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Comparison of inorganic chemical compositions of atmospheric TSP, PM₁₀ and PM_{2.5} in northern and southern Chinese coastal cities

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ABSTRACT

To compare the inorganic chemical compositions of TSP (total suspended particulate), PM₁₀ (particulate matter with an aerodynamic diameter less than 10 μm) and PM_{2.5} (particulate matter with an aerodynamic diameter less than 2.5 μm) in southern and northern cities in China, atmospheric particles were synchronously collected in Dalian (the northern city) and Xiamen (the southern city) in spring and autumn of 2004. The mass concentrations, twenty-three elements and nine soluble ions were assessed. The results show that in Dalian, the mass concentrations of Mg, Al, Ca, Mn and Fe in spring were 4.0–10.1, 2.6–8.0, 4.1–12, 1.2–3.6 and 2.9–7.9 times higher, respectively, than those in Xiamen. The dust storm influence is more obvious in Dalian in spring. However, in Xiamen, heavy metals accounted for 13.9%–17.9% of TSP, while heavy metals contributed to 5.5%–9.3% of TSP in Dalian. These concentrations suggest that heavy metal pollution in Xiamen was more serious. In addition, the concentrations of Na⁺, Cl[−], Ca²⁺ and Mg²⁺ were higher in Dalian due to the influence of marine aerosol, construction activities and soil dust. The NO₃[−]/SO₄^{2−} ratios in Dalian (0.25–0.49) were lower than those in Xiamen (0.51–0.62), indicating that the contributions of vehicle emission to particles in Xiamen were higher. Coefficient of divergence values was higher than 0.40, implying that the inorganic chemical composition profiles for the particles of Dalian and Xiamen were quite different from each other.

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Introduction

Atmospheric particulate matter, including PM₁₀ (particulate matter with an aerodynamic diameter less than 10 μm) and

PM_{2.5} (particulate matter with an aerodynamic diameter less than 2.5 μm), is reported to raise human health concerns and environmental problems (with regard to climate, visibility and biogeochemical cycles) (Liu et al., 2008). They are mixtures

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of thousands of substances with characteristic particle number and size and certain surface and chemical components (Götschia et al., 2005; Hueglin et al., 2005; Viana et al., 2007). Understanding the chemical composition of particulate matter is especially important in determining its sources and potential effects on the environment and human health. The coastal atmosphere adjacent to large urban and industrial centers can be strongly impacted by the emissions of air pollutants (Fang et al., 2006; Liu et al., 2008).

Understanding the chemical compositions of aerosols in coastal areas and islands, including both natural and anthropogenic components, can be used to characterize the sources, i.e., natural vs. anthropogenic, continental vs. marine and local source vs. long range transport (Qin et al., 1997). A number of studies on atmospheric aerosol compositions and their sources have been conducted in coastal areas and islands (Braga et al., 2005; Moreno et al., 2006; Mariani and Mello, 2007). In addition, characterization of coastal aerosols can provide information for the investigation of the atmospheric input of many important biogeochemical trace metals (Hsu et al., 2010; Uematsu et al., 2010) and inorganic nitrogen (NO_3^- and NH_4^+) (Gao, 2002; Kumar et al., 2008; Xia and Gao, 2010; Uematsu et al., 2010) to the adjacent marine and the ocean ecosystems.

In recent years, an increasing number of scientific studies addressing aerosol levels, size distributions, chemical compositions and sources in Chinese Coast Regions (CCR) have been published. Most of them have focused on the cities of Dalian (Wan et al., 2006), Tianjin (Kong et al., 2010), Qingdao (Davis and Guo, 2000; Zhang et al., 2001; Hu et al., 2002; Guo et al., 2003; Zhang et al., 2003; Guo et al., 2004), Shanghai (Wang et al., 2006; Du et al., 2011), Hangzhou (Cao et al., 2009; Hong et al., 2013), Xiamen (Zhao et al., 2011; Zhang et al., 2012), and Guangzhou (Tan et al., 2009) and Hong Kong (Cheng et al., 2000; Cheung et al., 2005), as these cities are on the boundary between Asia and the North Pacific Ocean. Aerosols from different sources transported over this region can be modified significantly before reaching the remote Pacific. However, each of these studies was conducted in one city, and none of them synchronously reported the chemical compositions of particles with different sizes in these cities. It should be noted that particle composition varies with size, time and locations. Chan and Yao (2008) indicated that various chemical species are likely to be unevenly distributed over different sizes of particles due to their specific formation pathways. The diversity of chemical compositions, sources and size distributions of aerosols in the north and south Chinese coastal regions are still not clear identified.

Therefore, the assessment of $\text{PM}_{2.5}$, PM_{10} and TSP (total suspended particulate) inorganic chemical composition data in the most industrialized and quickly developing area of eastern China is needed for the development of legislative and environmental protection. Other chemical composition such as elemental carbon (EC), organic carbon (OC) and organic compounds are also important and have drawn special attention in China (Li et al., 2016; Zong et al., 2015; Feng et al., 2009; Yang et al., 2005; Barletta et al., 2005), but not analyzed in this article. The objectives of this study are to quantify the various mass concentrations, inorganic chemical compositions and sources of TSP, PM_{10} and $\text{PM}_{2.5}$ from two coastal cities in northern and southern China.

1. Experiment

1.1. Sampling sites description

Dalian is located at $120^\circ 58' - 123^\circ 31' \text{E}$ and $38^\circ 43' - 40^\circ 10' \text{N}$. There are many hills and few plain areas. The climate is typically a territorial monsoon system within a warm-temperate zone. The annual average temperature and precipitation are 10.5°C and 550–950 mm (60%–70% concentrated in summer), respectively. The urban area of Dalian is approximately 2400 km^2 , with the population of the urban area being more than 3.7 million. The main industries in Dalian are shipbuilding, chemical engineering, locomotive building, tourism, exhibition and software. In Dalian, coal gas is a primary fuel for household cooking, and coal is a main fuel used for central heating in winter (Wan et al., 2006).

Xiamen ($118^\circ 04' 04'' \text{E}$, $24^\circ 26' 46'' \text{N}$) is located in the south-east of the Chinese mainland, adjacent to Taiwan Island. Hills, plains and tidal flats are its main soil types, accounting for 62.5%, 14.0% and 7.7% of the total area, respectively. It is typically a subtropical monsoon climate. The annual average temperature and precipitation are 21°C and 1200 mm, respectively. The dominate wind direction is to the northeast with wind speeds of 3.4–7.9 m/sec. Xiamen Island is the main part of the landform, with an area of 128.1 km^2 . The main industries in Xiamen are machine manufacturing, electronics industry and chemical engineering. Both Xiamen and Dalian are important harbors of CCR with port cargo throughput of 42.6 and 171 million tons in 2004, respectively. Intensive harbor activities may emit marker elements like V and Ni for heavy oil combustion for industrial use and maritime traffic (Manoli et al., 2002; Moreno et al., 2006; Koc-ak et al., 2007). This will be discussed in detail throughout the rest of this paper. For each city, one site was selected (Fig. 1), and a detailed description is listed in Table 1. Two sampling campaigns were conducted with one in spring and the other in autumn. Spring is the period when dust storms occur frequently in most regions of China (the average dust storm frequency was 52.97%) (Wang et al., 2004). Both Dalian and Xiamen are on the storm transport path and are thus important exit points of dust storms to the Pacific (Hsu et al., 2005).

