



Seasonal variations and chemical characteristics of sub-micrometer particles (PM₁) in Guangzhou, China

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ABSTRACT

Daily samples of ambient sub-micrometer particles (PM₁, particles with an aerodynamic diameter $\leq 1.0 \mu\text{m}$) were collected from July 2009 to April 2010 at an urban site over Guangzhou in southern China. Mass concentrations of water-soluble inorganic ions, organic carbon (OC) and elemental carbon (EC) were determined to characterize the chemical composition of PM₁. The mass concentration of PM₁ ranged from $14.6 \mu\text{g m}^{-3}$ to $143.3 \mu\text{g m}^{-3}$, with an annual mean value of $52.4 \pm 27.3 \mu\text{g m}^{-3}$. Seasonally-averaged PM₁ concentrations decreased in the order winter > autumn > spring > summer. The annual mean concentrations of OC and EC were 6.2 ± 3.5 and $5.0 \pm 2.9 \mu\text{g m}^{-3}$, respectively. The OC and EC concentrations were measured following the IMPROVE_A thermal/optical reflectance (TOR) protocol. Total carbonaceous aerosol (the sum of organic matter and elemental carbon) accounted for $23.0 \pm 4.4\%$ of PM₁ mass. Clear seasonal variations in OC and EC suggested sources of these two constituents were remarkable difference among the four seasons. Seasonally averaged OC/EC ratios were 1.2, 1.7, 1.4, and 1.5, from spring to winter respectively. Low OC/EC ratios in comparison with other cities in China revealed that vehicle emissions play an important role in carbonaceous aerosol levels in Guangzhou. SO_4^{2-} , NO_3^- and NH_4^+ were the three major inorganic ions in PM₁, collectively contributing $30.0\% \pm 6.3\%$ of the PM₁ mass. SO_4^{2-} and NH_4^+ were both the highest in autumn and the lowest in summer. In contrast, NO_3^- was the highest in winter. Sulfur oxidation ratio was positively correlated with solar radiation and O_3 , but negatively correlated with SO_2 . Nitrogen oxidation ratio was positively correlated with NO_2 , NH_4^+ and Cl^- , but showed a negative correlation with temperature. By applying the IMPROVE equation, PM₁ mass was reconstructed and showed that $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , OM and EC accounted for $(30.7 \pm 11.4)\%$, $(9.7 \pm 5.2)\%$, $(22.6 \pm 5.0)\%$ and $(9.7 \pm 2.3)\%$ of PM₁, respectively. Finally, source apportionment by positive matrix factorization revealed that (1) secondary aerosol and biomass burning, (2) diesel emissions, (3) gasoline emissions and sea salt, and (4) coal combustion were the greatest contributors to PM₁.

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1. Introduction

High levels of fine particles (PM_{2.5}, particles $\leq 2.5 \mu\text{m}$ in diameter) in the urban atmosphere have been found to

increase morbidity and mortality as well as respiratory symptoms in many epidemiological studies (Dockery et al., 1993; Pope et al., 1995; Schwartz et al., 1996; Pope, 2000; Cao et al., 2012). Tie et al. (2009) demonstrated that a dramatic increase in the frequency of air pollution events has been followed by a large increase in the incidence of lung cancer in Guangzhou. The submicron fraction (particles with

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an aerodynamic diameter $\leq 1 \mu\text{m}$, PM_{10}) should be more strongly associated with adverse health issues than larger particles (Huang et al., 2003). Studies of ambient PM_{10} and its chemical composition are still limited in comparison with the number of studies on $\text{PM}_{2.5}$.

Guangzhou is a mega city with a population of more than 10 million, located in the northern Pearl River Delta (PRD) in Guangdong province, China. Due to a rapid economic growth rate and corresponding rise in energy consumption and vehicle use over the past two decades, the PRD has experienced increasing degradation of regional air quality (Deng et al., 2008). For example, between 1980 and 2006, the occurrence of low visibility remains very high ($150 \text{ days year}^{-1}$), and the persistent low visibility was mainly resulted from small aerosol particles. During the past years, short-term studies on $\text{PM}_{2.5}$ chemical composition and their optical properties were conducted in Guangzhou (Zhang et al., 2008; Andreato et al., 2008; Liu et al., 2008; Tan et al., 2011; Huang et al., 2012), but a long time-scale series of observations is still lacking. In this study, PM_{10} and its major chemical composition (organic carbon (OC), elemental carbon (EC) and water-soluble inorganic ions) were determined over a one-year period. The objectives of this paper are 1) to evaluate pollution levels of PM_{10} and its major chemical compositions in Guangzhou; and 2) to quantitatively identify the sources of PM_{10} .

2. Methodology

2.1. Sample collection

PM_{10} samples were collected on 47 mm quartz microfiber filters (Whatman International Ltd, Maidstone, England, QMA) from the roof surface of a 50-m high building at the monitoring station of the South China Institute of Environmental Science (SCIES), which is located in the urban area of Guangzhou ($23^{\circ}07'N$, $113^{\circ}21'E$) (see Fig. 1). This monitoring station was a super-site SCIES monitoring station for aerosol and atmospheric haze research, representing the urban area of Guangzhou. There are no obvious industrial pollution sources around the monitoring station.

Daily 24-h PM_{10} (10:00 am to 9:30 am, local time) filter samples were collected using a sampler (BGI Incorporated,

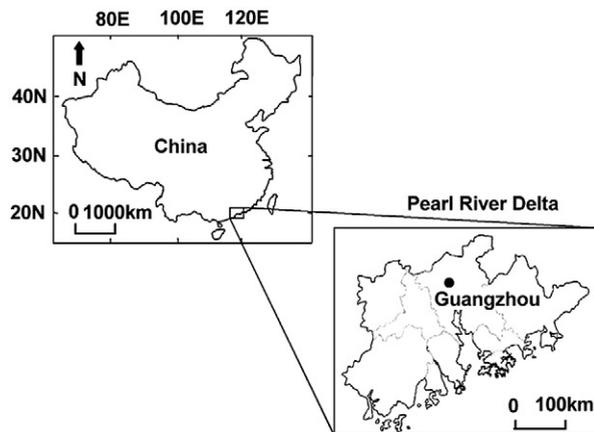


Fig. 1. Location of Guangzhou.

