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Source apportionment and secondary organic aerosol estimation of $PM_{2.5}$ in an urban atmosphere in China

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$PM_{2.5}$ is the key pollutant in atmospheric pollution in China. With new national air quality standards taking effect, $PM_{2.5}$ has become a major issue for future pollution control. To effectively prevent and control $PM_{2.5}$, its emission sources must be precisely and thoroughly understood. However, there are few publications reporting comprehensive and systematic results of $PM_{2.5}$ source apportionment in the country. Based on $PM_{2.5}$ sampling during 2009 in Shenzhen and follow-up investigation, positive matrix factorization (PMF) analysis has been carried out to understand the major sources and their temporal and spatial variations. The results show that in urban Shenzhen (University Town site), annual mean $PM_{2.5}$ concentration was 42.2 μg m^{-3}, with secondary sulfate, vehicular emission, biomass burning and secondary nitrate as major sources; these contributed 30.0%, 26.9%, 9.8% and 9.3% to total $PM_{2.5}$, respectively. Other sources included high chloride, heavy oil combustion, sea salt, dust and the metallurgical industry, with contributions between 2%–4%. Spatiotemporal variations of various sources show that vehicular emission was mainly a local source, whereas secondary sulfate and biomass burning were mostly regional. Secondary nitrate had both local and regional sources. Identification of secondary organic aerosol (SOA) has always been difficult in aerosol source apportionment. In this study, the PMF model and organic carbon/elemental carbon (OC/EC) ratio method were combined to estimate SOA in $PM_{2.5}$. The results show that in urban Shenzhen, annual SOA mass concentration was 7.5 μg m^{-3}, accounting for 57% of total organic matter, with precursors emitted from vehicles as the major source. This work can serve as a case study for further in-depth research on $PM_{2.5}$ pollution and source apportionment in China.

$PM_{2.5}$, source apportionment, secondary organic aerosol (SOA)

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As one of the major atmospheric pollutants, $PM_{2.5}$ has complex chemical compositions, relatively small sizes, and a long lifetime in the air. It can strongly contribute to visibility deterioration, cloud formation processes and climate change (Tang et al., 2006). Since it contains deleterious compositions such as acidic substances, polycyclic aromatic hydrocarbon (PAH), heavy metals and others, $PM_{2.5}$ has clear epidemiologic evidence to be harmful to human health, particularly to the respiratory system (Pope et al., 2006; Franklin et al., 2008; Huang et al., 2012). The complex sources of $PM_{2.5}$ can be divided into two classes: One is direct emission from sources, or primary sources; the other is via atmospheric chemical transformations that oxidize gas phase precursors to form new particles, such as sulfate, nitrate and organic matter, which represent secondary sources.

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Prior research results show that China is currently suffering very severe $PM_{2.5}$ pollution, with some cities having a $PM_{2.5}$ mass concentration more than 100 μg m^{-3}. Thus, $PM_{2.5}$ is a major atmospheric pollutant in the country (Yang et al., 2011). High $PM_{2.5}$ concentration is the main reason for haze events in the Pearl River Delta (PRD), Yangtze River Delta and Beijing-Tianjin-Hebei regions, which have seriously hindered urban and regional sustainable development, greatly influenced social economic development, and reduced public satisfaction with air quality. China promulgated new national air quality standards in March 2012, in which $PM_{2.5}$ has been added as a routine monitoring index, making it a key issue for pollution control and future research in the country. $PM_{2.5}$ pollution control is not only a practical demand for human health protection, air quality improvement and dealing with climate change, but also a strategic requirement necessary to achieve nationwide sustainable development.

A premise for effective control of $PM_{2.5}$ pollution is to meticulously study and accurately understand its sources. Different locations and times have variable causes of $PM_{2.5}$ pollution, which are closely related to local emission characteristics and meteorological conditions and are variable spatially and temporally. Source apportionment of $PM_{2.5}$ has commonly been based on analysis of its detailed chemical composition, using source-related information indicated by different chemical compositions to split the contributions from different sources. This must be accomplished by mathematical models, such as positive matrix factorization (PMF) and chemical mass balance (CMB) (Tang et al., 2006). Although many publications in China have focused on $PM_{2.5}$ chemical compositions (Yang et al., 2011), its source apportionment based on long-term and systematic observation in the country have rarely been reported in domestic or international publications. Based on $PM_{2.5}$ samples collected over 1 year in Shenzhen and complete analysis of their chemical compositions, we use the PMF model to identify major $PM_{2.5}$ sources and further explain their spatiotemporal variations. Secondary organic aerosol (SOA) content is also estimated effectively, using the source apportionment results. This study may serve as a method and case reference for further in-depth research on $PM_{2.5}$ source apportionment in China.

