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Spatial and seasonal variability of water-soluble ions in $PM_{2.5}$ aerosols in 14 major cities in China

Miao-Ching Cheng [a,1], Chen-Feng You [a,b,*], Junji Cao [c], Zhangdong Jin [c]

[a] Department of Earth Sciences, National Cheng Kung University, Tainan 701, Taiwan
[b] Earth Dynamic System Research Center, National Cheng Kung University, Taiwan
[c] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

HIGHLIGHTS

- 110 $PM_{2.5}$ samples in 14 major cities over China and analyze for WS ions in summer and in winter 2003.
- Anthropogenic activities are the main sources for WS ions in $PM_{2.5}$ particles.
- High concentrations of WS-Zn, Pb and S in winter are mainly due to coal burning.
- Location of industrial zones influence heavy metals of aerosols significantly.

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ABSTRACT

We analyzed $PM_{2.5}$ aerosols from 14 major cities in China for concentrations of water-soluble (WS) major and trace elements (Na, Mg, Ca, K, Fe, Mn, Zn, Rb, Sr, Ba, Pb, S and Cl). The main focus was to examine patterns in spatial distribution and seasonal variability. Using principal component analysis, we identified three general sources for WS-elements in aerosols as anthropogenic, seasalts and fine dust particles originating from soils. The spatial patterns identified show that anthropogenic activity is the most important factor influencing the concentration of heavy metals in aerosols. Concentrations of WS-S, Zn and Pb were correlated with the locations of major industrial zones, and regulated by topography and seasonal weather patterns. We found higher WS-metals concentrations during the winter season, probably related to coal combustion in northern China. Moderate correlations of WS-S, Zn, Pb and Cl suggest that coal combustion releases. The seasonal pattern in WS-Fe concentrations shows the importance of acid precipitation events where coal combustion contributes to additional Fe (II) deposition. The findings of this study support the argument that WS-S in fine particles enhanced the production of hydrogen ions act to reduce the pH values of precipitation. Our interpretation of these spatial and seasonal patterns in WS-major and trace elements in aerosols highlights the need for continued research on trends in acidic deposition in major industrial cities in China.

1. Introduction

$PM_{2.5}$ aerosols derived mainly from the combustion of fossil fuels, traffic, and smelting and metal processing (Mouli et al., 2005; Tie and Cao, 2009). Atmospheric transport delivers pollutants from industrial and other anthropogenic activities in Asia to the western Pacific and other surrounding areas (Zhou et al., 1990; Uematsu et al., 1992). For example, large quantities of suspended particulate matter (PM) and crustal materials are carried from desert regions in China (Arimoto et al., 2004; Zhang et al., 2011) and various components are mixed by seasonal winds to cause distinct variations in chemical compositions (Lee et al., 2009; Han et al., 2009).

Increased industrial development has increased the anthropogenic contribution from various sources to aerosol loadings around the world (Safai et al., 2010). Some of the concern is focused on Pb and Zn which are toxic metals largely associated with fine particles such as $PM_{2.5}$ (Schlesinger, 2007). These and other trace metals are mainly derived from industrial combustion at high temperature or transportation-derived emissions (Al-Momani, 2003; Garcia et al., 2006; Heal et al., 2005; Mihajlidi-Zelić et al., 2006).

* Corresponding author. Department of Earth Sciences, National Cheng Kung University, Tainan 701, Taiwan.
E-mail address: cfy20@mail.ncku.edu.tw (C.-F. You).
[1] Present address: Nan-Kwang Senior High School, No. 62, Zhongxing Rd., Xinying Dist., Tainan 730, Taiwan.

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Acid precipitation is another concern in China during the last few decades (Larssen et al., 2006). Acid precipitation is generated mainly from SO_2 and NO_x emissions linked to fossil-fuel combustion. The most important SO_2 and NO_x sources are coal combustion and oil-fired power plants, with some contribution from transportation (Larssen et al., 2006). Alkaline dusts are the most important components to neutralize acidic precipitation, which are derived mainly from soil particles in desert regions and from construction sites (Zhang et al., 2011). Air pollutants can be transported across long distances and eventually deposited with rains or

Table 1
Description of sampling site, meteorological data and energy structure in each city (modified from Cao et al., 2007).