1.2. PM sampling

The equipment used in Dalian was manufactured by China Geological Equipment Factory. Filter samples were collected with a flow rate of 78 L/min (Zhang et al., 2010). The equipment used in Xiamen was a TEOM-1400 from R&P in the United States for simultaneous collection of $\text{PM}_{2.5}$, PM_{10} and TSP with a flow rate of 16.7 L/min. Ambient air particulate matter was collected synchronously at the two sites. Polypropylene ($\varnothing = 90 \text{ mm}$, Pallflex2500 QAT-UP) (for elemental analysis) and quartz filters ($\varnothing = 90 \text{ mm}$, Pall Gelman Laboratory, Ann Arbor, MI) (for ion analysis) were used. Samplers were placed on the rooftop of buildings of national motoring sites. During each sampling period, PM samples were collected for 10 days. For each day, 24 hr sampling was conducted.

Before sampling, polypropylene and quartz fiber filters were calcined at 60°C for 0.5 hr and 600°C for 2 hr, respectively. Filters

Fig. 1 – Location of the sampling sites.

were weighed by a sensitive microbalance (Shimadzu Scientific Instruments, Inc., Japan) with balance sensitivity ± 0.010 mg, after being stabilized for at least 24 hr under constant temperature ($21^\circ\text{C} \pm 1^\circ\text{C}$) and humidity ($45\% \pm 5\%$). Prior to weighing, filters were equilibrated in a desiccator at room temperature within 48 hr. After sampling, the filters were removed from the inlet, folded in half and wrapped in a laminar-flow clean hood until use. As a control, blank filters were assessed in the same manner. After weighing, the filters were stored at -20°C until chemical analysis.

1.3. Analytical techniques

The filters were digested in a high-pressure Teflon vessel with 3 mL of concentrated HNO_3 , 1 mL of concentrated HCl , and 1 mL of concentrated HF . After cooling, the solutions were dried and diluted to 10 mL with deionized water. In total, 21 elements (Al, As, B, Ba, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, S, Sr, Ti, Zn and Zr) were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, General Electric Co., U.S.A.). Ten ions (SO_4^{2-} , NO_3^- , F^- , Cl^- , NH_4^+ , Na^+ , K^+ , Ca^{2+} and Mg^{2+}) were measured by ion chromatography (IC, Dionex 500, Dionex Co., U.S.A.). The samples were washed twice with deionized water in an ultrasonic cleaner and filtered through $0.47 \mu\text{m}$ microporous membranes before being injected into the IC (Zhang et al., 2010).

1.4. Data analysis

To identify the potential importance of different source regions at the sampling sites, air mass trajectories were calculated

using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) 4.8 model of NOAA's Air Resources Laboratory (ARL). The trajectories reflected the large-scale atmospheric transport characteristics of air masses to the sampling sites. At each sampling time point, a 48 hr back trajectory was computed at 00:00 UTC (coordinated universal time, local time is 8:00) and at 500 m above the end point location at ground level, using the National Centers for Environmental Prediction reanalysis meteorological data as input. Detailed descriptions of PCA, CMB and HYSPLIT analyses can be found in Kong et al. (2011).

2. Results and discussion

2.1. Characteristics of mass concentrations

2.1.1. Differences in mass concentrations of particles in Dalian and Xiamen

In Dalian, the mass concentrations for TSP, PM_{10} and $\text{PM}_{2.5}$ were 119.4 ± 98.7 , 83.2 ± 39.7 and $44.8 \pm 19.2 \mu\text{g}/\text{m}^3$ for spring and were 116.3 ± 51.7 , 64.8 ± 30.5 and $31.3 \pm 17.1 \mu\text{g}/\text{m}^3$ for autumn, respectively. In Xiamen, the average mass concentrations for TSP, PM_{10} and $\text{PM}_{2.5}$ were 29.3 ± 9.9 , 24.3 ± 8.7 and $20.5 \pm 7.7 \mu\text{g}/\text{m}^3$ for spring and were 69.2 ± 27.1 , 63.8 ± 25.6 and $56.2 \pm 23.1 \mu\text{g}/\text{m}^3$ for autumn, respectively (Fig. 2 and Table 2). In spring, the mass concentrations of TSP, PM_{10} and $\text{PM}_{2.5}$ in Dalian were 4.1, 3.4 and 2.2 times higher than those in Xiamen while in autumn, the corresponding values were only 1.9, 1.0 and 0.6 times of those in Xiamen, respectively. In spring, compared with in Xiamen, dust storms might influence particulate matter more obviously in Dalian because

Table 1 – Sampling sites and campaigns.

City	Sampling periods		Sites location	Description	Sampling height/m	No.
	Spring	Autumn				
Dalian	15/03/04–25/03/04 ^a	12/10/04–22/10/04 ^a	Fujiazhuang ($121^\circ 37' 20''$ E $38^\circ 51' 40''$ N)	Traffic, residential	6	20
Xiamen	(n = 10)	(n = 10)	Hongwen ($118^\circ 8' 42''$ E $24^\circ 28' 37''$ N)	and commercial site	9	20

No.: Numbers of samples collected.
 Sites locations are indicated in Fig. 1.
^a DD/MM/YY.

Fig. 2 – Time series of total suspended particulate (TSP), PM_{10} and $PM_{2.5}$ mass concentrations and the mass percentages for PM_{10}/TSP and $PM_{2.5}/PM_{10}$ in different seasons for Dalian and Xiamen.

Dalian is more adjacent to the source regions of dust. In autumn, local anthropological sources were the main contributors to particulate matter both in Dalian and Xiamen, especially for fine particles. Kong et al. (2010) indicated that for TSP, PM_{10} and $PM_{2.5}$ in Tianjin, their dominate sources were soil dust (accounting for 26% of TSP), coal combustion (accounting for 30% of PM_{10}) and vehicle emission (accounting for 34% of $PM_{2.5}$), respectively.

No significant seasonal variations of PM were observed in Dalian for all three types of particles, but for Xiamen, TSP, PM_{10} and $PM_{2.5}$ in autumn were significantly (t -test, $p < 0.001$) higher than those in spring, with the autumn/spring ratios of mass concentrations of 2.4, 2.6 and 2.7, respectively. Higher concentrations of TSP, PM_{10} and $PM_{2.5}$ were also found in autumn at a coastal site of Tianjin, and the author indicated that the thermal inversions and fog situations that appeared could cause a considerable accumulation of air pollutants in the lower layers of the atmosphere (Kong et al., 2010; Marcazzan et al., 2001). This finding indicated that both the thermodynamic conditions in the planetary boundary layer (which can either favorably or adversely affect pollutants dispersion) and sources variation during different seasons were other reasons for significant variations of PM_{10} and $PM_{2.5}$

concentrations. Meanwhile, from the linear regression analysis for TSP vs. PM_{10} and PM_{10} vs. $PM_{2.5}$, all correlation coefficients (r^2) were higher than 0.78 ($p < 0.0001$) for both the two cities and the two seasons (Table 3), indicating that they have common emission sources and could be used to estimate $PM_{2.5}$ from daily monitored PM_{10} and to estimate PM_{10} from TSP.