1 Instruments and methods

1.1 $PM_{2.5}$ sampling and analysis

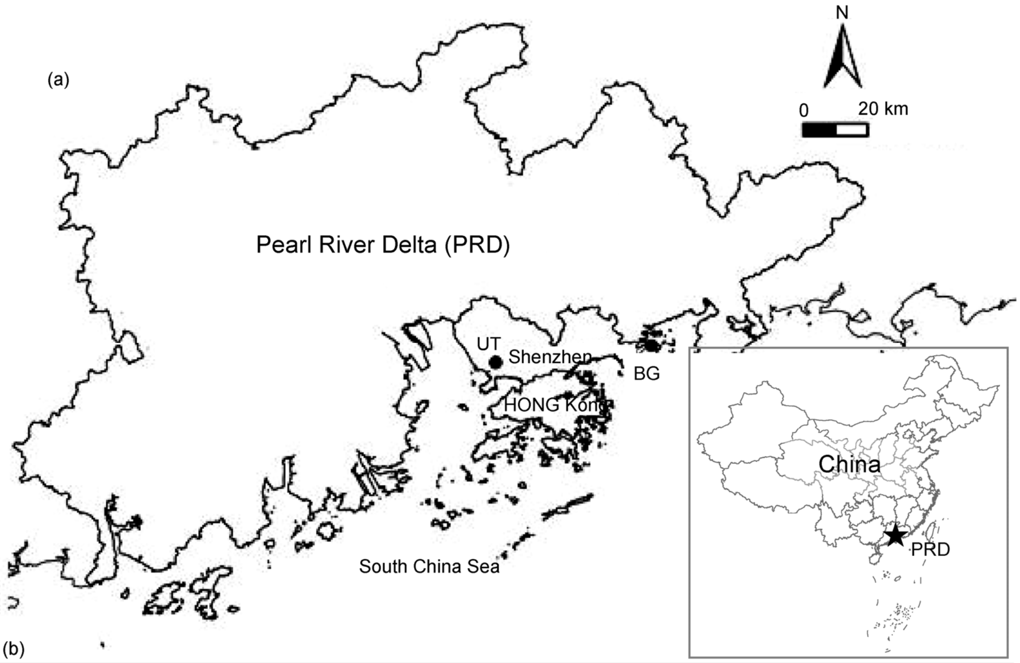
We conducted systematic sampling and analysis of $PM_{2.5}$ in Shenzhen. This city is in the PRD region of the southern China coastal area. Daya and Dapeng bays are to the east, the Pearl River estuary and Lingding Ocean are to the west, Hong Kong is to the south, and Dongguan and Huizhou are to the north. It has a subtropical marine monsoon climate, with annual mean temperature 22.4°C. The urban area is in a narrow band from east to west, and is one of the most developed cities in China. However, the city's rapid economic development has brought a sharp increase in population and energy consumption. As a result, air quality is impacted; among the most obvious phenomena are frequent haze events. According to observed data from the Shenzhen Meteorological Bureau, annual haze days in the city have remained above 100 since the 21st century. We chose a $PM_{2.5}$ sampling site on the campus of Peking University Shenzhen Graduate School (University Town site, UT), in the western part of urban Shenzhen. There were no obvious local emission sources nearby, making it a site representative of the urban environment (Figure 1(a)). A $PM_{2.5}$ sampler (Thermo 2300 4-channel sampler, Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA) was deployed atop a four-story university building. Two channels of this sampler (using 47 mm Teflon and quartz filters, respectively) were used for sampling, each with a flow rate of 16.7 L min^{-1}. Sampling was carried out intermittently over 24 h throughout 2009, with sampling dates shown on Figure 1b. Intensive observation was conducted during a typical pollution period (October 27–December 2 in autumn), with an adjusted daily sampling frequency and a regional background site added in the coastal village of Baguang (BG site) in east Shenzhen for simultaneous $PM_{2.5}$ sampling. Sampling at BG was via the same method as at UT (on some dates, BG had a sampling period of 12 h). A total of 165 sets of valid samples were collected at UT during all of 2009, and 54 sets at BG during the intensive observation period.

Teflon filters were weighed in a super clean laboratory (with temperature 21±1°C, and relative humidity RH of 40%±5%) before and after sampling, results of which were used to calculate the $PM_{2.5}$ daily average mass concentration. Teflon filter samples were then analyzed using an ICP-MS (7500c; Agilent Technologies, Santa Clara, California, USA) for 15 metallic elements. One part of each quartz filter sample (1.45 cm × 1 cm) was analyzed for organic carbon (OC) and elemental carbon (EC), using an OC/EC analyzer (Desert Research Institute, Reno, Nevada, USA) and IMPROVE heating protocol (Chow et al., 2001). Organic carbon mass was multiplied by an empirical factor 1.6 to convert to organic matter (OM) mass (He et al., 2011). The remaining part of each quartz filter was used for de-ionized water extraction in an ultrasonic bath, and then the extracted liquid was filtered and analyzed by ion-chromatograph (Dionex DX 500, Thermo Fisher Scientific Inc.) for anions and cations. Details of each analysis technique are found in our previous publication (He et al., 2008).

1.2 Source apportionment using PMF model

Based on $PM_{2.5}$ chemical composition in the Shenzhen atmosphere, the PMF receptor model was used to identify major $PM_{2.5}$ sources. A commonly used model in aerosol source apportionment, PMF requires no source profile,

(a)



(b)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Jan.					*						*						*						*						*		
Feb.				*						*						*						*						*	/	/	/
Mar.						*						*						*						*				*		*	
Apr.	*		*		*		*		*				*				*		*		*		*		*		*		*		/
May	*		*		*		*		*		*		*		*		*		*		*		*		*		*		*		*
June		*		*		*		*				*		*		*		*				*		*		*		*		*	/
July		*		*		*				*		*		*		*		*		*				*		*		*		*	
Aug.	*		*		*		*		*		*		*		*		*		*		*		*		*		*		*		*
Sep.		*		*		*		*		*		*		*		*		*		*		*		*		*		*		*	/
Oct.		*		*		*		*		*		*		*		*		*		*		*		*		*	*#	*#	*#	*#	*#
Nov.	*#	*#	*#	*##	*##	*##	*##	*##	*##	*#	*##	*#	*#	*#	*#	*#	*##	*##	*##	*#	*#	*##	*##	*#	*##	*##	*##	*##	*##	*##	/
Dec.	*#	*#	*				*		*		*		*		*		*		*		*				*		*		*	*	

Figure 1 Sampling sites and date distribution for Shenzhen $PM_{2.5}$ sampling. UT: University Town urban site; BG: Baguang regional site; *: UT sampling date; #: BG sampling date; ##: twice per day at BG, each lasting 12 h.

source inventory or photochemical reaction mechanisms. The model begins with inner connections within the observed dataset itself and then identifies major contributing factors according to their contribution magnitudes and the actual local situation. The source type each factor represents is determined by analyzing characteristic values of its various components. PMF was developed by Paatero at the University of Helsinki in Finland during the mid 1990s. Its basic principle (Paatero et al., 1994) follows below. In the model, observed data are represented by a bilinear unmixing model:

$$X_{ij} = g_{ip}f_{pj} + e_{ij},$$

where X_{ij} represents measured data for species j in sample i. The model uses a least-squares algorithm for data fitting, thereby calculating P values corresponding to fixed source profiles (f_j) and their contribution ratio variation over an observation period (g_i, time series). Residuals for each data point not fit by the model are e_{ij}, and the sum of squares of the ratios of the fitted residuals to estimated error of each data point is called Q. Therefore, the fitting process is for minimizing the Q value. We used the U.S. Environmental Protection Agency (EPA) PMF 3.0 software to do the simulation, using concentrations of NH_4^+, Cl^-, NO_3^-, SO_4^{2-}, OM, EC, Na, Mg, Al, K, Ca, V, Fe, Zn and Pb species in the 215 total samples from sites UT and BG. Other metallic elements were excluded from the model because of their very low concentrations and obscure indicative character. Analyzed deviations of the components were controlled within 10%, so model-input data of their uncertainties were all set to 10%. In the PMF analysis, two to twelve factors were analyzed. Results show that when the simulation output is nine factors, characteristic values and source profiles of each factor have a clear indicative character, completeness and independence (Figure 2). Characteristics of each factor are discussed in detail in Section 2.2.

