

# Characterizing PM<sub>2.5</sub> Pollution of a Subtropical Metropolitan Area in China

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## ABSTRACT

The chemical and physical characteristics of PM<sub>2.5</sub>, especially their temporal and geographical variations, have been explored in metropolitan Hangzhou area (China) by a field campaign from September 2010 to July 2011. Annual average concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> during non-raining days were 106 - 131  $\mu\text{g}\cdot\text{m}^{-3}$  and 127 - 158  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively, at three stations in urban breathing zones, while corresponding concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> at an urban background station (16 m above ground level in a park) were 78 and 104  $\mu\text{g}\cdot\text{m}^{-3}$ , respectively. For comparison, the annual average PM<sub>10</sub> concentration at a suburban station (5 m AGL) was 93  $\mu\text{g}\cdot\text{m}^{-3}$ . Detailed chemical analyses were also conducted for all samples collected during the campaign. We found that toxic metals (Cd, As, Pb, Zn, Mo, Cu, Hg) were highly enriched in the breathing zones due to anthropogenic activities, while soluble ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) and total carbon accounted for majority of PM<sub>2.5</sub> mass. Unlike most areas in China where sulfate was several times of nitrate in fine PM, nitrate was as important as sulfate and highly correlated with ammonium during the campaign. Thus, a historical shift from sulfate-dominant fine PM to nitrate-dominant fine PM was documented.

**Keywords:** PM Pollution; PM<sub>2.5</sub> Composition; Breathing Zone; Air Pollution Measurements; Personal Exposure

## 1. Introduction

PM<sub>2.5</sub> is an important air pollutant. Due to its relatively long suspension time in the air and special optical properties, PM<sub>2.5</sub> is responsible for the formation of regional haze [1-3]. Depending on its position in the air, PM<sub>2.5</sub> may be responsible for warming or cooling of surface [4]. When inhaled, PM<sub>2.5</sub> may cause severe health problems, such as asthma, lung cancer, and heart disease [5-10], though the exact component of PM<sub>2.5</sub> responsible for certain adverse health effect is uncertain [8,9].

To protect the public from PM<sub>2.5</sub> pollution, significant efforts have been conducted worldwide [11-15]. For example, US EPA has started to regulate ambient PM<sub>2.5</sub> pollution since 1998, and recently tightened its ambient air quality standards for 24-hour and annual averages to 35 and 15  $\mu\text{g}\cdot\text{m}^{-3}$  [16], respectively. As PM<sub>2.5</sub> pollution started to draw public attention in China, China Ministry of Environmental Protection recently released its first ambient air quality standard for PM<sub>2.5</sub>, to be effective in 2016; the standard sets the same PM<sub>2.5</sub> limits for recreational areas as US EPA, but allows non-recreational areas to have higher limits, namely, 70 and 35  $\mu\text{g}\cdot\text{m}^{-3}$  for 24-h

and annual averages, respectively.

While intensive field campaigns have been carried out in China and elsewhere [17-20], the temporal and geographical variations of PM<sub>2.5</sub> in urban breathing zones (0.5 - 2 m above ground) in China remain poorly documented. To obtain such detailed information about PM<sub>2.5</sub> pollution, an extensive field campaign was conducted in metropolitan Hangzhou area (HZ), China, during September 2010-July 2011. HZ is experiencing both fast urbanization and growing environmental issues: as of 2010, the population of HZ ranked sixth in China, and the population density was 1214/km<sup>2</sup>. The goals of this campaign were: 1) to determine the pollution level of PM<sub>2.5</sub> in the breathing zone of urban air; 2) to investigate chemical and physical characteristics of PM<sub>2.5</sub> pollution; 3) to identify areas for further research before next field campaign. Section 2 will describe experimental methods of the campaign, and Section 3 will present major findings. A summary will be presented in Section 4.

## 2. Experimental Methods

The sampling, analysis, and quality assurance procedures are described below.

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## 2.1. Sampling

### 2.1.1. Sites

HZ is situated in a subtropical area with distinct seasonal weather conditions, and is 50-km away from the western rim of the Pacific Ocean. As HZ is a traditional hotspot for national and international tourists, there are two automatic monitoring stations (“A” and “B”, **Table 1**) running since 2005 for PM<sub>2.5</sub> as well as other air pollutants, independent of this campaign: one (“A”) represents suburban recreational conditions, and the other (“B”) represents urban mixed conditions. Sampling inlets were at 5 m (“A”) and 16 m (“B”) above ground level (AGL) at the automatic stations. For this campaign, four additional stations were chosen to represent breathing zone conditions in various urban areas, namely, nearby highway (“C”), a college gate (“D”), a business area with peak hours (“E”), and a business area without peak hours but with dense population (“F”). At these special stations, sampling inlets were at 1 - 1.5 m AGL. **Figure 1** shows the sampling sites for this campaign.

### 2.1.2. Duration

Sampling was conducted at all stations from September 2010 to July 2011. During the sampling period, seasonal average temperatures in the area were 21°C for fall (September-November 2010), 6.9°C for winter (December 2010-February 2011), 16°C for spring (March-May 2011), and 29°C for summer (June-August 2011). As it was raining frequently in the sampling region, PM<sub>2.5</sub> samples were only collected at sites “A”-“E” concurrently during

non-raining days. On each sampling day, samples were collected for 18 - 24 hours; in each season, 7 - 10 days were selected for concurrent sampling. In addition, PM<sub>2.5</sub> samples were also collected at sites “B” and “F” during January-June 2008.

