

# Chemical Characteristics of Particulate Matter during a Heavy Dust Episode in a Coastal City, Xiamen, 2010

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# ABSTRACT

Xiamen, as a southeastern coastal city, is hardly affected by dust storms (DSs) sourced from the arid and semiarid areas in North or Northwestern China in spring. Unfortunately, during 21-23 March, 2010, the heaviest DS that had been recorded in past 50 years affected air quality seriously. Continuous particulate matter monitor was employed for the observation of PM2.5 (aerodynamic diameter less than 2.5 µm) and PM10 (aerodynamic diameter less than 10 µm) during 20-24 March 2010. Total suspended particulate (TSP) samples during this episode were also collected and their characteristics of element species and water-soluble ions were illustrated to characterize the heavy pollution in Xiamen. The DS peaked on 21 March, with the highest concentrations of 454.51  $\mu$ g/m<sup>3</sup> and 990.24  $\mu$ g/m<sup>3</sup> for PM<sub>2.5</sub> and PM<sub>10</sub>, respectively. The variations of ratio for  $PM_{25}/PM_{10}$  indicated that  $PM_{10}$  was the main particles that were influenced by DS. The higher ratios (DS/Non dust days) of Al, Fe, Mg, Mn, and Ba were over 5.0, which are primarily from a soil. However, the ratios of Zn, V, As, Ti, and Cr, mainly from anthropogenic sources, had a range of 1.3 to 3.4. These results suggested that the soil-sourced species made more contribution to DS particles compared to the anthropogenic species. The mass fractions of water-soluble ions in TSP indicated that the concentrations of K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, F<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup> were evidently higher in DS samples than those of non-DS samples. The compositions of ions in dust aerosols showed that the multi-sources of aerosol were ubiquitous during the dust episode. The highest concentrations of sulfate and nitrate occurred in the day when dust ended in Xiamen, which demonstrated the formation of secondary pollutants from dust during the long-range transport, as well as from local environmental pollution.

Keywords: Dust storm; Particle; Inorganic element; Water-soluble ion; Xiamen.

#### **INTRODUCTION**

Dust storms (DSs) are a common phenomena in the arid inland of China, and are the major forcing of soil erosion, together with the strong winds, high concentrations of particulate pollutants (Guo *et al.*, 2004). DSs are transported long distances by atmospheric circulation, which would contribute significant nutrients to river and ocean by dust deposition (McTainsh *et al.*, 2005), but more influencing chemical constituents of atmosphere (Wang *et al.*, 2007) and human health (Chan and Lippmann, 1980; Berico *et al.*, 1997), modifying cloud formation (Kaufman *et al.*, 2005) and affecting the energy balance of the Earth (Satheesh and Moorthy, 2005). Many cites in middle latitudes and northern Pacific Ocean tropical areas, including the Beijing (Xie *et*  *al.*, 2005), Qingdao (Guo *et al.*, 2004), Korea (Kim and Park, 2001; Lee *et al.*, 2006), Japan (Ma *et al.*, 2004, 2005; Nakamura *et al.*, 2005), Taiwan (Lin, 2001; Chen *et al.*, 2004), and even places as distant as Hawaii (Braaten and Cahill, 1986) are often influenced by DSs with wind speeds of 6–20 m/s (Natsagdorj *et al.*, 2003; Xuan *et al.*, 2004).Therefore, more and more researchers had focused on the dust emissions from the arid and semiarid areas in North or Northwestern China(Zhang *et al.*, 2001, 2003, 2008). However, little had been done to investigate the characteristics of pollution during the episode of DSs in Southeastern China, especially for coastal city, Xiamen.

Xiamen, a subtropical and coastal city in southeastern China, is a main economic and culture center of Fujian Province. The northern and northeastern are the prevailing wind in the whole year except summer, which can bring dust and pollutants when moving from northern or northeastern cities. However, no literature had reported DSs that occurred in Xiamen, where were far from deserted regions. Unfortunately, Xiamen occurred the largest DS on

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21 March 2010, which covered completely atmosphere of the city and aroused the public attention sharply.