Waltham, MA, U.S.A.; Model PQ200) operating at a flow rate of 16.7 L min^{-1} . Samples were collected over 1-month periods in all 4 seasons: summer (July 1st to July 31st, 2009), autumn (October 1st to October 31st, 2009), winter (January 1st to January 31st, 2010) and spring (April 1st to April 30th, 2010). A total of 123 aerosol samples of PM_{10} and 16 blank samples were collected. Before sampling, the quartz filters were baked at 800°C for at least 3 h to remove adsorbed organic vapors, and then equilibrated in desiccators for 24 h before sampling. Prior to measurement, the flow rate of the PM_{10} sampler was calibrated. The collected filter samples were stored in a freezer at -18°C to prevent the volatilization of particle constituents.

Aerosol mass loadings were determined gravimetrically using a Sartorius MC5 electronic microbalance ($\pm 1 \mu\text{g}$ sensitivity, Sartorius, Göttingen, Germany). Before weighing, the filters were equilibrated for 24 h at 20 to 23°C in a chamber with a relative humidity between 35% and 45%. Each filter was weighed at least three times before and after sampling following the 24 h equilibration period. The differences among the three repeated weightings typically were less than $10 \mu\text{g}$ for blanks and $20 \mu\text{g}$ for sample filters. The mean net mass for each filter was obtained by subtracting the pre-deployment weight from the average of the post-sampling readings.

2.2. Chemical analysis

A 0.5 cm^2 punch from the filter was analyzed for eight carbon fractions following the IMPROVE_A thermal/optical reflectance (TOR) protocol on a DIR model 2001 carbon analyzer (Atmoslytic Inc., Calabasas, CA) (Cao et al., 2007; Chow et al., 2007). This produced four OC fractions (OC1, OC2, OC3 and OC4 at 140°C , 280°C , 480°C and 580°C , respectively, in a helium [He] atmosphere); OP (a pyrolyzed carbon fraction determined when transmitted laser light attained its original intensity after oxygen [O_2] was added to the analysis atmosphere); and three EC fractions (EC1, EC2 and EC3 at 580°C , 740°C and 840°C , respectively, in a 2% $\text{O}_2/98\%$ He atmosphere). IMPROVE_TOR OC is operationally defined as $\text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP}$ and EC is defined as $\text{EC1} + \text{EC2} + \text{EC3} + \text{OP}$ (Chow et al., 2007). Inter-laboratory comparisons of samples between the IMPROVE_TOR protocol and the TMO (thermal manganese dioxide oxidation) approach have shown differences of $<5\%$ for TC and $<10\%$ for OC and EC (Chow et al., 2007). Average field blanks were 1.8 and $0.1 \mu\text{g}/\text{m}^3$ for OC and EC, respectively.

One quarter of each filter sample was used to determine the water-soluble ion mass concentrations. Four anions (SO_4^{2-} , NO_3^- , Cl^- and F^-) and five cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) in aqueous extracts of the filters were determined by ion chromatography (Dionex Corp, Sunnyvale, CA, Model Dionex 600). To extract the water-soluble inorganic species from the quartz filters, each sample was put into a separate 20 mL vial containing 10 mL distilled-deionized water ($18 \text{ M}\Omega$ resistivity), and shaken first by an ultrasonic instrument for 60 min and then by mechanical shaker for 1 h for complete extraction of the ionic compounds. The extracts were stored at 4°C in a pre-cleaned tube before analysis. Cation (Na^+ , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+}) concentrations were determined with a CS12A column

(Dionex Corp, Sunnyvale, CA.) and 20 mmol L⁻¹ MSA eluent. Anions (SO₄²⁻, NO₃⁻, Cl⁻ and F⁻) were separated by an AS11-HC column (Dionex Corp, Sunnyvale, CA) and 20 mmol L⁻¹ KOH eluent. The limits of detection were less than 0.05 mg L⁻¹ for anions and cations. Standard reference materials produced by the National Research Center for Certified Reference Materials, China, were analyzed for quality assurance purposes. Blank values were subtracted from sample concentrations (Shen et al., 2008; Zhang et al., 2011).

2.3. Continuous observation of meteorological parameters and gas pollutants

Meteorological parameters, including wind direction (WD), wind speed (WS), relative humidity (RH), temperature (TEMP), solar radiation (SR) and precipitation (PR), were measured every 30 min. Wind direction and wind speed were recorded by a wind monitor (Vaisala Company, Helsinki, Finland; model QMW110A); ambient RH and temperature were measured by a RH/temperature probe (Vaisala Company, Helsinki, Finland; model QMH102); solar radiation was measured by a silicon pyranometer (Kipp & Zonen Inc., Delft, Holland; model SP Lite2) and precipitation was measured by a rain gauge (Vaisala Company, Helsinki, Finland; model RG13). All meteorological instruments were mounted 3 m above the roof of the station (53 m above the ground).

Trace gases including sulfur dioxide (SO₂), nitride oxide (NO_x) and ozone (O₃) were measured every 5 min, by a sulfur dioxide analyzer, nitride oxide analyzer, and ozone analyzer (all from Thermo Fisher Scientific Inc., Franklin, MA; Model 43i, Model 42i, Model 49i), respectively. All gas analyzers were calibrated every week.

3. Results and discussion

3.1. Meteorological conditions and mass concentration of PM₁

Meteorological conditions influenced heavily on the PM levels and chemical species formation. The seasonal distributions of meteorological factors were summarized as shown in Table 1. RH is the highest in spring, following by winter, summer, and autumn. SR and TEMP ranked as a same decreasing order of summer > autumn > spring > winter. PR is one of important ways to reducing the particles levels by wet deposition. PR followed in a decreasing order as spring > summer > winter > autumn. Wind speed, which influenced heavily on the dilution of PM, ranked in a decreasing order summer > winter > spring > autumn.

