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Measurement of aerosol chemical, physical and radiative properties in the Yangtze delta region of China

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Abstract

In order to understand the possible influence of aerosols on the environment in the agricultural Yangtze delta region of China, a one-month field sampling campaign was carried out during November 1999 in Linan, China. Measurements included the aerosol light scattering coefficient at 530 nm, σ_{sp} , measured at both dry relative humidity (RH < 40%) and under ambient conditions (sample RH = $63 \pm 19\%$), and the absorption coefficient at 565 nm, σ_{ap} , for aerosol particles having diameters $< 2.5 \mu\text{m}$ (PM_{2.5}). At the same time, daily filter samples of PM_{2.5} as well as aerosol particles having diameters $< 10 \mu\text{m}$ (PM₁₀) were collected and analyzed for mass, major ion, organic compound (OC), and elemental carbon (EC) concentrations in order to determine which anthropogenic chemical species were primarily responsible for aerosol light extinction. The aerosol loading in the rural Yangtze delta region was comparable to highly polluted urban areas, with mean and standard deviation (S.D.) values for σ_{sp} , σ_{ap} and PM_{2.5} of 353 Mm^{-1} (202 Mm^{-1}), 23 Mm^{-1} (14 Mm^{-1}) and $90 \mu\text{g m}^{-3}$ ($47 \mu\text{g m}^{-3}$), respectively. A clear diurnal pattern was observed in σ_{sp} and σ_{ap} with minimum values occurring in the middle of the day, most likely associated with the maximum midday mixing height. The ratio of the change in light scattering coefficient at ambient RH to that at controlled RH (RH < 40%), $F_{\sigma_{sp}}$ (RH), indicates that condensed water typically contributed $\sim 40\%$ to the light scattering budget in this region. The mass scattering efficiency of the dry aerosol, $E_{\text{scat},2.5}$, and mass absorption efficiency of EC, $E_{\text{abs},2.5}$, have mean and S.D. values of $4.0 \text{ m}^2 \text{ g}^{-1}$ ($0.4 \text{ m}^2 \text{ g}^{-1}$) and $8.6 \text{ m}^2 \text{ g}^{-1}$ ($7.0 \text{ m}^2 \text{ g}^{-1}$), respectively. PM_{2.5} concentrations in Linan and two other locations in the Yangtze delta, Sheshan and Changshu (which have monthly mean values ranging from ~ 80 to $110 \mu\text{g m}^{-3}$), are all significantly higher than the proposed 24-h average US PM_{2.5} NAAQS of $65 \mu\text{g m}^{-3}$. Organic compounds are the dominant chemical species accounting for $\sim 50\%$ of the PM_{2.5} mass at all three sites. The results indicate that aerosol loadings in the agricultural Yangtze delta region of China are relatively high, and suggest that aerosols have a significant impact on visibility, climate, crop production, and human health in this region. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Light scattering coefficient; Light absorption coefficient; PM_{2.5}; Organic compounds; Yangtze delta

1. Introduction

China is the world's most populated and fastest growing nation. Concurrent with population growth is

extraordinary economic growth at a rate of increase of $\sim 10\%$ per year in gross domestic product (Freemantle, 1998). Along with economic growth are the associated increases in anthropogenic pollutants from industrial sources. It is estimated that emissions of various anthropogenic pollutants, such as aerosols and ozone precursors, will dramatically increase in the future. In particular, sulfur emissions (from the burning of coal which currently supplies China with $\sim 75\%$ of its total

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energy requirement) will roughly double by 2010 (Daniel, 1994; Wolf and Hidy, 1997). However, the impact of anthropogenic pollutants, in particular aerosols, on the environment remains uncertain in this region of the world due to the sparseness of measurements of aerosol chemical, physical and radiative properties on relevant temporal and spatial scales.

Through the absorption and scattering of solar radiation, aerosols influence visibility (Wagonner et al., 1981), and directly affect climate through the modification of the Earth's energy balance (Charlson et al., 1992; Schwartz, 1996). The magnitude of the direct radiative forcing of aerosols at a particular time and location depends on the amount of radiation scattered back to space, which itself depends on the size and optical properties of the particles, their abundance, and the solar zenith angle (Schwartz, 1996). Light extinction by aerosols also reduces the quantity and quality (relative amount of diffuse to direct solar irradiance) of solar radiation reaching the surface which may influence crop production, especially in areas of relatively high aerosol loadings such as China (Chameides et al., 1999). Li et al. (1995) report a $\sim 0.2\text{--}0.4^\circ\text{C}$ decrease in surface temperatures over the last ~ 40 yr in a broad region of China extending from Sichuan Province east over the Yangtze delta region. This cooling was accompanied by significant decreases in visual range, and is attributed to the direct influence of aerosols on the surface energy balance (Li et al., 1995).

Several studies report relatively high loadings of fine particulate matter (defined here as particles having aerodynamic diameters $< 2.5\ \mu\text{m}$, $\text{PM}_{2.5}$) in urban and near-urban regions of China. Waldman et al. (1991) report values of $\text{PM}_{2.5}$ mass concentration measured over a 2-week period in the industrialized city of Wuhan ranging from 54 to $207\ \mu\text{g m}^{-3}$, with a mean value of $139\ \mu\text{g m}^{-3}$. The ions SO_4^{2-} , NO_3^- and NH_4^+ accounted for $\sim 40\%$ of the $\text{PM}_{2.5}$ mass, and the remaining mass was attributed to carbonaceous compounds not directly measured (Waldman et al., 1991). Similarly, Salmon et al. (1994) report an annual $\text{PM}_{2.1}$ (particles having aerodynamic diameters $< 2.1\ \mu\text{m}$) concentration of $130\ \mu\text{g m}^{-3}$ in Datong (Shanxi Province) with the dominant chemical species being organic carbon which accounted for $\sim 50\%$ of the $\text{PM}_{2.1}$ mass. The mean $\text{PM}_{2.5}$ mass concentration measured in Beijing during a week period in June, 1999 was $136\ \mu\text{g m}^{-3}$ (S.D. $48\ \mu\text{g m}^{-3}$), with organic compounds (OCs) being responsible for $\sim 30\%$ of the $\text{PM}_{2.5}$ mass and sulfate, ammonium, nitrate and mineral aerosol contributing 15%, 8%, 5% and 16%, respectively (Bergin et al., 2001). Bergin et al. (2001) also measured the aerosol scattering and absorption coefficients and estimated the visibility to be ~ 6 km during the field study. Overall, prior measurements indicate relatively high concentrations of fine particulate mass in urban regions of China,

with OCs typically being the most dominant chemical species.