### 2.1.3. Samplers

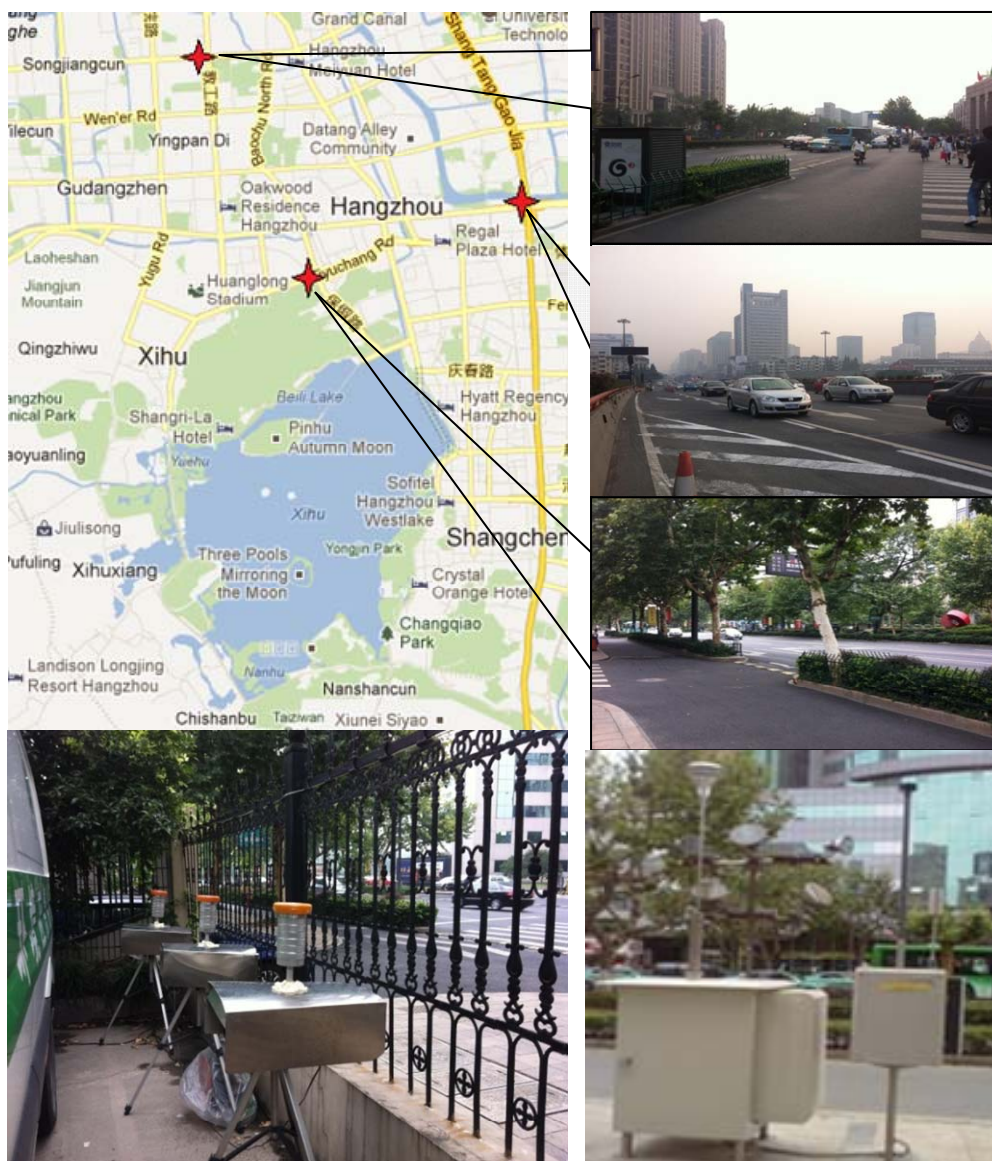
At sites “A”, “B”, “F”, air pollutants were continuously measured for PM<sub>2.5</sub>, O<sub>3</sub>, CO, NO<sub>2</sub>, CH<sub>4</sub>, and NMHC, using automatic monitoring equipment (Air Point, Austria; DURAG, Germany; SYNSPEC, Holland). At sites specially selected for this campaign, PM<sub>2.5</sub> samplers were the model TH-150C, manufactured by Wuhan Tianhong Instruments Co., Ltd. The operational volume flow rate for PM<sub>2.5</sub> samplers was set at 100 L·min<sup>-1</sup>, and the size cut was at 2.5 μm. At each site, three samplers were used to collect three concurrent PM<sub>2.5</sub> samples for analyzing inorganic elements, soluble ions, and carbon items, respectively. For inorganic elemental analysis, PTEF organic filters (Sumitomo Electric Fine Polymer, Inc.) were used. For organic analyses, quartz filters (Whatman 1851047) were used. The pore size was 0.3 μm for both types of filters, and the collection efficiency at 0.15 μm was 99.97% for organic filters and 99% for quartz filters.

## 2.2. Analyses

The bulk masses of PM<sub>2.5</sub> samples were weighed with a balance (0.0001 accuracy), and the speciation was conducted for 25 inorganic elements, 9 ions, and 3 carbon items. Details are elaborated below.

