



Chemical composition, diurnal variation and sources of PM_{2.5} at two industrial sites of South China

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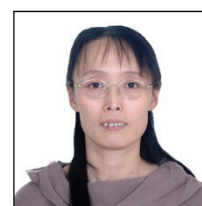
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ABSTRACT

Diurnal PM_{2.5} samples were collected during summer and winter at an industrial complex site (site A) and an electronic waste (e-waste) recycling site (site B) in Qingyuan, South China. The concentration of organic carbon (OC), elemental carbon (EC), water soluble ions (WSI) and elements were investigated for their seasonal and diurnal variations. Organic matter (OM) was the most abundant specie in winter, accounting for 40.2% and 48.8% of PM_{2.5} in sites A and B, respectively; while in summer, excluding the elemental portion, WSI was the biggest part, which accounted for 37% and 49.4% of PM_{2.5} mass in sites A and B, respectively. Significantly higher concentrations were observed for most of the analyzed chemical species in winter. Average acidity of PM_{2.5} at both sites was significantly higher in summer. Diurnal variation with elevated concentrations of PM_{2.5} in nighttime samples was found at site B. Secondary inorganic aerosols (NH₄⁺, NO₃⁻ and SO₄²⁻) exhibited clear day-to-night variation. Concentration of SO₄²⁻ was about 15% higher in daytime samples. NH₄⁺ and NO₃⁻ co-varied in winter, but were weakly associated with each other in summer. Sites A and B samples were almost all ammonium-rich in winter, whereas the summer samples were ammonium-poor during the daytime but ammonium-rich in the night. Positive matrix factorization (PMF) model analysis showed that secondary formation, biomass burning, regional industries, coal combustion and dust had significant contribution to PM_{2.5}. Among them, secondary formation and biomass burning together contributed approximately 50% of PM_{2.5} mass at both sites. Additionally e-waste recycling activities resulted in high pollution of Cu at Site B.

Keywords: PM_{2.5}, chemical composition, diurnal variation, e-waste, source apportionment

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1. Introduction

Particulate matter especially the fine particles with aerodynamic diameters smaller than 2.5 μm (PM_{2.5}) has recently been a concern of scientists since it is associated with a range of effects on human, such as health problems (Seaton et al., 1995) and atmospheric haze problems (Pryor et al., 1997). PM_{2.5} is composed of a large number of individual compounds and is widespread in the environment. The chemical composition of PM_{2.5} including organic carbon (OC), elemental carbon (EC), ions, major and trace elements, etc. has been extensively investigated in urban and rural areas (Takahashi et al., 2008; Terzi et al., 2010). A few studies on industrial areas were also carried out in some countries such as Spain, Belgium and Turkey (Rodriguez et al., 2004; Alastuey et al., 2006; Querol et al., 2008; Bencs et al., 2010; Pekey et al., 2010). The composition and sources of PM_{2.5} varied largely due to divergences of climate, location and industries of the sites, but were generally characterized with high OC/EC ratio, peaked sulfate, carbon content and elemental concentrations near industrial sites, indicating great impact of industrial activity.

The typical sources of PM_{2.5} include natural and anthropogenic emissions such as forest fires, volcanic eruptions, incomplete combustion of fossil fuels, wood, agricultural debris or leaves and fugitive emissions from industrial processes (Dan et al., 2004; Hopke et al., 2006). Additionally, secondary formation by the oxidation of atmospheric volatile matter may also be an important source. The contributions of various sources to PM_{2.5} can vary from location to location, which depend on the meteorological condi-

tions, geographical position and the emission strength of the sampling sites. Thus, it is important to understand the sources and atmospheric processes of PM_{2.5} in different parts of the world.

Several studies on the sources and chemical composition of atmospheric aerosols have been conducted in the urban and suburban areas of the Pearl River Delta (PRD), China. These studies showed that the main constituents of PM_{2.5} mass were OC, EC, sulfate and nitrate, and eight sources including secondary sulfates (32%), secondary nitrates (6%), biomass burning (15%), coal fly ash/cement (18%), sea salt (3%), crustal dust (5%), vehicle exhaust (6%) and coal-fired power plants (3%) were identified (Wang et al., 2006; Liu et al., 2008). However, to our knowledge, no studies on the chemical composition and sources of typical industrial areas have been reported in this region. Qingyuan is one of the biggest e-waste recycling areas in China. It is located in northwestern Guangdong province, adjacent to the PRD region. During the past few decades, the explosive increases in industrial productivity have led to serious atmospheric contamination. With numerous industries, the air pollution in Qingyuan may be influenced by the industrial activities. In this study, diurnal PM_{2.5} samples were collected at an industrial complex site and an e-waste recycling site from Qingyuan. In previous studies, the characteristics of polycyclic aromatic hydrocarbons (PAHs) at these two sites have been reported (Wei et al., 2011; Wei et al., 2012). The results showed that most of parent PAHs with 4–6 rings detected exhibited significant diurnal variations at the e-waste recycling site, and that the pollution patterns of PAH derivatives were similar at the two sites, indicating the contribution of regional pollution.

This study aims to: (1) characterize the major chemical composition of $PM_{2.5}$ in the two industrial sites; (2) analyze the seasonal and diurnal variations of the major species; and (3) identify possible sources and their contribution using principle component analysis (PCA) and positive matrix factorization (PMF) models. The results would expand the current knowledge of $PM_{2.5}$ sources, their distribution and transport mechanisms and would provide useful information for the evaluation of their risks to human health.