To our knowledge, there have not been measurements of aerosol chemical, physical and radiative properties reported for the rural Yangtze delta region of China. The Yangtze delta region is one of the largest agricultural areas of China, and is located within several hundred kilometers of large industrialized cities including Shanghai, Hangzhou, Nanjing, and Wuhan. It is also located downwind of the Sichuan province, which is a significant source of air pollution (Chameides et al., 1999). At this time, it is not possible to estimate the influence of aerosols on visibility as well as on regional climate and crop production in this area of China due to the lack of pertinent measurements of aerosol properties. For this reason, a field sampling campaign was conducted over a 5-week period in the early winter of 1999 in Linan, China which is a rural location in the Yangtze delta region.

2. Experimental methods

The aerosol light scattering coefficient, σ_{sp} , at both dry (RH $< 40\%$) and ambient relative humidity (RH), and absorption coefficient, σ_{ap} , were measured during the one-month intensive field sampling period from 28 October to 1 December, 1999 in Linan, China—a background air monitoring station operated by the Chinese government. At the same time, daily filter samples of $\text{PM}_{2.5}$ and PM_{10} were collected and analyzed for mass, major ion and organic and elemental carbon (EC) concentrations in order to determine which anthropogenic chemical species were primarily responsible for aerosol extinction. Meteorological parameters (wind speed, wind direction, temperature, RH, and precipitation) were measured by the Linan Background Air Monitoring Station personnel. As shown in Fig. 1, the station is located in an agricultural region of Yangtze delta in close proximity to large urban sources of anthropogenic pollutants (189 km west-southwest of Shanghai, with a population of ~ 12 million; 40 km west of Hangzhou, with a population of 1.1 million). The site is located at an elevation of 133 m (latitude $30^\circ 17' \text{N}$, longitude $119^\circ 45' \text{E}$), with access by a single road from the township of Linan (population 50,000) which is located ~ 10 km to the northwest. The site is unique in that it is removed from local point and mobile sources of pollutants, and therefore represents somewhat aged urban air in the vicinity of this region. In addition, as part of the NASA funded China-MAP study, daily $\text{PM}_{2.5}$ samples were collected at Linan and two other locations in the Yangtze delta: Sheshan ($31^\circ 5' \text{N}$, $121^\circ 11' \text{E}$) which is located ~ 163 km east-northeast of Linan, and Changshu ($31^\circ 41' \text{N}$, $120^\circ 46' \text{E}$) which is ~ 183 km north-northeast of Linan. $\text{PM}_{2.5}$ samples were

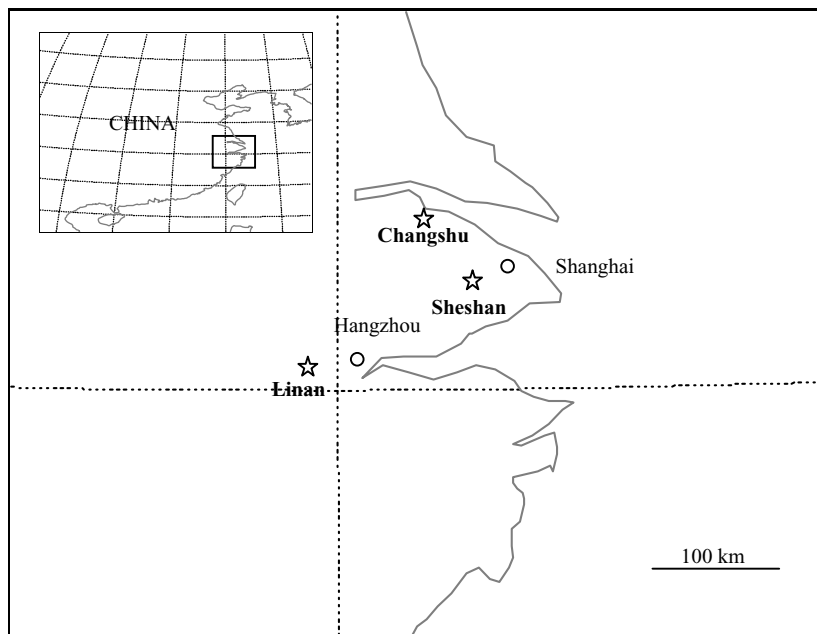


Fig. 1. Map of the Yangtze delta. Three sampling sites, Linan (latitude $30^{\circ}17'N$, longitude $119^{\circ}45'E$), Sheshan ($31^{\circ}5'N$, $121^{\circ}11'E$), and Changshu ($31^{\circ}41'N$, $120^{\circ}46'E$), are labeled on the map.

analyzed for elemental and organic carbon as well as major ions from these sites on an every other day schedule.

2.1. Measurements of aerosol radiative properties

Aerosol light scattering and absorption coefficients were measured at dry RH ($RH < 40\%$) at the Linan Background Air Monitoring Station. A radiance research nephelometer was used to measure the light scattering coefficient, σ_{sp} , at 530 nm. The instrument was calibrated prior to the field experiment using clean (particle-free) air as well as HFC-134a for the span gas. The aerosol light absorption coefficient, σ_{ap} , was measured at 565 nm using a radiance research particle soot absorption photometer (PSAP). The absorption coefficient was corrected for both light scattering and instrument overestimation as described by Bond et al. (1999). Air was sampled at a flow rate of 16.7 l min^{-1} at ambient temperature ($12 \pm 6^{\circ}\text{C}$) and pressure ($1008 \pm 5 \text{ mbar}$) through a URG corporation cyclone inlet that removed particles having diameters $> 2.5 \mu\text{m}$, in order to sample the particulate fraction that efficiently scatters light. The inlet was located on the roof of the monitoring room, and at a height $\sim 7 \text{ m}$ above the ground surface. The air then passed through 4 m of $\frac{3}{8}$ in. i.d. black conductive tubing and into the monitoring room. The sample flow was then gently heated to maintain an RH of $< 40\%$ using a capacity-type RH/

temperature sensor (Vaisala, Inc. Humicap, model 50 Y) interfaced to a RH controller (Watlow Instruments, Inc.) that heated a 1.27 cm i.d., 30 cm long section of stainless steel tubing. The aerosol was conditioned in order to ensure that the aerosol radiative properties being measured were intrinsic to the aerosol and not dependent on water content (Ogren and Sheridan, 1996). The flow was split into two separate sample streams using a URG Corporation flow splitter. A portion of the flow ($0.13\text{--}0.45 \text{ l min}^{-1}$ depending on atmospheric conditions) was sampled by the PSAP, with the remaining flow going to the nephelometer. An additional sampling line was also operated at 16.7 l min^{-1} at ambient temperature and pressure with a similar URG $\text{PM}_{2.5}$ cyclone upstream of a radiance research nephelometer which sampled air at ambient conditions. Both nephelometers have their own capacity-type RH/temperature sensors (Vaisala, Inc. Humicap, model 50 Y) to measure the sample temperature and RH. The RH within the ambient nephelometer had a mean value of 63% with an S.D. of 19%, which is $\sim 13\%$ lower than the actual ambient RH ($72 \pm 21\%$) because of the heat added to the sample by the nephelometer itself. In the following sections, the RH associated with the ambient nephelometer is always referred to as the sample RH. All of the flows were generated using a vacuum pump (Gast, Inc.) and maintained by critical orifices manufactured by O'Keefe Controls. Several times during the field study a HEPA capsule filter was placed upstream of each

sampling line in order to ensure the instruments were working properly. Typically, zero air σ_{sp} values were $<1 \text{ Mm}^{-1}$.