2 Results and discussion

2.1 $PM_{2.5}$ chemical composition and spatiotemporal variation

The Shenzhen observation during 2009 shows that daily mass concentrations of $PM_{2.5}$ were 8.5–132 μg m^{-3}, with an annual average of 42.2 μg m^{-3} (annual averages were calculated from monthly ones). The annual average chemical composition of $PM_{2.5}$ at site UT is shown in Figure 3(a). OM is the dominant species, constituting 31.6% of total $PM_{2.5}$, indicating that organic pollution is significant in the city. SO_4^{2-}, EC, NH_4^+, NO_3^- and Cl^- are other major components, representing 27.8%, 11.1%, 8.3%, 6.3% and 1.0% of total $PM_{2.5}$, respectively. Fifteen significant metallic elements were detected using ICP-MS, accounting for 5.7% of the total, among which K and Na had the most prominent contributions. The deviation between weighed mass and mass summed from all measured $PM_{2.5}$components is 8.2%, including contributions from undetermined mineral components such as SiO_2 and measurement errors from analysis methods. Compared with long-term systematic previously reported analyses of $PM_{2.5}$ in other Chinese mega cities (Table 1), the annual average $PM_{2.5}$ concentration in Shenzhen was significantly lower than that in Beijing, Shanghai and Guangzhou. This suggests that Shenzhen has relatively low pollution emissions and favorable diffusion conditions because of its coastal location. However, the Shenzhen observation is the most current, and effects of local government pollution reduction measures have gradually emerged. The concentration of EC in Shenzhen is not the lowest, and is related to the preponderance of heavy-duty diesel trucks associated with its role as a port city.

Figure 3(b) gives monthly average concentrations of chemical composition in 2009 at site UT. $PM_{2.5}$ pollution levels have obvious seasonal variation, lower in spring and summer, higher in autumn and winter. The lowest average concentration is 16.9 μg m^{-3} in July. The highest is 76.8 μg m^{-3} in January, 4.5 times the former. Major $PM_{2.5}$ components have similar seasonal variations. This variation in Shenzhen is closely related to its climate characteristics. Table 2 delineates average monthly variations for temperature, RH, wind direction, wind speed, atmospheric boundary layer height and precipitation in the city in 2009. In January, temperature, RH, and atmospheric boundary layer height were the lowest. There was almost no precipitation, forming a meteorological condition that was clearly unfavorable to diffusion and elimination of air pollution. Moreover, a predominant wind direction of northeast to north in January was favorable for transport of atmospheric pollutants emitted from the PRD inland region to Shenzhen (Table 1), fur-

Table 1 Comparison of atmospheric chemical composition of $PM_{2.5}$ in Shenzhen and other domestic cities

	Beijing 2005-03–2006-02	Shanghai 1999-03–2000-05	Guangzhou 2002-10–2003-06	Shenzhen 2009-01–2009-12
$PM_{2.5}$	118.5	67.6	70.6	42.2
OC	24.5	16.8	17.6	8.3
EC	8.19	6.49	4.4	4.7
SO_4^{2-}	15.8	13	14.7	11.7
NO_3^-	10.1	5.78	4	2.7
NH_4^+	7.3	5.66	4.5	3.5
Reference	Yang et al., 2011	Ye et al., 2003	Hagler et al., 2006	This study

Table 2 Major monthly average meteorological parameters in Shenzhen in 2009a)

Month	Average temperatures (°C)	Average relative humidity (%)	Predominant wind direction	Average wind speed (m s^{-1})	Atmospheric boundary layer height (m)	Precipitation (mm)
Jan.	14.6	53	NNE	2.5	690*	0.2
Feb.	20.8	74	E	2.2	700*	1.0
Mar.	19.1	79	NNE	2.4	710*	176.3
Apr.	22.1	72	E	2.7	860	125.5
May	25.5	79	E	2.5	900	268.8
June	27.9	77	WS	2.2	840	192.9
July	28.9	75	WS	2.5	910	254.9
Aug.	29.1	77	ENE	2.0	940	217.4
Sep.	28.7	70	NE	2.6	930	282.4
Oct.	26.1	62	NE	2.1	800	18.6
Nov.	19.5	63	NNE	2.6	740	32.6
Dec.	16.5	69	NNE	2.4	640	40.4

a) Some data provided by Shenzhen Meteorological Bureau . *: Observation results from the same month in 2010.