2. Methodology

2.1. Description of sampling sites and meteorological condition

Two sampling sites were chosen in the Qingcheng district and Longtang town of Qingyuan (Figure S1). Site A was located in an industrial complex area that included numerous factories for clothing, photocopier, automobile services, etc. The samples were collected on the rooftop of a five-story building approximately 15 m above ground. Site B was located in a primary school surrounded by e-waste lots and workshops, with electrical cables and wires being the major e-waste materials. Burning wires for copper recovery was an occasional event in this area. Site A was situated approximately 10 km northwest of site B.

Sampling was conducted between August 5 and 16, 2009 and between January 24 and February 4, 2010. During these periods, diurnal $PM_{2.5}$ samples were collected from 07:30 to 19:30 (local time) for the daytime samples and from 19:30 to 07:30 of the following day for the nighttime samples. Field blanks accompanying samples to the sampling sites were performed. The air samples were drawn at about $1.13\text{ m}^3\text{ min}^{-1}$ through the quartz fiber filters (QFFs, $20.3\text{ cm}\times 25.4\text{ cm}$, Whatman) using a high-volume sampler (GUV-15HBL1, Thermo, USA) equipped with a $PM_{2.5}$ size-selective inlet. Before and after sampling, the filters were kept under constant temperature (25°C) and relative humidity (RH) (50%) for 24 h before weighing. The sampled filters were wrapped with annealed aluminum foil and stored in a refrigerator at -40°C until analysis.

The ambient parameters during the sampling periods are listed in Table S1 of the Supporting Material (SM). During both sampling periods, no extreme weather conditions such as typhoon, dust and storm were observed. Back trajectory analysis revealed different wind patterns in the two sampling periods. In summer, southwesterly winds from ocean and northern winds from inland were equally represented. While in winter, northeasterly wind dominated, bringing in dirty air masses moving across northern coastal cities.

2.2. Chemical analysis

Samples were analyzed for carbonaceous species (OC and EC), water soluble ions (WSI), major and trace elements. The detection limits (DL) were defined as 3 times the standard deviation of blank measures, which were repeated for 7 times.

Carbonaceous species. OC and EC were determined by a DRI THERMAL OPTICAL Carbon Analyzer (Model 2001A) using thermal/optical transmittance (TOT) protocol. A punch of 0.525 cm^2 filter was heated in a completely oxygen-free He atmosphere, at four stepwise temperatures of 120°C (OC_1), 250°C (OC_2), 450°C (OC_3) and 550°C (OC_4) to release all organic carbon on the filter. Then the pure He eluent was switched to a 2% O_2 /He mixture and at 550°C (EC_1), 700°C (EC_2) and 800°C (EC_3), samples were determined for EC concentration. Optical pyrolyzed carbon (OP) was monitored by laser. The carbon that evolved at each temperature was oxidized to carbon dioxide (CO_2) and then reduced to methane (CH_4) for quantification with a flame ionization detector. When the analysis is done, all the 8 fractions are given out. OC is defined as $OC_1+OC_2+OC_3+OC_4+OP$ and EC is

defined as $EC_1+EC_2+EC_3-OP$. The DL of OC and EC were 0.82 and $0.19\text{ }\mu\text{g cm}^{-2}$, respectively.

Water soluble ions. Aliquots of filters were extracted with ultra-pure Milli-Q water in an ultrasonic bath for water soluble ions. The extract was filtered through a $0.45\text{ }\mu\text{m}$ pore size filter and analyzed for Li^+ , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+} , F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} using an ion chromatography (Dionex ICS-900) with an electrical conductivity detector. Anions were separated with an IonPac AS23 analytical column connected IonPac AG23 pre-column. Cations were separated with an Ion Pac CS12A analytical column connected Ion Pac CG12A pre-column. The corresponding DL of ions measured above were 0.02 , 0.03 , 0.18 , 0.16 , 0.1 , 0.29 , 0.009 , 0.033 , 0.033 , 0.044 , 0.066 , 0.083 and 0.083 mg L^{-1} , respectively.

Elements. Filters were digested using 3 mL concentrated nitric acid in closed Teflon bombs at 150°C for one week. The bombs were ultrasonically operated for 1 h every day. Then the solutions were evaporated near to dryness and were diluted to 8 mL using Milli-Q water to reach a final solution of acidity $<2\%$. Trace elements were then analyzed by ICP-MS (ELAN6000). Before analyzed, 20 ppb Rh was added as internal standard. Major elements were analyzed by ICP-AES (VARIAN VISTA PRO). For each batch of samples, two blanks were performed with the same procedure of samples during the whole process. Totally 25 elements were measured including Al, Ca, Fe, K, Mg, Na, Ti, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, Cs, Ba, Pb, Mo, Cd, Rb, Sr, Y, U and Th, and the corresponding DL were 0.9 , 0.01 , 0.3 , 0.3 , 0.05 , 0.2 , 0.024 , 0.124 , 0.008 , 0.022 , 0.016 , 0.04 , 0.217 , 0.002 , 0.011 , 0.001 , 0.009 , 0.01 , 0.004 , 0.002 , 0.002 , 0.002 , 0.012 , 0.0002 and $0.0007\text{ }\mu\text{g L}^{-1}$, respectively. Most of elements were measured because they accounted for large proportions of metals, or they were tracers for specific sources, and may give us some information on the source characterization. Other trace elements were measured in order to get a full knowledge of the elements composition. Quartz fiber filters contains high Al, Ca, Mg, Na background and low levels of trace elements, while in our study, the sample to blank ratios for most of the measured metals were larger than 3, making the results usable. All the results were then corrected for filter blanks. For some analytical reasons, only winter results were obtained.