**Table 1. PM concentration in a subtropical metropolitan area (HZ, CHINA).**

Monitoring sites	Period	Mass concentration(μg/m <sup>3</sup> )		PM <sub>2.5</sub> /PM <sub>10</sub>
		PM <sub>10</sub>	PM <sub>2.5</sub>	
C: nearby highway (1 - 1.5 m AGL)	Winter	185.2	164.4	0.888
	Spring	157.3	138.3	0.879
	Summer	111.6	97.6	0.875
	Autumn	177.6	122.0	0.687
	All Seasons	157.9	130.6	0.827
D: college gate (1 - 1.5 m AGL)	Winter	149.9	119.6	0.798
	Spring	94.7	86.6	0.914
	Summer	87.3	77.8	0.891
	Autumn	191.2	140.3	0.734
E: business area with peak hours (1 - 1.5 m AGL)	All Seasons	130.8	106.1	0.811
	Winter	121.0	100.2	0.828
	Spring	122.4	107.2	0.876
	Summer	113.2	87.7	0.775
B: urban mixed conditions (16 m AGL)	Autumn	149.4	134.9	0.903
	All Seasons	126.5	107.5	0.850
	All Seasons	104	77.5	0.745
A: suburban recreational conditions (5 m AGL)	All Seasons	93	/	/



**Figure 1. Monitoring stations and sampling setup. The distributions of the sampling locations are marked with red stars in the Google map.**

### 2.2.1. Inorganic Elements

After sampling, organic filters loaded with  $PM_{2.5}$  were carefully cut along the inner rim and put into a 50 ml microwave digestion tank. 6 ml  $HNO_3$  and 2 ml  $H_2O_2$  were then added into the tank to dissolve  $PM_{2.5}$  at pre-designed procedures. Then, the bulk solution was moved into a 50 mL flask. High-purity water was used to fix the volume and for mixing well. Finally, the solution was used for instrumental analyses.

Instrumental analyses were conducted by Inductively Coupled Plasma (ICP, Optima 7300DV) emission spectrometers for elements (Li, V, Cr, Co, Ni, Cd), by Atomic Fluorescent Spectrometers (AFS-9230) for elements (Hg, As, Se), and by ICP-Mass Spectrometers (MS, X Series 2) for elements (Al, Ba, Ca, Cu, Fe, K, Mg, Mn,

Mo, Na, P, Pb, S, Si, Ti, Zn).

For the AFS analysis, sample solutions were first heated in acidic media to convert all mercury into  $Hg^{2+}$ , and  $Hg^{2+}$  was then reduced by  $KBH_4$  to form Hg vapor that was drawn into AFS for detection. As and Se were detected similarly.

### 2.2.2. Soluble Ions

After sampling, a piece of organic filters loaded with  $PM_{2.5}$  were put into a 25-ml colorimetric tube. Then, 20.00-ml deionized water was added to and bubbles expelled from the tube. The tube was placed in a supersonic cleaner running for 20 minutes. After still for a while, clear solution in top layer was drawn and filtered before being analyzed by Ion Chromatography for water-soluble

anions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ; Dionex IC DX600) and cations ( $NH_4^+$ ,  $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ; Dionex ICS-90).

### 2.2.3. Carbon Analysis

After sampling, quartz filters loaded with  $PM_{2.5}$  were put on new and clean aluminum foil, and a representative piece was obtained carefully. A second piece with the same area was obtained and processed as follows to remove carbonate. First, the second piece was merged in concentrated HCl solution in a covered container. Then, the container was placed in a ventilator cabinet for about an hour to remove carbonate in the form of  $CO_2$  and for another hour to let remaining HCl evaporate. The sample was then kept at low temperature and saved for subsequent analyses.

The organic, elemental, and total carbon contents of  $PM_{2.5}$  samples were determined with a thermo-photometric carbon analyzer (DRI Model 2001A). A piece of processed sample filter ( $0.495\text{ cm}^2$ ) was put in an environment with pure He gas without  $O_2$ , and was heated progressively at  $120^\circ\text{C}$ ,  $250^\circ\text{C}$ ,  $450^\circ\text{C}$ , and  $550^\circ\text{C}$  first to determine organic carbon contents OC1, OC2, OC3, and OC4, respectively. Then, in an environment with 2%  $O_2$  and 98% He, the sample was further heated progressively at  $550^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $800^\circ\text{C}$  to determine elemental carbon contents EC1, EC2, and EC3. The  $CO_2$  produced within each temperature ladder was reduced into  $CH_4$ , catalyzed by  $MnO_2$ , for being detected with Fire Ionization Detectors. During heating processes, part of organic carbon was converted into black carbon, which hindered clear distinction between organic carbon and elemental carbon. Hence, the reflection intensity of the He-Ne laser light at 633 nm by a monitoring filter was used to gauge the starting temperature of the oxidation of elemental carbon, to ensure science-based distinction between organic carbon and elemental carbon.

## 2.3. QA/QC Procedures

### 2.3.1. Sampling

All sampling instruments used for this study were calibrated by the Technology Supervision Bureau of Zhejiang Province within valid periods. Before each sampling, pump volumes of  $PM_{2.5}$  samplers were calibrated, and so were sampling volumes of other instruments. During filter sampling, a specialist was responsible for checking conditions of volume-flow meters of sampling pumps, and the project manager randomly checked conditions of flow meters at a frequency. Records were made to ensure the precision of sampling volumes and subsequent calculations of pollutant concentrations. No sample was collected in raining weather, and filter samples were ensured to conserve particulate matter during transportation.