The annual average PM₁ mass concentration was 52.4 ± 27.3 μg m⁻³, ranging from 14.6 to 143.3 μg m⁻³, and therefore exceeded the U.S. National Ambient Air Quality Standards (NAAQS) for annual PM_{2.5} (15 μg m⁻³) by more than a factor of 3. Clear seasonal variations in PM₁ concentration were observed (Table 1 and Fig. 2), with seasonal averages decreasing in the order winter (63.4 μg m⁻³) > autumn (62.1 μg m⁻³) > spring (54.4 μg m⁻³) > summer (29.9 μg m⁻³). Summer PM₁ levels were the lowest of the four seasons, mainly due to high wind speeds and frequent rainfall in comparison with those in other seasons. As shown in Table 1, summer WS was much higher than in other seasons. The high wind speeds in summer favor the dilution of pollutants and thus decrease PM₁ levels. Intense solar radiation in summer helps to destroy the stable boundary layer and also favors the pollution dilution. In addition, the summer monsoon from the South China Sea introduces clean air and high precipitation. By contrast, higher PM₁ levels in spring, autumn and winter may be attributed to more mild conditions arising from the lower wind speed and weaker solar radiation. Although the greatest precipitation

Table 1

Mean mass concentrations of PM₁, its chemical constituents, gas pollutants and meteorological parameters in the four seasons.

	Annual (n = 123)	Summer (n = 31)	Autumn (n = 31)	Winter (n = 31)	Spring (n = 30)
PM ₁	52.4 ± 27.3	29.9 ± 13.3	62.1 ± 21.5	63.4 ± 30.2	54.4 ± 27.5
OC	6.8 ± 3.9	4.6 ± 1.7	7.3 ± 2.7	8.8 ± 5.7	6.5 ± 3.1
EC	5.0 ± 2.9	3.0 ± 1.3	5.5 ± 2.4	6.1 ± 3.6	5.6 ± 2.8
OC/EC	1.4 ± 0.4	1.7 ± 0.6	1.4 ± 0.3	1.5 ± 0.4	1.2 ± 0.2
Na ⁺	1.6 ± 0.6	1.8 ± 0.2	1.8 ± 0.2	1.8 ± 0.4	0.9 ± 0.7
NH ₄ ⁺	3.4 ± 2.5	1.2 ± 1.1	4.5 ± 1.7	4.1 ± 2.6	3.7 ± 3.0
K ⁺	0.5 ± 0.4	0.2 ± 0.1	0.8 ± 0.3	0.7 ± 0.4	0.4 ± 0.3
Mg ²⁺	LD	LD	LD	LD	LD
Ca ²⁺	0.3 ± 0.3	0.1 ± 0.1	0.4 ± 0.1	0.2 ± 0.2	0.3 ± 0.5
F ⁻	LD	LD	LD	LD	LD
Cl ⁻	1.2 ± 1.2	0.6 ± 0.3	0.6 ± 0.4	2.2 ± 1.7	1.4 ± 0.9
NO ₃ ⁻	4.6 ± 4.5	1.3 ± 0.7	4.0 ± 4.1	7.3 ± 4.3	5.6 ± 5.4
SO ₄ ²⁻	11.3 ± 6.5	7.6 ± 4.2	19.2 ± 5.3	10.1 ± 4.4	8.0 ± 4.0
SO ₂	50.6 ± 33.8	68.3 ± 20.0	37.8 ± 25.3	52.0 ± 45.9	44.1 ± 31.4
NO	52.0 ± 49.1	26.0 ± 15.9	28.1 ± 22.1	90.9 ± 66.0	63.5 ± 42.0
NO ₂	69.6 ± 31.2	45.1 ± 14.4	111.1 ± 49.5	79.0 ± 34.4	71.3 ± 28.6
O ₃	29.4 ± 28.4	11.9 ± 11.5	68.3 ± 22.8	18.4 ± 8.7	18.6 ± 21.4
WS	0.9 ± 0.8	1.8 ± 0.7	0.3 ± 0.3	0.9 ± 0.5	0.6 ± 0.6
Temp	23.2 ± 6.4	29.9 ± 1.6	27.1 ± 1.3	15.2 ± 4.0	20.5 ± 3.3
RH	67 ± 15	68 ± 8	50 ± 12	71 ± 14	72 ± 11
SR	138 ± 79	215 ± 62	177 ± 45	77 ± 44	79 ± 52
PR	319.8	68.0	21.0	50.6	180.2

LD: low detection.