2.3. Statistical analysis

The PCA (SPSS V18) and PMF (EPA PMF3.0) were applied to the concentration dataset to find the groups of chemicals with similar behaviors for the identification of $PM_{2.5}$ sources and their relative contributions. Detailed information is presented in the Supporting Material (SM) (Figures S3 and S4). Correlations between selected major chemicals and meteorological parameters were tested using the Pearson coefficients (Table S2). The non-parametric Mann-Whitney U test was employed to detect the differences between sites, diurnal and seasonal variations. A p value of <0.05 was considered to be of statistical significance (Table S3).

3. Results and Discussion

3.1. Reconstruction of $PM_{2.5}$

In this study, the chemical components of $PM_{2.5}$ could be divided into six classes as follows: crustal material (CM), trace elements (TE), WSI, organic matter (OM), EC and particle-bound water (PBW). For the reconstruction of crustal and elemental material, crustal and trace elements are converted to their mineral oxides. Si was an important crustal species, but was not measured in this study, so it was estimated as $[Si]=3.41[Al]$ based on crustal composition given by Mason and Moore (1982). WSI is calculated as sum of major ions including Na^+ , K^+ , Ca^{2+} , NH_4^+ , Cl^- , PO_4^{3-} , SO_4^{2-} and NO_3^- . PBW were derived using the Extended AIM Aerosol Thermodynamics Model III (E-AIM, 1998), which is an equilibrium

thermodynamic model of the system $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$. Typical filter equilibration conditions of 25 °C (298.15 K) temperature and 50% RH were used. On average, retained PBW accounted for 9% and 7.67% of $\text{PM}_{2.5}$ mass in the winter samples of sites A and B, 13.4% and 12.4% in the summer samples of sites A and B, respectively. Then the transformation factors k of OC to OM were derived using the SANDWICH method (Frank, 2006; Dabek-Zlotorzynska et al., 2011), which estimates OM by subtracting non-carbon components of $\text{PM}_{2.5}$ from measured mass. Using this method, the average k values were estimated to be 2.25 and 3.47 at winter sites A and B, respectively. For summer samples, because of sample contamination, the elemental data (CM and TE) were invalid. Assuming the same proportion of elements in $\text{PM}_{2.5}$ samples, the average k values in summer sites A and B were estimated to be 2.46 and 1.36. It is worth noting that the transformation factor suffered great variability at site B in the two seasons, this might be due to differences in the organic aerosol composition. Turpin and Lim (2001) reported that aerosol heavily impacted by wood-smoke have high ratios (2.2–2.6), the ratios of more water-soluble (polar) organic compounds could be even higher (1.5–3.8). The higher ratio in winter site B than site A might be ascribed to greater photochemical formation of secondary organic aerosol (SOA) or more serious biomass burning at site B. However, the low ratio of 1.36 in summer at site B is confusing. Unfortunately the detailed organic composition of $\text{PM}_{2.5}$ was not measured in this study and it needs further investigation.

The reconstructed chemical compositions based on average concentrations of $\text{PM}_{2.5}$ are shown in Figure 1. In general, OM and WSI were two most important contributors to $\text{PM}_{2.5}$ mass: in winter, OM was the most abundant at both sites, accounting for 40.2% and 48.8% of $\text{PM}_{2.5}$ in sites A and B, respectively; while in summer, excluding the elemental part, WSI was the biggest part, which accounted for 37% and 49.4% of $\text{PM}_{2.5}$ mass in sites A and B, respectively. WSI contribution was the highest in summer at site B due to large increment of PO_4^{3-} . Bi et al. (2010) reported the major particle components in a typical e-waste workshop of south China and found that P was the most abundant element, which was mainly due to organic phosphates. Organophosphates are usually used as flame retardants for electrical appliances, or act as insecticides during farming (site B has several farmlands). With both higher atmospheric oxidation species and solar radiation in summer, the degradation of these compounds might be enhanced (Watts and Linden, 2008; Gatidou and Iatrou, 2011), resulting in high concentrations of PO_4^{3-} in summer.

3.2. $\text{PM}_{2.5}$ mass concentrations

$\text{PM}_{2.5}$ concentrations in summer and winter were $50.5 \pm 17.5 \mu\text{g m}^{-3}$ and $120.4 \pm 54.3 \mu\text{g m}^{-3}$ at site A, respectively and $51.5 \pm 14.2 \mu\text{g m}^{-3}$ and $111.0 \pm 57.2 \mu\text{g m}^{-3}$ at site B, respectively. The average levels of $\text{PM}_{2.5}$ at both sites significantly exceeded the 24-hour air quality standard of $35 \mu\text{g m}^{-3}$ established by USEPA and was comparable to Guangzhou (Tao et al., 2012), but much higher than that of other PRD cities such as Hong Kong, Shenzhen and Zhuhai (Lai et al., 2007), or other Asian cities (Shon et al., 2012). $\text{PM}_{2.5}$ increased by about a factor of 2 in winter. However, the variation between sites A and B was rather small.