### 2.3.2. Weighing

Before and after sampling, organic filters were baked at  $60^\circ\text{C} \pm 2^\circ\text{C}$  for 8 hours and blank quartz filters were baked at  $500^\circ\text{C}$  for 4 hours. Then, filters were put in dryers for at least 48 hours before weighing. This procedure is expected to remove the disturbance of water, and to provide weighting results comparable with other studies though some compounds such as ammonium nitrate may evaporate if original samples were collected at relatively humid condition, e.g., when relative humidity was over 80%. During weighing, samples were put into glass agar plates and covered to avoid the effect of static electricity.

### 2.3.3. Elemental Analyses

Each container used for this study was cleaned first, and then washed with warm, 10%  $HNO_3$ . Then, the container was rinsed with tap water. Finally, the container was rinsed repeatedly with deionized water (Mill-Q,  $>18.2\text{ M}\Omega\cdot\text{cm}$  at  $25^\circ\text{C}$ ), in order to reduce blank background. For each batch of samples, at least three blank samples were analyzed to determine blank background value. During sample analyses, a standard sample was added for every 10 - 15 samples, to check instrumental stability. When an element showed abnormally high content, analysis was stopped and the inlet system was rinsed with 2%  $HNO_3$ . Then, standard solutions were used to calibrate instruments, and samples were diluted before subsequent analyses.

### 2.3.4. Ionic Analyses

Glass containers were cleaned, and soaked in deionized water for over 24 hours. Then, containers were cleaned with supersonic waves for 30 minutes. Blank background was determined in the same way as for elemental analyses, and so was the use of standard samples.

### 2.3.5. Carbon Analysis

At the beginning and the end of each day when samples were analyzed,  $CH_4/CO_2$  standard gases were used to calibrate instruments. For every 10 samples, one was randomly chosen for parallel analysis. Two standard samples were analyzed every two weeks. Compared with DRI (USA) instruments which have the same model or use different methods [21-28], the detection precision was  $<5\%$  for TC and  $<10\%$  for OC and EC in this study.

## 3. Results and Discussions

PM mass concentrations and  $PM_{2.5}$  compositions are presented below.

### 3.1. Mass Concentration

**Table 1** lists average PM concentrations in the metropolitan breathing zones, at an urban background station,

and at a suburban background station during this campaign. It is shown that the average PM<sub>2.5</sub> concentration in the breathing zone ranged from 106 to 131  $\mu\text{g}\cdot\text{m}^{-3}$  annually and from 78 to 164  $\mu\text{g}\cdot\text{m}^{-3}$  seasonally, with peak values nearby highway in winter and in business areas in fall. PM<sub>2.5</sub> accounted for 81% - 85% of PM<sub>10</sub> annually and 69% - 91% of PM<sub>10</sub> seasonally. Concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> at the metropolitan background station (16 m AGL in a park) were lower than in the breathing zones by (27 - 41)% and (18 - 34)%, respectively. The concentration of PM with diameters between 2.5 - 10  $\mu\text{m}$  was  $\sim 25 \mu\text{g}\cdot\text{m}^{-3}$  in urban stations during the campaign.

### 3.2. Elemental Composition

**Table 2** lists concentrations of 25 elements detected in PM<sub>2.5</sub> samples collected in the breathing zones during the campaign. A number of metals, including toxic heavy metals (Hg, Cd, Cr, Pb, As), were detected, and Fe showed the highest concentration of 2.1  $\mu\text{g}\cdot\text{m}^{-3}$  on seasonal average basis. Sulfur concentration ranged 3.0 - 9.7  $\mu\text{g}\cdot\text{m}^{-3}$  seasonally, corresponding to 9 - 29  $\mu\text{g}\cdot\text{sulfate}\cdot\text{m}^{-3}$  if all sulfur element existed as sulfate in PM<sub>2.5</sub>. Total concentration of non-sulfur elements ranged 2.6 - 11  $\mu\text{g}\cdot\text{m}^{-3}$  seasonally. Together, elemental concentrations accounted for 7.5 - 18  $\mu\text{g}\cdot\text{m}^{-3}$ , or 9% - 23%, of PM<sub>2.5</sub> concentration seasonally while oxygen, nitrogen, and carbon elements were excluded.

**Table 3** lists average enrichment factors (EF) of 25 elements during the campaign. It is shown that the EF value exceeded 1000 for (Cd, Se, S, Mo, Zn), and exceeded 100 for (Pb, Cu, As) in this campaign, while an EF value larger than 10 suggests that the element is an-

thropogenic [29]. Compared with 5 years ago, the EF value decreased for (S, Mo, Zn) and especially for (Se, As), which indicate the decrease in coal-related emissions; meanwhile, the EF value increased for (Pb, Cu, Mn, Fe, V), which suggests the increase in vehicle emissions.

### 3.3. Ionic Composition

Nine detected soluble ions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ;  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) contributed an average of 42  $\mu\text{g}\cdot\text{m}^{-3}$  to PM<sub>2.5</sub> concentration measured in breathing zones during this study, and three major ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) accounted for 85% of total ionic mass. On seasonal average basis, concentrations of soluble ions ranged 10 - 86  $\mu\text{g}\cdot\text{m}^{-3}$  while the three major ions accounted for 9 - 74  $\mu\text{g}\cdot\text{m}^{-3}$  with maximum occurred in winter and minimum in summer. Sulfate concentration ranged from 5.6 to 21  $\mu\text{g}\cdot\text{m}^{-3}$  seasonally.