Different sizes of atmospheric particles probably originate from different sources; the $PM_{2.5}/PM_{10}$ ratio can be used for identifying their sources (Sun et al., 2004; Chan and Yao, 2008). High ratios (e.g., larger than 0.6) were generally ascribed to secondary particulate formation of species such as NO_3^- , SO_4^{2-} , NH_4^+ and organics, while low ratios were ascribed to the overwhelming contribution from fugitive dust or sand dust from long-distance transport (Duan et al., 2006; Chan and Yao, 2008; WHO, 2006). These relationships indicated that the proportion of particles in fine and coarse sizes was dependent on local geography, meteorology and specific PM sources. The typical $PM_{2.5}/PM_{10}$ ratio was 0.50 for developing country urban areas and 0.5–0.8 for developed country urban areas (WHO, 2006). From Fig. 2, the range of $PM_{2.5}/PM_{10}$ ratios in Dalian during the whole period was 0.39–0.67, with an average value of 0.51; while the ratios varied between 0.78 and 0.93 with an

Table 2 – Statistic values for mass concentrations of TSP, PM₁₀ and PM_{2.5} at Spring and Autumn in Dalian and Xiamen.

		Mass concentration (μg/m ³)			Mass percentage (%)	
		TSP (n = 10)	PM ₁₀ (n = 10)	PM _{2.5} (n = 10)	PM ₁₀ /TSP	PM _{2.5} /PM ₁₀
Dalian						
Spring	Min	43.0	37.0	22.0	41.8	45.0
	Max	383.0	160.0	72.0	89.4	66.7
	Median	96.5	78.0	39.5	82.9	56.0
	Mean	119.4	83.2	44.8	78.8	55.4
	SD	98.7	39.7	19.2	13.9	7.5
Autumn	Min	43.3	23.0	11.6	48.3	39.4
	Max	192.4	107.7	61.4	67.8	57.0
	Median	119.4	60.5	28.4	53.6	48.6
	Mean	116.3	64.8	31.3	55.5	47.5
	SD	51.7	30.5	17.1	6.3	5.9
Xiamen						
Spring	Min	13.0	10.0	9.0	76.9	78.3
	Max	44.0	39.0	34.0	88.6	90.0
	Median	30.5	25.0	20.5	82.0	84.5
	Mean	29.3	24.3	20.5	82.3	84.2
	SD	9.9	8.7	7.7	4.0	3.6
Autumn	Min	34.8	31.0	26.3	85.8	81.0
	Max	121.1	113.1	100.3	95.4	92.7
	Median	68.8	64.5	57.3	92.7	88.3
	Mean	69.2	63.8	56.2	91.8	87.8
	SD	27.1	25.6	23.1	3.1	3.7

average value of 0.86 in Xiamen. These observations indicated that fine particles comprise a large fraction of PM₁₀ for both Dalian and Xiamen. The high PM_{2.5}/PM₁₀ ratios in Xiamen were the same as those of the Pearl River Delta (PRD) region of China where the ratios observed were 0.86 (Wang et al., 2008) and 0.92 (Xu et al., 2002). Most of the coarse particles were primary in origin and included biological particles, particles produced by agricultural and construction works, marine aerosols, and some traffic-related particles (e.g., from brakes and tires). Moreno et al. (2004) indicated that the fine fraction was, in contrast, mainly dominated by secondary particles like nitrates and sulfates produced in the atmosphere as a result of condensation of nitrogen and sulfur oxides. Other major sources of fine particles were the primary emissions from power industrial plants (fly-ash) and the combustion of hydrocarbon fuels (particles from vehicle exhaust).

2.1.2. Comparison with other locations

As Table 4 shows, for Dalian, PM₁₀ concentrations were similar to those in Bandung (Oanh et al., 2006), Hong Kong (Ho et al., 2003) and Mexico City (Vega et al., 2002), while for Xiamen, its PM₁₀ concentrations were similar to those in Istanbul (Karaca et al., 2005), Rio de Janeiro (Mariani and Mello, 2007), Buenos Aires (Bogo et al., 2003) and Spain (Querol et al., 2004). For PM_{2.5}, the mass concentrations in Dalian and Xiamen were similar to those in Bangkok (Oanh et al., 2006), Beirut (Shaka and Saliba, 2004), Buenos Aires (Vega et al., 2002), Buenos Aires (Bogo et al., 2003) and Mexico City (Vega et al., 2002). For Asian cities, PM₁₀ had the highest mass concentrations with an average value of 131.2 μg/m³. This level was 3.1, 3.0 and 4.7 times those for South American, European and North American cities, respectively; the mean concentration of PM_{2.5} in Asia was also the highest at 76.6 μg/m³. This level was 3.6, 2.8 and 6.9 times those for South American, European and North American cities, respectively. It should also be noted that the PM₁₀ and PM_{2.5} concentrations were especially high for Chinese mainland cities (CMC), with average values of 164.6 and 104.3 μg/m³, respectively. Meanwhile, the average PM_{2.5}/PM₁₀ ratios for CMC were high (0.67), higher than those for South American (0.47), European (0.61) and North American cities (0.40). Therefore, the PM pollution, especially for fine particles, should be paid more attention in CMC.

2.2. Differences in inorganic element concentrations in Dalian and Xiamen

The absolute concentration of the various inorganic elements is highly differentiated, ranging from a few ng/m³ up to some μg/m³ during the sampling period (Tables 5 and 6). The European Commission proposed a directive for limiting toxic metals with the mean annual concentration proposed as 6 ng/m³ for As, 20 ng/m³ for Ni and 5 ng/m³ for Cd in PM₁₀. The World Health Organization (WHO) proposed an annual average concentration of 150 ng/m³ for Mn in PM₁₀ (Chan and Yao, 2008). The National Ambient Air Quality Standards (GB 3095-2012) gave seasonal limited values for Pb of 1 μg/m³. The measurements in this study suggested concentrations exceed the safe levels for particles both in Dalian and Xiamen at the two study periods compared with the above proposed value. Mn and Pb were at safe levels. Ni was not safe for PM₁₀ in Dalian in spring or for Xiamen in autumn.

Table 3 – Linear regression analysis for total suspended particulate (TSP) vs. PM₁₀ and PM₁₀ vs. PM_{2.5} for the two cities and two seasons.

	Seasons	Combination	Linear regression equation	r ²
Dalian	Spring	TSP vs. PM ₁₀	PM ₁₀ = 0.3576 TSP + 40.5	0.7886 ^a
		PM ₁₀ vs. PM _{2.5}	PM _{2.5} = 0.4527 PM ₁₀ + 7.1365	0.8747
	Autumn	TSP vs. PM ₁₀	PM ₁₀ = 0.5731 TSP - 1.8102	0.9429
		PM ₁₀ vs. PM _{2.5}	PM _{2.5} = 0.5446 PM ₁₀ - 4.0346	0.9408
Xiamen	Spring	TSP vs. PM ₁₀	PM ₁₀ = 0.8781 TSP - 1.4297	0.9841
		PM ₁₀ vs. PM _{2.5}	PM _{2.5} = 0.8771 PM ₁₀ - 0.8124	0.9903
	Autumn	TSP vs. PM ₁₀	PM ₁₀ = 0.943 TSP - 1.443	0.9938
		PM ₁₀ vs. PM _{2.5}	PM _{2.5} = 0.8973 PM ₁₀ - 1.0691	0.9921

r²: correlation coefficients.