For $\text{PM}_{2.5}$ mass, more pronounced diurnal variation was observed at site B, especially in summer, with higher values observed in the night. However, site A did not show the similar trend. Site A was located at an industrial complex area with numerous industries. The industrial emissions were strong during daytime. Moreover, the sampling site was close to several high-traffic roads. Higher traffic exhausts were expected in the daytime, which could be proved by the higher EC values in the daytime of site A in both seasons. Higher emissions during daytime might offset the concentrating of chemical species due to shallower boundary layer in the night, resulting in the weak diurnal variation

at this site. In contrast, the industrial activities at site B were much simpler, the major industrial activity was e-waste recycling and the sampling site was located in a school with no heavy-traffic road around, making the variation more pronounced.

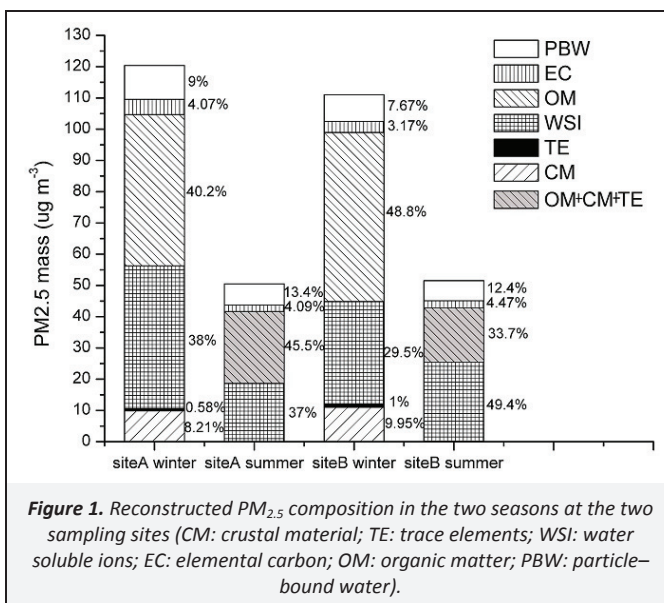


Figure 1. Reconstructed $\text{PM}_{2.5}$ composition in the two seasons at the two sampling sites (CM: crustal material; TE: trace elements; WSI: water soluble ions; EC: elemental carbon; OM: organic matter; PBW: particle-bound water).

The variation of chemical species might be influenced by meteorological conditions such as temperature, RH and wind speed. For example, a strong negative correlation between $\text{PM}_{2.5}$ and temperature (see the SM, Table S2) suggested that condensation of gaseous phase to particle played an important role on the concentration elevation of $\text{PM}_{2.5}$ under colder conditions. The negative correlation between $\text{PM}_{2.5}$ and wind speed implied the importance of local sources. Similar results were observed for carbonaceous species and major ions. For more details, please refer to the SM.

3.3. Characterization of carbonaceous species

Average concentrations of carbonaceous species are shown in Table 1. It can be seen that site B showed higher OC and EC concentrations than site A in summer, while site A showed higher concentrations than site B in winter. Note that the increment of OC and EC values in summer at site B was mainly due to increase of night concentrations, which indicates that in the night, there might be more primary emissions, such as e-wastes burning.

Correlation analysis showed excellent correlation between OC and EC concentrations at both sites in winter (site A, $r=0.95$; site B, $r=0.93$), while obviously weaker correlations were spotted in summer (site A, $r=0.59$; site B, $r=0.65$). The strong correlation in winter implies that OC and EC were either originated from the same sources or underwent similar processes. Whereas for summer samples, due to enhanced secondary formation, OC and EC data were much more scattered. The average OC/EC ratio in winter and summer was 4.33 and 3.68 at site A and 4.40 and 3.78 at site B, respectively, and was comparable to the typical value of 4.22 in winter Guangzhou, but higher than that of 2.26 in summer (Duan et al., 2007). An enrichment in organic carbon (given by OC/EC values) has been observed both in rural and remote locations and in summer time (Castro et al., 1999), while in this study, enhanced OC/EC ratio in winter was found at both sites, which could be interpreted by stronger biomass burning contribution in this season (He et al., 2011).

Table 1. Average concentrations ($\mu\text{g m}^{-3}$) of $\text{PM}_{2.5}$, OC and EC, major cations, anions in the two sites (the in-situ $[\text{H}^+]$ in nmol m^{-3})