**Figure 2** shows seasonal variations of ionic concentrations in the breathing zones during the campaign. All ions showed the lowest concentration in summer, and most ions peaked in winter. Ions ( $\text{SO}_4^{2-}$ ,  $\text{K}^+$ ,  $\text{F}^-$ ,  $\text{Mg}^{2+}$ ) showed high values in fall and winter, and  $\text{Ca}^{2+}$  peaked in spring. As major ions are secondary in origin and their formation time from corresponding precursors is long enough for regional transport to take place, one could argue that seasonal trends of ionic concentrations might reflect the fact that the study area was cleaner than surrounding regions in the nation, though local emissions and the absolute pollution level are also rather significant. This hypothesis was, however, not supported by further analyses using concurrently measured concentrations of

**Table 2. Concentrations of 25 elements ( $\mu\text{g}/\text{m}^3$ ) detected in PM<sub>2.5</sub> samples.**

Element	Winter	Spring	Summer	Autumn	Year	Element	Winter	Spring	Summer	Autumn	Year
Al	0.596	1.175	0.293	0.875	0.735	Mn	0.084	0.075	0.039	0.097	0.074
As	0.022	0.012	0.015	0.023	0.018	Mo	0.0028	0.0120	0.0064	0.0028	0.0060
Ba	0.058	0.058	0.036	0.047	0.050	Na	0.504	0.731	0.545	0.282	0.491
Ca	1.934	1.979	1.349	1.530	1.698	Ni	0.0051	0.0269	0.0055	0.0047	0.0105
Cd	0.006	0.0052	0.0032	0.0106	0.0061	P	0.018	0.022	0.018	0.043	0.025
Co	0.0006	0.0008	0.0003	0.0007	0.0006	Pb	0.186	0.127	0.109	0.194	0.154
Cr	0.0064	0.0086	0.0057	0.0053	0.0065	S	5.725	4.465	5.068	5.299	5.139
Cu	0.102	0.069	0.049	0.088	0.077	Se	0.0080	0.0047	0.0035	0.0099	0.0065
Fe	1.303	1.304	0.634	1.525	1.191	Si	0.610	0.5212	0.0000	1.270	0.6002
Hg	0.0001	0.0001	/	0.0003	0.0001	Ti	0.0216	0.0232	0.0054	0.022	0.0179
K	1.571	1.137	0.293	1.972	1.243	V	0.0060	0.0077	0.0054	0.0063	0.0063
Li	0.0017	0.0015	0.0010	0.0015	0.0015	Zn	0.495	0.471	0.343	0.689	0.499
Mg	0.255	0.184	0.096	0.202	0.184	Sum/					
Sum	13.5	12.4	8.9	14.2	12.2	PM <sub>2.5</sub> (%)	10.5	11.2	10.1	10.7	10.6

**Table 3. Enrichment factors of 24 elements in PM<sub>2.5</sub> samples.**

Element	Sites				Average of Hangzhou in 2006
	Highway	College Gate	Business Area with Peak Hours	Average	
As	361	683	543	529	1114
Ba	21.3	18.3	15.3	18.3	/
Ca	19.1	26.1	38.2	27.8	18.43
Cd	4746	7874	7959	6860	/
Co	8.6	12.8	8.7	10.0	/
Cr	17.3	28.7	16.8	20.9	42.84
Cu	441	710	611	588	574
Fe	5.5	6.6	5.5	5.9	3.15
Hg	92.3	221	182	165	/
K	7.8	13.8	9.7	10.4	9.13
Li	6.8	12.4	8.3	9.2	/
Mg	2.4	2.7	3.4	2.8	6.96
Mn	23.0	37.9	24.4	28.4	21.62
Mo	1960	2240	1000	1733	/
Na	2.7	5.1	4.2	4.0	6.66
Ni	104	55.1	38.6	65.8	79.65
P	4.9	5.2	4.2	4.7	21.51
Pb	693	1350	832	958	797
S	2794	3850	2710	3118	3332
Se	1994	5675	3545	3738	14496
Si	0.1	0.1	0.2	0.1	0.8
Ti	0.6	0.8	0.8	0.8	13.88
V	11.2	20.9	16.1	16.1	10.88
Zn	742	1608	944	1098	1242

(sulfate, SO<sub>2</sub>) and (nitrate, NO<sub>2</sub>) in this campaign. On molar basis, sulfate accounted for 10% - 30% of total sulfur in breathing zones, and nitrate accounted for 1% - 20% of total oxidized nitrogen during this study. Thus, seasonal variations of ionic concentrations may also result from changes in relative humidity near sampling sites during this campaign.

Also shown in **Figure 2** is the ratio of cation/anion in PM<sub>2.5</sub> samples. The ratio ranged 1.0 - 1.6 with the average of 1.2 in breathing zones, and was 1.1 at a routine automatic monitoring station. Thus, organic anions might be present significantly during the campaign.

As sulfate concentration was measured concurrently with the concentration of elemental sulfur in this study, a comparison between the two concentrations may offer unique insights into the existence of organic sulfur compounds. During this study, the average concentration of S was 5.14 µg·m<sup>-3</sup>, and that of sulfate 14.5 µg·m<sup>-3</sup>; thus, it is likely that organic sulfur concentration was minor (~0.3 µg·S·m<sup>-3</sup>) compared with inorganic sulfur.

