon; Temp: air temperature; RH: relative humidity; WS: wind speed.

### Table 4

Stepwise Regression results for the empirical model of light scattering coefficient in the metropolitan Kaohsiung in January and March of 2000

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values of β</th>
<th>Standard error of β</th>
<th>Estimated regression coefficient (a)</th>
<th>Estimated standard deviation of a</th>
<th>Standard t(28)ᵇ</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>β₁=0.254</td>
<td>0.110</td>
<td>a₁=0.0046</td>
<td>0.0020</td>
<td>2.300</td>
<td>0.029</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>β₂=0.305</td>
<td>0.084</td>
<td>a₂=0.0067</td>
<td>0.0018</td>
<td>3.627</td>
<td>0.001</td>
</tr>
<tr>
<td>TC</td>
<td>β₃=0.236</td>
<td>0.130</td>
<td>a₃=0.0033</td>
<td>0.0016</td>
<td>2.064</td>
<td>0.048</td>
</tr>
<tr>
<td>PM₂.⁵-remainder</td>
<td>β₄=0.195</td>
<td>0.103</td>
<td>a₄=0.0032</td>
<td>0.0017</td>
<td>1.897</td>
<td>0.068</td>
</tr>
</tbody>
</table>

ᵃ Units of parameters: light scattering coefficient, km⁻¹; ammonia sulfate, ammonia nitrate, total carbon (TC), and PM₂.⁵-remainder, μg/m³.

ᵇ t critical(0.975; 28)=2.045 at a 95% significant level.

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C.-S. Yuan et al. / Atmospheric Research 82 (2006) 663–679
Table 5
Comparison of literature values of mass scattering efficiency from various urban locations

<table>
<thead>
<tr>
<th>Location</th>
<th>Mass scattering efficiency (m² g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(NH₄)₂SO₄          NH₄NO₃  Carbon</td>
<td></td>
</tr>
<tr>
<td>Denver, USA</td>
<td>6.6  2.8            3.2⁹(C)  3.4⁹(C)  4.0⁹(C)</td>
<td>Groblicki et al. (1981)</td>
</tr>
<tr>
<td>Los Angeles, USA</td>
<td>4.9  6.3            4.5⁹(C)  4.9⁹(C)  5.7⁹(C)</td>
<td>Appel et al. (1985)</td>
</tr>
<tr>
<td>Brisbane, Australia</td>
<td>12.4  –             5.7⁹(C)  5.7⁹(C)  5.7⁹(C)</td>
<td>Chan et al. (1999)</td>
</tr>
<tr>
<td>Kwangju, Korea</td>
<td>4.125  –             –  3.6⁹(C)  2.4⁹(C)</td>
<td>Kim et al. (2001)</td>
</tr>
<tr>
<td>Taichung, Taiwan</td>
<td>8.8  5.2            3.6⁹(C)  3.3³⁰(C)</td>
<td>Tsai (1999)</td>
</tr>
<tr>
<td>Kaohsiung, Taiwan</td>
<td>4.6  6.7            4.6⁹(C)  4.6⁹(C)  4.6⁹(C)</td>
<td>This study</td>
</tr>
</tbody>
</table>

As shown in Table 2 and Fig. 6, a strong inverse correlation between visibility and light scattering coefficient was observed (r = −0.9). Although visibility degradation is caused by both the absorption and scattering of light, the effect of scattering is considered to be much stronger than the effect of absorption as shown in the aforementioned section and in previous studies (Chan et al., 1999; Dzubay et al., 1982). Hence, this study tried to establish the correlation between visibility and light scattering coefficient. Fig. 9 presents the hourly visibility (Lv), the corresponding hourly scattering coefficient (b_sp), and the best-fit curve during the investigation period. Although the mathematical expression is not exactly the same as the Koschmieder’s equation (Lv = 3.91/b_ext, where denotes the overall extinction coefficient in the air) (Hinds, 1982), the inverse relationship between L_v and b_sp still conserved. Because the overall extinction coefficient is certainly more comprehensive than the scattering coefficient, it is noted that the power of b_sp in the fitted formula, 0.67, is obviously lower than that of b_ext, 1.0, in the Koschmieder’s equation. Another approach was also tried in this study by substituting the light scattering coefficient with the reconstructed extinction coefficient in the previous formula herein. It showed that the power of b_ext in the