Species	Site A						Site B					
	Winter			Summer			Winter			Summer		
	Day	Night	Average	Day	Night	Average	Day	Night	Average	Day	Night	Average
OC	19.1	20.3	20.1	7.81	7.25	7.53	13.9	16.0	15.6	7.74	9.55	8.62
	± 8.83	± 13.0	± 10.4	± 1.85	± 3.92	± 2.61	± 7.17	± 9.75	± 8.01	± 2.74	± 3.86	± 2.86
EC	4.45	4.60	4.57	2.23	1.91	2.07	3.12	3.66	3.52	1.91	2.60	2.30
	± 2.07	± 2.71	± 2.25	± 0.50	± 0.94	± 0.53	± 1.56	± 1.99	± 1.69	± 0.52	± 1.18	± 0.62
OC/EC	4.39	4.40	4.33	3.65	3.90	3.68	4.54	4.26	4.40	4.03	4.00	3.78
	± 1.30	± 1.58	± 1.06	± 1.16	± 0.95	± 0.95	± 1.29	± 1.30	± 1.25	± 0.71	± 1.47	± 0.96
$\text{PM}_{2.5}$	125	104	120	49.7	51.4	50.5	111	105	111	48.6	58.7	51.5
	± 56.2	± 59.2	± 54.3	± 15.6	± 21.3	± 17.5	± 59.2	± 66.0	± 57.2	± 24.4	± 17.8	± 14.2
Na^+	1.96	2.03	1.99	1.00	0.75	0.87	0.47	0.49	0.49	2.77	2.45	2.64
	± 0.95	± 1.11	± 0.93	± 0.78	± 0.64	± 0.67	± 0.28	± 0.36	± 0.28	± 0.28	± 0.54	± 0.21
NH_4^+	8.52	7.09	8.01	2.56	2.83	2.70	7.23	6.29	6.88	2.78	3.68	3.24
	± 5.19	± 4.87	± 4.77	± 2.01	± 0.97	± 1.38	± 4.04	± 3.78	± 3.73	± 1.74	± 1.90	± 1.59
K^+	1.10	1.09	1.11	0.48	0.39	0.44	0.81	0.93	0.88	0.38	0.48	0.44
	± 0.51	± 0.64	± 0.51	± 0.23	± 0.15	± 0.15	± 0.32	± 0.43	± 0.34	± 0.11	± 0.12	± 0.10
Mg^{2+}	0.04	0.05	0.05	0.06	0.04	0.05	0.06	0.06	0.05	0.06	0.05	0.05
	± 0.02	± 0.04	± 0.02	± 0.02	± 0.02	± 0.02	± 0.02	± 0.07	± 0.02	± 0.02	± 0.02	± 0.02
Ca^{2+}	0.42	0.44	0.44	0.56	0.48	0.51	0.37	0.34	0.35	0.66	0.53	0.61
	± 0.22	± 0.25	± 0.20	± 0.17	± 0.16	± 0.11	± 0.13	± 0.38	± 0.24	± 0.19	± 0.23	± 0.17
Cl^-	3.47	3.74	3.67	0.24	0.91	0.57	2.39	3.64	3.14	0.50	2.17	1.46
	± 2.08	± 2.37	± 2.09	± 0.21	± 1.25	± 0.66	± 1.73	± 2.30	± 1.95	± 0.33	± 1.48	± 0.87
NO_3^-	12.8	9.22	11.3	1.89	3.14	2.52	9.44	6.92	8.27	2.61	4.42	3.50
	± 8.93	± 7.40	± 7.76	± 2.06	± 3.25	± 2.49	± 7.00	± 5.17	± 5.55	± 1.90	± 3.52	± 2.49
PO_4^{3-}	3.04	3.09	3.04	0.77	0.42	0.60	0.40	0.37	0.40	3.32	2.76	3.07
	± 1.89	± 1.83	± 1.66	± 1.42	± 0.98	± 1.10	± 0.35	± 0.60	± 0.51	± 1.17	± 0.90	± 0.77
SO_4^{2-}	14.7	12.2	13.8	11.6	9.33	10.5	13.1	11.1	12.3	11.2	9.75	10.5
	± 7.25	± 6.33	± 6.51	± 5.29	± 4.08	± 4.17	± 6.99	± 5.79	± 5.88	± 4.69	± 2.79	± 3.39
SIA ^a	36.1	28.5	33.1	16.0	15.3	15.7	29.8	24.3	27.4	16.6	17.8	17.2
	± 20.7	± 18.0	± 18.5	± 7.76	± 6.61	± 6.56	± 17.1	± 13.7	± 14.3	± 6.88	± 6.18	± 6.29
SIA% ^b	0.74	0.68	0.72	0.83	0.84	0.84	0.84	0.76	0.80	0.66	0.66	0.65
	± 0.13	± 0.15	± 0.12	± 0.06	± 0.08	± 0.06	± 0.07	± 0.12	± 0.10	± 0.10	± 0.12	± 0.10
K^+/EC	0.27	0.26	0.25	0.21	0.24	0.22	0.29	0.31	0.28	0.22	0.21	0.20
	± 0.12	± 0.14	± 0.09	± 0.08	± 0.12	± 0.08	± 0.13	± 0.15	± 0.10	± 0.08	± 0.08	± 0.05
Cl^-/Na^+	2.17	2.36	1.97	0.42	1.12	0.68	5.47	10.5	7.31	0.18	0.87	0.54
	± 1.92	± 2.31	± 1.42	± 0.64	± 1.03	± 0.50	± 4.78	± 9.28	± 5.34	± 0.12	± 0.52	± 0.32
$[\text{NH}_4^+]/[\text{SO}_4^{2-}]$	2.94	2.90	2.95	1.17	1.77	1.47	2.99	2.89	2.94	1.29	2.00	1.62
	± 0.80	± 0.97	± 0.86	± 0.74	± 0.61	± 0.53	± 0.75	± 0.88	± 0.70	± 0.58	± 0.18	± 0.70
$[\text{H}^+]_{\text{in-situ}}$	9.63	6.60	7.92	51.7	32.7	42.2	5.57	5.03	5.30	45.6	27.5	37.0
	± 7.26	± 7.61	± 6.99	± 46.2	± 30.2	± 27.8	± 5.25	± 6.61	± 4.26	± 53.0	± 31.4	± 29.0

^a SIA: secondary ionic species, sum of NH_4^+ , NO_3^- , SO_4^{2-} ^b SIA%: SIA percent of total ions

Different diurnal patterns of carbonaceous species were observed at the two sites (Table 1, Figure 2). No significant day-to-night difference was observed in winter at both sites because of the complex sources, while more pronounced diurnal variation appeared in summer at site B where industries were dominated by e-waste activities.