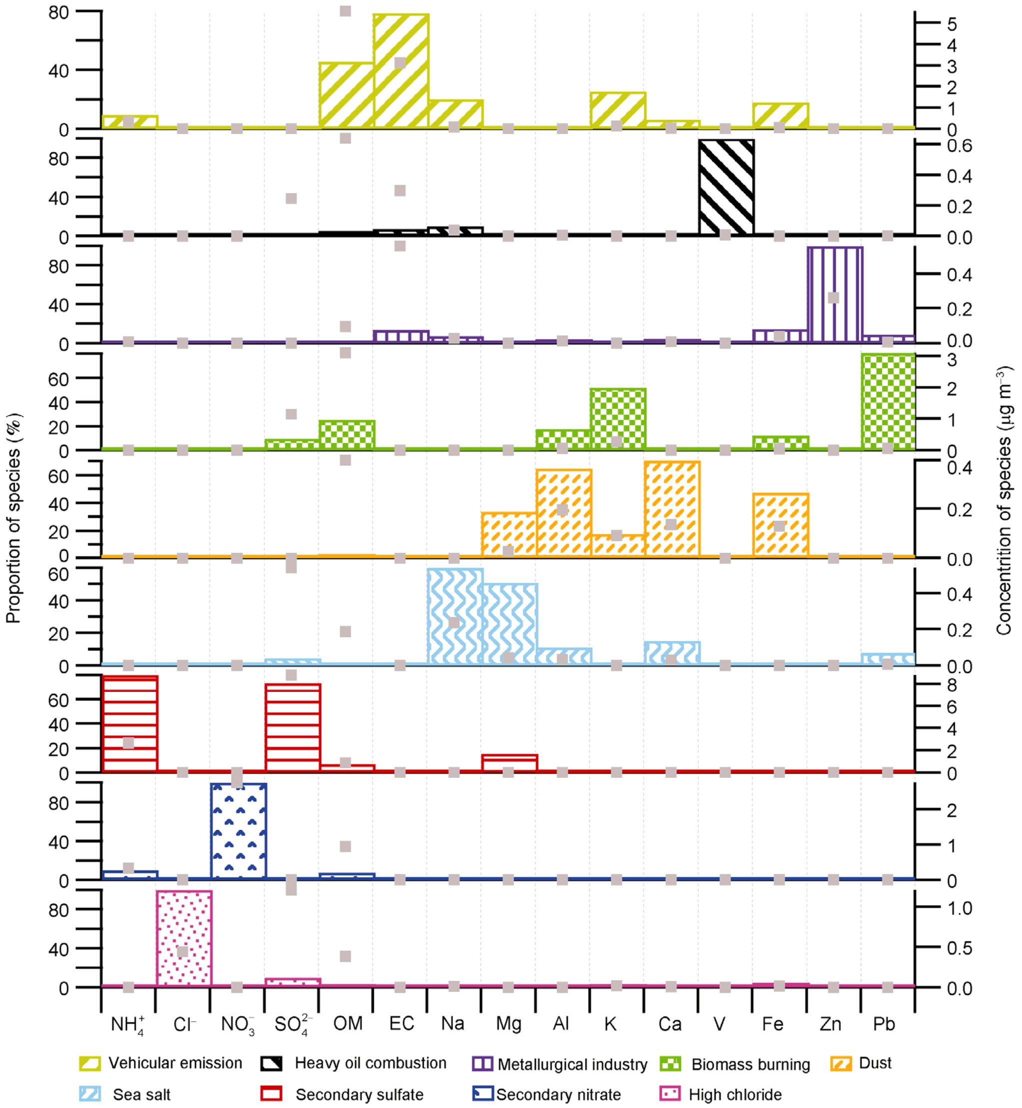


Figure 2 PMF characteristic values and source profiles for $PM_{2.5}$ in Shenzhen. Histograms are for proportion of species, and gray squares for concentration of species.

ther aggravating the city's $PM_{2.5}$ pollution. In contrast, during July, atmospheric boundary layer height and precipitation were relatively high. The predominant wind direction was favorable, bringing air masses of oceanic origin mainly from the southwest. These conditions in July facilitate diffusion and elimination of air pollution, resulting in the least $PM_{2.5}$ pollution. Meteorological conditions in other months were in transition between winter and summer, and $PM_{2.5}$ pollution remained at medium levels all year round.

During the intensive observation period in autumn, average mass concentrations of $PM_{2.5}$ at UT and BG were 52.0 and 32.6 μg m^{-3}, respectively. Comparison of their chemical compositions is shown in Figure 3(c). Entering autumn, the predominant wind direction in Shenzhen changed to northeast (Table 2). Located in a seaside holiday village in the far east of the city, site BG has a sparse surrounding population and lacks pollution from urban and industrial areas. This makes it representative of a regional background level of upwind pollutant input. $PM_{2.5}$ concentration at BG still reached 0.63 times that at UT, clearly indicating that in autumn, regional pollutant transport significantly influenced $PM_{2.5}$ pollution levels in Shenzhen. Regarding chemical compositions, sulfate had a prominent contribution at BG, with a concentration of 13.4 μg m^{-3}; this is very close to the 13.1 μg m^{-3} at UT. This reveals that sulfate was evenly distributed over the city, and has a regional pollution characteristic. EC accounted for 11.5% of total mass at UT, with a mass concentration 6.0 μg m^{-3}, much higher than at BG. This indicates that EC has a concentrated local source in the urban area, i.e., vehicular emission.

2.2 Source apportionment of $PM_{2.5}$ using PMF model

The PMF was used to identify major sources of $PM_{2.5}$, and a factor number of nine was found to be optimum. Characteristic values and source profiles of each factor are shown in

Figure 2. Figure 4(a) and 4(b) show seasonal variations of the contributions of each factor to $PM_{2.5}$ mass concentration at UT, as well as comparison between contributions of corresponding factors at UT and BG during the autumn intensive observation period.

(i) Vehicular emission

For the first factor, characteristic values of OM and EC are the highest, which were apparently from a combustion source. This source has clear seasonal variation, lower in spring and summer, and higher in autumn and winter. During the intensive observation, average contribution of this source at UT reached 6.3 times than at BG, indicating emission intensity was much stronger than that of the background region. Thus, the source is ascertained to be vehicular emission.

(ii) Heavy oil combustion

Vanadium (V) is a tracer of heavy oil combustion emission (Chow et al., 2002). For the second factor, V has the highest characteristic value, so this factor is determined to be heavy oil combustion. A prominent source of such com-