2.2. Measurement of aerosol chemical and physical properties

Daily $\text{PM}_{2.5}$ and PM_{10} filter samples (beginning and ending at 9:00 a.m. local standard time (LST) each day) were collected and analyzed for mass, major ionic as well as OC and EC concentrations. The filter sampling system consisted of an URG Corporation $\text{PM}_{2.5}$ cyclone followed by a URG Corporation flow splitter, which diverted the flow into 3 lines, each with a flow rate of 5.6 l min^{-1} . An additional line was operated at a flow rate of 16.7 l min^{-1} , and had an URG corporation PM_{10} cyclone inlet. The flows were generated using another vacuum pump (Gast, Inc.), maintained by critical orifices, and measured by Dwyer rotameters. A Gallus 2000 air meter was used to monitor the total air volume through the sampling system. Flow balance and leak checks were conducted each day to ensure there were no system leaks. The flows calculated from the readings of the rotameters and from the readings of the air meter agreed to within 5% over the entire sampling period. Pall Gelman Teflon Zefluor filters ($2 \mu\text{m}$ pore size and 47 mm diameter) were used to collect $\text{PM}_{2.5}$ and PM_{10} samples for mass analyses. The Zefluor filters were conditioned for 2 weeks, both before and after sampling. Filter masses were determined using a Mettler Toledo MT5 electronic mass balance located in a clean room (temperature $21 \pm 1^\circ\text{C}$, RH $35 \pm 3\%$) at the Georgia Tech Southern Center for Integrated Studies of Secondary Air Pollutants (SCISSAP) analytical laboratory. Several of the $\text{PM}_{2.5}$ filters ($n = 5$) were also used to determine the water insoluble $\text{PM}_{2.5}$ mass fraction, following $\text{PM}_{2.5}$ mass concentration determination. This was done by drawing 5 l of ultrapure deionized water through the filters, reconditioning the filters in the clean room, and reweighing the filters. Pall Gelman Zefluor filters were also used to collect samples for analysis of major anions (SO_4^{2-} , NO_3^- , and Cl^-) and cations (NH_4^+ , Ca^{2+} and Na^+). After sampling, filters were placed in pre-cleaned 22 ml bottles, along with 20 ml of ultrapure deionized water, and sonicated in a water bath for 30 minutes. The extracts were analyzed for cations and anions using a Dionex DX 500 Chromatograph System located at the Georgia Tech SCISSAP laboratory. Pallflex #2500 QAT-UP Quartz fiber filters (47 mm diameter) were used to collect aerosol particles for EC/OC analysis. Elemental and organic carbon mass concentrations were determined using the thermal evolution technique described by Birch and Cary (1996). The organic carbon concentrations were then multiplied by a factor of 1.4 (White and Roberts, 1977; Countess et al., 1980; Japar et al., 1984) to determine the

concentrations of the OC. Prior to sampling, the Quartz filters were pre-baked at 600°C for 2 h at Georgia Tech SCISSAP laboratory. Several field blanks for $\text{PM}_{2.5}$, PM_{10} , EC/OC and ions were also collected and analyzed in order to quantify the level of contamination during filter handling, shipping and analysis. The average concentrations of the field blanks were $<4\%$ of the concentrations of the samples. The mean concentration of each species measured on the field blanks was subtracted from the field samples to estimate atmospheric concentration.

At the same time, as part of the NASA funded China-MAP study, $\text{PM}_{2.5}$ samples were also collected at Linan, as well as at Changshu and Sheshan. Daily filter samples were obtained on an every-other day sampling schedule, alternating collection of samples for ionic and EC/OC concentration estimation. At Linan, an Andersen $\text{PM}_{2.5}$ RAAS-2.5-1 Ambient Air Sampler from Andersen Instruments Inc. was used to collect samples. At Changshu, aerosol samples were collected by a Rupprecht & Patashnick (R&P) Partisol Sampler 2000-H with a 10 l min^{-1} URG $\text{PM}_{2.5}$ cyclone inlet. A 3-channel particle composition monitor (PCM) manufactured by URG according to the specifications of SCISSAP was used to collect $\text{PM}_{2.5}$ aerosol samples at Sheshan. Samples were analyzed for ions and EC/OC at Georgia Tech as described above.

2.3. Meteorological measurements

Ambient temperature and RH were measured every minute using a capacity-type RH/temperature sensor (Vaisala, Inc. Humicap, model 50 Y). The sensor was located outside of the monitoring room, at a height $\sim 5 \text{ m}$ above the ground surface, and was shielded from direct solar radiation. At the same time, meteorological parameters including wind speed, wind direction, pressure, and precipitation were measured by the staff of the Linan Background Air Monitoring Station on an hourly basis. The temperature and RH presented in this paper are hourly averages of the measurements.

3. Results and discussions

The local meteorology during the field study was characterized by relatively low wind speeds (mean and S.D. of 1.7 and 1.1 m s^{-1} , respectively). In general, the wind direction was north to northeast during the daytime and south to southwest during the night. No clear relationship was found between atmospheric aerosol properties (i.e., σ_{sp} and σ_{ap}) and wind direction. Several days had precipitation as follows: 31 October (14 mm), 1 November (1.4 mm), 11 November (3.2 mm), 15 November (0.2 mm), and 26–28 November (2.4, 16.3 and 1.1 mm). Although light rains occurred on several

days, the period was characterized by generally dry conditions.

3.1. Aerosol radiative properties

Table 1 shows the mean and S.D. values of the hourly averaged aerosol light scattering coefficient, σ_{sp} , absorption coefficient, σ_{ap} , and single scattering albedo, ω , measured at dry RH which are 353 Mm^{-1} (202 Mm^{-1}), 23 Mm^{-1} (14 Mm^{-1}), and 0.93 (0.04), respectively. The mean scattering coefficient is only $\sim 25\%$ lower than the mean value of 488 Mm^{-1} (S.D. of 370 Mm^{-1}) reported for Beijing, China during a week in June, 1999 (Bergin et al., 2001). This is somewhat surprising given that Linan is a rural location more removed from both stationary and mobile sources of aerosols and their precursors compared to a large urban area such as Beijing. The mean aerosol absorption coefficient in Linan of 23 Mm^{-1} is more than a factor of 3 lower than the mean value of 83 Mm^{-1} (S.D. of 40 Mm^{-1}) measured in Beijing during June, 1999. This is most likely due to the greater emissions of EC from diesel engines in Beijing. Based on these measurements, the mean single scattering albedo is significantly higher in Linan during the field study (0.93) than the mean value measured during June, 1999 in Beijing (0.81) (Bergin et al., 2001). The visibility is estimated to be $\sim 7 \text{ km}$ during the field study assuming that visibility = $1.9/\sigma_e$ (value represents 75th percentile) (Husar et al., 1994), which is roughly the same as that estimated in Beijing ($\sim 6 \text{ km}$) by Bergin et al. (2001).