In this study, the dust samples in air were collected during DS on 21–22 March 2010. The observation of fine particle ( $PM_{2.5}$ , aerodynamic diameter less than 2.5 µm) and inhaleble particle ( $PM_{10}$ , aerodynamic diameter less than 10 µm) was conducted to illuminate the mass concentrations of particulate during this DS appeared in coastal city. Furthermore, major metal elements and watersoluble ions (WSIs) in total suspended particles (TSP) were determined to describe the pollution characteristics of this heaviest DS that had been ever recorded in past 50 years. Our work maybe the first documentation about pollution characteristics of dust event in Xiamen, which should be in favor of evaluating the environmental and social risks caused by DS, as well as the impact on the air quality of coastal city far from dust storm source.

#### **EXPERIMENT**

#### Aerosol Sample Collection

The sampling site is located in Jimei District of Xiamen city and surrounded by highway, schools, residential building and Xinglin bay. The sampler was placed at rooftop of one building in Institute of Urban Environment, Chinese Academy of Sciences, about 30 m above the ground. During the sampling periods, meteorological parameters, including ambient temperature, relative humidity (RH), wind speed, and visibility were recorded by Xiamen meteorological agency and real-time monitor.

Two types of particulate matter (PM), which are  $PM_{2.5}$  and  $PM_{10}$  samples were observed by continuous particulate matter monitor (TEOM 1405-D, Thermo Co. Ltd., USA).  $PM_{2.5}$  and  $PM_{10}$  data were achieved from 20 March, 2010 to 24 March, 2010, the value of which was recorded every 30 min automatically. Two high-volume samplers (TH-1000C, Wuhan Tianhong Co. Ltd., China) with quartz fiber filters (QFFs, Whatman, 20.3 cm × 25.4 cm) were employed to collect TSP samples at the flow rate of 1.0 m<sup>3</sup>/min from 21 March 2010 to 22 March 2010. During this period, the TSPs were collected from about 8:00 to 16:00 as the daytime samples, and 20:00 to 4:00 as the nighttime samples. In addition, three samples before and after DSs were collected on 14–16 March 2010 and 28 March 2010, each of which were sampled every 24 h on non-DS days.

The QFFs were previously annealed for 5 h at 450°C in a furnace and then stored in baked aluminum foil within sealed polyethylene plastic bags before use. After sampling, loaded QFFs were wrapped with prebaked aluminum foils and sealed with double layers of polyethylene bags, and stored at -20°C until extraction. All of those filters were weighted before and after sampling with an analytical balance (Sartorius T-114, Germany) after stabilizing under constant temperature ( $25 \pm 1$ °C) and humidity ( $50 \pm 1$ %).

#### METAL ELEMENTS ANALYSIS

#### Analytical Procedure

The filters of samples, which loaded more than 1 mg

particulate, were digested with 5 mL concentrated nitric acid (ultra-pure) in the sealed Teflon pipes at 150°C for 6 days, and digested solutions were extracted by an ultrasonic bath (KQ300DE, Kunshan Ultrasonic Instrument Co., Ltd, China) every 24 h during the process. After digestion, the samples were filtered and then diluted to less than 2% acidity with Mill-Q water. Finally, the diluted solutions were quantified by inductively coupled plasma mass spectrometry instrument (ICP-MS, 7500C, Agilent Co. Ltd, USA). Standard multi-element solutions (National Information Center for Standard Substance, China) from 5 to 250 ng/mL were used for calibration, and Ru of 50 ng/mL was added as internal standard.