3.5. Correlation of visibility with light extinction coefficients

intensive measuring period (in March 2000), the 5-h average b_ext was 371 Mm⁻¹ with a range of 145–676 Mm⁻¹. The relative contributions of the four major components to b_ext are illustrated in Fig. 8. Light extinction budget analysis showed that b_sp was the dominant component of b_ext in metropolitan Kaohsiung, accounting for approximately 72–78% of b_ext. The particulate absorption coefficient (b_ap) was the second important contributor, accounting for approximately 17–23% of b_ext, while the remaining 5% of b_ext was attributed to gas molecules.

Table 6
Stepwise Regression results for the empirical model of atmospheric visibility in the metropolitan Kaohsiung in January and March of 2000 (L_v=a₁×[NH₄NO₃]+a₂×[(NH₄)₂SO₄]+a₃×[PM₂.₅-remainder]+a₄×RH; R²=0.98)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values of β</th>
<th>Standard error of β</th>
<th>Estimated regression coefficient (a)</th>
<th>Estimated standard deviation of a</th>
<th>Standard t(28)²</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH₄)₂SO₄</td>
<td>β₁=−0.38</td>
<td>0.07</td>
<td>a₁=−0.74</td>
<td>0.24</td>
<td>−3.04</td>
<td>0.005</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>β₂=−0.20</td>
<td>0.10</td>
<td>a₂=−0.37</td>
<td>0.14</td>
<td>−2.73</td>
<td>0.015</td>
</tr>
<tr>
<td>PM₂.₅-remainder</td>
<td>β₃=−0.27</td>
<td>0.10</td>
<td>a₃=−0.45</td>
<td>0.12</td>
<td>−3.64</td>
<td>0.001</td>
</tr>
<tr>
<td>RH</td>
<td>β₄=−0.15</td>
<td>0.07</td>
<td>a₄=−0.34</td>
<td>0.16</td>
<td>−2.12</td>
<td>0.038</td>
</tr>
</tbody>
</table>

*Units of parameters: atmospheric visibility, km; RH, %; ammonia nitrate, ammonia sulfate and PM₂.₅-remainder, μg/m³.

*Critical t (0.975; 28) = 2.045 at a 95% significant level.
fitted formula increased from 0.67 to 0.75, as shown in Fig. 10.

Moreover, the aforementioned stepwise multiple linear regression method was further applied to reconstruct an empirical regression model of visibility as a function of (NH₄)₂SO₄, NH₄NO₃, remaining amount of PM₂.₅ (denoted as PM₂.₅-remainder), and relative humidity. The details of regression results are tabulated in Table 6. Judging by the value of β (regression coefficient that specifies the magnitude of the effects of each of the independent variables on the dependent variable), sulfates in PM₂.₅ were revealed to be most sensitive to visibility change among all of the parameters because of its domination of light scattering in the air. Nitrates and remaining amount in PM₂.₅ were, however, less sensitive than sulfates to visibility change. Moreover, relative humidity was the only meteorological parameter that affects visibility although the effect of relative humidity on visibility change was much less than the aforementioned three aerosol species. The estimated regression coefficients in the visibility model were examined through t-test, and the P-values were less than 0.05 at the 95% confidence level.

3.6. Impact of Asian dusts

During the fourth intensive sampling period (March 24–30, 2000), an Asian dust storm intruded the East Asia and happened to be observed in metropolitan Kaohsiung. The intrusion of Asian dusts to metropolitan Kaohsiung was validated by the following two pieces of evidence: the pathways of backward air mass trajectory as illustrated in Fig. 11 and the extraordinarily high concentrations of coarse particle (PM₂.₅–10) on March 29–30, 2000 as shown in Figs. 6 and 12.

