Seasonal Variation of Aerosol Optical Properties in an Urban Site of the Yangtze Delta Region of China

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ABSTRACT

The characteristics of aerosol optical properties during 2012 at Hangzhou (30°14′N, 120°10′E), an urban site in the Yangtze Delta Region of China, were analyzed, including aerosol scattering and absorption coefficients, aerosol optical depth (AOD), Ångström exponent (α), single scattering albedo (SSA), and aerosol size distribution. Both aerosol absorption and scattering coefficients were lowest in summer; the highest absorption coefficient was observed in autumn; while the scattering was highest in winter. There were no significant differences in the seasonal average of AOD, with values of approximately 1.0 in spring, autumn and winter, and 0.72 in summer. The averaged Ångström exponent was found to be relatively high throughout the year, with a minimum value of 1.14 in spring and a maximum of 1.35 in autumn. The fine modes of the aerosol volume size distributions showed the highest peak around radius 0.15 µm in spring, autumn and winter, and radius 0.25 µm in summer, while the coarse modes showed maximum peaks at radius 2.9 µm in all seasons. The volume concentrations of coarse mode aerosols over Hangzhou were highest in spring compared with other seasons. The mean total SSA values were 0.89, 0.93, 0.89 and 0.88 at 440 nm for spring, summer, autumn and winter, respectively, indicating that the aerosols were mainly composed of scattering particles in Hangzhou. Furthermore, it was found continuous pollution events appeared in East China as a result of biomass burning during June 10–13 in 2012. The main causes of extremely severe air pollution and poor visibility in Hangzhou were related to the long-distance transport of pollutants, local pollution emission and stagnant weather conditions. Aerosol optical properties exhibited high value in absorption AOD and high aerosol volumes, low SSA in coarse mode after biomass burning.

Keywords: Aerosol optical properties; Pollution processes; Hangzhou.

INTRODUCTION

Aerosols are one of the most important factors in current assessments and predictions of global climate change, but are associated with large uncertainties (IPCC, 2001). Aerosols are a key component of the processes of atmospheric physics, such as the formation of precipitation and the radiative transfer of light waves in the atmosphere. Aerosol particles can change the earth-atmosphere energy balance and affect the climate directly by scattering and absorbing solar and terrestrial radiation, in addition to acting as cloud condensation nuclei and altering cloud microphysical properties (Twomey, 1991; Hansen et al., 1997). Aerosols also play an important role in reduced visibility (Horvath, 1995) and implicated in human health hazard because sub-micron aerosols can irritate the respiratory system (Dockery and Pope 1994; Zhang et al., 2013).

Parameters to describe aerosol properties are necessary...
to accurately assess the radiative properties of aerosols (Carrico et al., 2003). Aerosol optical properties are affected by the particle size, chemical composition as well as the shape of aerosol (Kiehl and Briegleb 1993; Che et al., 2009a; Liu et al., 2011; Wang et al., 2010). Aerosol optical properties are usually retrieved from in situ instruments or ground-based remote sensing instruments. Many studies focus on the aerosol optical properties and their variation using a nephelometer, photometer or aethalometer at multiple sites (Arnott et al., 2003; Aalto nen et al., 2006; Pereira et al., 2008; Ma et al., 2011; Pandolfi et al., 2011). Other investigations have also reported aerosol optical properties in detail using ground-based remote sensing networks for several locations (Raes et al., 2000; Smirnov et al., 2001; Eck et al., 2005; Li et al., 2007; Yu et al., 2009; Che et al., 2009b; Alam et al., 2012; Che et al., 2013; Alam et al., 2014; Che et al.; 2014; Che et al., 2015). Such studies have helped to reduce the uncertainties associated with direct aerosol radiative forcing.

With the rapid urbanization and the economy growth in China, emissions of anthropogenic aerosols have increased dramatically in recent years, especially in the Yangtze Delta region. Aerosol optical properties still have large uncertainties in these areas. There has been considerable attention paid to aerosol optical properties in some areas of the Yangtze Delta region of China, such as Shanghai, Nanjing and Taihu (Xia et al., 2007; Pan et al., 2010; Xu et al., 2011; He et al., 2012; Xu et al., 2012). However, there are few studies about aerosol optical properties from ground-based measurements over Hangzhou. This paper therefore reports aerosol optical properties measured both at the surface and in the atmospheric column at an urban site of Hangzhou in the Yangtze Delta region of China. The characteristics and variations of scattering coefficients, absorption coefficients, aerosol optical depth (AOD), Ångström exponent, single scattering albedo, aerosol size distribution and aerosol volume at Hangzhou were analyzed based on the measurements during 2012. Moreover, the aerosol optical properties during serious pollution in the middle of June 2012 were discussed by analyzing the meteorological observations, aerosol observations and the back-trajectory HYSPLIT model.