#### Quality Assurance and Quality Control (QA/QC)

The evaluations of the analytical procedures were performed with the standard soil as reference material (National Information Center for Standard Substance, China). The recovery of 18 elements (Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Sr, Sn, Ba, Pb, and Ga) were 80-110%. Four blank filters and three blank aluminum foil (originally used to package QFFs) were also analyzed and the sample results were corrected by the average of blank concentrations. The instrumental detection limit of trace elements was 0.10 ng/L. Only those elements exceeding the detection limit by 5 times were discussed in this study. Metal materials should be avoided through the whole experiment. Detection limits corresponding to 3 times the standard deviation of 10 replicate blank level measurements were 0.09 mg/mL for Na, 0.02 mg/mL for K, and 0.06 mg/mL for Mg, 0.04 mg/ml for Cr, and below 0.2 mg/mL for the rest of the trace metals. All blank values below 0.05 mg/mL.

# Water-soluble Ions Analysis

#### Analytical Procedure

The water-soluble components were extracted from the filters (6.0 cm<sup>2</sup> pieces of filter) into 20 mL Mill-O water in 50 mL polypropylene tubes by ultrasonic bath for 1 h, then the solutions were filtered with a 0.45 µm PTFE syringe filter (Pall Co. Ltd, USA) and stored in 2 mL glass bottles. Ion chromatography system (ICS-3000, Dionex, USA) was employed to detect the concentrations of five anions (F, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) and five cations (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>,  $Ca^{2+}$ ,  $Mg^{2+}$ ) species. The anions were analyzed with an IonPac ASRS-4 suppressor and an IonPac AS11-HC × 250 mm analytical column. The eluent for anion analysis was 10 mmol/L Na<sub>2</sub>CO<sub>3</sub>. The cations were analyzed with an IonPac CSRS-4 suppressor and an IonPac CS12A  $\times$  250 mm analytical column. The eluent for anion analysis was 10 mmol/L CH<sub>4</sub>O<sub>3</sub>S. Injection of the samples was done automatically using a 10 µL loop.

#### QA/QC

All standard solutions of 10 WSIs were obtained from National Information Center for Standard Substance, China. The resistance of Mill-Q water is more than  $18 \text{ M}\Omega$ .

Before real sample analysis, standard solutions and blank tests were experimented, the correlation coefficient of standard curves was more than 0.999. The method detection limit for major anions and cations, including  $F^-$ , Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>, were 0.026, 0.058, 0.017, 0.013, 0.010, 0.013, 0.087, 0.048, 0.084 and 0.067 mg/L, respectively.

There were three blank samples and three parallel random samples among every 15 samples extracted by ultrasonic bath and a standard solution among every 10 samples during analysis. All the measured concentrations of WSIs were subtracted by the filter blanks.

# **RESULTS AND DISCUSSION**

# Mass Concentrations of $PM_{2.5}$ and $PM_{10}$ during DSs, before and after DSs

Fig. 1 is the time series variation of concentrations for  $PM_{2.5}$  and  $PM_{10}$  from 20 March to 24 March 2010, which showed that the mass concentrations of  $PM_{2.5}$  and  $PM_{10}$  reached a striking high level during DS episode (21–22 March 2010) and peaked at 454.51 µg/m<sup>3</sup> and 990.24 µg/m<sup>3</sup> in the afternoon of 21 March 2010, respectively. Therefore, air quality in Xiamen deteriorated seriously. Fig. 2 is aerosol index from Earth Probe Total Ozone Mapping Spectrometer (TOMS) (http://toms.gsfc.nasa.gov/aerosols), which was available to confirm the phenomena of DS transport, and also presented the heaviest aerosol pollution appeared on 21 March in Xiamen.