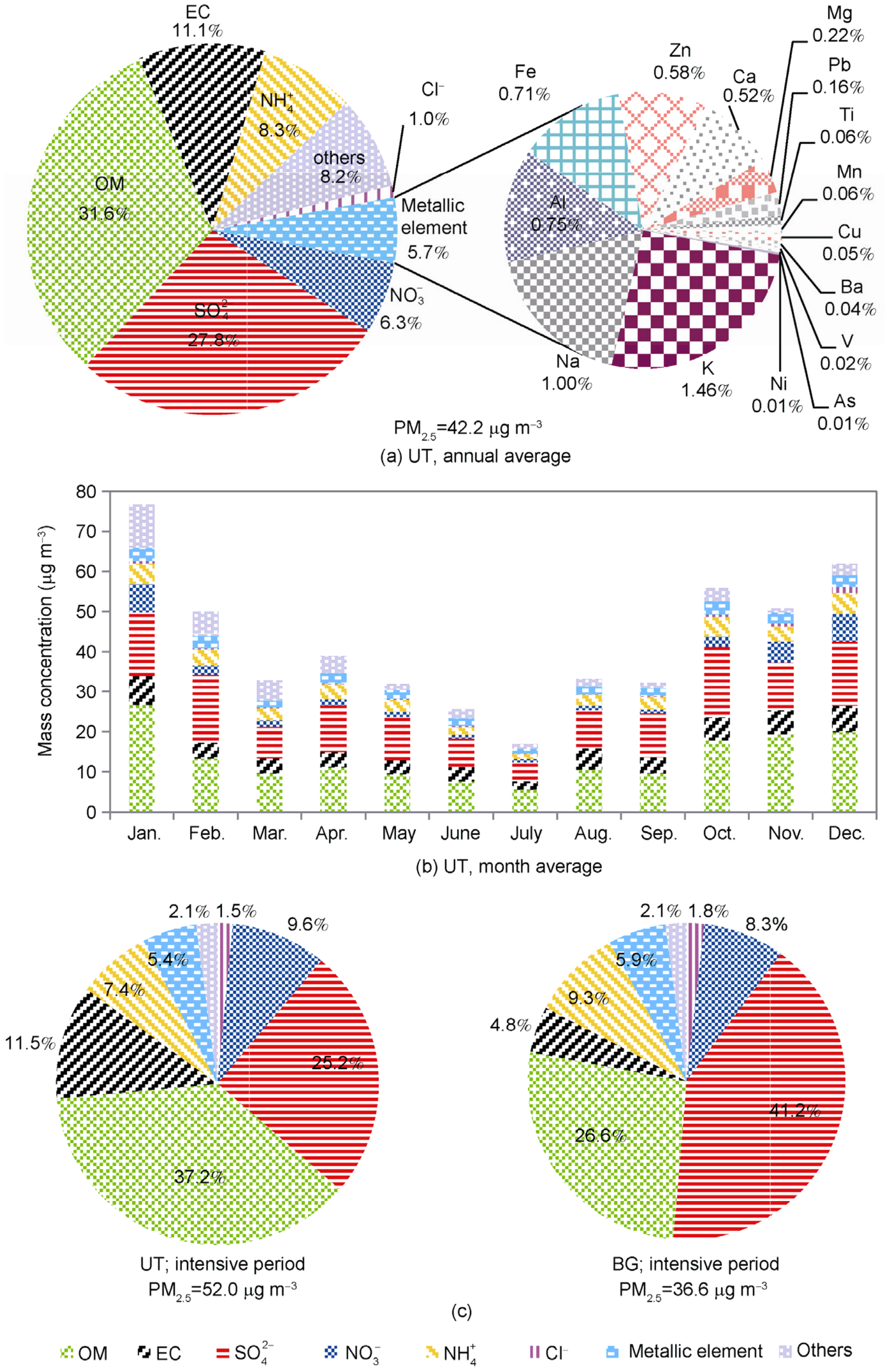


Figure 3 $PM_{2.5}$ average chemical composition in Shenzhen.

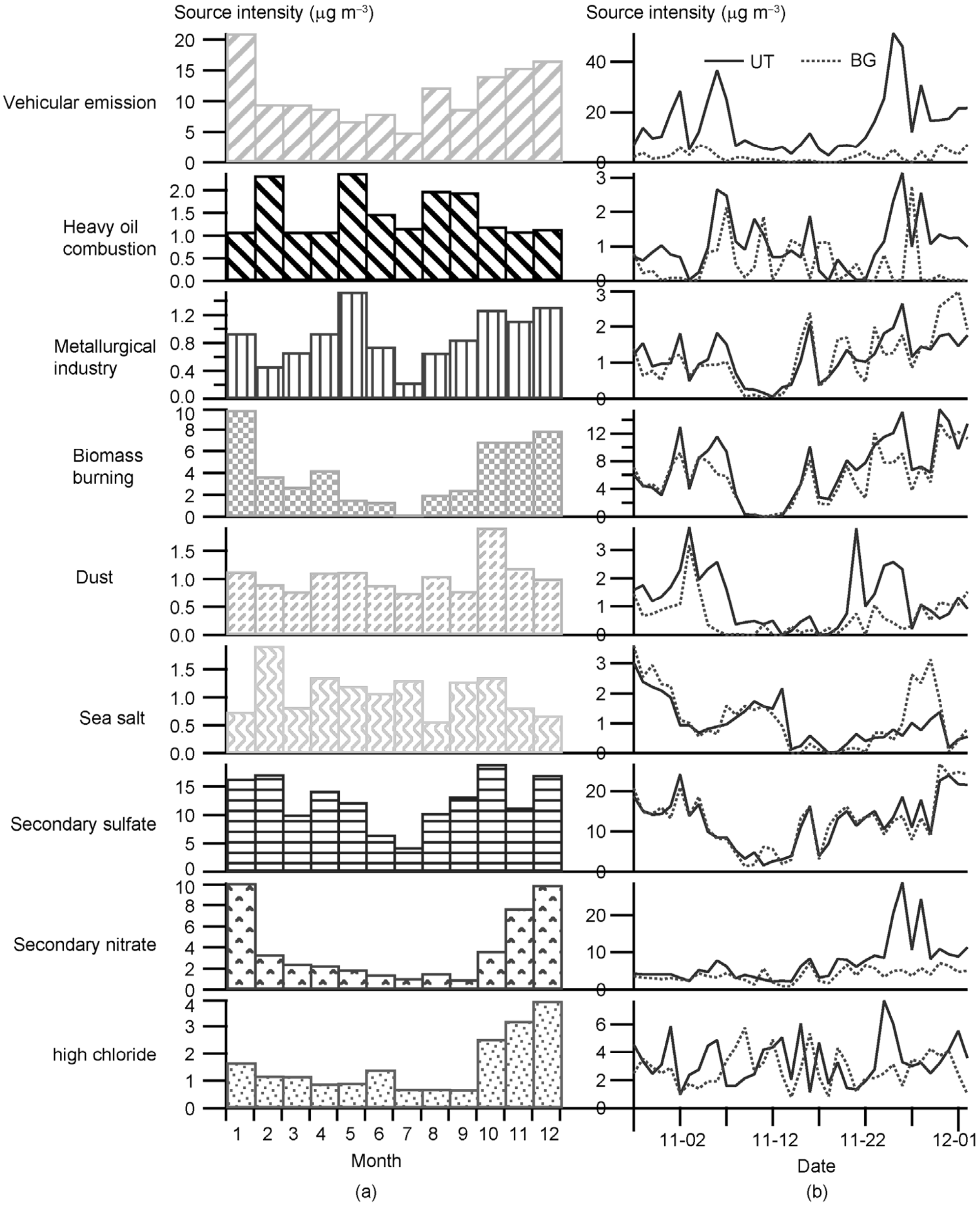


Figure 4 Temporal variations of contributions of each factor, from PMF model output.

bustion in Shenzhen is ship emissions, apart from which oil-fired power plants and industry uses may also contribute. Yuan et al. (2006a) also found a heavy oil combustion source with V as its tracer, using PMF analysis for PM_{10} source apportionment in Hong Kong. They believed this source to be mainly ship emissions. The contribution of this source to $PM_{2.5}$ at the UT site has unclear seasonal variation, probably being largely influenced by ship sailing conditions. During the intensive observation period in autumn, the average contribution of this source at UT was 2.2 times that at BG, and with time they differed greatly. This may be due to the proximity of UT to a high-traffic ship sailing area in the Pearl River estuary.