^a All significant level as $p < 0.001$.

Table 4 – Comparison of PM concentrations ($\mu\text{g}/\text{m}^3$) in Xiamen and Dalian with other studies for urban sites.

Regions	Location	Sampling time	PM ₁₀	PM _{2.5}	PM _{2.5} /PM ₁₀	Reference
Asian	Dalian	2004	74.0	38.1	0.51	This study
	Xiamen		44.1	38.4	0.86	
	Yangtze delta region	1999	98.0	90.0	0.92	Xu et al. (2002)
	Hong Kong	2000–2001	78.9	50.2	0.60	Ho et al. (2003)
	Nanjing	2001	316	222	0.70	Wang et al. (2003)
	Beirut	2003	119	39.9	0.34	Shaka and Saliba (2004)
	Istanbul, Turkey	2002–003	47.1	20.8	0.46	Karaca et al. (2005)
	Beijing	2002–2003	210	116	0.55	Sun et al. (2004)
	Kanpur	2002–2003	211	101	0.50	Sharma and Maloo (2005)
	Taichung, Taiwan	2004–2005	26.7	16.9	0.63	Fang et al. (2006)
	Beijing	2001–2004	221	136	0.62	Oanh et al. (2006)
	Bangkok		54.5	34.0	0.62	
	Bandung		72.5	45.5	0.63	
	Manila		54.5	43.5	0.80	
	Hanoi		132.5	78.5	0.59	
	Chennai		157	44.0	0.28	
	Taiwan	2002–2003	104	64.7	0.62	Tsaia and Chen (2006)
	Shanghai	2004–2005	118	68.0	0.57	Chen et al. (2008)
	Urumqi	2004–2007	373	187	0.50	Li et al. (2008)
	Pearl River Delta, China	2004	113	97.0	0.86	Wang et al. (2008)
South America	Mexico city	1997	71.3	35.9	0.50	Vega et al. (2002)
	Buenos Aires	1999	48.0	37.0	0.77	Bogo et al. (2003)
	Candiota region	2000–2003	14.9	5.2	0.35	Braga et al. (2004)
	Sao Paulo	2002	33.6	11.9	0.35	Bourotte et al. (2007)
	Rio de Janeiro	1998–1999	42.8	17.1	0.38	Mariani and Mello (2007)
Europe	Milan	1997–1998	85.5	54.5	0.64	Marcazzan et al. (2001)
	Thessaloniki, Greece	1994–1995	127	97.0	0.76	Manoli et al. (2002)
	Spain	1999–2001	47.5	30.0	0.63	Querol et al. (2004)
	Porto, Italy	2002	27.0	15.0	0.56	Braga et al. (2005)
	Edinburgh	1999–2000	15.5	8.5	0.55	Heal et al. (2005)
	Duisburg	2002	21.9	14.7	0.67	Sillanpaa et al. (2006)
	Prague	2002–2003	35.0	29.6	0.85	
	Amsterdam	2003	34.8	25.4	0.73	
	Helsinki	2003	21.1	8.3	0.39	
	Barcelona	2003	46.3	20.0	0.43	
	Athens	2003	54.0	25.3	0.47	
	Moitinhos, Portugal	2002–2003	35.8	23.0	0.64	Oliveira et al. (2007)
	Helsinki, Finland	2002	56.7	20.3	0.36	Aarnio et al. (2008)
North America	Edmonton, Canada	1984–1994	29.1	11.2	0.38	Cheng et al. (1998)
	Calgary, Canada		26.3	11.1	0.42	

The ratios were calculated based on arithmetic average of PM₁₀ and PM_{2.5} mass concentrations for each site during sampling periods.

Na, Al, S, Ca, Fe and Zn were the most abundant inorganic elements for all the three size fractions of particles in Dalian and Xiamen. They comprised 85.9%–88.2% of the concentrations for all the detected inorganic elements in spring, and there were no obvious diversities in the two cities. While in autumn, they occupied 86.1%–87.5% and 46.2%–46.4% of the concentrations for all the detected inorganic elements for particles in Dalian and Xiamen, respectively. In spring, all inorganic elements were higher in Dalian than those from Xiamen, with the Dalian/Xiamen ratios ranging from 1.2–25.0 except for Ti (for all the three fractions), Cr and Zn (only for PM_{2.5}). It may be that dust could influence the particles in Dalian more strongly than Xiamen during spring as the Dalian/Xiamen ratios were especially higher for crustal elements such as Mg (4.0–10.1), Al (2.6–8.0), Ca (4.1–12.7), Mn (1.2–3.6) and Fe (2.9–7.9). Meanwhile, the ratios in decreasing order were TSP > PM₁₀ > PM_{2.5} for all of the above elements.

In autumn, all V, Mo and Ni were higher in Xiamen than in Dalian, with the Dalian/Xiamen ratios of 0.04–0.08, 0.01–0.04 and 0.10–0.38, indicating that there were more emission sources for these elements in Xiamen. V and Ni are widely accepted as markers for heavy oil combustion (Janssen et al., 1997; Manoli et al., 2002; Hsu et al., 2005; Almeida et al., 2006; Moreno et al., 2006; Koc-ak et al., 2007; Wu et al., 2007). Therefore, there were more heavy oil combustion sources in Xiamen, like vessel and industrial activities. For S, Zn and Ba, their Dalian/Xiamen ratios were in the range of 242–524, 95–315 and 3.5–16.1, respectively, indicating that coal combustion and vehicle exhaust were more important sources for particles in Dalian in autumn than those in Xiamen. Ba and Zn were source signatures for vehicle exhaust (Hueglin et al., 2005; Hagler et al., 2007; Wu et al., 2007; Viana et al., 2008). S was a marker for almost all of the fugitive dusts in a coal-based city in China (Kong et al., 2011). Heavy elements (V, Cr,

Table 5 – Statistical analysis of chemical species in TSP, PM₁₀ and PM_{2.5} at spring of Dalian and Xiamen (ng/m³).