It was obviously found that concentrations of  $PM_{10}$  exceeded Xiamen daily concentration (about 80 µg/m<sup>3</sup> that was monitored by Xiamen EPA during normal days) during this DS episode, which lasted almost three days until 24 March 2010. The average concentrations of  $PM_{2.5}$  and  $PM_{10}$  on 21 March 2010, the heaviest particulate

pollution day, touched  $265.55 \pm 134.07 \ \mu\text{g/m}^3$  and 584.48 $\pm$  267.32 µg/m<sup>3</sup>. Therefore, the average PM<sub>2.5</sub> concentration of the heaviest pollution day exceeded the 24-h American air quality standard of 35  $\mu$ g/m<sup>3</sup> and yearly mean value of 15  $\mu$ g/m<sup>3</sup> (EPA, 2006). The average of PM<sub>2.5</sub> and PM<sub>10</sub> concentrations during 20–24 March 2010 were 141.50  $\pm$  $108.82 \ \mu g/m^3$  and  $322.03 \pm 237.38 \ \mu g/m^3$ , respectively. The average concentration of PM<sub>2.5</sub> in Xiamen during DS period was slightly higher than that of Xi'an (137.6  $\mu$ g/m<sup>3</sup>) during DS in 2006-2007 (Shen et al., 2009), and also much higher than that of in Taiwan (107.0  $\mu$ g/m<sup>3</sup>) during DS in 2000–2001(Chen et al., 2004). However, the average PM<sub>10</sub> concentration in Xiamen was significantly lower than that in north city, such as Beijing (898 µg/m<sup>3</sup>) (Xie et al., 2005), while higher than that of in Taiwan (260  $\mu$ g/m<sup>3</sup>) (Chen et al., 2004).

On 22 March 2010, the average concentrations of  $PM_{2.5}$ and  $PM_{10}$  dropped to 144.22 ± 37.46 µg/m<sup>3</sup> and 356.53 ± 76.94 µg/m<sup>3</sup>, which were only accounted for 56% and 61% compared to those on past day. However, the concentrations of  $PM_{10}$  always kept high, although the average concentrations exhibited a trend of decrease on 21–24 March 2010, which clearly suggested that coarse particles were the main contributor for this heavy episode among 22–24 March 2010.

Backward wind trajectories (http://www.arl.noaa.gov/ HYSPLIT.php) show that air parcels arriving in Xiamen during the DS originated 48 h earlier in northern China (Fig. 3). The strong winds (indicated by the extended length of the 48-h backward trajectory), which aided long-range transport, passed through the economically developed regions along the east of China, adding their



Fig. 1. Time series variation of concentrations for  $PM_{2.5}$  and  $PM_{10}$  from 13:05 20 March to 08:05 24 March 2010.

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Fig. 2. Variations of aerosol index for dust on March 20–23, 2010. Location of Xiamen shown as large red dots.



**Fig. 3**. Backward trajectories for air parcels that affected Xiamen during the 20–21 March 2010 dust storm (http://www.arl. noaa.gov/HYSPLIT.php).

aerosol pollutants to the mix before it arrived in Xiamen. Therefore, the backward wind trajectories further reveal that the elevated levels of  $PM_{2.5}$  and  $PM_{10}$  during DS in Xiamen are caused by sand dust from the deserts of Mongolia and northeastern China.

Fig. 4 shows the correlations among PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>2.5-10</sub> (coarse particulate, particulate diameter more than 2.5 µm and less than 10 µm) during DS in Xiamen. From Fig. 4, it was obviously found that PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>2.5-10</sub> presented good correlation coefficient with 0.92 and 0.95, respectively, which not only demonstrated that there were the same sources for PM10, PM2.5 and PM2.5-10, but also revealed that DS impacted both these particles dramatically, especially for PM<sub>10</sub> and PM<sub>2.5-10</sub>. These results were similar with the researches of other coastal cites, such as Taiwan (Chen et al., 2004) and Hong Kong (Lee et al., 2010), which implied that DS originated from northern or northwestern regions evidently influenced these coastal cities by long-range transport. In general, fine particle occupied much higher fraction of the PM<sub>10</sub> mass during normal days (Wang et al., 2009), which reached to 54% before and after DS in Xiamen. However, fine particles only accounted for 42% of the PM<sub>10</sub> mass during the DS period, which revealed that most of the  $PM_{10}$  components collected in Xiamen during the DS period consisted of a coarse particle fraction rather than a fine particle fraction.