City name	Code	City description	Location	Sampling site	Sampling date	
					Sumner	Winter
Northern China						
Beijing	BJ	Capital of China, developed megacity	39.9°N, 116.4°E	Roof (14 m) of a building in Institute of Atmospheric Physics, Chinese Academy of Sciences (CAS)	2003.07.11, 2003.07.13, 2003.07.15, 2003.07.19	2003.01.11, 2003.01.15, 2003 01.16, 2003.01.17
Changchun	CC	Continental & developed industrial city	43.9°N, 125.3°E	Roof (6 m) of a building in Jilin University	2003.07.09, 2003.07.20, 2003.07.23	2003.01.06, 2003.01.09, 2003 01.11, 2003.01.17
Jinchang	JC	Asian dust source region, Developing city	383°N, 101.1°E	Roof (10 m) of a building in Jinchang Meteorological Bureau	2003.07.16, 2003.08.01, 2003.08.13, 2003.08.19	2003.01.06, 2003.01.08, 2003.01.10, 2003.01.18
Qingdao	QD	Developing coastal city	36°N, 120.3°E	Roof (10 m) of a building in Chinese Ocean University	2003.07.06, 2003.07.07, 2003.07.24, 2003.07.26	2003.01.07, 2003.01.09, 2003.01.11, 2003.01.15
Tianjin	TJ	Developed industrial city	39.1°N, 117.2°E	Roof (20 m) of a building in Nankai University	2003.07.13, 2003.07.17, 2003.07.21, 2003.07.24	2003.01 07, 2003 01 10, 2003.01.11, 2003.01.16
Xi'an	XA	Continental & developing industrial city	34.2°N, 108.9°E	Roof (10 m) of a building in Institute of Earth Environment, CAS	2003.07.03, 2003.07.28, 2003.08.16, 2003.08.20	2003.01.07, 2003.01.11, 2003.01.19
Yulin	YL	Continental developing city, close to a desert	38.3°N, 109.8°E	A observation tower (10 m) in Shaanxi Desert Institute	2003.06.15, 2003.07.01, 2003.07.09, 2003.08.02	2003.01.07 2003.01.11, 2003.01.12, 2003 01.15
Southern China						
Chongqing	CQ	Continental & developing industrial city	29.5°N, 10.6°E	Roof (10 m) of the Chongqing Academy of Environmental Sciences	2003.07.11, 2003.07.13, 2003.07.14, 2003.07.17	2003.01.06, 2003.01.07, 2003.01.10, 2003.01.17
Guangzhou	GZ	Developed Industrial & commercial megacity	23.1°N, 113.2°E	Roof (10 m) of a building in Zhongshan University	2003.07.08, 2003.07.11, 2003.07.13, 2003.07.14	2003.01.12, 2003.01.17, 2003.01.18, 2003.01 19
Hong Kong	HK	Coastal & commercial city, developed city	22.2°N, 114.1°E	A monitoring site (10 m) in Hong Kong Polytechnic University	2003.07.07, 2003.07.09, 2003.07.12, 2003.07.14	2003.01.09, 2003.01.18, 2003.01.20, 2003.01.21
Hangzhou	HZ	Developing continental city	302°N. 120.1°E	A sub-station (20 m) in Hangzhou Environmental Monitoring Station	2003.07.09, 2003.07.14, 2003.07.16, 2003.07.21	2003.01.06, 2003.01.08, 2003.01.12, 2003.01.17
Shanghai	SH	Developed industrial & commercial megacity	31.2°N, 121.4°E	Roof (8 m) of a building in Donghua University	2003.07.12, 2003.07.16, 2003.07.19, 2003.07.21	2003.01.06 2003.01.11, 2003.01.17, 2003.01.19
Wuhan	WH	Developed industrial & commercial city	30.5°N, 114.2°E	Roof (8 m) of a building in Chinese University of Geosciences	2003.07.12, 2003.07.13, 2003.07.17, 2003.07.20	2003.01.09, 2003.01.11, 2003.01.18, 2003.01.19
Xiamen	XM	Coastal & commercial city, developing city	24.4°N, 118.1°E	Roof (8 m) of a building in Xiamen University	2003.07.06, 2003.07.12, 2003.07.20, 2003.07.28	2003.01.09, 2003 01.11, 2003.01.16, 2003.01.18

as aerosol particles. Trace metals in anthropogenic aerosols are readily extracted at low pH value (Heaton et al., 1990; Migon et al., 1993).

WS-ions are major components of atmospheric aerosols, especially $PM_{2.5}$. They can compose up to 60–70% of the total mass in aerosols (Ali-Mohamed, 1991). The water-soluble chemical composition of fine aerosols, therefore, has been one focus of atmospheric pollution research (Zhang et al., 2011). Previous studies of atmospheric pollution in China have included studies of aerosols. However, most of these studies were focused on major ions using chromatographic methods (He et al., 2001; Hu et al., 2002; Wang et al., 2002, 2006; Yao et al., 2002; Shen et al., 2009; Tan et al., 2009; Zhang et al., 2011). Some studies have focused mainly on Pb concentrations or isotopes in bulk suspended or dissolved particles (Sakata et al., 2006; Hsu et al., 2006). Only limited effort has been directed towards the relationships between trace metals in fine particles and their contribution to acid precipitation.

In this study, we conducted leaching experiments using deionized water to separate WS-ions from $PM_{2.5}$ aerosols and measured the concentrations for major and trace elements (Na, Mg, Ca, K, Fe, Mn, Zn, Rb, Sr, Ba, Pb, S and Cl) using ICP-MS. Our main objectives were to understand the spatial patterns and seasonal variation in WS-components in fine aerosols and examine the relationships between industrial activities and acid precipitation in 14 major cities in China.