The mean σ_{sp} value at Linan is roughly 3 times greater than the mean value of 120 Mm^{-1} measured in Atlanta, Georgia (a relatively polluted city in the US) during August 1999 as part of the Atlanta SuperSite experiment (Carrico et al., 2001). The aerosol scattering coefficient in Linan is also significantly higher than the values reported by Waggoner et al. (1981) for urban areas of the US during the 1970s which range from 30 to 210 Mm^{-1} . Mean values of σ_{ap} reported for several locations in the US range from 27 to 118 Mm^{-1} (Waggoner et al., 1981). Recent measurements of σ_{ap} during the month of August in Atlanta have a mean and S.D. of 16 Mm^{-1} (12 Mm^{-1}) (Carrico et al., 2001). The

value of 23 Mm^{-1} in Linan is within the range of values reported for urban areas within the US, although it is roughly a factor of 1.5 greater than recent measurements in Atlanta. Continuous measurements of σ_{sp} and σ_{ap} made at Bondville, Illinois, a rural location in the south central region of the state, by the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL) have values ranging from 8 to 80 and $0.5\text{--}5.0 \text{ Mm}^{-1}$, respectively (Sheridan et al., 1998). The σ_{sp} and σ_{ap} values at the rural location in the US are roughly a factor of 4 lower than in Linan. In general, aerosol radiative properties in Linan are more representative of prior measurements in urban rather than rural areas.

Fig. 2 shows the 24-h average σ_{sp} , σ_{ap} , and ω values for each day of the field study. There is a significant amount of day-to-day variability in both σ_{sp} and σ_{ap} . The lowest values are found on 31 October and 27 November. On these days, rainfall occurred (14 and 16 mm, respectively), which scavenged aerosols from the atmosphere. Both σ_{sp} and σ_{ap} steadily increase over several day periods following the rainfall events. The results indicate that, not surprisingly, precipitation has a significant impact on the observed aerosol radiative properties. Fig. 3 shows values of σ_{sp} and σ_{ap} averaged for each hour of the day (error bars represent S.D.) as a function of local time. There is a clear diurnal pattern in both σ_{sp} and σ_{ap} , with minimum values occurring in the early afternoon between 12:00 and 14:00, and statistically similar values throughout the rest of the day. The hourly averaged ambient Temperature, T , and RH, for each hour of the day is given in Fig. 4. The daily maximum in temperature and minimum in RH occurs at 12:00, which generally corresponds to minimum values for σ_{sp} and σ_{ap} . This suggests that as the atmospheric temperature, and hence mixing height, increases to peak values in the early afternoon, σ_{sp} and σ_{ap} decrease in part due to dilution of surface air with air aloft. From the early morning to afternoon both σ_{sp} and σ_{ap} decrease by $\sim 40\%$. In the late afternoon, σ_{sp} and σ_{ap} begin to rise as the temperature decreases and the atmospheric boundary layer becomes more stable, thus decreasing the depth at which aerosols emitted from the surface are being mixed into the atmosphere. The values of σ_{sp} and σ_{ap} are relatively constant from 20:00 in the

Table 1
Mean and S.D. values of aerosol physical, chemical and radiative properties (measured from 28 October to 30 November, 1999)^a

	PM _{2.5} ($\mu\text{g m}^{-3}$)	PM ₁₀ ($\mu\text{g m}^{-3}$)	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	Sodium ($\mu\text{g m}^{-3}$)	Ammonium ($\mu\text{g m}^{-3}$)	Nitrate ($\mu\text{g m}^{-3}$)	Sulfate ($\mu\text{g m}^{-3}$)	σ_{sp} (Mm^{-1})	σ_{ap} (Mm^{-1})	ω
Mean	90	98	44	3.4	3.0	8.6	7.7	21.2	353	23	0.93
S.D.	47	51	25	1.7	1.2	5.2	7.0	11.5	202	14	0.04

^a Aerosol mass concentration and chemical composition data are means and S.D. of daily values. σ_{sp} (530 nm), σ_{ap} (565 nm), and ω represent dry (RH < 40%) conditions, and are means and S.D. of hourly averaged values.

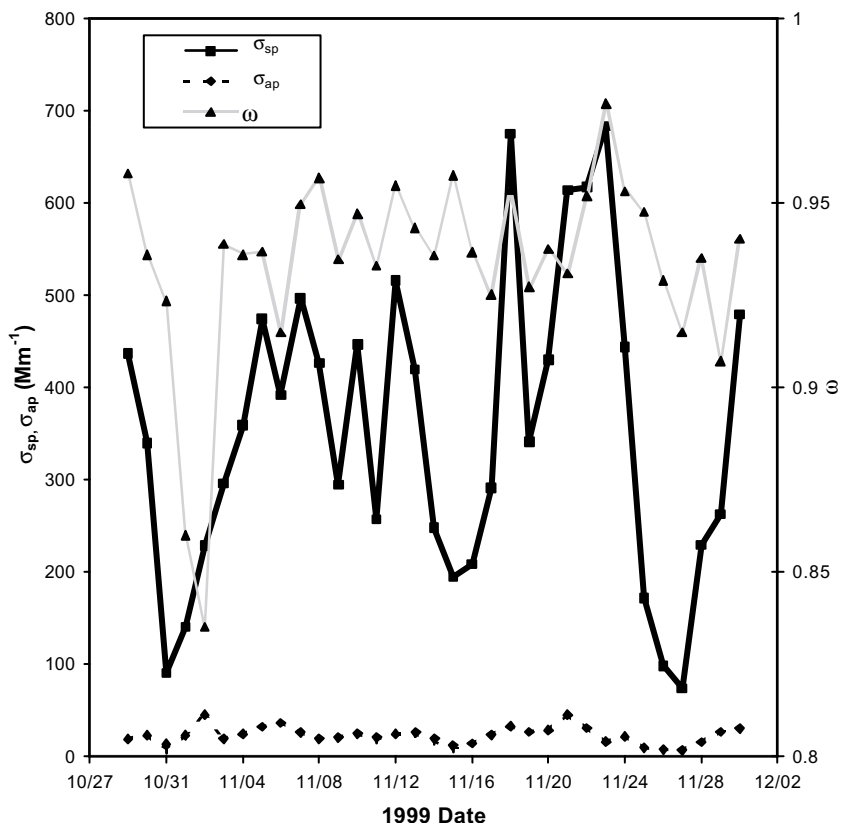


Fig. 2. Daily average aerosol scattering coefficient, σ_{sp} (530 nm), absorption coefficient, σ_{ap} (565 nm) and single scattering albedo, ω , measured at dry RH (RH < 40%).

evening to 06:00 in the morning. This suggests that the emission of aerosol particles into the stable atmospheric boundary layer does not significantly increase the aerosol loading overnight (i.e. the sources of aerosols during the late evening and early morning are insignificant compared to other times of the day). This is quite possibly due to the onset of darkness, and the end of the workday which corresponds to decreases in the emissions of aerosols from agricultural activities (biomass burning, and combustion linked with farm equipment) and small local industries. It is possible that the relatively high values of aerosol extinction coefficient measured at Linan decrease the mixing height compared to clean conditions by influencing the amount of radiation reaching the surface, and hence surface heating.