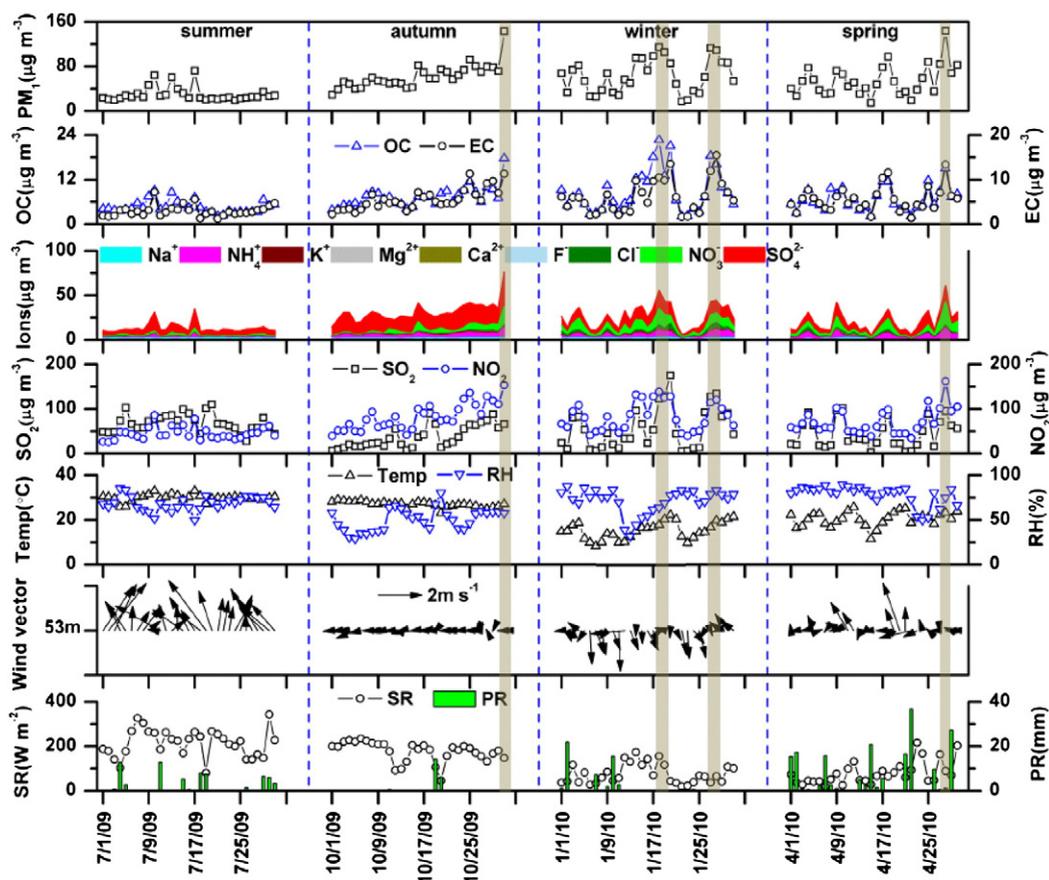


Fig. 2. Temporal variations of PM_{10} mass concentrations, its chemical species, gas pollutants and selected meteorological parameters in four seasons (2009–2010).

occurred during spring, the unfavorable meteorological conditions mentioned above lead to the high PM_{10} levels.

During the whole sampling period, four pollution events were found (Fig. 2). In this study, pollution events were defined as periods when daily PM_{10} concentrations exceeded the annual mean concentration plus two standard deviations; here, this threshold was $107 \mu\text{g m}^{-3}$. The first pollution event occurred on Oct 31, 2009, with PM_{10} concentrations of $142.7 \mu\text{g m}^{-3}$. This high PM_{10} concentration was mainly due to continuous calm weather, despite sunny conditions, leading to a gradual accumulation of PM. The second and third pollution events both occurred in winter (Jan 18 2010, and Jan 27–Feb 8 2010, with respective mean PM_{10} values of $114.8 \mu\text{g m}^{-3}$ and $111.3 \mu\text{g m}^{-3}$). The fourth pollution event, on April 28 2010, had a mean PM_{10} level of $143.3 \mu\text{g m}^{-3}$. Each of these high PM_{10} episodes was associated with a continuously low atmospheric boundary layer during overcast weather (weak solar radiation, as shown in Fig. 2).

From a wider perspective, the PM_{10} concentration measured in this study can be compared with the loadings studied in other mega cities. As shown in Table 2, the average PM_{10} concentration was lower than that in Xi'an (Shen et al., 2010), close to that in Kaohsiung (Lin and Lee, 2004), but higher than in Milan (Vecchi et al., 2004). Although the PM_{10} concentration in Guangzhou was not at very serious levels when compared with other cities, some actions should be

undertaken to lower down the PM_{10} levels, owing to the adverse health effects of PM_{10} .

3.2. Chemical composition of PM_{10}

3.2.1. Carbonaceous species

The annual mean concentrations of OC and EC in PM_{10} were $6.2 \pm 3.5 \mu\text{g m}^{-3}$ and $5.0 \pm 2.9 \mu\text{g m}^{-3}$, respectively (Table 1). Total Carbon (TC), calculated as the sum of OC and EC concentrations, accounted for $23.0 \pm 4.4\%$ of PM_{10} by mass. The seasonal variations of OC concentrations decreased in the order winter ($8.8 \pm 5.7 \mu\text{g m}^{-3}$) > autumn ($7.3 \pm 2.7 \mu\text{g m}^{-3}$) > spring ($6.5 \pm 3.1 \mu\text{g m}^{-3}$) > summer

Table 2

Levels of PM_{10} in the urban areas of mega cities ($\mu\text{g m}^{-3}$).

Locations	Period	Spring	Summer	Autumn	Winter	References
Guangzhou (PM_{10})	2009–2010	54.4	29.9	62.1	63.4	This study
Xi'an (PM_{10})	2007–2008	139.2	72.5	120.8	178.2	Shen et al. (2010)
Kaohsiung (PM_{10})	2000–2001	–	24.5	52.2	67.1	Lin and Lee (2004)
Milan (PM_{10})	2002	–	16.4	–	41.0	Vecchi et al. (2004)

($4.6 \pm 1.7 \mu\text{g m}^{-3}$), therefore following a similar pattern to the mass of PM_{10} . However, the seasonal pattern of EC showed some differences when compared with OC and PM_{10} . The highest and lowest EC concentrations were in winter and summer, and the spring EC concentration was slightly (although insignificantly) higher than that in autumn. The difference in seasonal pattern between OC and EC may imply changes in the strengths of their sources during the four seasons.

In a previous study of PM_{10} , OC concentrations at an urban site in Xi'an were respectively $18.2 \mu\text{g m}^{-3}$, $9.6 \mu\text{g m}^{-3}$, $23.2 \mu\text{g m}^{-3}$ and $33.3 \mu\text{g m}^{-3}$ from spring through to winter (Shen et al., 2010). A similar seasonal pattern in OC concentration was observed in Xi'an and Guangzhou. However, the OC concentrations in Xi'an were remarkably higher than those in Guangzhou. The seasonal concentrations of EC in Xi'an were slightly higher than those in Guangzhou, except in summer; however, these differences in EC concentrations were insignificant when compared with the contrast in OC concentration.