	Dalian			Xiamen		
	TSP	PM ₁₀	PM _{2.5}	TSP	PM ₁₀	PM _{2.5}
B	15.1 ± 11.4	11.2 ± 5.5	6.3 ± 2.1	4.4 ± 2.2	3.8 ± 1.9	3.3 ± 1.8
Na	813.9 ± 673.0	555.3 ± 286.2	298.7 ± 123.8	266.2 ± 80.3	230.6 ± 69.7	205.7 ± 64.5
Mg	596.8 ± 462.1	368.0 ± 167.9	152.2 ± 66.6	59.1 ± 18.7	45.5 ± 14.0	38.2 ± 11.4
Al	2195.4 ± 1639.8	1473.0 ± 636.7	547.0 ± 219.9	273.1 ± 87.3	237.9 ± 77.2	212.3 ± 71.0
P	83.8 ± 67.6	56.3 ± 25.8	30.6 ± 12.2	20.8 ± 6.6	17.6 ± 5.8	15.2 ± 4.8
S	4553.6 ± 1992.3	3788.8 ± 1789.1	2131.8 ± 799.5	1271.4 ± 489.3	1053.9 ± 391.1	913.6 ± 326.7
K	586.2 ± 460.4	417.8 ± 210.6	205.6 ± 78.8	147.1 ± 46.7	126.6 ± 45.1	115.3 ± 41.8
Ca	4437.7 ± 3662.9	2798.6 ± 1424.3	1018.3 ± 421.7	348.4 ± 110.0	287.4 ± 87.5	246.0 ± 77.9
Ti	22.1 ± 18.3	14.1 ± 7.8	6.4 ± 2.6	24.0 ± 7.0	21.2 ± 6.7	18.1 ± 5.7
V	19.6 ± 8.1	15.4 ± 5.9	8.5 ± 2.8	8.5 ± 2.8	7.4 ± 2.6	6.4 ± 2.4
Cr	10.4 ± 7.7	7.7 ± 3.9	4.2 ± 1.9	7.6 ± 2.2	6.6 ± 2.1	5.5 ± 1.8
Mn	53.0 ± 45.6	35.6 ± 16.2	18.1 ± 7.2	14.9 ± 4.9	12.1 ± 4.0	14.5 ± 12.8
Fe	2376.2 ± 1882.6	1567.7 ± 699.6	632.3 ± 269.9	302.0 ± 96.3	251.3 ± 78.0	219.3 ± 72.4
Mo	5.8 ± 4.4	4.2 ± 2.1	2.5 ± 1.0	0.6 ± 0.5	0.2 ± 0.4	0.1 ± 0.3
Ni	43.7 ± 37.9	28.1 ± 13.6	15.4 ± 6.2	6.8 ± 2.4	5.9 ± 1.7	5.3 ± 1.6
Cu	147.0 ± 110.3	96.8 ± 45.8	52.5 ± 20.6	35.6 ± 9.9	30.3 ± 8.6	27.5 ± 8.0
Zn	362.5 ± 271.4	275.8 ± 122.2	137.4 ± 45.8	263.7 ± 78.0	229.1 ± 76.3	202.8 ± 67.7
Sr	18.5 ± 16.1	12.1 ± 6.0	4.3 ± 1.8	2.6 ± 1.0	2.2 ± 0.8	1.9 ± 0.6
Zr	3.9 ± 3.1	2.7 ± 1.5	1.1 ± 0.7	0.4 ± 0.7	0.3 ± 0.5	0.1 ± 0.3
As	28.9 ± 12.6	23.7 ± 10.6	16.1 ± 6.1	16.7 ± 6.1	14.8 ± 5.5	13.0 ± 4.8
Cd	10.3 ± 9.2	6.5 ± 3.1	3.8 ± 1.8	3.6 ± 1.0	3.0 ± 0.7	2.4 ± 0.8
Ba	116.4 ± 93.1	72.7 ± 35.7	30.8 ± 13.2	38.5 ± 17.8	31.6 ± 15.2	27.4 ± 13.4
Pb	124.4 ± 77.1	93.3 ± 46.7	42.9 ± 17.7	45.0 ± 15.4	39.0 ± 12.7	34.6 ± 11.4
Na ⁺	727.9 ± 580.8	504.8 ± 262.7	277.2 ± 115.1	235.3 ± 70.8	207.8 ± 61.2	190.1 ± 60.9
NH ₄ ⁺	3002.0 ± 1371.7	2353.3 ± 1009.8	1667.2 ± 668.4	1273.3 ± 482.9	1069.4 ± 403.1	891.5 ± 329.3
Mg ²⁺	494.9 ± 380.6	318.8 ± 141.4	132.6 ± 56.5	48.5 ± 14.9	39.0 ± 12.0	32.7 ± 10.1
K ⁺	528.1 ± 408.2	386.8 ± 209.1	189.7 ± 69.8	132.6 ± 42.3	114.3 ± 41.7	103.4 ± 39.4
Ca ²⁺	3703.5 ± 2917.7	2454.5 ± 1223.4	923.7 ± 371.1	319.3 ± 100.6	265.9 ± 81.9	223.2 ± 73.3
F ⁻	44.0 ± 35.6	26.6 ± 13.9	14.2 ± 7.2	2.9 ± 1.6	1.7 ± 0.7	1.2 ± 0.8
Cl ⁻	1300.0 ± 1138.3	850.3 ± 431.9	481.0 ± 194.6	351.8 ± 99.8	302.8 ± 90.3	266.4 ± 84.6
NO ₃ ⁻	3327.2 ± 1443.0	2635.0 ± 1223.5	1564.1 ± 809.1	1891.6 ± 648.6	1609.6 ± 568.2	1294.9 ± 505.2
SO ₄ ²⁻	11,855.1 ± 5419.4	10,079.8 ± 4843.1	5711.1 ± 2223.6	3354.0 ± 1282.4	2855.7 ± 1077.1	2462.7 ± 862.9

Mean ± Standard deviation are listed.

Ni, Cu, Zn, As, Cd, Ba and Pb), in total, account for 5.5%–6.1% and 13.9%–14.6% of particles in Dalian and Xiamen in spring, respectively, while in autumn the corresponding values were 7.9%–9.3% and 17.7%–17.9%, respectively. It could be concluded that the heavy metal pollution in Xiamen was more serious than in Dalian and was more serious in autumn than in spring for both of the two cities.

The inorganic elements have different behaviors not only in their absolute concentrations in air but also in the relative sharing of the two fractions that constitute PM₁₀: fine particles and coarse particles (Chan and Yao, 2008; Fang et al., 2005). These authors reported that As, Ca, Fe, Mg, Na and Ti appear to accumulate in the larger fraction while anthropogenic sources such as V, Pb and Zn were observed to accumulate in the fine fraction. Sharma and Maloo (2005) also noted that metals associated with the finer fraction mostly originate from the incomplete combustion of carbon-containing materials from motor vehicles, power plants, smelters, incinerators, cement kilns and home furnaces, while the metals derived from natural sources were usually present in the coarse fraction. Moreno et al. (2006) found that Ti, Mn, Sr, Sb and Ce were always preferentially concentrated in the coarser sample, whereas V, Ni, Co, As, Se, Cd, Sn, Yb, Lu, Tl, Pb, Bi and Th were more enriched in PM_{2.5}. In this study, when compared

with Dalian, all of the inorganic elements preferentially concentrated in the fine fraction for both spring and autumn. Their mass percentages in PM_{2.5} were in the range of 55.6%–78.4% and 72.2%–92% of TSP for spring and autumn, respectively, in Xiamen (Fig. 3). In Dalian, their mass percentages in PM_{2.5} varied between 22.9%–55.7% and 12.6%–42.4% for spring and autumn, respectively. It could be concluded that particles in Xiamen were more hazardous than those in Dalian, as the fine particles can be deposited deeper in the respiration system than coarse particles. Meanwhile, for most inorganic elements in the fine particles from Xiamen, their mass percentages were correspondingly higher in autumn than spring (except for Ti and Sr); for those in Dalian, it was the opposite (except for Zr and Sr). Heal et al. (2005) reported that in Birmingham, the PM_{2.5}/PM₁₀ ratios for Fe, Cu, Ni and Zn were 30%, 35%, 75% and 75%, respectively; Kyotani and Iwatsuki (2002) reported that the PM_{2.5}/PM₁₀ ratios for Ti, Fe, Mn, V, Pb, Cu and Zn were 15%, 25%, 40%, 60%, 75% and 75%, respectively in Kofu, Japan. These results were different than those in this study. For inorganic elements in Dalian, the PM_{2.5}/PM₁₀ ratios were in the range of 35% (for Sr)–68% (for As) and 39% (for Fe)–66% (for P) for spring and autumn, respectively. For inorganic elements in Xiamen, the ratios ranged from 65% (for Zr)–91% (for Cu) and 85% (for Sr)–96% (for Cr) for

Table 6 – Statistical analysis of chemical species in TSP, PM₁₀ and PM_{2.5} at autumn of Dalian and Xiamen (ng/m³).