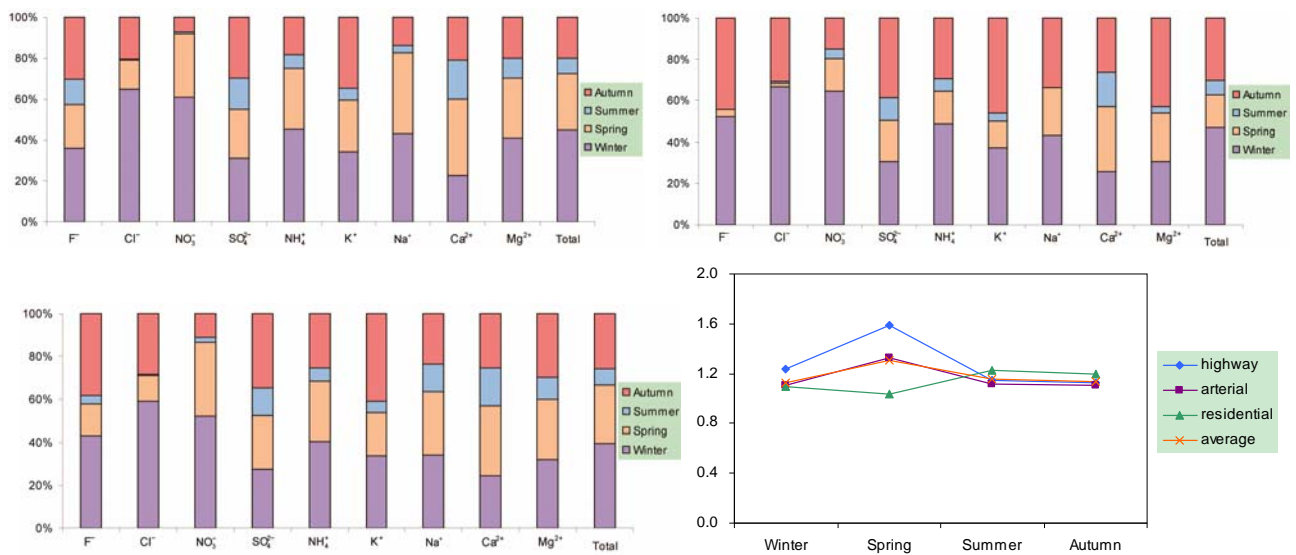
### 3.4. Carbon Distribution

Concentrations of total carbon (TC), organic carbon (OC), and elemental carbon (EC) in PM<sub>2.5</sub> were measured to be 32, 21, and 11 µg·m<sup>-3</sup>, respectively, during the campaign. Total carbon accounted for 28% of PM<sub>2.5</sub> concentration in the breathing zones.

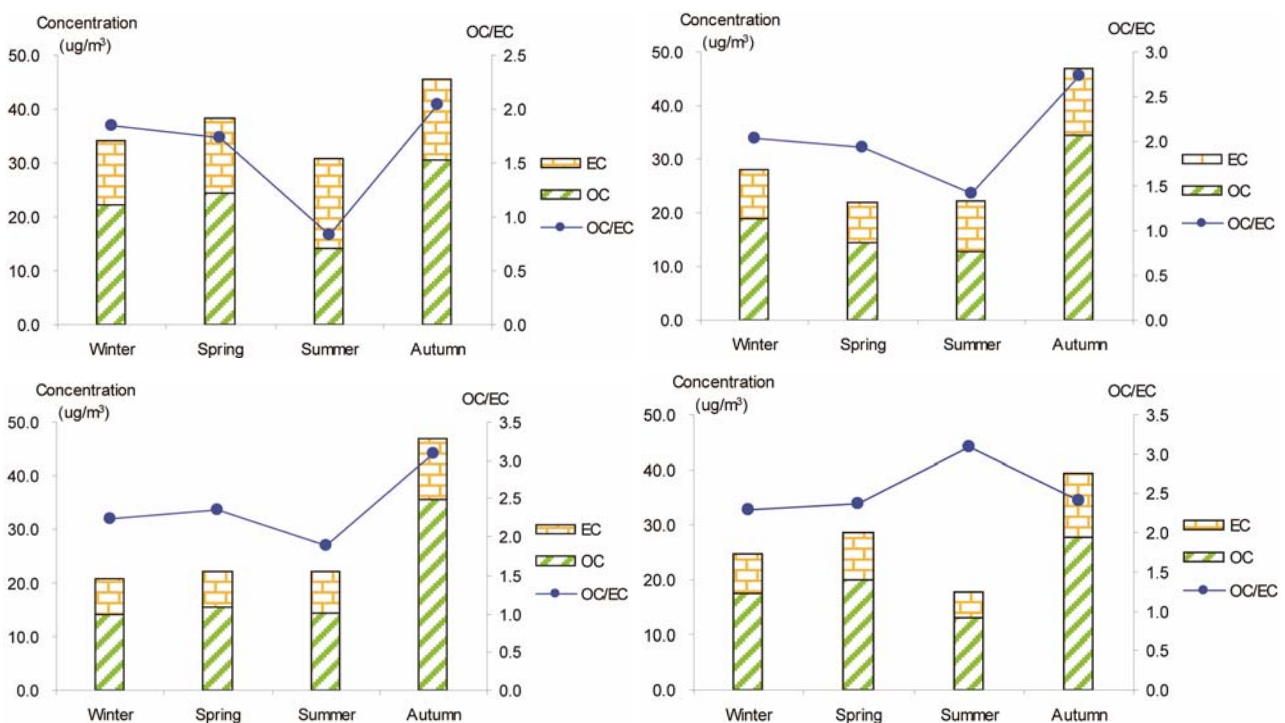
**Figure 3** shows seasonal concentrations of OC and EC in PM<sub>2.5</sub> and corresponding ratio of OC/EC at various stations. It is shown that seasonal TC and OC concentrations peaked in fall and showed minimal values in summer, while EC showed much smaller seasonality; thus, OC drove the seasonal trend of TC in the campaign. The seasonal ratio of OC/EC showed minimum value in summer, and peaked in fall in breathing zones. At the suburban background station (5 m AGL), the ratio of OC/EC peaked in summer while the TC concentration was the lowest.