The sources of carbonaceous aerosols can be qualitatively evaluated by studying the relationship between OC and EC concentrations (Turpin and Huntzicker, 1995; Cao et al., 2007; Zhang et al., 2007). A high correlation coefficient ($R = 0.89$, $p < 0.001$) was found between OC and EC for the full set of PM_{10} samples, indicating that the OC and EC in PM_{10} were mainly derived from the same sources. However, when seasonally stratifying the dataset (Fig. 3), the results showed some distinct differences: the strongest correlations between OC and EC were found in spring ($R = 0.96$, $p < 0.001$), followed by winter ($R = 0.89$, $p < 0.001$), autumn ($R = 0.84$, $p < 0.001$) and summer ($R = 0.70$, $p < 0.001$). These results demonstrate that the sources and chemistry controlling OC and EC loadings were varied and complex in autumn and especially so in summer. The strong solar radiation and high temperature in summer can favor photochemical reactions that produce secondary organic carbon (SOC) (Cao et al., 2004, 2007), and should therefore be considered when estimated SOC levels during the four seasons.

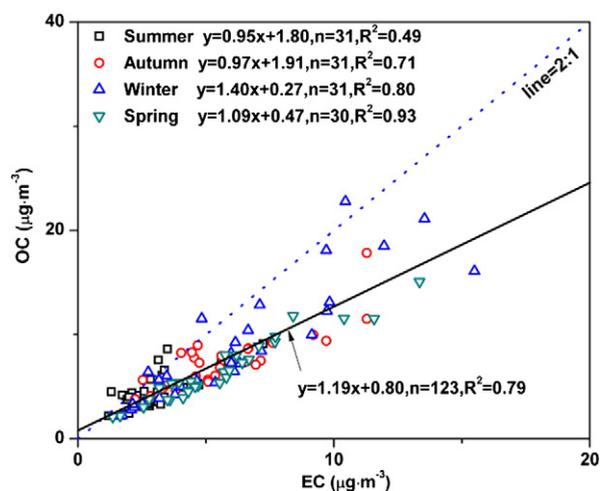


Fig. 3. Correlations between organic carbon (OC) and elemental carbon (EC) in the four seasons.

OC/EC ratios provide a valuable tool to indicate the sources and formation processes of carbonaceous particles (Cao et al., 2003). The overall annual average OC/EC ratio was 1.4, with a range from 1.0 to 3.5. Seasonal OC/EC ratios decreased in the following order: summer (1.7) > winter (1.5) > autumn (1.4) > spring (1.2). The seasonal average OC/EC ratios were much lower than those observed at Xi'an, which showed the highest OC/EC ratio in winter (5.6) and lowest in spring (3.2) (Shen et al., 2010). Differences in the OC/EC ratios between Guangzhou and Xi'an imply that PM_{10} from Guangzhou is either relatively more abundant in EC or depleted in OC, highlighting variations in the sources of carbonaceous aerosol and PM_{10} mass.

Watson et al. (2001) found that the OC/EC ratios for coal combustion, vehicle emission and biomass burning were 2.7, 1.1 and 9.0, respectively. Considering the characteristics of these emissions profiles and as Guangzhou is located in the most highly developed regions of Pearl River Delta Region in China, the relatively lower OC/EC ratios indicated that vehicle emissions play an important role in the origin of carbonaceous aerosol. In addition, coal combustion from power plants located around the PRD is likely to be another important emission source of carbonaceous aerosol. Meanwhile, the role of biomass burning should be negligible. The lower OC/EC ratios also implied that SOC is a less important constituent of PM_{10} OC in Guangzhou than in Xi'an. In contrast, Xi'an is located in a developing region of Northwest China where coal combustion and biomass burning led to high OC/EC ratio (Shen et al., 2010).

3.2.2. Ionic species in PM_{10}

The annual average value of total water-soluble ionic species was $22.8 \pm 12.7 \mu\text{g m}^{-3}$, accounting for $43.2 \pm 7.7\%$ of PM_{10} mass and indicating that ionic species contributed the major fraction of PM_{10} mass in Guangzhou. Seasonal variations of total water-soluble ion loadings were observed, and loadings decreased in the order autumn ($31.4 \pm 10.8 \mu\text{g m}^{-3}$) > winter ($26.4 \pm 12.8 \mu\text{g m}^{-3}$) > spring ($20.3 \pm 12.2 \mu\text{g m}^{-3}$) > summer ($12.9 \pm 5.9 \mu\text{g m}^{-3}$). The annual and seasonal mean concentrations of the four anions followed the same sequence of SO_4^{2-} > NO_3^- > Cl^- > F^- , while the five cations ranked in the order NH_4^+ > Na^+ > K^+ > Ca^{2+} > Mg^{2+} . Clearly, sulfate, nitrate and ammonium dominated the water-soluble inorganic species, accounting for $82.1 \pm 7.6\%$ of the total ions concentration.

Anion and cation concentrations showed very different seasonal patterns. SO_4^{2-} , NH_4^+ and K^+ exhibited the same seasonal pattern, decreasing in the order autumn > winter > spring > summer, while Cl^- and NO_3^- followed the order winter > spring > autumn > summer. SO_4^{2-} , NO_3^- and NH_4^+ were formed from the gas-particle conversion process, as reported in many studies. High temperatures in autumn favored the conversion of SO_2 to SO_4^{2-} . Lowest SO_4^{2-} in summer was mainly because of dilutions of clean summer monsoon and abundance of precipitation. In addition, strong atmospheric oxidation (O_3 level as a surrogate) in autumn than in summer is another important reason for seasonal SO_4^{2-} formation. NH_4^+ and K^+ were enriched in autumn, mainly due to biomass burning in the harvest season (Hays et al., 2005). The high nitrate in winter may be due to lower temperatures, which would favor the conversion of gaseous nitric acid to aerosol particles (Russell et al., 1983). A

previous study also showed that there is a positive correlation between RH and nitrogen oxidation ratio (Shen et al., 2008), and we note in this context that we observed high RH in winter. High RH was also observed in spring, but has relative low nitrate level in contrast with winter, this is mainly because: 1) the precursor's levels for nitrate, NO plus NO₂, were the highest in winter than in spring; 2) higher precipitations in spring than in autumn can also explain the seasonal nitrate levels difference; and 3) the wind speed in winter was a little higher than spring, so one can expect that the regional transport contribution to high nitrate in winter. Na⁺ concentrations were highest in summer, followed by autumn and winter, and lowest in spring. Compared with Na⁺ and Cl⁻ concentrations were lower in autumn and summer than those in winter and spring, which suggested chlorine loss occurred during the sunny summer and autumn months. Ca²⁺ concentrations were much lower than those of other ions except F⁻ and Mg²⁺. In general, Ca²⁺ was derived from road traffic and construction activities in the urban area (Shen et al., 2008). Ca²⁺ ranked in the order autumn>spring>winter>summer, but no evident difference was found between the four seasons.