	Dalian			Xiamen		
	TSP	PM ₁₀	PM _{2.5}	TSP	PM ₁₀	PM _{2.5}
B	13.4 ± 5.5	10.6 ± 5.2	5.3 ± 2.8	21.0 ± 7.3	18.5 ± 6.6	16.8 ± 6.3
Na	1029.0 ± 472.8	434.0 ± 193.4	204.4 ± 102.9	246.2 ± 85.5	220.3 ± 81.2	195.0 ± 76.3
Mg	796.3 ± 325.4	316.2 ± 116.1	148.2 ± 83.4	102.2 ± 37.0	88.6 ± 32.8	80.4 ± 29.1
Al	995.2 ± 439.0	452.9 ± 212.9	206.5 ± 100.2	221.0 ± 80.6	197.2 ± 69.7	173.1 ± 65.8
P	66.9 ± 25.7	33.5 ± 13.7	22.1 ± 12.5	151.0 ± 56.4	135.7 ± 53.4	122.1 ± 50.3
S	1676.8 ± 699.6	1017.4 ± 542.6	653.3 ± 367.0	3.2 ± 1.2	3.2 ± 1.2	2.7 ± 0.9
K	789.1 ± 344.4	355.9 ± 155.1	195.3 ± 102.3	395.8 ± 142.7	351.3 ± 133.0	322.4 ± 128.5
Ca	7594.3 ± 3657.8	3997.8 ± 2276.4	1648.3 ± 921.8	385.8 ± 127.2	342.9 ± 119.3	308.8 ± 109.3
Ti	25.0 ± 10.2	9.8 ± 4.1	6.4 ± 3.9	12.5 ± 4.6	10.9 ± 4.2	9.4 ± 3.9
V	19.8 ± 7.8	12.9 ± 6.5	7.0 ± 3.6	238.5 ± 88.1	213.7 ± 80.2	191.7 ± 75.2
Cr	15.5 ± 6.7	7.8 ± 3.7	4.0 ± 2.3	10.1 ± 4.1	9.0 ± 4.1	8.6 ± 3.8
Mn	94.6 ± 56.7	49.4 ± 25.1	22.1 ± 12.6	35.5 ± 11.9	32.5 ± 10.9	28.6 ± 10.4
Fe	2104.7 ± 916.0	671.5 ± 294.4	265.1 ± 141.3	345.4 ± 113.5	315.4 ± 105.3	286.7 ± 99.9
Mo	9.4 ± 4.1	4.0 ± 1.8	2.4 ± 1.2	246.2 ± 85.5	220.3 ± 81.2	195.0 ± 76.3
Ni	20.3 ± 8.3	7.9 ± 3.8	4.3 ± 2.6	53.0 ± 18.8	47.9 ± 17.3	42.5 ± 15.7
Cu	105.8 ± 46.9	41.9 ± 18.8	25.6 ± 13.5	19.2 ± 7.1	17.7 ± 6.4	16.2 ± 5.8
Zn	788.1 ± 318.9	456.6 ± 201.4	218.6 ± 101.2	2.5 ± 0.8	2.4 ± 1.0	2.3 ± 0.9
Sr	17.8 ± 6.7	11.3 ± 5.9	6.2 ± 3.8	9.0 ± 3.2	7.7 ± 2.9	6.5 ± 2.4
Zr	4.3 ± 1.8	2.4 ± 1.2	1.3 ± 1.1	2.1 ± 0.7	1.9 ± 0.7	1.7 ± 0.6
As	27.8 ± 11.2	20.7 ± 10.3	11.8 ± 6.4	19.8 ± 7.1	17.8 ± 6.2	16.1 ± 5.7
Cd	8.7 ± 4.6	4.6 ± 2.4	2.6 ± 1.5	2.9 ± 1.0	2.7 ± 0.7	2.6 ± 0.8
Ba	122.6 ± 56.4	54.2 ± 25.1	21.5 ± 10.7	7.6 ± 3.0	7.0 ± 2.5	6.2 ± 2.4
Pb	102.5 ± 46.2	59.5 ± 28.1	29.0 ± 15.5	72.1 ± 27.2	66.0 ± 24.9	62.3 ± 23.9
Na ⁺	923.7 ± 438.3	400.6 ± 189.9	184.0 ± 89.9	221.6 ± 81.1	197.5 ± 76.0	178.6 ± 70.9
NH ₄ ⁺	683.3 ± 332.7	459.1 ± 198.7	446.9 ± 282.8	10,451.1 ± 3748.8	9559.5 ± 3495.7	8794.9 ± 3249.8
Mg ²⁺	607.9 ± 246.8	260.8 ± 103.6	119.7 ± 64.8	89.4 ± 33.0	77.7 ± 28.5	72.9 ± 26.0
K ⁺	715.1 ± 324.6	319.5 ± 154.3	134.1 ± 63.7	361.6 ± 136.9	333.9 ± 115.6	290.4 ± 118.8
Ca ²⁺	4906.9 ± 2100.1	3169.5 ± 1854.2	1384.0 ± 755.9	340.3 ± 113.1	309.5 ± 104.6	284.9 ± 96.9
F ⁻	460.9 ± 230.3	194.7 ± 98.1	79.0 ± 43.5	81.7 ± 32.1	72.6 ± 26.9	63.1 ± 24.5
Cl ⁻	1605.8 ± 731.1	712.9 ± 346.5	318.4 ± 163.9	347.3 ± 125.5	315.1 ± 126.7	287.6 ± 102.7
NO ₃ ⁻	1721.6 ± 689.8	1276.5 ± 596.3	620.8 ± 289.6	11,754.1 ± 4092.4	10,655.2 ± 3771.9	9343.5 ± 3532.4
SO ₄ ²⁻	4340.2 ± 1768.6	2675.4 ± 1436.4	1746.3 ± 974.3	19,252.9 ± 7589.5	17,849.1 ± 6857.2	17,042.9 ± 6549.7

Fig. 3 – Size distribution of chemical species in atmospheric particulate matter from Dalian and Xiamen in spring and autumn. PM_{2.5–10} particle matters with aerodynamic diameter between 2.5 μ m and 10 μ m; PM_{10–100} particle matters with aerodynamic diameter between 10 μ m and 100 μ m.

spring and autumn, respectively. These ranges might be related to the different dominate sources of fine particles in different periods of the two cities.