The history of air mass transported from North China and/or Mongolia to the metropolitan Kaohsiung was determined by plotting 3-day backward trajectories using the HYSPLIT-4 model developed by the Air Resource Laboratory of National Oceanic and Atmospheric Administration (Draxler and Hess, 1997). The backward trajectories at three height levels (500, 1000, and 1500 m above sea level)
were plotted every 6 h during the period of March 27–29, 2000. The apparent transport pathways showed that the Asian dust storm did pass the metropolitan Kaohsiung (Fig. 11). Moreover, the time-series plots of particulate matter shown in Fig. 6 indicated that the concentrations of coarse particles (PM_{2.5-10}) increased dramatically under the impact of Asian dusts, while the concentrations of the fine particles (PM_{2.5}) did not vary much. Relatively higher ratios of coarse to fine particles (C/F) were observed on March 29–30, 2000, while compared to other days. Similar results were observed in the variation of particle size distribution as shown in Fig. 12. It showed that a bi-modal distribution (both the fine and coarse modes) on March 27 shifted to a single-modal distribution (the coarse mode only) in the afternoon of March 28, 2000. Moreover, high mass concentrations of the

Fig. 10. The relationship between 5-h averaged visibility ($L_v$) and light extinction coefficient ($b_{ext}$) in January and March of 2000.

Fig. 11. Backward trajectories of air mass originating at Kaohsiung Meteorology Station on March 29, 2000 during the intrusion period of Asian dusts.
coarse mode further extended to March 29–30, and would be expected to shift back to its original bimodal distribution once the Asian dusts passed over the metropolitan Kaohsiung. However, the visual air quality, including the light scattering coefficient and the visibility, did not vary much during the Asian dust storm period since they are affected mainly by the fine particles only (Yuan et al., 2002). It explained why the expected significant variation of the visual air quality was not present in the metropolitan Kaohsiung under the impact of Asian dusts.

4. Conclusions

Several conclusions drawn from this study are summarized as follows. First of all, the seasonal

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**Fig. 12.** Variation of particle size distributions on March 27–30 during the intrusion period of Asian dusts.
average visibilities observed in the metropolitan Kaohsiung in spring, summer, fall and winter were 5.4, 9.1, 8.2, and 3.4 km, respectively. A diurnal variation of visibility was observed and showed that the visibility was generally lower in the morning and higher in the afternoon. Secondly, a mass light scattering efficiency of 3.6 m² g⁻¹ for PM₂.₅ and a much lower value (0.3 m² g⁻¹) for PM₂.₅–₁₀ indicated that the visible light was mainly scattered by the fine aerosol particles. The derived MLR model of light scattering coefficient yielded the mass scattering efficiencies of 4.6 m² g⁻¹ for (NH₄)₂SO₄, 6.7 m² g⁻¹ for NH₄NO₃, 3.3 m² g⁻¹ for total carbon, and 3.2 m² g⁻¹ for PM₂.₅-remainder with an $R^2$ of 0.97. On average, the percentage contributions of the visibility-degrading species to the light scattering coefficient were 29% for sulfates, 28% for nitrates, 22% for total carbon, and 21% for PM₂.₅-remainder. Thirdly, a regression model of visibility based on sulfates, nitrates, PM₂.₅-remainder, and relative humidity was also developed. The results showed that the variation of sulfate in PM₂.₅ aerosols was most sensitive to visibility change among the parameters. Finally, the analysis of light extinction budget indicated that $b_{ap}$ was the dominant component of $b_{ext}$ in the metropolitan Kaohsiung, accounting for approximately 75% of the overall light extinction coefficient. The light absorption by particles ($b_{ap}$) was the second important contributor, accounting for approximately 20% of $b_{ext}$, while the remaining 5% of $b_{ext}$ was attributed to gases.

Acknowledgments

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