Ion balance calculations are commonly used to evaluate the acid–base balance of aerosol particles. To calculate the cation/anion balance of PM₁, we converted the ion mass concentrations into microequivalents. The cation and anion microequivalents were calculated as follows:

$$C(\text{cation microequivalents m}^{-3}) = \text{Na}^+/23 + \text{NH}_4^+/18 + \text{K}^+/39 + \text{Mg}^{2+}/12 + \text{Ca}^{2+}/20 \quad (1)$$

$$A(\text{anion microequivalents m}^{-3}) = \text{F}^-/19 + \text{Cl}^-/35.5 + \text{NO}_3^-/62 + \text{SO}_4^{2-}/48. \quad (2)$$

Strong correlations between anion and cation equivalents were observed (Fig. 4), which indicated that the nine ionic species were the major ions in PM₁. Most samples were positioned above a 1:1 anion:cation (A:C) line, implying that PM₁ in Guangzhou was acidic. Ion balance calculations stratified by season showed summer and autumn samples

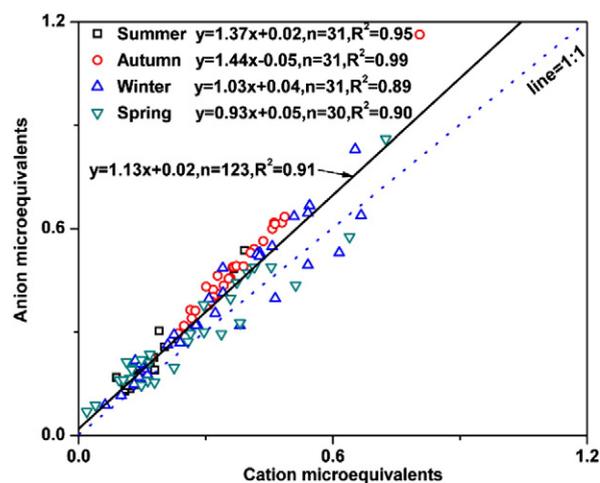


Fig. 4. Total anions versus total cations.

plotted farther above the A:C unity line, indicating that they were more acidic. In contrast, the spring and winter samples were more scattered than those in summer and autumn. The slopes of the regression equations showed that winter samples were weakly acid, while spring samples were alkaline. In general, the seasonal trends of anion/cation ratios suggest that PM₁ particle acidity was mainly due to SO₄²⁻, NO₃⁻ and Cl⁻, whereas NH₄⁺, Na⁺ and K⁺ tended to buffer the acidity.

SO₄²⁻ and NO₃⁻ are formed mainly via the conversion of gaseous precursors, and therefore they are considered as secondary species. To evaluate the transformation efficiency of trace gases (SO₂ and NO₂ to SO₄²⁻ and NO₃⁻), the sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were defined as follows (Wang et al., 2005):

$$\text{SOR} = n - \text{SO}_4^{2-} / (n - \text{SO}_4^{2-} + n - \text{SO}_2) \quad (3)$$

$$\text{NOR} = n - \text{NO}_3^- / (n - \text{NO}_3^- + n - \text{NO}_2) \quad (4)$$

where n denotes the molar quantity of the chemical species.

Higher SOR and NOR values indicate increased formation of secondary aerosols in the atmosphere. Ohta and Okita (1990) suggested that SO₂ oxidation occurs in the atmosphere, as SOR was greater than 0.10. In this study, the average values of SOR were 0.14, 0.07, 0.31 and 0.16 from spring to winter, respectively. The corresponding values for NOR were 0.05, 0.02, 0.03 and 0.06, respectively. The SOR of PM₁ samples was higher than 0.10 in autumn, winter and spring, but lower than 0.10 in summer, indicating that secondary formation of SO₄²⁻ from SO₂ was strong in autumn, winter and spring, but limited in summer. Seasonal variations in NOR were different from those of SOR, suggesting a different formation process. NOR values were higher in winter and spring than in summer and autumn.

Normally, the heterogeneous formation of nitrate and sulfate on pre-existing particles is much more efficient than homogeneous formation in the atmosphere, and the heterogeneous conversion efficiency is influenced heavily by the ambient meteorological factors (Seinfeld, 1986; Li-Jones and Prospero, 1998). To determine the factors affecting the formation of secondary species (SO₄²⁻ and NO₃⁻), the seasonal variations of SOR, NOR, Temp, RH and O₃ were considered (Fig. 5).

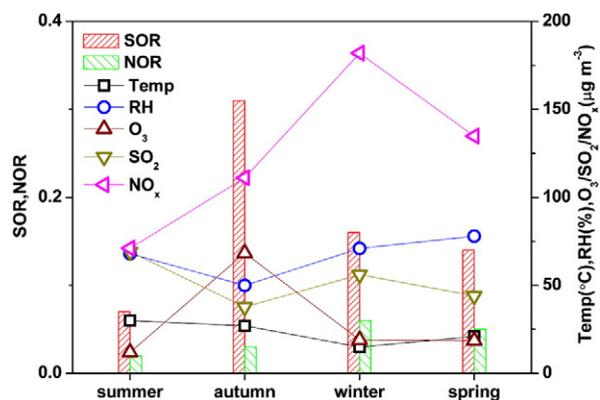


Fig. 5. Seasonal variations of SOR, NOR, Temp, RH, O₃, SO₂ and NO_x.