The ratio ($F_{\sigma_{sp}}(\text{RH})$) of aerosol light scattering coefficient measured at ambient RH, $\sigma_{sp}(\text{RH})$, to that at controlled dry conditions (RH < 40%), $\sigma_{sp}(40\%)$, based on hourly averaged data for the entire field study is shown in Fig. 5. The $F_{\sigma_{sp}}(\text{RH})$ values at each RH are relatively constant, suggesting that the properties that influence the hygroscopic growth such as the dry size

distribution, refractive index, and aerosol hygroscopicity (McInnes et al., 1998) did not significantly vary during the field study. At an RH of 80%, $F_{\sigma_{sp}}(\text{RH})$ varies from 1.7 to 2.0, in agreement with previous measurements of $F_{\sigma_{sp}}(80\%)$ made at continental locations within the US (Waggoner et al., 1981; Charlson et al., 1984; Rood et al., 1987). For the mean daytime ambient RH of 72%, approximately 40% of the light attenuation by aerosols is due to light scattering by condensed water.

3.2. Aerosol physical and chemical properties

Daily integrated filter samples for $\text{PM}_{2.5}$, elemental and organic carbon, and major ionic aerosol concentrations are presented in Fig. 6. The concentrations of calcium and chloride are not shown because they were relatively low for the entire sampling period (mean concentrations were 0.16 and $0.48 \mu\text{g m}^{-3}$, respectively). The aerosol mass concentration denoted as 'unidentified' in Fig. 6 was determined by subtracting the $\text{PM}_{2.5}$ mass concentration from the summation of the mass concentrations for the individual chemical species for each sample. The unidentified fraction is on average

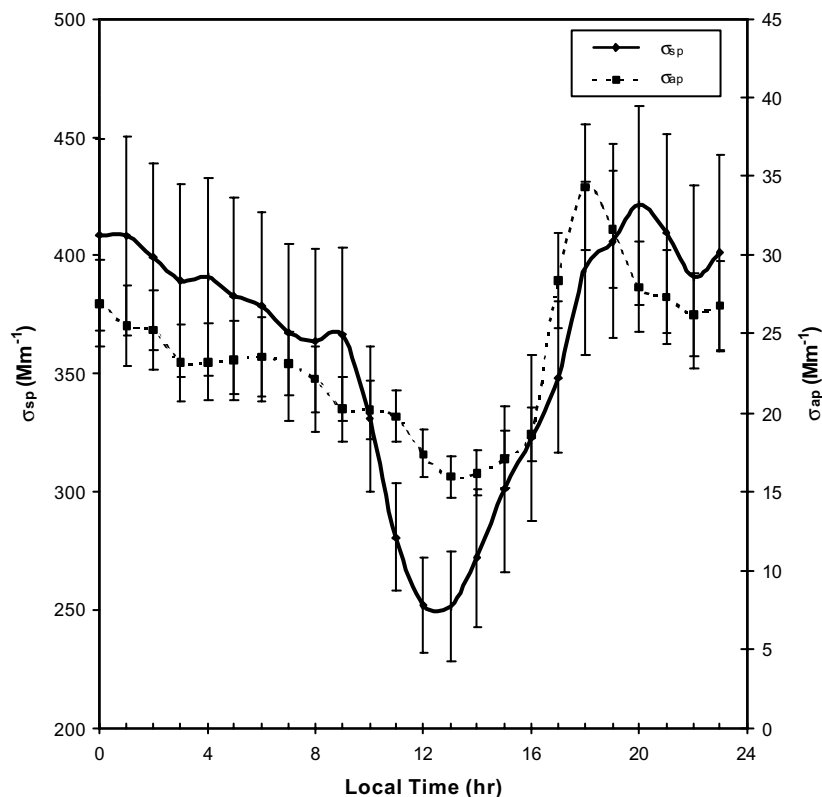


Fig. 3. Diurnal variability of aerosol scattering coefficient, σ_{sp} (530 nm), and absorption coefficient, σ_{ap} (565 nm). The values are averaged for each hour of the day (error bars represent S.D.) for the entire sampling period (28 October–30 November, 1999).

~3% of the $PM_{2.5}$ mass concentration suggesting that the majority of the chemical species are accounted for in the chemical analyses. The trend in the daily $PM_{2.5}$ mass concentration is similar to that observed for the daily averaged aerosol radiative properties, with low values corresponding to the days that had precipitation. Moreover, the ratio of OC (which is primarily composed of water insoluble compounds) to sulfate concentration increased from ~1.5 to ~4 after the precipitation, which further suggests that precipitation removal is a major process that is responsible for the lower aerosol concentrations. Mean and S.D. values for the daily filter measurements of $PM_{2.5}$, PM_{10} as well as chemical composition of the $PM_{2.5}$ aerosol are given in Table 1. The majority of the aerosol mass is located in the fine ($D_p < 2.5 \mu m$) particle mode, as reflected in the 0.92 ratio of $PM_{2.5}$ to PM_{10} . The lack of coarse mode aerosol is likely due to the relatively low wind speed during the field study (mean wind speed of $1.7 m s^{-1}$), that did not favor the generation and transport of wind blown dust, which exists primarily in the coarse size mode. Also, the unidentified fraction of $PM_{2.5}$ is relatively insignificant (~3% of the total $PM_{2.5}$ mass) suggesting that wind

blown dust was not an appreciable fraction of the aerosol mass during the field study. The mean and S.D. of the 24-h average $PM_{2.5}$ mass concentration is $90 \mu g m^{-3}$ ($47 \mu g m^{-3}$). This mean value is only ~30% lower than the mean daily $PM_{2.5}$ mass concentration value of $136 \mu g m^{-3}$ reported in Beijing during June, 1999 (Bergin et al., 2001). In addition, the mean $PM_{2.5}$ mass concentration at Linan is nearly a factor of 1.5 greater than the proposed 24-h average US NAAQS for $PM_{2.5}$ of $65 \mu g m^{-3}$, and a factor of 6 greater than the proposed annual average US NAAQS for $PM_{2.5}$ of $15 \mu g m^{-3}$.