2.3. Characteristic of soluble ion concentrations in Dalian and Xiamen

2.3.1. Differences in mass concentrations

Tables 5 and 6 show that secondary ions, including SO_4^{2-} , NO_3^- and NH_4^+ (Chen et al., 2003; Xiu et al., 2004; Wang et al., 2006), were the dominant ions, in total, accounting for 72.7%–81.6% and 85.0%–85.6% for particles in Dalian and Xiamen, respectively, in spring. In autumn, the corresponding values were 42.2%–55.9% and 96.6%–96.7% for Dalian and Xiamen, respectively. SO_4^{2-} , NO_3^- and NH_4^+ showed higher mass concentrations in Dalian in spring but were lower in autumn compared with those in Xiamen. Na^+ and Cl^- were related to marine aerosol (Chen et al., 2003), and their concentrations in Dalian were 1.0–4.2 and 1.1–4.6 times those in Xiamen for spring and autumn, respectively. This observation indicates that marine aerosol was more important to the particulate matter in Dalian compared with Xiamen. The mass concentrations of Ca^{2+} were higher in Dalian than those in Xiamen and were approximately 10 times higher for TSP and PM_{10} and 5 times higher for $\text{PM}_{2.5}$. In Dalian, Mg^{2+} was 4.1–10.2 (for spring) and 1.6–6.8 (for autumn) times those in Xiamen, and the values were higher for spring. Wang et al. (2006) noted that Ca^{2+} and Mg^{2+} were mainly from crustal sources and construction dust. Therefore, the particles in Dalian might be influenced more by local construction activities and soil dust.

For K^+ , a marker for biomass burning (Wang et al., 2006; Tao et al., 2009; Kumar and Sarin, 2010), its mass concentrations in Dalian were 1.8–4.0 and 0.5 (for $\text{PM}_{2.5}$)–2.0 times those in

Xiamen for spring and autumn, respectively. Elevated K^+ concentrations were also observed in Xi'an by Shen et al. (2009) in the straw burning period, indicating that in autumn, fine particles in Xiamen might be influenced more by biomass burning when compared with those in Dalian. This influence of biomass burning was verified by the backward mass trajectories as shown in Fig. 4. For Dalian, the air masses mainly travel across northern and northeastern China (including Liaoning, Jilin, Hebei and Shandong province). For Xiamen, a large fraction of air masses travel from the ocean, and in autumn, some originate from the eastern coastal area of China, including Jiangsu, Shandong and Liaoning Provinces. Lu et al. (2011) indicated that the emission amounts of $\text{PM}_{2.5}$ from biomass burning were 208.3, 144.8, 119.2, 210.9, 252.9 and 271.5 kg for Hebei, Liaoning, Jilin, Jiangsu, Shandong and Henan Provinces of China, respectively, in 2007. In most cases, the air masses traveling to Dalian were influenced more by biomass burning when compared with Xiamen. While in autumn (the harvest time in China), the higher emission amounts of particles from Jiangsu and Shandong Provinces might explain the higher K^+ concentrations in $\text{PM}_{2.5}$ in autumn in Xiamen.

Considering the size distribution of ions, in Dalian, there was no obvious diversity of ion distribution in $\text{PM}_{2.5}$, particle matters with aerodynamic diameter between 2.5 μm and 10 μm ($\text{PM}_{2.5-10}$), particle matters with aerodynamic diameter between 10 μm and 100 μm (PM_{10-100}), with the ranges of average mass percentages of 24.9%–55.5%, 22.9%–41.3% and 15%–39.5%, respectively, in spring. In autumn, the corresponding values were 11.3%–65.4%, 1.8%–38.1% and 2.9%–59.8%, respectively, as Fig. 3 shows. For Xiamen, it is clear that ions of $\text{PM}_{2.5}$ dominate, with mass percentages of 41.9%–80.8% and 77.2%–89.2%. Tao et al. (2009) and Yang et al. (2007) calculated

Fig. 4 – Forty-eight hour air parcel backward trajectories (every 1 hr in each day) for spring and autumn in Dalian and Xiamen.

that $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 contributed to 56.1% and 61% of the light extinction coefficient of $\text{PM}_{2.5}$ in Guangzhou and Jinan, respectively. Considering the higher mass concentrations of secondary inorganic ions in Xiamen in autumn and the higher mass percentages of these ions in fine particles, the haze pollution in Xiamen should be paid more attention because these ions were the main contributors to visibility degradation.

2.3.2. Differences in specific ionic ratios

2.3.2.1. Anions/cations (A/C) ratio. This ratio is a good indicator of the acidity of particles (Wang et al., 2006). Total anions were well correlated with cations, with correlation coefficients (R^2) higher than 0.99 ($p < 0.001$) for all fractions of particles in Dalian and Xiamen in both spring and autumn, as shown in Fig. 5. For Xiamen, all slopes were higher than 1.0, implying insufficient cations to neutralizing anions. While for Dalian, most slopes were lower than 1.0, indicating insufficient anions, except for $\text{PM}_{2.5}$ and PM_{10} in spring. This result indicated that in Xiamen, the particles were acidic during the sampling periods, while in Dalian, the particles were alkaline, except for PM_{10} and $\text{PM}_{2.5}$. From Fig. 4, a fraction of the air masses of Dalian were from Shandong Province where industrial activities, including coal-fired power plants, emit the highest amounts of $\text{PM}_{2.5}$ and PM_{10} (Zhang et al., 2006). In Kong et al. (2012), higher SO_4^{2-} mass concentrations were observed in a coal-based city, and the author attributed it to local coal combustion. In the current study, high SO_4^{2-} mass concentrations were also found in spring in Xiamen, as shown in Table 5.

2.3.2.2. Non-sea salt (nss) ions/total ions ratio. The chemical composition of sea-salt particles was assumed to be the same as that of sea water, and the soluble Na^+ in particulate samples was assumed to come solely from sea-salts. nss-SO_4^{2-} , nss-Cl^- , nss-Mg^{2+} , nss-K^+ and nss-Ca^{2+} can be calculated by the following equations. Typical sea water compositions are from Das et al. (2011).

$$\text{nss-SO}_4^{2-} = [\text{SO}_4^{2-}] - 0.125[\text{Na}^+] \quad (1)$$

$$\text{nss-Cl}^- = [\text{Cl}^-] - 1.167[\text{Na}^+] \quad (2)$$

$$\text{nss-Mg}^{2+} = [\text{Mg}^{2+}] - 0.022[\text{Na}^+] \quad (3)$$

$$\text{nss-K}^+ = [\text{K}^+] - 0.227[\text{Na}^+] \quad (4)$$

$$\text{nss-Ca}^{2+} = [\text{Ca}^{2+}] - 0.044[\text{Na}^+] \quad (5)$$

Fig. 6 lists the mass concentrations and mass percentages of nss-ions in Dalian and Xiamen. In Dalian, nss-SO_4^{2-} and nss-Ca^{2+} hold the higher mass concentrations, ranging from 1.7–11.3 and 0.8–4.8 $\mu\text{g}/\text{m}^3$, respectively; while in Xiamen, nss-SO_4^{2-} dominates, with the mass concentrations ranging from 2.1–19.2 $\mu\text{g}/\text{m}^3$. In spring, the nss-SO_4^{2-} in Dalian was 3.5, 3.1 and 2.2 times that in Xiamen for TSP, PM_{10} and $\text{PM}_{2.5}$, respectively. However, in autumn, it was the opposite. nss-SO_4^{2-} concentrations were higher for particles in Xiamen,

Fig. 5 – Relationship between equivalent concentrations for anions and cations of particles from Dalian and Xiamen in spring and autumn. Cations = $[\text{Na}^+] / 23 + [\text{NH}_4^+] / 17 + [\text{K}^+] / 39 + 2 \times [\text{Mg}^{2+}] / 24 + 2 \times [\text{Ca}^{2+}] / 40$; Anions = $[\text{F}^-] / 19 + [\text{Cl}^-] / 35.5 + [\text{NO}_3^-] / 62 + 2 \times [\text{SO}_4^{2-}] / 96$.