3.4. Distribution of water soluble ions

Concentrations and diurnal variations of major ions are shown in Table 1 and Figure 2. At both sites, major anions were SO_4^{2-} , NO_3^- and Cl^- , while dominant cations were NH_4^+ , Na^+ , K^+ and Ca^{2+} , among which secondary ionic aerosols (SIA: sum of NH_4^+ , SO_4^{2-} and NO_3^-) were the most abundant, making up 65%–84% of total ions at the two sites. SIA exhibited different variation patterns in the two seasons, which might be associated with the differences in the acidity of particles in the different sampling periods. The in-situ acidity ($[\text{H}^+]_{\text{in-situ}}$) in $\text{PM}_{2.5}$ was estimated using the E-AIM model (E-AIM, 1998) and is given in Table 1. As we can see, average acidity in both sites were significantly higher in summer, with the value of 42.2 nmol m^{-3} at site A and 37.0 nmol m^{-3} at site B respectively and was about 7 times higher than that in winter.

As shown in Figure 3, sulfate and nitrate equivalents in winter samples were almost fully balanced by ammonium, but were not fully neutralized in the summer samples. Considering $[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$ as ammonium-rich (AR) and $[\text{NH}_4^+]/[\text{SO}_4^{2-}] \leq 1.5$ as ammonium-poor (AP) (Pathak et al., 2004), the site A and site B samples were almost all ammonium-rich in winter, whereas the summer samples were ammonium-poor during the daytime but ammonium-rich in the night. In AR samples, high nitrate concentrations were observed. Excess NH_3 that doesn't react with sulfate can lead to the formation of ammonium nitrate (NH_4NO_3) (Shon et al., 2012), resulting in the co-varying of NH_4^+ and NO_3^- in winter ($r=0.97$ and 0.94 at sites A and B respectively). In AP samples in summer, due to relative lacking of NH_4^+ (concentration of NH_4^+ decreased while that of SO_4^{2-} increased in the daytime), neutralization of sulfate is favored over the formation of ammonium nitrate (Pathak et al., 2003), thus lower correlations between NH_4^+ and NO_3^- was found ($r=0.70$ and 0.66 at sites A and B respectively).

The average concentrations of sulfate showed an increase of about 15% in daytime samples in both seasons at both sites. Sulfate is formed by photochemical and heterogeneous reactions of its precursor gas SO_2 (Guo et al., 2011; Deshmukh et al., 2012). Unlike nitrate, sulfate is less ammonium dependent, and the

stability of ammonium sulfate makes it less vulnerable to the temperature changes. A higher abundance of SO_4^{2-} in daytime aerosols could be explained by enhanced local emission and increased photochemical reactions in the daytime (Ziemba et al., 2007; Kundu et al., 2010).