SOR decreased in the order autumn (0.31) > winter (0.16) > spring (0.14) > summer (0.07), while NOR decreased in the order winter (0.06) > spring (0.05) > autumn (0.03) > summer (0.02). The similar patterns of SOR and O₃ suggested atmospheric oxidation influenced heavily on SOR. Shen et al. (2008) reported that SOR is positively correlated with temperature. Earlier studies suggested that solar radiation is one of several important factors influencing O₃ production (Thompson et al., 2001; Wang et al., 2012). Although solar radiation in summer is higher than in autumn, SOR and O₃ in autumn were higher than in summer. This is mainly because precipitation in summer is much higher than in autumn. The seasonal values of NOR were lower than the corresponding SOR values. NOR showed an opposite pattern to that of temperature, which is mainly because of the increased evaporation of NO₃⁻ at higher temperature (Hu et al., 2008). The seasonal variations of NOR and RH were similar, consistent with a previous study which found that a high RH is favorable in producing NO₃⁻ (Shen et al., 2008). As we mentioned above, the highest precursor levels (NO plus NO₂) and possible transportation also contributed to highest NOR in winter, even the RH in spring is a little higher than winter. It was also noticed that the spring precipitation was three times in comparison with winter (as shown in Table 1), and this should be another reason for low nitrate in spring.

3.2.3. 3 Reconstruction of PM₁ mass concentration

In general, dry PM_{2.5} mass concentration can be reconstructed by the IMPROVE equation (Hand and Malm, 2006), and we attempt to do so here. Organic matter (OM), EC and water-soluble ions are the major constituents in PM₁. The elemental composition of PM₁ was not determined in this study, therefore, the unidentified fractions in PM₁ recorded as “remainders” refer to chemical components that were not analyzed, including water content, soil dust, insoluble elements, and others. The concentration of OM was calculated by multiplying OC by 1.6 (Cao et al., 2007).

PM₁ concentrations reconstructed with the IMPROVE equations are presented in Fig. 6. The Pearson correlation

coefficient between measured and reconstructed PM_{2.5} mass concentration was 0.96 (n = 123, p < 0.001), which indicated that the dominant species in the IMPROVE equation can closely represent the measured PM₁, although the slope was 1.28. The reconstructed mass accounted for 72.7 ± 9.4% of the measured PM₁ mass in the urban area of Guangzhou. On average, (NH₄)₂SO₄, NH₄NO₃, OM, and EC accounted for (30.7 ± 11.4) %, (9.7 ± 5.2) %, (22.6 ± 5.0) % and (9.7 ± 2.3) % of PM₁ mass, respectively. The dominant components were (NH₄)₂SO₄ and OM in summer and autumn. The proportion of NH₄NO₃ increased in winter and spring, perhaps due to its greater stability at lower temperatures.

3.3. Source apportionments of PM₁

Positive matrix factorization (PMF) was developed by Paatero and Tapper (1994) and Paatero (2004), and has been widely used as a method to identify and evaluate the origins of PM_{2.5} and PM₁ (Song et al., 2006; Hwang and Hopke, 2007; Lestari and Mauliadi, 2009; Shen et al., 2010). PMF was recommended by the United States Environmental Protection Agency when identifying PM sources. Here, PMF1.1 was used to apportion the sources of detected components in PM₁. In this study, the values below the detection limit were substituted by the half value of the detection limit, and missing values were substituted by the geometric average of relevant chemical species (Lee et al., 2002). Five factors were identified by the PMF model in this study (Fig. 7). Each source and its relative contributions are discussed below.

The first factor comprised Ca²⁺, Mg²⁺, Na⁺, Cl⁻ and SO₄²⁻, which are significant crustal markers. The second factor, enriched with four OC fractions, EC1, Cl⁻, and NO₃⁻ represents exhaust from gasoline-powered engines and sea spray (Watson et al., 1994; Cao et al., 2005). The third factor was loaded with three EC fractions, such as EC2 and EC3, representing the emissions from diesel exhausts and (Watson et al., 1994; Cao et al., 2005). The fourth factor, characterized by OC1-4, EC1, SO₄²⁻, NO₃⁻, and NH₄⁺, was consistent with coal combustion emissions (Watson et al.,

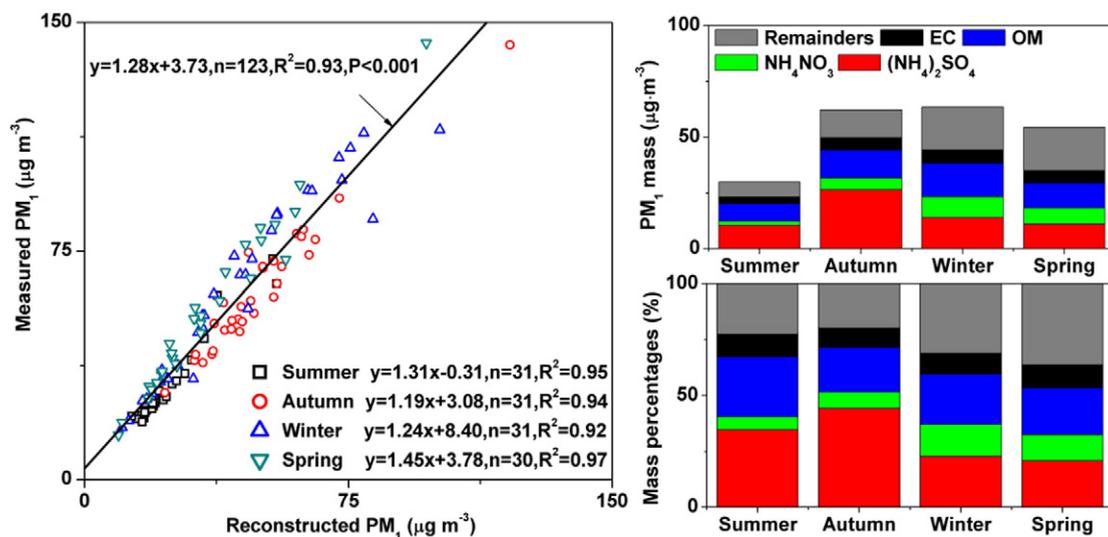


Fig. 6. Measured versus reconstructed PM₁ mass during the four seasons (2009–2010).