METHODS AND DATA

Site Description

Hangzhou is situated in the eastern coast of China and is one of the most developed areas of the Yangtze River Delta region. It has 8.9 million population and 2.7 million vehicles according to the 2014 Statistical Bulletin of Hangzhou. As reported by Hangzhou meteorological records, Hangzhou belongs to the subtropical monsoon climate, with an average temperature of 17.0°C, relative humidity of 75.4% and rainfall of 1438 mm over the past 30 years (1981-2010). In this study, all in situ measurements of aerosol optical properties and meteorological factors were conducted at the Hangzhou National Reference Climatological Station (30°14’N, 120°10’E, 41.7 m above sea level). The site is situated at the convergence of the West Lake scenic area and commercial and residential areas in the south of city. There are no local industrial pollution sources around the site. Thus, aerosol optical properties at this site can be representative of the urban areas of Hangzhou.

Instrument and Data

Aerosol scattering coefficients ($\sigma_{scat}$) were measured at three wavelengths (450, 525, and 635 nm) using an integrating nephelometer (Model Aurora 3000, Ecotech, Australia). The scattered light in the angular range of 10–170° was measured and the scattering coefficients were derived after the correction for the truncation error according to Müller et al. (2011). Similar correction scheme was developed for another commercial nephelometer (TSI model 3563) by Anderson and Ogren (1998). Müller et al. (2011) also compared the Aurora 3000 and TSI 3563 integrating nephelometers using ammonium sulphate and ambient air. Maximum differences in total scattering are 4% (450 nm), 2% (525 nm) and 5% (635 nm). Moreover, Green light (525 nm) interacts strongly throughout the human range of visibility. In order to better data comparison, $\sigma_{scat}$ at the wavelength of 525 nm was analyzed in this study. A background (zero) check was automatically performed at midnight every Friday and a span check was manually performed weekly by using particle-free HFC-R134a gas recommended by the manufacturer. If the deviation was greater than 2 M m$^{-1}$ for zero checks and 10% for span checks, a full calibration was executed. A relative humidity in the cell of the instrument was controlled below 60% by an automatic heating inlet device in order to prevent the presence of liquid particles inside the sampling cell, and consequently the effects of hygroscopicity enhancing the scattering of particles.

The concentrations of black carbon (BC) were measured using an aethalometer (Model AE-31, Magee Scientific, USA). The instrument operates by continuously measuring the attenuation of light transmitted through a sample collected on a quartz fiber filter (Hansen et al., 1984). The absorption coefficients ($\sigma_{abs}$) were indirectly obtained from the recorded BC concentrations ([BC]) at 880 nm according to the empirical equation (Yan et al., 2008):

$$\sigma_{abs} = \delta \times [\text{BC}]$$

(1)

where $\delta$ is a conversion factor with the value 8.28 m$^{2}$ g$^{-1}$. Note that the wavelength ($\lambda$) of the $\sigma_{abs}$ acquired from the above equation is 532 nm; thus, an empirical relationship between the $\sigma_{abs}$ and wavelengths (i.e., $\sigma_{abs} \propto \lambda^\beta$) was applied to convert the $\sigma_{abs}$ at 532 nm to those at 525 nm. The absorption exponent $\beta$ is equal to –1 for BC in the wavelength range of 450 to 750 nm (Bodhaine, 1995).

The AOD measurements at 1640, 1020, 870, 670, 500, 440, 380 and 340 nm were conducted by a sun photometer (Model CE-318, Cimel Electronique, France) with a 1.2° full field-of-view (Holben et al., 1998). The valid AOD data are calculated by the ASTPwin software (Cimel Ltd. Co.) for the Level 1.0 AOD (raw result without cloud screening), the Level 1.5 AOD (cloud-screened AOD based on the work of Smirnov et al. (2000)) The Ångström exponent ($\alpha$) was calculated by linear regression of the AODs against the wavelengths in the range of 440 to 870 nm on the
showed a similar seasonal variation, with gradually increasing with a value of 368.3 ± 207.8 M m⁻¹, on average in 2012.

meteorological conditions in autumn and winter. In summer (Fig. 1), indicating a strong day-to-day variability, with Beijing in China (He et al., 2009), the annual mean \( \sigma_{\text{abs}} \) is lower. The higher \( \sigma_{\text{abs}} \) in Beijing may be related to the larger contribution of BC emitted from coal consumption in the residential heating season from November to March.