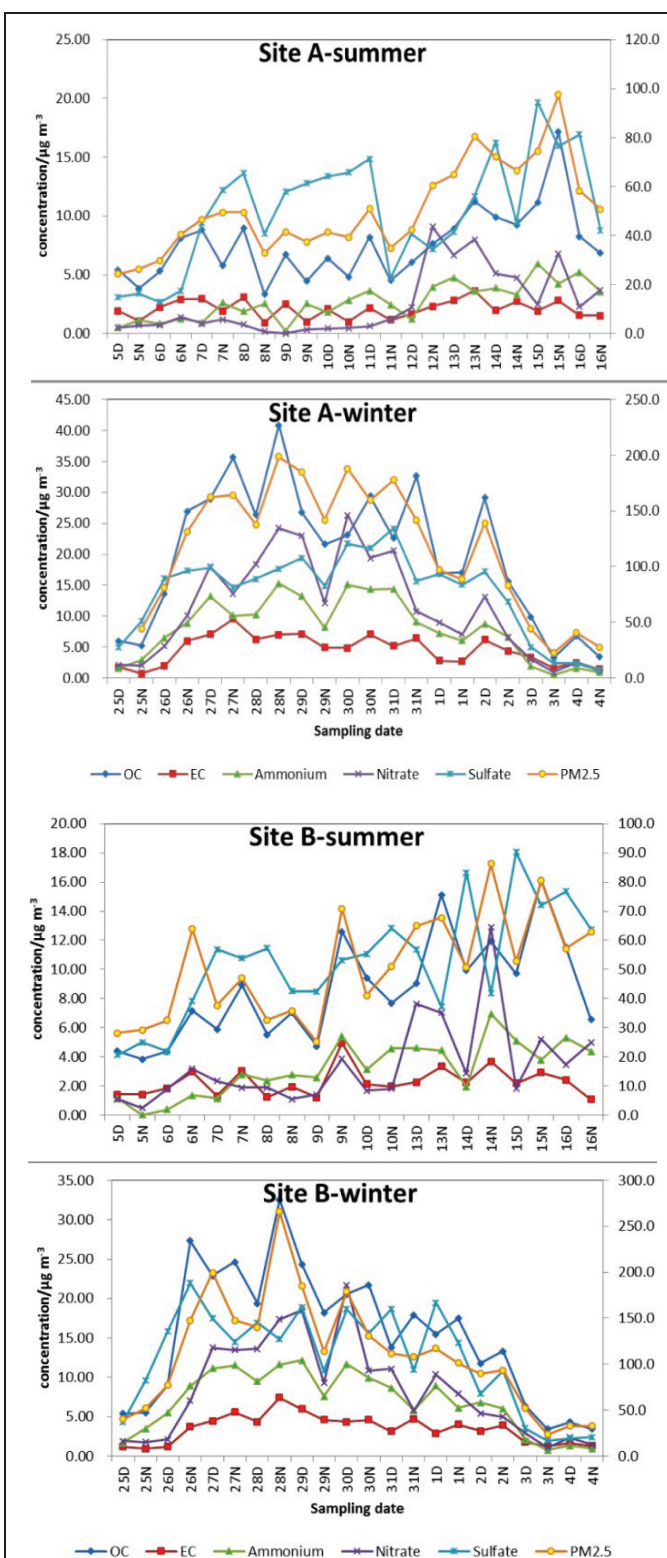


Figure 2. Diurnal variations of selected major species during summer and winter at the two sampling sites: the right Y-axis stands for the concentration of $\text{PM}_{2.5}$ mass; "D" represents daytime samples and "N" represents nighttime samples.

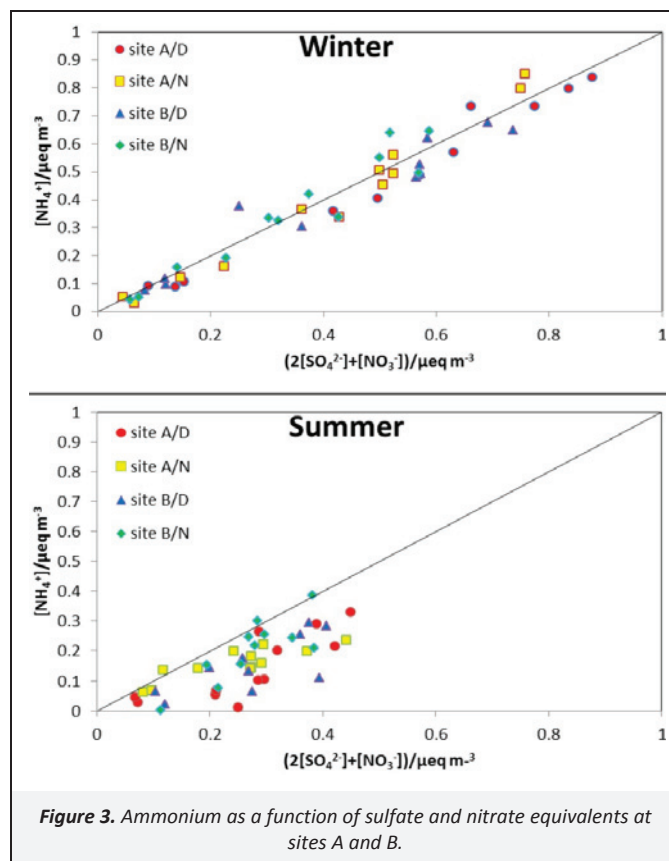


Figure 3. Ammonium as a function of sulfate and nitrate equivalents at sites A and B.

Both NH_4^+ and NO_3^- concentrations were found to be significantly higher in the nighttime of summer. NH_4^+ and NO_3^- are not thermally stable in summer. In the daytime, they suffer from large evaporation losses under higher temperatures (Kundu et al., 2010; Li et al., 2011; Ram and Sarin, 2011). Also, heterogeneous formation of NO_3^- via hydrolysis of N_2O_5 under high humidity conditions might contribute to higher concentration of NO_3^- at night. However, the two ions were observed to be more abundant in the daytime of winter. NH_4^+ in aerosol is produced from the reaction between NH_3 and acidic species (H_2SO_4 , HNO_3 etc.) present in gas or particle-phase (Kundu et al., 2010), so elevation of either NH_3 or acidic species may contribute to the NH_4^+ concentration. Trebs et al., (2004) studied the diel variation of trace gases and found that both NH_3 and HNO_3 reached their peaks in the daytime, which was due to the increase of air temperature after sunrise causing re-evaporation of deposited gases from wet surfaces. This may interpret the higher values in daytime samples of winter.

3.5. Variation of elemental compositions

Diurnal and average concentrations of measured elements are displayed in Table S4. In this study, only winter results were obtained. Crustal elements Al, Ca, K, Na, Mg and Fe were the most abundant, taking up 89% and 82% of all the elements measured at sites A and B, followed by elements related to anthropogenic activities such as Cu, Zn and Pb.

Although diurnal variation was not statistically significant for elements in both sites, elevated concentration at daytime was found for most elements at site A, this may be due to more vehicle emission and dust resuspension. At site B, crustal elements such as Al, Ca and Mg also showed the same trend, but other non-crustal elements only showed slight differences between day and night. It is worthy to note that elements related to e-waste recycling such as Cu and Pb were almost twice in the night as much as in the day, the increment was much higher than other elements, which might be attributed to more e-waste burning activities in the night.