(iii) Metallurgical industry

Zinc (Zn) is a trace element of metallurgical industry emission (Hien et al., 2001). For the third factor, Zn has the highest characteristic value, so this factor is determined to be metallurgical industry. The contribution of this source to $PM_{2.5}$ at the UT site has unclear seasonal variation. Its temporal variation may be connected with the intensity of industrial activity. During the intensive observation, the contribution of this source at UT was similar to that at BG, and their time series were similar. Therefore, the source was from regional transportation, which is in accord with the fact that there is scarcely any metallurgical industry in Shenzhen.

(iv) Biomass burning

The fourth factor has prominent characteristic values of

Pb and K. Since K is a tracer of biomass burning (Yamasoe et al., 2000), this source is closely related with biomass burning events. In rural areas of China, open-field biomass burning is usually mixed with garbage burning, the smoke of which may contain Pb. Yuan et al. (2006a) also found, in PMF source apportionment for PM_{10} in Hong Kong, that K and Pb coexisted in one factor, which they explained as a regional biomass and waste burning source. This source strongly contributed to $PM_{2.5}$ at site UT in autumn and winter, which is consistent with the seasonal characteristic of biomass burning. During the intensive observation, the contribution of this source at UT was only a little higher than at BG, and they had very similar time series. This is consonant with the fact that biomass burning events, as a regional source, were largely in rural areas.

(v) Dust

The fifth factor has relatively high characteristic values of mineral elements such as Ca, Al and Fe, so it is considered to be soil and road dust. The contribution of this source to $PM_{2.5}$ at UT has indistinct seasonal variation. During the intensive observation, the two time series at UT and BG greatly differed, indicating that this source has a strong local character. This is consistent with the pollution characteristic of dust.

(vi) Sea salt

The sixth factor has prominent characteristic values of Na and Mg, signifying that this source was chiefly sea salt particles with sizes less than 2.5 μm. Since Shenzhen is a coastal city, the contribution of this source to $PM_{2.5}$ at UT has unclear seasonal variation. During the intensive observation in autumn, the contribution of this source at BG was slightly greater than at UT, which is consistent with the fact that BG is a coastal site.

(vii) Secondary sulfate

For the seventh factor, SO_4^{2-} has the highest characteristic value, indicating that this source is a secondary formation process of sulfate. The source has clear seasonal variation, lower in spring and summer, and higher in autumn and winter. During the autumn observation, both contributions and temporal variations of this source at the two sites were very consistent. This reveals that secondary sulfate in Shenzhen was almost entirely from regional transportation.

(viii) Secondary nitrate

For the eighth factor, NO_3^- has the highest characteristic value, signifying that this source is a secondary formation process of sulfate. The source has evident seasonal variation, lower in spring and summer, and higher in autumn and winter. During the intensive observation, the average contribution of this source at site UT was 1.9 times that at BG. There were high values at the former site, indicating that substantial urban vehicular emission of NO_x was a significant contributor to locally heavy pollution of secondary nitrate. At other times, both the contributions and temporal variations of this source were similar at the two sites, showing that regional transportation had a leading role in secondary nitrate pollution.

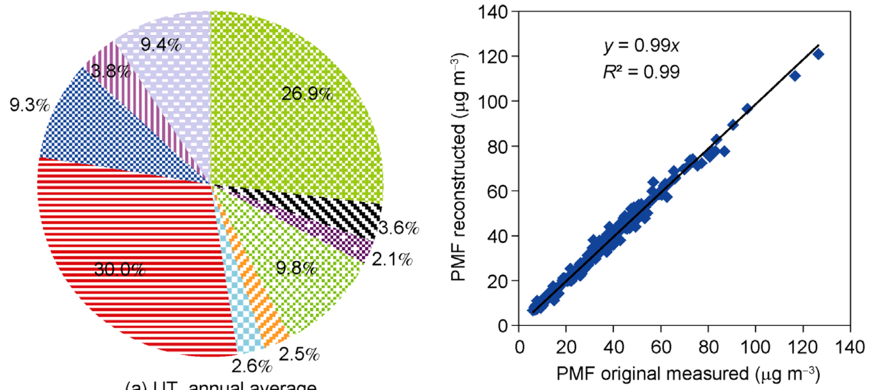
(ix) High chloride

For the ninth factor, Cl^- had the highest characteristic value. Cl^- in $PM_{2.5}$ may come from garbage burning emissions, or the secondary reaction of HCl and NH_3 in the atmosphere. HCl could be a direct emission of coal burning, or secondary formation from the heterogeneous reaction of sea salt, SO_2 or other acid gases (Zhuang et al., 1999). Contributions of this source to $PM_{2.5}$ at site UT were prominent in autumn. During the intensive observation in this season, the two time series at UT and BG strongly differed. All the above information shows that this factor has relatively complex sources. A strong source of Cl^- was identified in research on urban $PM_{2.5}$ in a western U.S. city, and was explained to be from disinfectant used in a nearby hospital (Kim et al., 2003). We could not identify accurate sources for this factor, thus it is termed high chloride and further research is needed to understand specific sources.

Based on the PMF source apportionment results above, annual $PM_{2.5}$ source structure at the UT site in 2009 is shown in Figure 5(a). Secondary sulfate, vehicular emission, biomass burning and secondary nitrate were the four major sources, contributing 30.0%, 26.9%, 9.8% and 9.3% of $PM_{2.5}$ total mass, respectively. High chloride, heavy oil combustion, sea salt, dust and metallurgical industry each contribute 2%–4% of $PM_{2.5}$ total mass. Of this mass, 9.4% was excluded from model input and source apportionment. The corresponding relationship between reconstructed mass from the nine factors and model-input total mass of each sample is depicted in Figure 5(b). Very strong correlation (R^2 = 0.99, slope = 0.99) is evident, indicating that these nine factors well simulated the major sources and their contributions to $PM_{2.5}$ in the Shenzhen atmosphere. During the intensive observation in autumn, the major two sources contributing to $PM_{2.5}$ at UT were vehicular emission (29.5%) and secondary sulfate (24.0%), while those at BG were secondary sulfate (39.2%) and biomass burning (17.7%). Song et al. (2006) used PMF for source apportionment of $PM_{2.5}$ in Beijing in 2000, identifying eight sources. These were coal burning (19%), secondary sulfate (17%), secondary nitrate (14%), biomass burning (11%), road dust (9%), vehicles (6%), industry (6%) and desert dust. Both cities have secondary sulfate, secondary nitrate and biomass burning as major sources. A significant difference is that coal burning is one of the major sources in Beijing in North China, whereas vehicular emission is a major contributor in Shenzhen.