As shown in Table 1, OC are the dominant chemical species accounting for ~50% of the $PM_{2.5}$ mass during the field study. The other main contributors to the $PM_{2.5}$ mass are sulfate (24%), nitrate (9%) and ammonium (10%). The results suggest that, under dry conditions ($RH < 40\%$), OC dominate the attenuation of solar radiation and hence the direct shortwave aerosol radiative forcing during the field sampling period. The mean and S.D. of the ratio of organic carbon to EC $PM_{2.5}$ mass are 11.0 (7.5), which is similar to the ratio of 11.6 (1.3) in Beijing (Bergin et al., 2001), but with

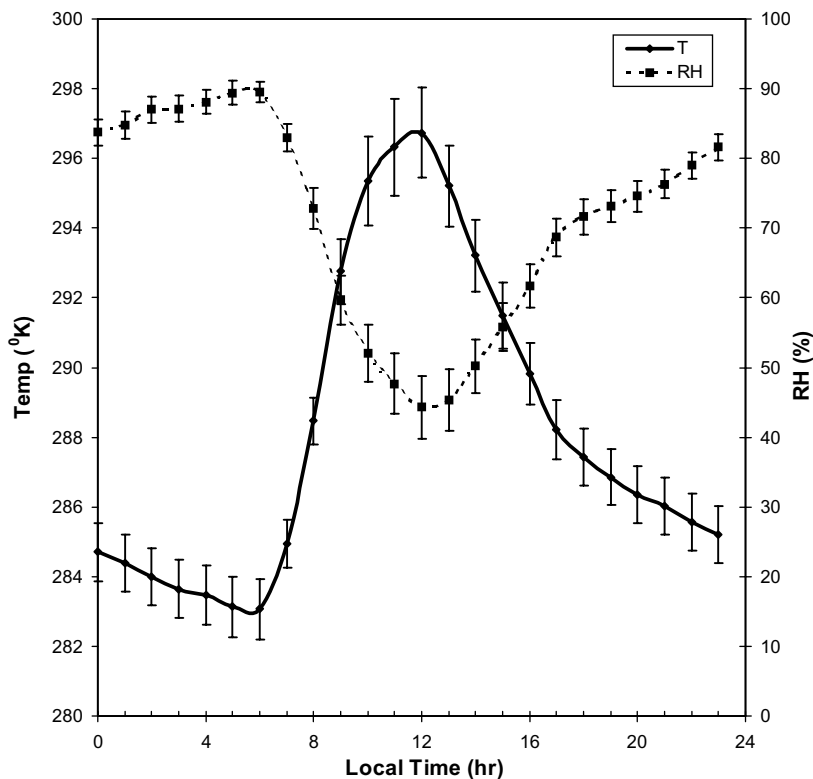


Fig. 4. Temperature (T) and relatively humidity (RH) versus local time. The values are averaged for each hour of the day (error bars represent S.D.) for the entire sampling period (28 October–30 November, 1999).

relatively greater variability. The large variability in the Linan OC/EC ratio may be due to the presence of a small activated carbon plant located ~ 1 km from the station, which operated sporadically during the field sampling campaign, and may have influenced local EC concentrations. The OC concentration measured in Linan is more than an order of magnitude greater than the continental US background value for OC of $\sim 3 \mu\text{g m}^{-3}$ reported by Malm et al. (1994), suggesting that the majority of the OC is anthropogenic. The field sampling campaign coincided with the rice harvest, and the burning of biomass after the harvest was evident throughout the region for the duration of the field study. It is likely that a significant fraction of the OC originated from biomass burning during this time of year in the Yangtze delta region. The water insoluble $\text{PM}_{2.5}$ mass fraction for several samples ($n = 5$) is 0.38 (with a S.D. of 0.05). Therefore, it would appear that a significant fraction of the OC ($\sim 80\%$) are not soluble in water. Aerosol produced from biomass burning in Brazil was found to consist primarily of organic carbon, with OC accounting for 70–80% of the aerosol mass (Ferek et al., 1998). In addition, the change in light scattering as a

function of RH for the biomass burning aerosol was relatively low ($F_{\sigma_{sp}}$ (RH = 80%) ~ 1.16) compared with measurements of other continental aerosols (Kotchenruther and Hobbs, 1998), which suggests that organic aerosols from biomass burning are water insoluble. Although the measurements were made at different locations for different types of vegetation and burning conditions, the data suggest that aerosol from biomass burning is composed of primarily OC that are relatively insoluble in water. Although, since analysis of specific OC was not performed on the Linan samples, it cannot be conclusively shown that the organic carbon originated from biomass burning. The presence of a significant fraction of water insoluble organic carbon aerosol in this rural location in conjunction with observed biomass burning suggests that a major part of organic aerosol is from biomass burning sources. A large fraction of the aerosol mass ($\sim 60\%$) is soluble in water. This suggests that the aerosols in Linan also have other important anthropogenic sources, probably from local industries and mobile sources, as well as from aerosols transported into the region from nearby urban areas (i.e. Hangzhou and/or Shanghai).

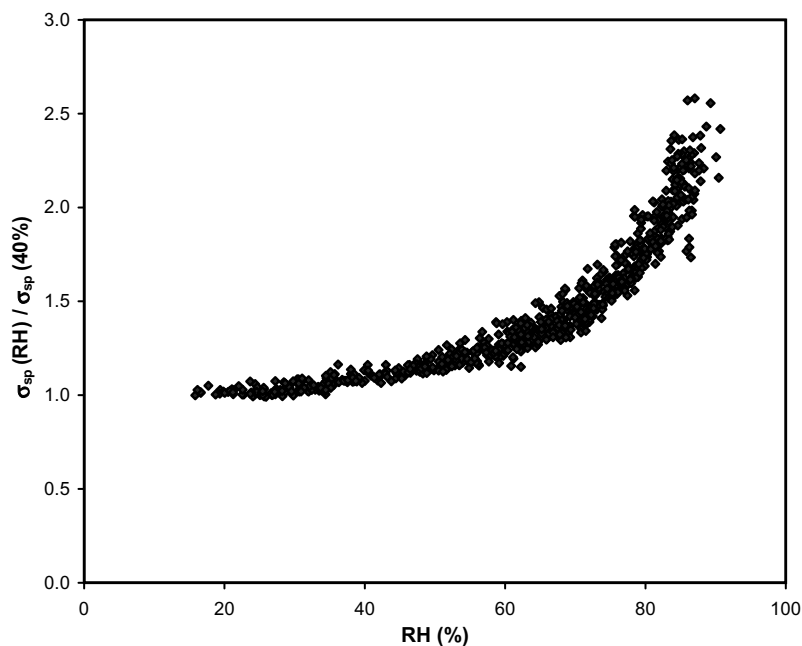


Fig. 5. Ratio of aerosol light scattering coefficient measured at ambient RH, σ_{sp} (RH), to that at controlled dry conditions (RH < 40%), σ_{sp} (40%), based on hourly averaged data for the entire sampling period (28 October–30 November, 1999).