The correlation between OC and EC concentrations is often used to determine whether they come from the





**Figure 2.** Seasonal variations of soluble ions in  $PM_{2.5}$  samples. Top left: highway; top right: arterial; bottom left: residential; bottom right: C/A ratios.



**Figure 3.** Seasonal average concentrations of OC and EC and their ratios in  $PM_{2.5}$  samples. Top left: arterial; top right: highway; bottom left: residential road, bottom right: residential areas.

same origin [30-32], as OC may be either produced by gas to particle conversion processes or directly emitted, while EC is usually directly emitted from fossil fuel combustion and biomass burning [33]. **Figure 4** shows seasonal scatterplots of OC versus EC measurements in breathing zones during the campaign. It is shown that OC and EC concentrations were highly correlated in winter ( $R^2 = 0.85$ , slope = 2.0) and spring ( $R^2 = 0.78$ , slope =

1.7). In summer and especially in fall, the OC concentration was poorly correlated with EC. In summer, data points split into two groups: one with a slope about 2, and the other with a slope about 0.5. In fall, data points may be bracketed by two lines with the ratio of OC/EC equals 2 and 4, respectively. The higher ratio of OC/EC was likely due to photochemical aging, and the lower ratio of OC/EC was likely due to fresh emissions or due

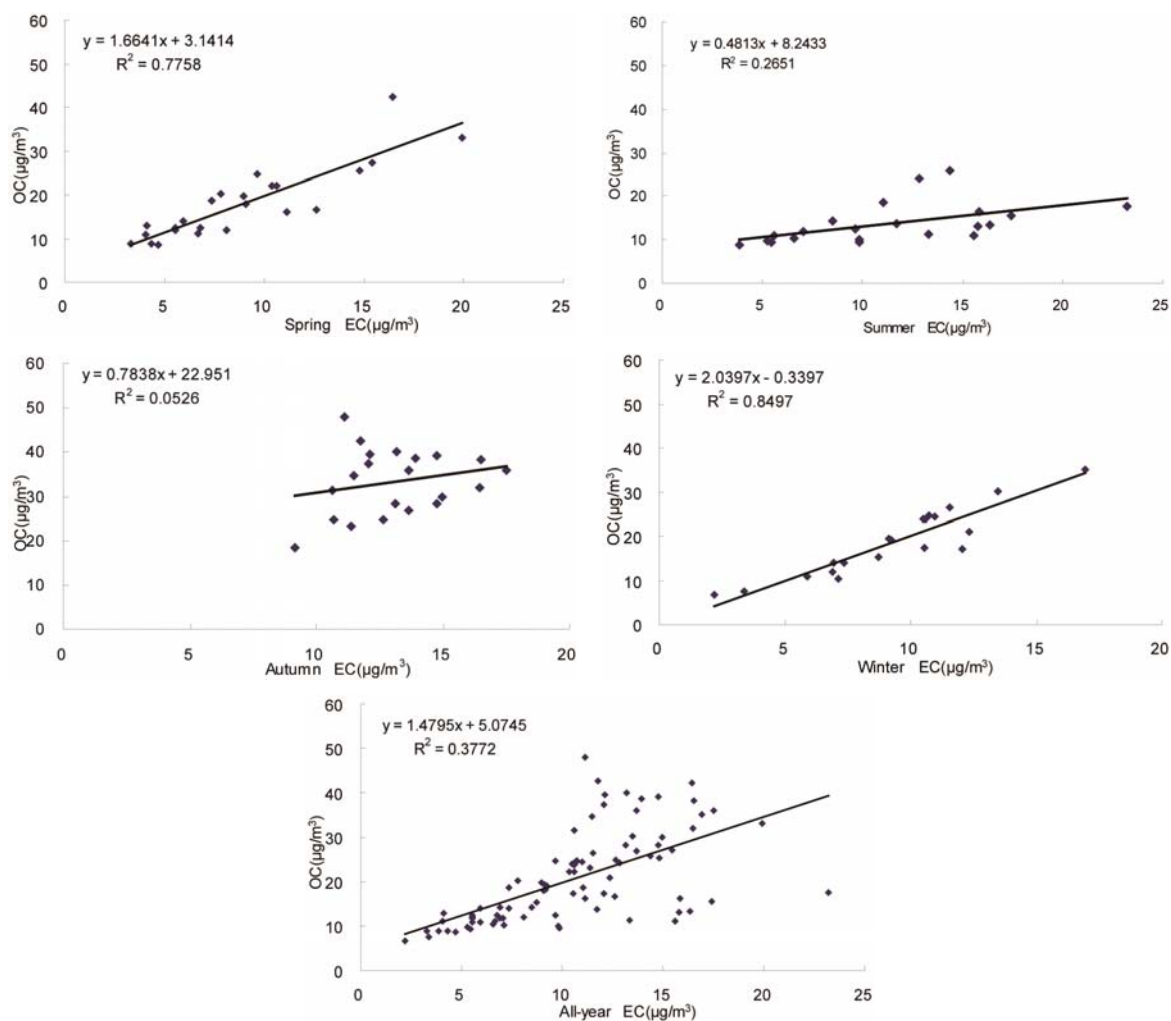


Figure 4. Scatter-plots of PM<sub>2.5</sub> OC and EC concentrations in four seasons.

to frequent rainfall that might remove more OC than EC from the air besides other factors.