The annual means of AOD at urban area of Hangzhou in 2012 were 0.34 ± 0.19, 0.41 ± 0.25, 0.56 ± 0.34, 0.80 ± 0.46 and 0.91 ± 0.51 at 1020, 870, 670, 500 and 440 nm, respectively. The AOD_{440 nm} at Hangzhou was slightly higher than Taihu (Xia et al., 2007), Pudong and Lin’an (Pan et al., 2010). Hangzhou has a rapidly vehicle increasing as well as many other industrial and anthropogenic activities in recent years. Moreover, Hangzhou is surrounded by high mountains, which causes poor pollution diffusion conditions. As a result, Hangzhou has become one of the heaviest aerosol loading area in the Yangtze Delta region.

Fig. 3 shows the seasonal variation of AODs at 1020, 870, 670, 500 and 440 nm in Hangzhou. The lowest AOD appeared in summer, with mean value of 0.72 ± 0.58 at 440 nm. The average AODs at 440 nm in spring, autumn and winter were almost steady, with values of 0.97 ± 0.46, 1.00 ± 0.50 and 1.00 ± 0.39, respectively. The high value in spring may have been caused by a dust event involving long-distance transport from North China, and local pollution sources (Gong et al., 2003). Precipitation increased substantially in summer and decreased the concentration of atmospheric aerosol. The value of AOD was therefore relatively lower in summer than other seasons. In winter, the weather was stable, dry and cold which usually caused poor pollutant diffusion conditions. Moreover, fog/haze events frequently occurred in winter, leading to a dramatic increase in AOD (Che et al., 2014).

Fig. 3 also shows the seasonal variation of \( \alpha_{440-870} \). It reached a maximum value of 1.35 ± 0.22 in autumn and a minimum of 1.14 ± 0.23 in spring. The higher \( \alpha_{440-870} \) in autumn indicates a higher contribution of fine mode particles to AOD, which are mainly produced from anthropogenic emissions or photochemical reactions of polluted precursors (Xu et al., 2002). This is also suggested in the results of Pan et al. (2010), similarly based on measurements in the Yangtze River Delta region.

The relatively lower \( \alpha_{440-870} \) in spring may have been caused by the long-distance transport of dust particles from North China (Gong et al., 2003). As seen from Fig. 3, the 25% quantiles of \( \alpha_{440-870} \) values in different seasons were considerably larger than 0.8, indicating that the AODs are dominated by fine particles in Hangzhou. Eck et al. (2005) found that \( \alpha_{440-870} \) was higher than 0.80, even during dust events, at East Asian sites, suggesting that fine mode aerosols emitted from population centers in East Asia dominate aerosol optical properties, even in spring when pollution aerosols are mixed with coarse mode particles.

Volume Size Distribution

Fig. 4 shows the seasonal variation of aerosol volume size distributions. In general, the size distribution in each season appeared to have a bimodal logarithm normal structure: fine mode with radius < 0.6 µm and a coarse
mode with radius > 0.6 µm (Dubovik et al., 2002). As shown in Fig. 4, the fine modes reach the maxima peak at radius of 0.15 µm in spring, autumn and winter but reach the peak at a larger radius of 0.25 µm in summer. The coarse modes reach the maxima peak at radius of 2.94 µm in all seasons. The larger radius of the fine mode in summer is likely to be related to the hygroscopic growth of particles as a result of the higher relative humidity (Che et al., 2014).

Fig. 5 shows the seasonal variation of volumes of total, fine and coarse mode particles. The total particle volumes did not vary substantially, with the seasonal mean values of 0.25, 0.24, 0.21 and 0.22 µm³ in spring, summer, autumn and winter, respectively. Unlike summer, autumn and winter, the volume of the coarse mode was larger than that of fine mode in spring, which is likely to be related to the long-distance transport of the coarse dust particles. The volume of the fine mode (0.18 µm³) was three times higher than that of the coarse mode particles in summer because of the more efficient removal of coarse particles by precipitation and the hygroscopic growth of fine particles under humid conditions.