# Major Elements in TSP during DSs, before and after DSs

Table 1 lists the mass concentrations of 18 inorganic elements in TSP during non-dust and DS periods. As shown in Table 1, the concentrations in non-dust periods were lower than Chinese TSP standard (24-h mean value of  $300 \ \mu g/m^3$ ), which were 1.74 to 3.90 times than Chinese TSP standard in DS periods, especially on first day (21 March 2010). 18 Inorganic elements in TSP samples which the concentrations of Na, Mg, Fe, A1 and Cu were higher than that of other elements (Table 1). The concentrations of

the soil originated species, such as Al and Fe, increased remarkably during DS periods. In addition, the concentrations of the anthropogenic species, such as Zn, V, K, Ni, and As, did not show much different between non-dust and DS periods. Based on above explains, it was clearly concluded that the soil-sourced species were much more contributive to DS particles compared to the anthropogenic species.

Fig. 5 shows the concentration ratios (DS/non-DS) of 18 elements in TSP. It showed that the concentrations of all species increased during DS periods. The ratios of Al, Fe, Mg, Mn, and Ba (Kang *et al.*, 2009), were over 5.0 (Fig. 5), while the concentration ratios of Zn, V, As, Ti, and Cr had a range from 1.3 to 3.4. These results not only reasserted that the soil-sourced species were much more contributed to DS particles compared to the anthropogenic species, but also implied that the concentration of elements from soil would be increased evidently by long-range transport of air mass from northern regions.

Table 1 also exhibited that concentration of K was the highest in anthropogenic species, which reached to 200 ng/m<sup>3</sup> before and after DS days. It has been known that K was a diagnostic tracer for biomass burning source (Andreae, 1983; Andreae et al, 1998), and therefore, it reveals that there is biomass burning affected Xiamen air quality. Frequent anthropogenic activities, such as combustion of leaf and natural gas (Zhao et al., 2010a), would be a main reason contribute to higher K concentration. During DS periods, however, K concentration was almost 8 times than that of before and after DS days, indicating non-local emissions but source originated from northern regions may be responsible for the difference. Vehicle exhaust and coal combustion were the main sources for Pb, it was reported that ash accounted for about 20% in exhaust gas after coal combustion, and one third of which would be released in atmosphere and form dust (Zhao et al., 2008). Fig. 5 showed the highest ratio (17.3) of Pb before DS, after DS and DS



Fig. 4. Correlations among PM<sub>10</sub>, PM<sub>2.5</sub> and PM<sub>2.5-10</sub> during dust storm in Xiamen.

Date	Before DS day		After DS day			
	3/15	3/21(AM)	3/21(PM)	3/22(AM)	3/22(PM)	3/28
TSP	239.06	1169.23	896.14	783.75	522.64	75.62
Na	1135.80	2824.76	3404.13	3524.51	3124.51	1681.94
Mg	2193.76	11317.29	10072.54	8891.66	8931.16	186.68
AĪ	1989.76	21359.49	22234.44	21525.62	22225.12	1096.06
Fe	5110.78	21482.89	18770.92	18628.44	18227.74	310.74
Ti	265.60	376.58	359.98	318.00	348.10	9.20
Zn	184.48	484.50	215.36	289.40	318.80	54.36
Mn	227.54	661.78	609.68	598.56	578.86	16.60
Ba	119.48	292.69	280.88	332.15	318.84	5.82
Κ	215.46	1809.48	1816.04	1655.38	1695.88	198.56
V	12.82	41.25	39.12	42.68	39.88	10.88
Cr	22.48	24.60	19.22	26.66	21.36	4.67
Со	1.89	10.58	8.64	10.02	7.52	1.26
Ni	2.20	14.65	16.97	16.46	18.15	1.60
As	18.82	23.34	22.13	16.36	14.86	10.46
Sr	53.90	268.28	212.26	161.64	173.16	4.08
Sn	5.82	2.60	7.84	5.83	8.12	2.84
Pb	25.88	472.42	638.98	464.22	324.21	28.98
Ga	29.15	54.02	53.39	62.49	60.89	11.12
Total	13256.96	62146.81	60366.67	57517.8	57312.69	3819.72

Table 1. Mass concentrations of elements in TSP at different sampling days in Xiamen (ng/m<sup>3</sup>).