Secondary organic aerosols are important for many scientific reasons, and consist of many compounds which are only partly identified [34]. Yu *et al.* [35] for the first time estimated the spatial distribution of secondary organic carbon (SOC) over USA in summer, 1999. During the study period, major sources of primary OC were agricultural burning, soil dust, paved road dust and non-road diesel, while major sources of EC were non-road diesel, on-road heavy-duty diesel vehicle, agricultural burning and jet fuel combustion in USA. They showed that, on seasonal scale, modeled ratio of primary (OC/EC) changed significantly at specific locations, with values ranging from 0.8 to 3.5 at stations due to various combinations of emission sources. Meanwhile, the contribution of SOC to total OC ranged 50% - 80% based on combined analyses of observational and modeled data. In a subsequent study employing US EPA CMAQ, simulated seasonal average ratio of primary (OC/EC) over various

regions of USA ranged from 2.0 to 3.6, and estimated that SOC contributed less to total OC in 2001 compared with that in 1999 [36,37].

While it is elegant to estimate SOC from modeled ratio of primary (OC/EC) and measured EC, using measured EC as a tracer for primary OC may provide a preliminary estimate for measured SOC, with all possible uncertainties embedded in field data [35]. Using empirical formula (F1) below, SOC may be estimated from OC, EC, and the minimum ratio of OC/EC during a period.

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC}/\text{EC})_{\min} \quad (\text{F1})$$

On seasonal basis,  $(\text{OC}/\text{EC})_{\min}$  ranged 0.71 - 2.3 in this campaign, and SOC was estimated to range from 1.2 to 9.6  $\mu\text{g}\cdot\text{m}^{-3}$  in breathing zones using formula (F1).

#### 4. Conclusions

In this work, we observed significant temporal and geographical variations in PM pollution over a subtropical



metropolitan area through a multi-institutional field campaign in Hangzhou, China. During the campaign, we captured serious PM<sub>2.5</sub> pollutions in the breathing zone of the scenic city in all seasons. A number of toxic metals were highly enriched in the breathing zone due to anthropogenic activities. The annual average concentration of PM<sub>2.5</sub> ranged from 106 to 131  $\mu\text{g}\cdot\text{m}^{-3}$  in the metropolitan breathing zones, which were 40% - 70% higher than at typical ambient stations. Speciation of PM<sub>2.5</sub> was carried out for 25 elements using instrumental analyses by ICP, ICP-MS, and AFS, for 9 soluble ions using IC, and for (TC, OC, EC) using a thermo-photometric method.

A number of toxic metals were highly enriched in the breathing zone due to anthropogenic activities. Elemental analyses revealed significant presences of toxic heavy metals (Hg, Cd, Cr, Pb, As) in PM<sub>2.5</sub> and that, among 25 detected elements, (S, Ca, K, Fe) showed concentrations larger than 1.0  $\mu\text{g}\cdot\text{m}^{-3}$ . Enrichment factor analysis revealed that (Cd, Se, S, Mo, Zn, Pb, Cu, As) in PM<sub>2.5</sub> were dominated by anthropogenic sources. Nine soluble ions detected during the campaign contributed 42  $\mu\text{g}\cdot\text{m}^{-3}$  to PM<sub>2.5</sub> concentration on average, and three secondary inorganic ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) accounted for 85% of total ionic concentration. Nitrate concentration was close to and occasionally exceeded sulfate concentration during the campaign, which reflects rising vehicle activities. Molar ratios of sulfate/(total sulfur) and nitrate/(total oxidized nitrogen) frequently exceeded 10%, which suggests significant effects of photochemical reactions on PM<sub>2.5</sub> pollution in the breathing zones.

The average total carbon concentration was 32  $\mu\text{g}\cdot\text{m}^{-3}$ , and the average ratio of OC/EC was 2. During the campaign, seasonal variation of TC was dominated by OC, and both concentrations peaked in fall and were low in summer. The EC concentration showed little seasonality, and OC was well correlated with EC in winter and spring. Secondary organic carbon was estimated to contribute 1.2 - 9.6  $\mu\text{g}\cdot\text{m}^{-3}$  to PM<sub>2.5</sub> concentration in the breathing zones. Comparison of concurrent measurements of sulfur element and sulfate suggests that the average concentration of organic sulfur (0.3  $\mu\text{g}\cdot\text{S}\cdot\text{m}^{-3}$ ) in PM<sub>2.5</sub> samples was relatively small compared with inorganic sulfur during the campaign.

## 5. Declaration

This work has been reviewed by staff at Zhejiang Environmental Protection Agency, China, and has been approved for publication. Approval does not signify the endorsement of commercial products mentioned in this article, and opinions in this article are solely those of authors.

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