Fig. 6 – Distribution of non-sea salt ions in Dalian and Xiamen in spring and autumn.

especially for fine particles, at approximately 4.5, 6.6 and 9.8 times that in Dalian for TSP, PM₁₀ and PM_{2.5}, respectively. It may be that in spring, nss-SO₄²⁻ in Dalian might be more easily influenced by soil dust, which is more obvious for coarse particles, but in autumn, nss-SO₄²⁻ in Xiamen might be influenced more by coal combustion from long-range transport as discussed before.

In this study, SO₄²⁻, Ca²⁺ and Mg²⁺ were mostly from anthropogenic sources with nss-SO₄²⁻, nss-Mg²⁺ and nss-Ca²⁺ contributing higher than 87% of the corresponding ions in both of the two cities. Nss-Ca²⁺ was formed by the neutralization of acidic species (SO₄²⁻ and NO₃) by alkaline dust (CaCO₃) (Das et al., 2011). Nss-K⁺ accounts for 67%–75% of soluble K⁺ in Dalian. In Xiamen, it was occupied by 55%–60% and 85.7%–86% of K⁺ in spring and autumn, respectively. It seems that biomass burning dominates the contributions of K⁺ in Dalian, while in Xiamen, its contributions were only 26%–29% in autumn. For Cl⁻, only 31%–34% and 16%–28% were contributed by non-sea-salt sources in Dalian and Xiamen, respectively. These sources include waste incineration (Xia and Gao, 2010).

2.3.2.3. NO₃/nss-SO₄²⁻ ratio. The mass ratio of NO₃/nss-SO₄²⁻ has been used as an indicator of the relative importance of mobile vs. stationary sources of sulfur and nitrogen in the atmosphere (Wang et al., 2006). All of the ratios were lower than 1 (Fig. 7), the low mass ratios implying stationary emissions were predominant for atmospheric particulate matter (Aneja et al., 2006; Gu et al., 2013) in both northern and southern cities of China. In the current study, the NO₃/SO₄²⁻ ratios in Dalian (0.25–0.49) were lower than those in Xiamen (0.51–0.62) for the three types of particles in both spring and autumn, indicating that the contributions of vehicle emission to total particles in Xiamen were higher than those in Dalian.

2.4. Differences of chemical composition profiles between the two cities

To assess the degree of similarity between inorganic chemical compositions of particles from Dalian and Xiamen,

coefficient of divergences (CDs) were calculated for the three types of particles in spring and autumn. CD is defined as (Wongphatarakul et al., 1998):

$$CD_{jk} = \sqrt{\frac{1}{p} \sum_{i=1}^p \left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}} \right)^2} \quad (6)$$

where, x_{ij} represents the average concentration for a chemical component i at site j , j and k represent two sampling sites and p is the number of chemical components. If the CD approaches zero, the data from the two sites are considered similar. If the CD approaches one, they are considered to be very different (Wongphatarakul et al., 1998; Zhang and Friedlander, 2000; Han et al., 2010). Wongphatarakul et al. (1998) thought that the CD value of 0.269 reflected the similarity between particles of the two cities. In addition, mass concentration diagrams were characterized by scatter plots of chemical components' mass concentration for j against k . The mass concentration scatter diagrams of these three types of particles for spring and autumn are shown in Fig. 8. In this study, all

Fig. 7 – Ratios for NO₃⁻/SO₄²⁻ of particles from Dalian and Xiamen in spring and autumn.

Fig. 8 – Comparison of chemical species profiles for different size of particles among two cities in spring and autumn.

of the inorganic chemical composition profiles for TSP, PM₁₀ and PM_{2.5} of Xiamen and Dalian in spring and autumn were quite different from each other, with the CD values all higher than 0.40.

3. Conclusions

Inorganic chemical compositions of atmospheric TSP, PM₁₀ and PM_{2.5} in two of the most industrialized and quickly developing cities of eastern China were investigated and compared in this study. The analytical results suggested that economic structure, geographical location and meteorological factors contributed to the difference in inorganic chemical compositions of particulate matter from northern and southern Chinese cities.

The mass concentrations for TSP, PM₁₀ and PM_{2.5} were 117.9 ± 76.7 , 74.8 ± 35.7 and 38.0 ± 19.0 $\mu\text{g}/\text{m}^3$ for Dalian and 49.3 ± 28.5 , 44.1 ± 27.5 and 38.4 ± 24.8 $\mu\text{g}/\text{m}^3$ for Xiamen, respectively. In spring, the dust might influence the particulate matter more strongly in Dalian than in Xiamen, especially for coarse particles. This influence was verified by the

distribution of crustal elements such as Mg, Al, Ca, Mn and Fe. Heavy metals (V, Cr, Ni, Cu, Zn, As, Cd, Ba and Pb) accounted for 13.9%–17.9% of particles in Xiamen, higher than the 5.5%–9.3% in Dalian, indicating the heavy metal pollution in Xiamen was more serious than in Dalian.

Secondary ions, including SO_4^{2-} , NO_3^- and NH_4^+ , were the dominant ions, in total, accounting for 42.2%–81.6% and 85.0%–96.7% of particles in Dalian and Xiamen, respectively. They had higher mass concentrations in Dalian in spring but were lower in autumn when compared with those in Xiamen. Na^+ and Cl^- in Dalian were 1.0–4.6 times those in Xiamen, indicating marine aerosol was more important to particles in Dalian. The mass concentrations of Ca^{2+} and Mg^{2+} were higher in Dalian than those in Xiamen due to the influence of local construction activities and soil dust. In most cases, the air masses transported in Dalian were influenced more by biomass burning when compared with Xiamen. However, in autumn, the higher emission amounts of particles for Jiangsu and Shandong Province might explain the higher K^+ concentrations in PM_{2.5} in autumn in Xiamen.

Anions/cations ratios indicate that in Xiamen, the particles were acidic, but in Dalian, the particles were alkaline, except

for PM₁₀ and PM_{2.5}. In the current study, SO₄²⁻, Ca²⁺ and Mg²⁺ were mostly from anthropogenic sources, with the nss-SO₄²⁻, nss-Mg²⁺ and nss-Ca²⁺ contributing higher than 87% of the corresponding ions in both of the cities. NO₃/nss-SO₄²⁻ mass ratios were lower than 1, implying stationary emissions were predominant for atmospheric particulate matter in both northern and southern cities of China. The NO₃/SO₄²⁻ ratios in Dalian (0.25–0.49) were lower than those in Xiamen (0.51–0.62) for the three types of particles in both spring and autumn. This difference indicates that the contribution of vehicle emissions to particles in Xiamen were higher than that in Dalian. Coefficient of divergence values were higher than 0.40, suggesting that the location of cities and season contributed to the differences in the inorganic chemical composition profiles for TSP, PM₁₀ and PM_{2.5}.

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