Note: unit of TSP is  $\mu g/m^3$ .



periods, suggesting that the polluted plume originated from northern regions, such as the Yangtze Delta (Zhao *et al.*, 2010b), had a stronger effect on inorganic competitions in TSP in Xiamen by long-range transport under DS periods. Zn, as an important trace element for anthropogenic activities, exhibited high concentration before and after DS days, which was associated with the large number of vehicles in Xiamen, especially for brakes wear.

The enrichment factor (*EF*) is defined as formula 1 (Erel *et al.*, 2006), where  $(C_X/C_{Al})_{aerosol}$  is the concentration ratio of a given element X to Al in aerosol, and  $(C_X/C_{Al})_{crust}$  is

the concentration ratio of a given element X to Al in the average crustal abundance. Al is the common reference element for crustal particles in EF calculations based on the crustal chemical composition given by Erel (2006).

$$EF_{crust} = \frac{(C_X / C_{Al})_{aerosol}}{(C_X / C_{Al})_{crust}}$$
(1)

Depending on the *EFs* (Table 2), all analyzed trace element were considered in different days (before DS day,

Date	Before DS day		After DS day			
	3/15	3/21(AM)	3/21(PM)	3/22(AM)	3/22(PM)	3/28
Na	$19.72 \pm 2.89$	$4.56 \pm 3.15$	$5.28 \pm 5.12$	$5.66 \pm 7.19$	$4.86 \pm 4.22$	$53.00 \pm 7.24$
Mg	$55.00 \pm 3.58$	$26.43 \pm 8.71$	$22.60 \pm 3.21$	$20.60 \pm 5.11$	$20.04 \pm 9.11$	$8.50 \pm 4.12$
Al	1.00	1.00	1.00	1.00	1.00	1.00
Fe	$9.49 \pm 1.51$	$3.72 \pm 4.12$	$3.12 \pm 1.18$	$3.20 \pm 1.87$	$3.03 \pm 1.64$	$1.04 \pm 2.13$
Ti	$3.99 \pm 0.18$	$0.52 \pm 0.87$	$0.48 \pm 1.21$	$0.44 \pm 1.71$	$0.46 \pm 1.53$	$0.25 \pm 1.11$
Zn	$161.66 \pm 13.12$	$39.55 \pm 8.54$	$16.90 \pm 3.22$	$23.44 \pm 5.67$	$25.01 \pm 6.67$	$86.48 \pm 10.65$
Mn	$15.32 \pm 2.89$	$4.15 \pm 2.57$	$3.68 \pm 3.12$	$3.72 \pm 2.54$	$3.49 \pm 3.11$	$2.02 \pm 1.11$
Ba	$12.74 \pm 1.51$	$2.90 \pm 2.54$	$2.68 \pm 3.11$	$3.27 \pm 3.54$	$3.04 \pm 2.78$	$1.12 \pm 2.14$
Κ	$0.43 \pm 0.11$	$0.34 \pm 0.57$	$0.32 \pm 0.37$	$0.30 \pm 0.51$	$0.30\pm0.28$	$0.71 \pm 1.54$
V	$12.44 \pm 1.73$	$3.72 \pm 2.47$	$3.40 \pm 4.87$	$3.82 \pm 3.21$	$3.46\pm2.98$	$19.16 \pm 5.57$
Cr	$41.07 \pm 4.31$	$4.18 \pm 2.58$	$3.14 \pm 1.87$	$4.50 \pm 4.61$	$3.49 \pm 3.51$	$15.49 \pm 4.88$
Со	$13.98 \pm 6.97$	$7.29 \pm 2.72$	$5.72 \pm 2.87$	$6.85 \pm 1.33$	$4.98 \pm 1.66$	$16.92 \pm 5.57$
Ni	$11.03 \pm 1.57$	$6.84 \pm 3.44$	$7.61 \pm 2.13$	$7.62 \pm 3.71$	$8.14 \pm 3.89$	$14.56 \pm 7.87$
As	$193.04 \pm 22.51$	$22.30 \pm 7.51$	$20.31\pm8.28$	$15.51 \pm 5.34$	$13.64 \pm 6.71$	$194.76 \pm 17.61$
Sr	$40.54 \pm 5.11$	$18.78 \pm 6.15$	$14.28 \pm 9.17$	$11.24 \pm 5.51$	$11.66 \pm 5.87$	$5.57 \pm 2.51$
Sn	$53.60 \pm 6.37$	$2.23 \pm 1.88$	$6.46 \pm 2.13$	$4.96 \pm 1.89$	$6.69\pm2.69$	$47.48 \pm 11.59$
Pb	$24.96 \pm 9.51$	$42.44 \pm 13.55$	$55.14 \pm 13.87$	$41.38 \pm 12.88$	$27.99 \pm 7.75$	$50.73 \pm 11.61$
Ga	$70.35 \pm 6.77$	$12.14 \pm 5.56$	$11.53 \pm 6.87$	$13.94 \pm 4.77$	$13.16 \pm 5.57$	$48.72 \pm 12.62$