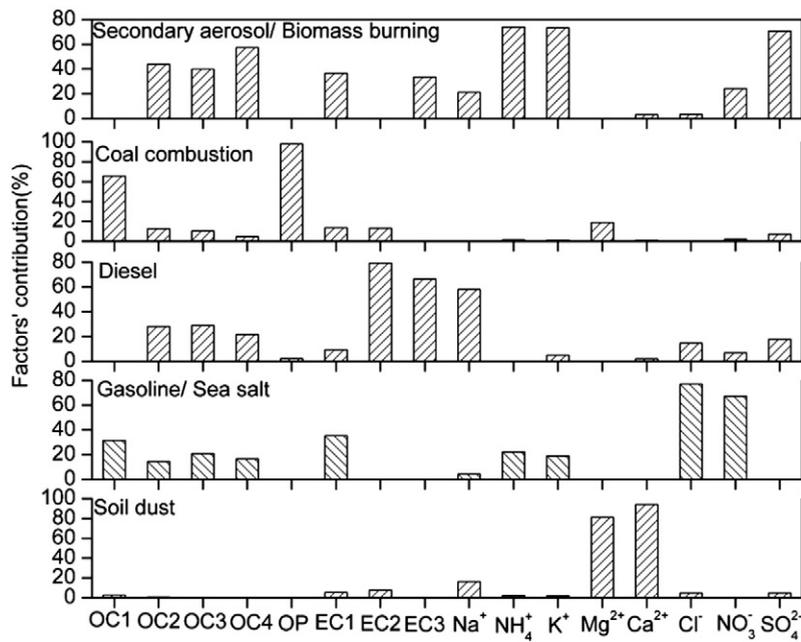


Fig. 7. The source profiles for PM₁ in Guangzhou.

1994; Hwang et al., 2003; Cao et al., 2005). Secondary aerosol and biomass burning was considered as the fifth factor, which was characterized by SO₄²⁻, NH₄⁺, NO₃⁻, K⁺, OC and EC (Song et al., 2001; Shen et al., 2010). A previous study has also demonstrated that biomass burning activities have been conducted in rural areas around Guangzhou (Zhang et al., 2010).

The contributions of the five factors to detected PM₁ mass are plotted in Fig. 8. Secondary aerosol and biomass burning contributed significantly to the detected PM₁ mass (49.4%), followed by gasoline emissions and sea salt (21.0%), diesel (16.5%), and coal combustion (8.7%). To understand the contributions of local/regional emission sources in more detail it will be necessary to measure more chemical species, such as the major/sub-major elements and organic components, in the near future.

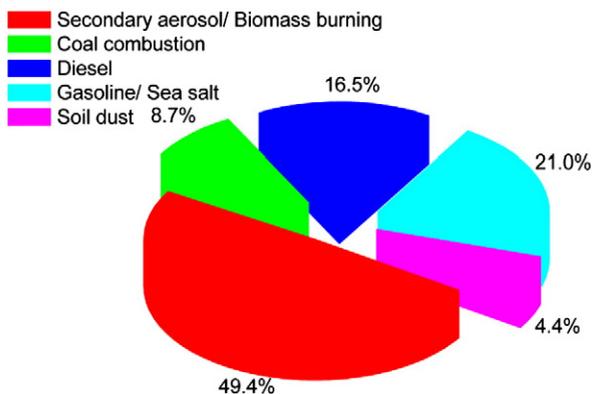


Fig. 8. The contributions of major PM₁ sources.

4. Conclusions

The PM₁ mass concentration ranged from 14.6 to 143.3 μg m⁻³, with an annual arithmetic mean value of 52.4 ± 27.3 μg m⁻³. Seasonally averaged mass loadings decreased in the order winter > autumn > spring > summer. Solar radiation, wind speed and precipitation strongly influenced PM₁ mass concentration. The average PM₁ concentration in Guangzhou was lower than in Xi'an in every season, and close to levels in Kaohsiung but higher than in Milan.

Seasonally averaged OC values decreased in the following order: winter > autumn > spring > summer, while PM₁ EC levels followed a different order: winter > spring > autumn > summer, revealing that the sources of these constituents were different to some extent. The annual average OC/EC ratio was 1.4, ranging from 1.0 to 3.5, and seasonal averages decreased in the following order: summer (1.7) > winter (1.5) > autumn (1.4) > spring (1.2). Considering the characteristics of vehicle emissions, the low OC/EC ratios indicated that vehicle emissions play an important role in carbonaceous aerosol origins in Guangzhou.

The annual average concentration of water-soluble ionic species was 22.8 ± 12.7 μg m⁻³, which accounted for (43.2 ± 7.7) % of PM₁ mass. Sulfate, nitrate and ammonium were the dominant water-soluble species. The ion balance highlighted that most PM₁ samples were acidic, especially in summer and autumn, owing to the higher SO₄²⁻ concentrations. Solar radiation heavily influenced SOR, while NOR was positively correlated with RH.

PM₁ mass concentrations were reconstructed using the IMPROVE equations. (NH₄)₂SO₄, NH₄NO₃, OM and EC accounted for (30.7 ± 11.4) %, (9.7 ± 5.2) %, (22.6 ± 5.0) % and (9.7 ± 2.3) % of PM₁ mass, respectively.

Source apportionment by PMF yielded five factors, indicating that secondary aerosol and biomass burning,

gasoline emissions and sea salt, diesel emissions, and coal combustion were the most dominant contributors to PM₁. As a result, pollution control methods, such as reducing motor vehicle emissions, may be an effective means of alleviating the PM₁ levels in Guangzhou.

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