**Single Scattering Albedo**

The SSA is defined as the ratio of the scattering coefficient to the extinction coefficient and is one of the key determinants of the radiative effect used in assessing climatic change (Jacobson et al., 2000). Even a small bias in SSA might change the estimated cooling or warming effect of aerosols (Takemura et al., 2002). Theoretically, SSA should increase rapidly with increased wavelength during dust events but decrease during periods of increased urban aerosol pollution (Bergstrom et al., 2007; Alam et al., 2012).
Fig. 6(a) shows Spectral variations of SSAT, SSAF and SSAC at Hangzhou, the mean SSAT at 440 nm, 670 nm, 870 nm and 1020 nm is 0.89 ± 0.04, 0.91 ± 0.04, 0.89 ± 0.04 and 0.88 ± 0.05, respectively; the mean values of SSAF are 0.92 ± 0.03, 0.93 ± 0.03, 0.92 ± 0.04 and 0.90 ± 0.05, respectively; the mean SSAC is 0.70 ± 0.07, 0.81 ± 0.07, 0.83 ± 0.07 and 0.84 ± 0.06, respectively. The SSAC value showed an increasing trend with increasing wavelength while the SSAT and SSAF value showed a decreasing trend with increasing wavelength in the visible bands. It is clearly that the SSAC was obviously lower than SSAT and SSAF, which indicates that there is a decrease in the scattering contribution of coarse particles. The SSAT value at 440 nm in Hangzhou was close to the value observed in Taihu (0.90), Mexico City (0.89), Kanpur (~0.90) and Karachi (~0.91) (Dubovik et al., 2002; Singh et al., 2004; Xia et al., 2007; Alam et al., 2011). However, this value was far lower than the results in other urban sites; for example, the value of SSA at 440 nm was measured 0.96 in Maldives, 0.93 in Paris, 0.92 in Shouxian and 0.95 in Hefei (Dubovik et al., 2002; Fan et al., 2010; Wang et al., 2014). This suggests that the aerosols in Hangzhou are less absorptive than in other cities.
Fig. 3. Seasonal variations of AOD and $\alpha_{440-870}$. The bars represent the 95th percentile, 75th percentile, median, 25th percentile and 5th percentile, from top to bottom, respectively, and “+” represents the mean value.

Fig. 4. Seasonal volume size distributions of aerosols

Fig. 6(b) shows the seasonal variations of total, fine and coarse mode SSA (SSAT, SSAF and SSAC) at 440 nm. The mean SSAT is $0.89 \pm 0.04$, $0.93 \pm 0.04$, $0.89 \pm 0.04$ and $0.88 \pm 0.05$ in spring, summer, autumn and winter, respectively. The mean SSAF is $0.92 \pm 0.02$, $0.94 \pm 0.03$, $0.91 \pm 0.03$ and $0.91 \pm 0.05$ in spring, summer, autumn and winter, respectively. Both SSAT and SSAF were highest in summer and lowest in winter. The high values in summer could be probably related to aerosol hygroscopic growth under high relative humidity (Xia et al., 2007). In contrast, biomass burning emitted black and organic carbon in winter which resulted in the low SSA. Compared with northern cities of China, such as Beijing (Xia et al., 2006), the SSA in Hangzhou in winter is relatively higher, due to the absence of a heating period during which more absorptive aerosols are produced. The mean SSAC is $0.73 \pm 0.05$, $0.71 \pm 0.09$, $0.68 \pm 0.07$ and $0.66 \pm 0.07$ for spring, summer, autumn and winter, respectively. The highest SSAC value was in spring, which reflects greater emissions of scattering coarse-mode particles or dust particles caused by cold air outbreaks from North China.

Aerosol Optical Properties during Pollution Events Processes

Typical pollution events happened during 10–13 June, 2012 was examined with the purpose of further investigating the air pollution in Hangzhou. The surface meteorological conditions during 10–13 June are shown in Fig. 7. As shown in Fig. 7(a), northerly winds with a velocity generally lower than 2.0 m s$^{-1}$ prevailed during this event, which was
not conducive to the spread of pollutants. Low visibility and high relative humidity were also observed during the events (Figs. 7(b) and 7(c)). The average $\sigma_{\text{abs}}$ and $\sigma_{\text{scat}}$ was 68.6 M m$^{-1}$ and 1133.4 M m$^{-1}$, respectively, during this event, indicating a very serious pollution process. Hennigan et al. (2008) suggested that the formation of secondary aerosols, such as NO$_3^-$, SO$_4^{2-}$, and secondary organic compounds, could be enhanced under high humidity conditions, thus enhancing the scattering of light.

It is clear from the synoptic analysis that a weak shear formed between a ridge behind the Northeast China low vortex and a subtropical high in north-central Zhejiang Province was gradually deepening from 18:00 UTC on 10 June. It became a low vortex and quickly moved into the East China Sea at 06:00 UTC 11 June. A saddle field was subsequently formed by this low vortex and the Northeast China low vortex. Hangzhou Bay was near the center of the saddle field (Fig. 8). A typical calm weather system was formed and sustained until 12:00 UTC on 13 June, during which both horizontal winds at ground level and vertical motion were weak (Fig. 9).