Table 2. Summary of Enrichment Factor Values for Trace Elements in TSP Xiamen during DS.

during DS days and after DS day). Elements having enrichment factors less than 1.0, such as K and Ti, were not taken into account in the calculation, as they were identified to be of exclusive crustal original. Elements having EFs between 1 and 5 were identified as originating from two sources, (i.e., anthropogenic and crustal sources). Elements having EFs more than 5.0 were identified to be dominated by anthropogenic origins (Hsu *et al.*, 2010). The data in Table 1 clearly showed that most of EFs for metals were higher before or after DS days than that in DS days, which indicated that mixed sources contributed to Xiamen aerosols.

The EFs crustal values of Fe, Al and Mn were approach 1 during DS days, indicating that larger amounts of these dust elements were derived from soil. However, compared with the dust-derived elements, the EF values of Pb, As and Zn, which were often enriched through anthropogenic emissions (Nriagu and Pacyna, 1988), were ranged from 15 to 55, reflecting the dominant effects to these elements from anthropogenic pollutant sources in upwind regions. Similar to dust elements, the EF value of Na was also likely to uniformity, except the value on 28 March 2010, suggesting that Na in our samples was mostly from not sea salt but surface soil. The EF values of these elements in Xiamen were lower than that of in Beijing (Cheng et al., 2005) and Shanghai (Fu et al., 2008), whereas, values of pollutant elements for Zn, As and Pb before or after DS days were higher than that of in these cities, which maybe relate with municipal waste incineration and metalliferous industry apart from brake wear (Hsu et al., 2005).

# Distribution of Water-soluble Ions among DS, before and after DS Periods

TenWSIs, Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, had been detected. Fig. 6 shows the distributing characteristics of these ions in DS, before and after DS periods, it was easily found that Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub> were the major ions in the samples collected during the dust episodes, while SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, and K<sup>+</sup> were the major ions in that of normal days. The average concentrations of Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> in DSs were 1.34, 4.20, 2.77, 9.04, 4.90, 5.54, 3.75, 5.54, 3.64 and 2.93 times than those before and after DSs, respectively.