Table 2. Average source contribution (both in percentage (%) and mass ($\mu\text{g m}^{-3}$) form) estimated to $\text{PM}_{2.5}$ in the two sites

Major chemicals	Source	Contribution, % ($\mu\text{g m}^{-3}$)	
		Site A	Site B
		PMF results	
NO_3^- , NH_4^+ , SO_4^{2-}	Secondary formation	35.6 (40.6)	42.6 (46.2)
EC, K^+ , Cl^-	Biomass burning	14.3 (16.3)	16.5 (17.9)
Al, Ca, Mg, Na, Ti	Crustal	10.2 (11.6)	6.1 (6.6)
Cd, Pb, SO_4^{2-}	Coal combustion	12.7 (14.5)	14 (15.2)
Cr, Co, Ni	Regional industrial	12 (13.7)	14.5 (15.7)
Zn, Mo	Traffic exhaust	13.7 (15.6)	
Na^+ , PO_4^{3-}	Dust re-suspending	1.4 (1.6)	
Cu	e-waste		6.4 (6.9)

Table S5 (see the SM) compares concentrations of highly enriched elements with other sites in Asia. The results showed that concentration of Cu at site B was significantly higher than other sites, even another notorious e-waste site Guiyu in which Cr was the highest (Deng et al., 2006). Other elements at both sites were higher than those Asian cities but comparable with or even lower than Chinese metropolitan cities such as Shanghai and Guangzhou (Ye et al., 2003; Wang et al., 2006).

3.6. Source appointment of $\text{PM}_{2.5}$

In order to quantitate the contribution of each source, PCA was first employed to estimate the possible number of sources and PMF was then employed successively for their distribution. Detailed source profiles are presented in the SM.

At site A, 7 factors were characterized. Factor 1 with high loadings of SIA was defined as secondary formation factor. Factor 2 was heavily loaded by EC, K^+ and Cl^- . EC, K^+ and Cl^- are possibly emitted during biomass burning process, so factor 2 represented biomass burning. Factor 3 which was dominated by Al, Ca, Mg, Ti undoubtedly represented crustal origin. Factor 4 contained high Cd, Pb and SO_4^{2-} , these species are good tracers of coke and coal combustion (Alleman et al., 2010; Chakraborty and Gupta, 2010), so this factor could be explained as coal combustion factor. Factor 5 was heavily loaded by Cr, Co and Ni. These elements are probably related to anthropogenic activities such as non-ferrous metal industries, chromium plating or fertilizer use (Hueglin et al., 2005; Wang et al., 2006), so factor 5 indicated regional industrial pollution. Factor 6 was highly loaded with Zn and Mo. Mo and Zn are likely associated with vehicle exhausts, such as additives in lubricant oil (Na and Cocker III, 2009), or wearing out of rubber tires on roads (Hao et al., 2007; Chakraborty and Gupta, 2010), so factor 6 could be a traffic factor. Factor 7 with high loadings of Na^+ and PO_4^{3-} is possibly related to the dust re-suspending. At site B, except for secondary formation, biomass burning, crustal, coal combustion and regional industrial sources, one more factor with high loadings of Cu was identified, which might be an e-waste factor.

Table 2 displays source contributions at the two sites estimated by PMF model and the simulated source profile for sites A and B is shown in Figures S3 and S4. From the simulated results, it's clear that both sites were significantly influenced by the same factors like secondary formation, biomass burning, regional industry, coal combustion and dust, which was 35.6%, 14.3%, 12%, 12.7% and 10.2% at site A and 42.6%, 16.5%, 14.5%, 14% and 6.1% at site B, respectively. In the industry complex area (site A), traffic also played an important role, which contributed 13.7% to the $\text{PM}_{2.5}$ mass, while at the e-waste site (site B), Cu emission through the metal recovery process was distinct.

Several other approaches were applied for further confirming of specific sources, e.g., K^+/EC ratios and enrichment factor (EF) analysis (for detailed results please refer to the SM). The results

confirmed that at both sites, anthropogenic activities bear great responsibility for the air pollution.

4. Conclusions

Day and night-time $\text{PM}_{2.5}$ samples were collected at an industrial complex site and an e-waste recycling site in Qingyuan city, China were analyzed for carbonaceous species, water soluble ionic species and elements. The reconstructed chemical composition based on the average concentrations of $\text{PM}_{2.5}$ in winter revealed that the major components in the two sites were organic matter and SIA. Carbonaceous species and most of ions especially for SIA showed significant seasonal variation and notable diurnal variation. Source characterization using PMF model revealed that both sites were significantly influenced by the same factors like secondary formation, biomass burning, regional industry, coal combustion and dust. Moreover, at site A, traffic source was also important, while at site B, Cu pollution acted as a distinctive e-waste feature.

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Supporting Material Available

Detailed information on the effect of meteorological conditions, Principle component analysis, Positive matrix factorization analysis, Enrichment factor analysis, K^+/EC ratios, Location of the two sampling sites (Figure S1), Enrichment factors of elements in $\text{PM}_{2.5}$ samples at the two sampling sites (Figure S2), Source profile (% of species) of $\text{PM}_{2.5}$ at site A (Figure S3), Source profile (% of species) of $\text{PM}_{2.5}$ at site B (Figure S4), Ambient parameters during the two sampling periods (Table S1), Pearson correlation analyses of major species with ambient parameters (Table S2), The statistical significance tested using non-parametric Mann-Whitney U for the diurnal and seasonal variation of major chemical species as well as the difference between site A and B (Table S3), Average concentrations (ng m^{-3}) of major elements in $\text{PM}_{2.5}$ samples at the two sampling sites (Table S4), Comparison of atmospheric concentrations of heavy metals (ng m^{-3}) in $\text{PM}_{2.5}$ between Qingyuan and other sites in Asia (Table S5). This information is available free of charge via Internet at <http://www.atmospolres.com>.

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