3.3. Aerosol mass scattering and absorption efficiencies

The mass scattering efficiency of the dry aerosol, $E_{scat,2.5}$, estimated from the ratio of σ_{sp} and the 24-h average $PM_{2.5}$ filter mass concentrations has a mean and S.D. of $4.0 \text{ m}^2 \text{ g}^{-1}$ ($0.4 \text{ m}^2 \text{ g}^{-1}$). This value is at the upper end of the range of the $E_{scat,2.5}$ values ($2.3\text{--}3.6 \text{ m}^2 \text{ g}^{-1}$) estimated in Beijing by Bergin et al. (2001). This is due to the fact that Beijing aerosol often had a significant coarse mode that contributed mass to the larger, less efficiently scattering particle sizes of the $PM_{2.5}$ aerosol. The mean $E_{scat,2.5}$ value in Linan is slightly larger than the values reported by Waggoner et al. (1981) for various locations within the US which range from 2.9 to $3.2 \text{ m}^2 \text{ g}^{-1}$. This could be due to the larger inlet cut-size ($3 \mu\text{m}$) used by Waggoner et al. (1981) as well as due to differences in aerosol physical and chemical properties between Linan and the measurement locations within the US. The $E_{scat,2.5}$ value at Linan is within the range of $3.3\text{--}4.2 \text{ m}^2 \text{ g}^{-1}$ reported by Reid et al. (1998a, b) for aerosols from biomass burning in Brazil.

The mean and S.D. for the mass absorption efficiency of EC, $E_{abs,2.5}$, estimated from σ_{ap} measurements and 24-h averaged EC concentrations determined from filters is $8.6 \text{ m}^2 \text{ g}^{-1}$ ($7.0 \text{ m}^2 \text{ g}^{-1}$). These values are within the range of values reported for the US by Wagoner et al. (1981) ($5\text{--}11 \text{ m}^2 \text{ g}^{-1}$) as well as for a variety of other locations presented by Horvath (1993). It is possible that the source of the EC is regional burning of biomass associated with the rice harvest as previously mentioned.

It is also possible that local industries as well as mobile sources contribute to the EC concentrations, although it is not possible to estimate the contribution of various sources with our data.

3.4. Aerosol chemical compositions at two other locations in the Yangtze delta region

As previously mentioned, $PM_{2.5}$ samples were collected at the same time at Linan, as well as at Changshu and Sheshan for ionic and EC/OC concentrations. Table 2 shows the monthly mean values of $PM_{2.5}$ OC, EC and major ions based on daily samples shown in Fig. 6 as well as every other day samples collected in Linan, Changshu and Sheshan as part of the China-MAP project. Mean concentrations of the major $PM_{2.5}$ chemical species measured from the filters collected daily and every other day in Linan agree to within $\sim 15\%$, and are not statistically different at a 95% confidence interval. Also, at a 95% confidence interval, the mean aerosol chemical concentrations at Linan and Sheshan are statistically similar. Mean concentrations of the major chemical species OC and Sulfate in Changshu are $\sim 40\%$ and 20% higher than in Linan. The possible reason for this may be that both Linan and Sheshan had no observable large industrial facilities within several kilometers. On the other hand, the sampling station of Changshu had several large factories within 1 km, and was also within 500 m of a busy roadway. It is expected that the Changshu sampling site was more influenced by

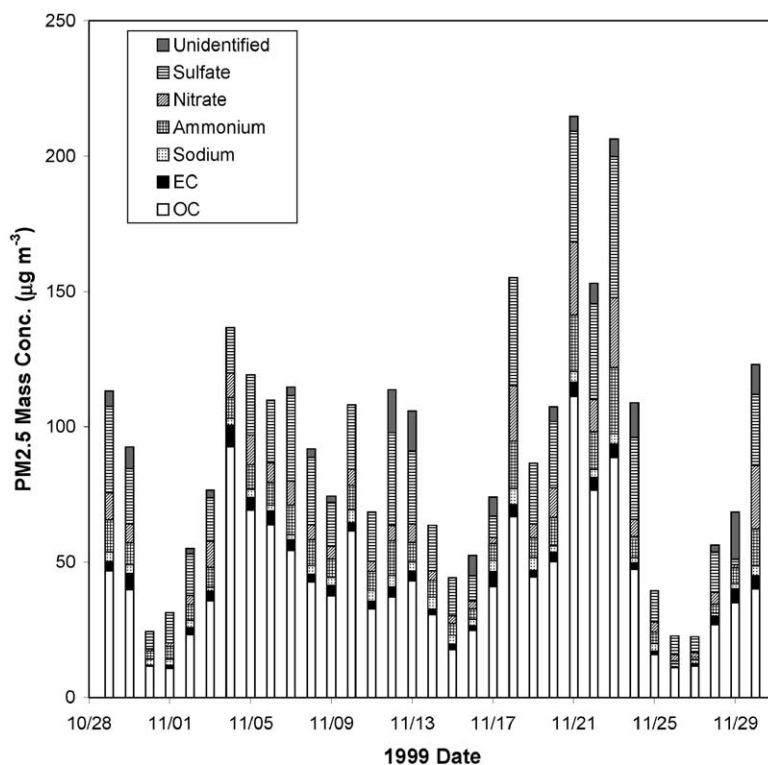


Fig. 6. Daily average $PM_{2.5}$ chemical concentrations. Filter samples were collected from 9:00 a.m. to 9:00 a.m. the next day (local standard time).

Table 2

Mean and S.D. values of daily average concentrations for major aerosol chemical compositions in Linan, Sheshan and Changshu (measured from 28 October to 30 November, 1999)

	OC ($\mu\text{g m}^{-3}$)	EC ($\mu\text{g m}^{-3}$)	Ammonium ($\mu\text{g m}^{-3}$)	Nitrate ($\mu\text{g m}^{-3}$)	Sulfate ($\mu\text{g m}^{-3}$)
Linan	44 (25)	3.4 (1.7)	8.6 (5.2)	7.7 (7.0)	21.2 (11.5)
Linan (Andersen)	42 (22)	3.0 (1.4)	7.7 (3.4)	7.3 (4.7)	17.2 (6.5)
Sheshan (PCM)	51 (24)	3.2 (1.9)	7.8 (4.5)	10.7 (6.6)	15.8 (7.8)
Changshu (R&P Partisol)	61 (28)	3.6 (1.7)	10.3 (4.0)	12.3 (7.2)	21.8 (12.3)

local sources than both Linan or Sheshan. Therefore, it is not surprising that aerosol concentrations are higher at Changshu than the other two sites. Fig. 7 shows the daily mean $PM_{2.5}$ concentrations of OC at the three sampling sites. The general trends in the data for each location are similar, with the lowest OC concentrations occurring during periods associated with precipitation. Although, peak OC values do not occur simultaneously at each of the sites. For instance, on 20 November the highest OC concentration measured during the field study at Changshu ($\sim 140 \mu\text{g m}^{-3}$) does not correspond to extremely high concentrations at either Linan or Sheshan. This may be due to several reasons including the day-to-day differences in aerosol sources and source strengths in each of the sub-regions as well as in local

meteorology. The monthly mean $PM_{2.5}$ concentrations of the major chemical species (OC + EC + major ions) over the field sampling period at the three sampling sites range from ~ 80 to $110 \mu\text{g m}^{-3}$. These concentrations are all significantly higher than the proposed 24-h average US $PM_{2.5}$ NAAQS of $65 \mu\text{g m}^{-3}$. At all three sites, OC are the dominant chemical species accounting for $\sim 50\%$ of the $PM_{2.5}$ mass.