The concentrations of the "crust" ions,  $Ca^{2+}$ ,  $Na^+$ , and  $Mg^{2+}$ , enhanced in dust episodes obviously, except for  $Mg^{2+}$  (the reason may be explained that  $Mg^{2+}$  was much more influenced by sea-salt in this coastal city); they were mainly from the mineral dust. The concentrations of the "pollution-crust" ions,  $SO_4^{2-}$ ,  $Cl^-$ , and  $K^+$ , were higher in dust episodes than in non-dust days in TSP samples (Fig. 6), which revealed that these ions in the TSP might be more from the crustal dust sources by long-range transport. The concentrations of the "pollution" ions,  $NO_3^-$ ,  $NH_4^+$ , F<sup>-</sup>, and  $NO_2^-$ , were also mostly higher in the dust episodes than those before and after DS days (Fig. 6), suggesting that they were also partly influenced by the long-range transported polluted plume and local pollution sources.

To verify three group classifications, Al was chosen as a reference element as it was a good tracer of the crustal aerosol, and  $Ca^{2+}$ ,  $SO_4^{2-}$ , and  $NO_3^-$  were selected to represent the crust, the pollution-crust, and the pollution groups, respectively. Fig. 7 illustrates the relationships of  $Ca^{2+}$ ,  $SO_4^{2-}$ ,  $NO_3^-$  to Al. It could be seen clearly that  $Ca^{2+}$  agreed with Al quite well ( $R^2 = 0.94$ ) among DS, before and after DS days. This indicated that  $Ca^{2+}$  could be from the same source as Al, i.e. the crustal source.  $NO_3^-$  and  $SO_4^{2-}$  had a good relationship with Al at some degree in the dust episodes, but showed a weaker correlation coefficient with Al in the non-dust days ( $R^2 = 0.89$  and  $R^2 = 0.82$ ) indicating that a certain part of  $NO_3^-$  and  $SO_4^{2-}$  were from the crustal source in dust episodes, while in the non-dust days they were mainly from the local pollution sources.



Fig. 6. Concentrations of water-soluble ions in TSP components among DS, before and after DS periods.



Fig. 7. Correlations among  $Ca^{2+}$ ,  $NO_3^-$ ,  $SO_4^{2-}$  and Al for all the collected samples.

Fig. 6 also obviously displayed that the highest concentrations of NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> appeared on day when the DS passed (22(PM) March 2010), which reached 31.30  $\mu$ g/m<sup>3</sup> and 53.34  $\mu$ g/m<sup>3</sup>, respectively. It was, on the one hand, demonstrated that the heterogeneous reactions of SO<sub>2</sub> and NO<sub>x</sub> with dust particles occurred during the transport of DSs. Furthermore, the increased ions from secondary pollutants (NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) implied that the transformation of primary pollutants, such as SO<sub>2</sub> and NO<sub>x</sub>, might take place on the conditions of adverse atmosphere.

# CONCLUSIONS

This study presents the first investigation of chemical characteristics for particle matter sampled in Xiamen during the heaviest DS event in March 2010.

The average concentrations of  $265.55 \pm 134.07 \ \mu g/m^3$ and  $584.48 \pm 267.32 \ \mu g/m^3$  for  $PM_{2.5}$  and  $PM_{10}$  on 21 March 2010 were almost 2.4 and 3.0 times than those of before DS day (20 March 2010). The correlations among  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_{2.5-10}$  during DS were 0.92 and 0.95, respectively, which not only demonstrated that there were the same sources for  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_{2.5-10}$ , but also revealed that DS impacted the mass of  $PM_{10}$  and  $PM_{2.5-10}$ dramatically. In addition, the decreased trend of average ratio for  $PM_{2.5}/PM_{10}$  implied that most of the  $PM_{10}$  in Xiamen during the DS period consisted of a coarse particle fraction rather than a fine particle fraction.

The compositions and characteristics of distribution for 18 elements and 10 WSIs all showed the higher concentration for these elements and WSIs in DS days than before and after DS periods. The different *EF* values for crustal and anthropogenic species during DS periods were corresponding to reflect the soil-derived sources and anthropogenic pollutant sources from northern China by long-range transport. The different groups of WSIs in dust aerosols also showed that contributors not only included local pollution sources, but also long-range transported polluted plume.

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