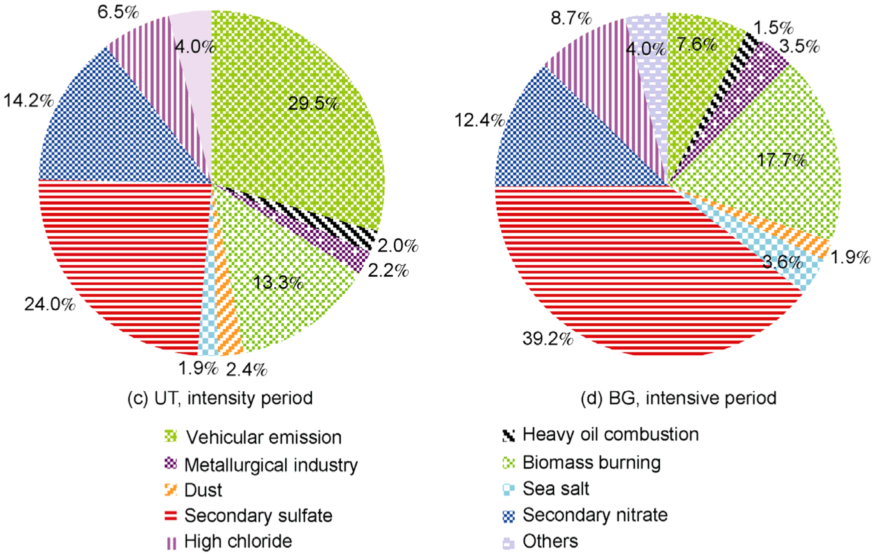
2.3 Estimation of secondary organic aerosol in $PM_{2.5}$

Organic aerosol (OA) is a significant component of $PM_{2.5}$, including primary organic aerosol from direct emission and



(a) UT, annual average

(b)



(c) UT, intensity period

(d) BG, intensive period

Figure 5 Average source composition of $PM_{2.5}$ in Shenzhen.

SOA formed from atmospheric photochemical reaction processes. Given the complexity of OA composition, there is no direct method that can discriminate between primary and secondary OA. Usually indirect methods are used for estimation, such as Turpin et al. (1995) and Cao et al. (2003) who estimated SOA concentration using the OC/EC ratio method at an early stage. Yuan et al. (2006b) applied the PMF model to identify and quantify SOA. They used it to analyze the major components in PM_{10} sampled in Hong Kong, and determined OA apportioned into factors with secondary character (the factors of secondary sulfate and secondary nitrate formation) as SOA, because they were probably formed simultaneously with sulfate and nitrate in atmospheric reactions.

In the present PMF model results, OA was apportioned into five sources; namely, secondary sulfate, secondary nitrate, vehicular emission, heavy oil combustion and biomass burning. OA apportioned into factors together with sulfate and nitrate should be classified as SOA (Yuan et al., 2006b). Moreover, we found that SOA can also exist within the factors of vehicular emission, heavy oil combustion and biomass burning. In our PMF model results, the OC/EC ratio is 1.12 in the source profile of the vehicular emission factor, which is remarkably higher than the ratio of 0.49 found by He et al. (2008) in freshly emitted $PM_{2.5}$ from vehicles inside tunnels in the PRD. However, during air mass transport from emission sources to receptor sites, gas phase precursors emitted from the sources will continually oxidize and form SOA. This causes the observed air mass at the receptor site to be somewhat aged and have a relatively high OC/EC ratio. Recent studies show that primary emission sources contain large amounts of semi-volatile OA, which may rapidly oxidize into SOA in the atmosphere (Robinson et al., 2007; Gouw et al., 2011). Thus, the OA that the PMF model apportioned into factors such as vehicular emission could contain both primary OA and SOA, which may be estimated using the OC/EC ratio method as shown in the following equation:

$$\begin{aligned}&[\text{secondary organic carbon}]_{\text{vehicular emission factor}}\\&=[\text{organic carbon}]_{\text{vehicular emission factor}}-[\text{EC}]_{\text{vehicular emission factor}}\times\\&\quad(\text{OC/EC})_{\text{vehicular fresh emission}}.\end{aligned}\tag{1}$$

SOA for the heavy oil combustion factor may be estimated by the same method. An OC/EC ratio of 0.39 measured in fresh emissions of diesel vehicles in the PRD by He et al. (2008) was selected as the ratio for freshly emitted $PM_{2.5}$ from heavy oil combustion. For the biomass burning factor, the characteristic value of EC is 0, indicating that its contribution to EC in Shenzhen $PM_{2.5}$ from biomass burning can be ignored; thus, the OC/EC method for SOA estimation is no longer applicable. We used an analogous OC/K method to estimate SOA for the biomass burning factor, in which K is a biomass burning tracer, as

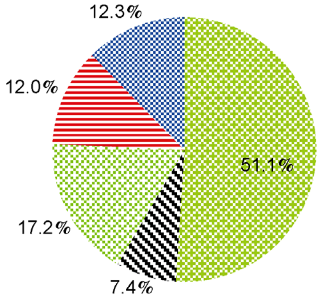
$$\begin{aligned}&[\text{secondary organic carbon}]_{\text{biomass burning factor}}\\&=[\text{organic carbon}]_{\text{biomass burning factor}}-[\text{K}]_{\text{biomass burning factor}}\times\\&(\text{OC/K})_{\text{biomass burning fresh emission}}.\end{aligned}\tag{2}$$

A value of 3.8 measured in $PM_{2.5}$ from a fresh biomass burning smoke plume in the PRD (Lin et al., 2010) was chosen for $(\text{OC/K})_{\text{biomass burning fresh emission}}$. Using PMF model results, SOA concentration in Shenzhen $PM_{2.5}$ was ultimately calculated as