To better understand the transport of particles from distant sources, 48-h back-trajectories at altitudes of 100, 300 and 500 m were calculated using the HYSPLIT mode. It is clear

Fig. 5. Seasonal volume of aerosols. The vertical bars are the standard deviations from the mean of the observation.

Fig. 6. (a) Spectral variations of SSAT, SSAF and SSAC at Hangzhou. The vertical bars are the standard deviations from the mean of the observation. (b) Seasonal variations of SSAT, SSAF and SSAC at Hangzhou. The bars represent the 95th percentile, 75th percentile, median, 25th percentile and 5th percentile, from top to bottom, respectively, and “+” represents the mean value.
Fig. 7. Time series of surface (a) wind vector, (b) relative humidity and (c) visibility at Hangzhou during 10–13 June, 2012.

Fig. 8. The contours (black line) and wind vector field at 850 hPa at 12:00 UTC on June 11, 2012.

Fig. 9. Cross-section of vertical velocity at 30°N at 12:00 UTC on June 11, 2012. Solid line represent downdraft and dotted line represent updraft.
that air masses originated from Qiandaohu, a county-level city of Hangzhou Province, and transported at low levels before arriving at Hangzhou on 10 June (Fig. 10(a)). In contrast, although initiated at high levels, air masses reaching Hangzhou on 13 June gradually declined when passing over Hebei, Shandong, Anhui and Jiangsu provinces, where human activity is intense (Fig. 10(b)). Based on the Fire Information for Resource Management System (FIRMS) (http://firms.modaps.eosdis.nasa.gov/firemap/), we examined the 1 km resolution fire product from MOD14 provided by MODIS. As shown in Fig. 11, a large area of fires caused by straw burning in the period 11–12 June was found in the provinces north of Hangzhou. Therefore, emissions from those regions would have been transported to Hangzhou.

Two typical days were selected to compare the difference of aerosol optical properties under the influence of local emissions (June 10, 2012) and long-distance transport (June 13, 2012). Fig. 12 show the size distribution, volumes, AAOD and SSA on 10 and 13 June in Hangzhou. From Figs. 12(a) and 12(b), it is clear from the volume size distribution on June 10, before biomass burning long-distance transport, that fine mode particles (radius < 1 mm) were predominant in local emissions. The fine mode particle volumes were about 0.21 µm$^3$, which was 2.6 times higher than the coarse mode particle volumes. In contrast, there was a clear increase in coarse mode particles on June 13, which could have

Fig. 10. 48-h backward trajectories at (a) 12:00 UTC on 10 June, 2012 and (b) 18:00 UTC on 12 June, 2012.
Fig. 11. Distribution of fire spots in central and east China during 11–12 June, 2012.

Fig. 12. Daily averaged (a) aerosol volume size distributions, (b) aerosol volumes, (c) AAOD and (d) SSA670nm on 10 and 13 June, 2012.
resulted from the long-distance transport of biomass burning particles. The coarse mode particle volume was 0.18 µm³, which was equal to the fine mode particle volume, but much higher than the value (0.08 µm³) on June 10. Fig. 12(c) shows that the AAOD value on June 13 was larger than the value on June 10, by 0.043, 0.020, 0.016 and 0.016 at 440, 670, 870 and 1020 nm, respectively. Fig. 12(d) shows that the SSAF value (0.93 at 670 nm) on June 10 was equal to the value on June 13. However, SSAC (0.76 at 670 nm) on June 10 was much higher than that of 0.72 (at 670 nm) on June 13. This suggests that biomass burning emitted coarse particles, such as black and organic carbon, which caused the observed low SSAC and high AAOD.

SUMMARY

The aerosol optical properties over Hangzhou, an urban site in the Yangtze Delta region of China, were analyzed using one year’s observational data collected from photometer measurements. Both absorption and scattering coefficients were lowest in summer, while the highest values appeared in winter for the scattering coefficients and in autumn for absorption coefficients. The high AOD values during the study period were found due to anthropogenic activities. Angstrom exponent is larger than 1.0 throughout the year which suggests the small aerosol particle size was dominant. The lower value of Angstrom exponent in spring possibly reflects the influences of dust aerosols from north China. The aerosol volume size distributions in fine modes showed the higher peak around radius in summer than in other seasons while maximum peaks observed the same in coarse modes in all seasons. The volume concentrations in coarse mode are larger in spring than in other seasons. SSA show low fluctuations and high value throughout the year, indicating that the aerosols in Hangzhou were mainly composed of scattering particles. Agricultural burning emissions can exert marked influences on air quality in surrounding and downwind regions. It makes aerosol properties more complex in Hangzhou. By continuing observations, more opportunities will be provided to perform further investigations over this region.

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