4. Conclusions

The mean and S.D. values of the aerosol light scattering coefficient, σ_{sp} , absorption coefficient, σ_{ap} , and single scattering albedo, ω measured at dry RH in

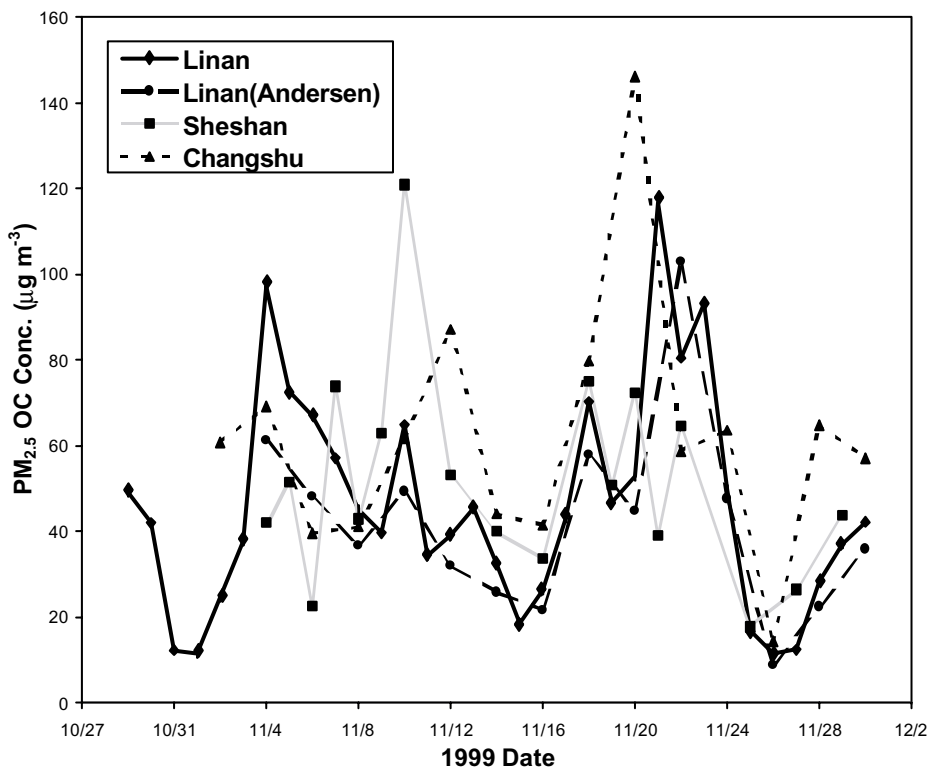


Fig. 7. Daily average $PM_{2.5}$ organic compound (OC) concentrations at Linan, Sheshan and Changshu. Filter samples were collected from 9:00 a.m. to 9:00 a.m. the next day (local standard time).

Linan, China during November, 1999 are $353 Mm^{-1}$ ($202 Mm^{-1}$), $23 Mm^{-1}$ ($14 Mm^{-1}$), and 0.93 (0.04), respectively. Aerosol radiative properties in Linan are more representative of values reported for urban regions rather than rural locations. There is a significant amount of day-to-day variability in both σ_{sp} and σ_{ap} , which is primarily associated with precipitation events that scavenge aerosols from the boundary layer. A clear diurnal pattern is observed in both σ_{sp} and σ_{ap} , with minimum values corresponding to daily maxima in temperature and minima in RH, suggesting σ_{sp} and σ_{ap} decrease in part due to an increase in the daily mixing height. At an RH of 80%, $F_{\sigma_{sp}}$ (80%) varies from 1.7 to 2.0, in agreement with previous measurements of $F_{\sigma_{sp}}$ (80%) made at continental locations within the US. The mean daytime RH is 72%, which suggests that approximately 40% of the light attenuation by aerosols is due to light scattering by condensed water.

The majority of the aerosol mass in Linan, China during our field campaign is located in the fine ($D_p < 2.5 \mu m$) particle mode, as demonstrated by the 0.92 ratio of $PM_{2.5}$ to PM_{10} . The mean and S.D. of the 24-h average $PM_{2.5}$ mass concentration is $90 \mu g m^{-3}$ ($47 \mu g m^{-3}$), which is nearly a factor of 1.5 greater than

the proposed 24-h average US NAAQS for $PM_{2.5}$ of $65 \mu g m^{-3}$. OC are the dominant chemical species accounting for $\sim 50\%$ of the $PM_{2.5}$ mass during the field study. The other main contributors to the $PM_{2.5}$ mass are sulfate (24%), nitrate (9%) and ammonium (10%). The results suggest that OC dominated the attenuation of solar radiation and hence the direct shortwave aerosol forcing during the field sampling period under dry conditions. Measurements also show that a significant fraction of the OC ($\sim 80\%$) are not soluble in water. The presence of a significant fraction of water insoluble organic carbon aerosol in this rural location in conjunction with observed biomass burning suggests that a major part of the organic aerosol is from biomass burning sources. Local anthropogenic sources as well as longer range transport from nearby urban areas (i.e. Hangzhou and/or Shanghai) also probably have important contributions to the aerosol loading in this area. The mass scattering efficiency of the dry aerosol, $E_{scat,2.5}$, and mass absorption efficiency of EC, $E_{abs,2.5}$, have mean and S.D. values of $4.0 m^2 g^{-1}$ ($0.4 m^2 g^{-1}$) and $8.6 m^2 g^{-1}$ ($7.0 m^2 g^{-1}$).

The mean $PM_{2.5}$ mass concentration of the major chemical species over the sampling period is similar for

Linan and Sheshan (located 163 km to the east-northeast of Linan), but is ~40% less than in Changshu (located 183 km to the north-northeast of Linan). This may be due to the fact that the sampling station in Changshu has several large factories within 1 km, and is also within 500 m of a busy roadway. Therefore it is expected that the Changshu sampling site is more influenced by local sources than either Linan or Sheshan. The mean PM_{2.5} concentration of the major chemical species ranges from ~80 to 110 µg m⁻³ at all three sites, and is therefore significantly higher than the proposed 24-h average US PM_{2.5} NAAQS of 65 µg m⁻³. For all locations, OC are the dominant chemical species accounting for ~50% of the PM_{2.5} mass.

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