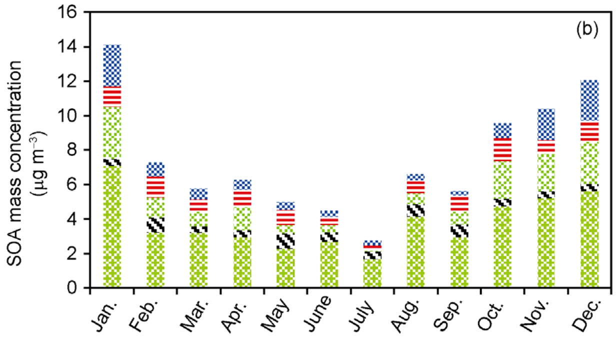
$$\begin{aligned}&[\text{SOA}]=[\text{OA}]_{\text{secondary sulfate factor}}+[\text{OA}]_{\text{secondary nitrate factor}}\\&+[\text{SOA}]_{\text{vehicular emission factor}}+[\text{SOA}]_{\text{heavy oil combustion factor}}+\\&[\text{SOA}]_{\text{biomass burning factor}}.\end{aligned}\tag{3}$$

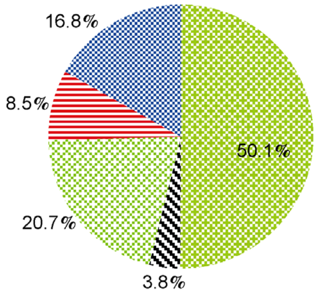
As shown in Figure 6, the average mass concentration of SOA in $PM_{2.5}$ at site UT in 2009 was 7.5 μg m^{-3}, representing 57% of total OA mass. Among all SOA sources, vehicle-related SOA formation reached 51% of total SOA, indicating that vehicles not only produce large amounts of primary OA, but also emit volatile and semi-volatile organic materials that form substantial SOA. Monthly average SOA mass concentration has obvious seasonal variation, lower in spring and summer, and higher in autumn and winter (Figure 6). During the intensive observation, average mass concentration of SOA at site UT was 10.3 μg m^{-3}, with vehicle emission-related SOA formation (50%) as its major source. The average mass concentration of SOA at BG was 4.6 μg m^{-3}, with biomass burning-related SOA formation (39%) as its major source.

During the autumn intensive observation, a state-of-the-art, high-resolution time-of-flight aerosol mass spectrometer (Aerodyne Research Inc., Billerica, Massachusetts, USA) was also used for a simultaneous PM_1 online observation at site UT. Based on the high-resolution OA mass spectra obtained, source apportionment of OA was done using the PMF model. The identified semi-volatile oxidized organic aerosol (SV-OOA) and low-volatility oxidized organic aerosol (LV-OOA) could represent the fresh and aged SOA, respectively. Details can be found in our previous publication (He et al., 2011). Based on the results from aerosol mass spectra during the autumn intensive observation, the average mass concentration of SOA (SV-OOA + LV-OOA) in PM_1 at site UT was 8.3 μg m^{-3}, representing 47% of total OA mass. This conclusion is close to that drawn in the present study: SOA in $PM_{2.5}$ was 7.5 μg m^{-3}, representing 57% of total OA mass. Considering the fact that fine particles within the size range of 1–2.5 μm are mostly from aged secondary aerosols (Huang et al., 2006; Lan et al., 2011), mass concentration of SOA and its ratio of total OA should be higher in $PM_{2.5}$ than in PM_1. In conclusion, during the autumn intensive observation at site UT, results from the two independent SOA identification methods indicate that SOA has a prominent contribution to atmospheric fine particles in Shenzhen.

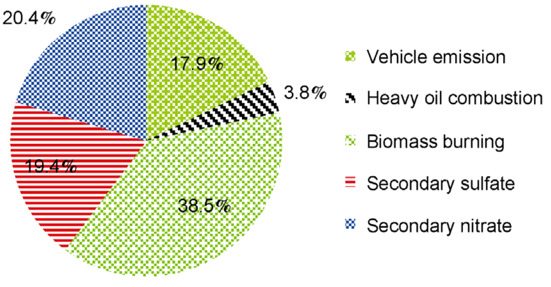


(a) UT, annual average





(c) UT, intensive period



(d) BG, intensive period

Figure 6 Source composition of SOA in $PM_{2.5}$ in Shenzhen.

3 Conclusions

Through full-year systematic observation and comprehensive analysis of PM$_{2.5}$ in Shenzhen, we obtained the following major conclusions:

(1) In urban Shenzhen, annual PM$_{2.5}$ concentration was 42.2 μg m^{-3}. OM, SO$_4^{2-}$, EC, NH$_4^+$, NO$_3^-$, Cl$^-$ and 15 major metallic elements composed 31.6%, 27.8%, 11.1%, 8.3%, 6.3%, 1.0% and 5.7% of total mass, respectively. Organic pollution in the atmosphere is significant. PM$_{2.5}$ pollution levels show clear seasonal variations, lower in spring and summer, and higher in autumn and winter; monthly average concentrations varied by as much as a factor of 4.5. In the typical pollution season of autumn, PM$_{2.5}$ mass concentration at the regional background site reached 0.63 times that at the urban site, demonstrating that regional transport significantly modulated PM$_{2.5}$ pollution in urban Shenzhen.

(2) Source apportionment results of PM$_{2.5}$ in the atmosphere using the PMF model showed that secondary sulfate, vehicular emission, biomass burning and secondary nitrate were the major sources in the urban area, accounting for 30.0%, 26.9%, 9.8% and 9.3% of PM$_{2.5}$ total mass, respectively. High chloride, heavy oil combustion, sea salt, dust and metallurgical industry contributed between 2%–4% of the total mass. Of this mass, 9.4% was excluded from model input and source apportionment. Spatiotemporal variation patterns of different sources show that vehicular emission sources were primarily local, secondary sulfate and biomass burning were mostly regional, and secondary nitrate had both local and regional sources.

(3) The PMF model and OC/EC ratio method were associated for identification and estimation of SOA in PM$_{2.5}$. The average SOA mass concentration in urban PM$_{2.5}$ was 7.5 μg m^{-3}, representing 57% of total OA mass. Among all SOA sources, vehicle-related SOA formation reached 51% of total SOA. At the regional background site in autumn, the major source of SOA was biomass burning-related SOA formation (39%).

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