2. Sample location and analytical methods

There were 110 $PM_{2.5}$ aerosols sampled from 14 major cities in China during 2003 (Table 1 and Fig. 1). Sampling was carried out simultaneously in all 14 cities during winter (January) and summer (July–August) 2003. The sampling locations are shown in Fig. 2.

Detailed descriptions for the sampling sites and periods are summarized in Table 1. At each site, 24 h aerosol sampling (0900–0900 local time) was performed in winter (January 6–20) and summer (June 3–July 30). The winter samples were collected from each city approximately daily during the sampling period in January 2003 (Cao et al., 2007). The summer samples were collected from each city between June 3 and 17. $PM_{2.5}$ samples were collected on 47 mm Whatman QM-A quartz filters, using a mini-volume air sampler (Airmetrics, Eugene, OR, USA) at a flow rate of 5 L min^{-1}. The samplers were set up on rooftops at various heights of 6–20 m above the ground (Table 1), which represented the air at each sampling location and avoided single point emission sources (Cao et al., 2007).

One-fourth of each aerosol filter was leached using deionized water to extract the WS-ions for chemical determinations. Filters were placed into Telfon vials, 8 ml of deionized water was added (resistivity ~18.3 MΩ), and sonicated for 90 min. The extracts were filtered through a syringe membrane (0.45 μm) and stored at 4 °C for later analysis. The filtrate was acidified using double-distilled nitric acid (~13 N) to 0.3 M HNO_3 for measuring concentrations of major and trace elements (Na, Mg, Ca, K, Fe, Mn, Zn, Rb, Sr, Ba, Pb, S and Cl) using HR-ICP-MS (Element 2, Finnigan) at the EDSRC, NCKU.

Each sample was measured twice by HR-ICP-MS. Average analytical precision was <3% for most of the elements in this study. Unknown concentrations were calibrated against a set of matrix-matched standards, prepared by using ICP high-purity standards. Analytical blanks were analyzed using the same experimental procedure as for the samples, including a blank filter. The concentrations in analytical blanks were below the detection limit of the ICP-MS (<1 ppt).

3. Results

3.1. WS-major and trace elements

The average concentrations of WS-Na, Mg, Ca, K, Fe, Mn, Zn, Rb, Sr, Ba, Pb, S and Cl in aerosol particles are summarized in Tables 2 and 3 for summer and winter, respectively. In summer, the highest WS-Na, Ca, Ba, Zn, Pb, S and Cl concentrations were found in JC, TJ, JC, XA, HZ, BJ, and TJ. The lowest concentrations of Na, Ca, Ba, Zn, Pb, S and Cl were found in QD, SH, QD, HK, HK, QD and YL. In winter, the highest WS-Na, Ca, Zn, Pb and Cl concentrations were in TJ, XA,

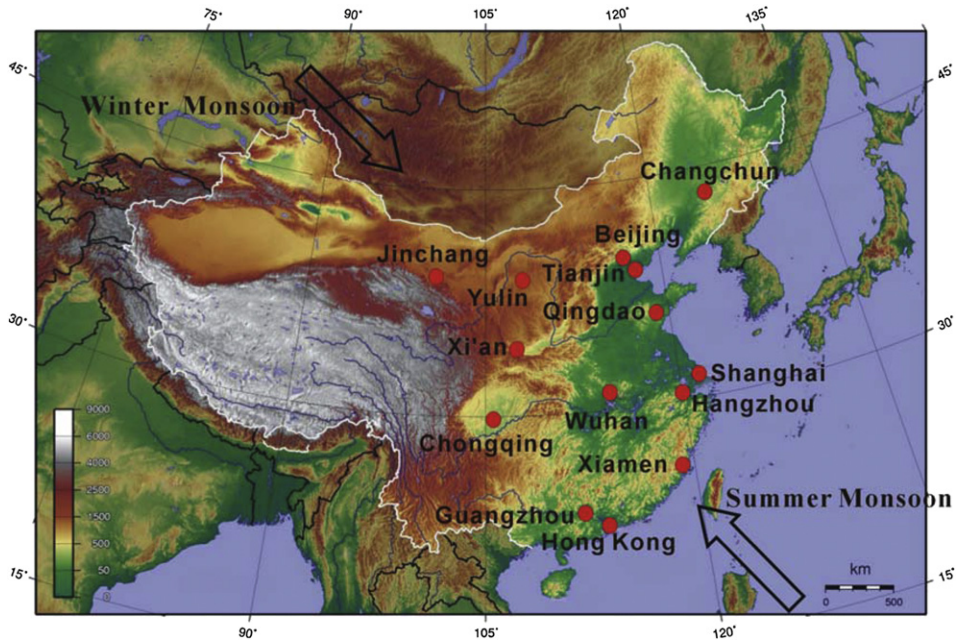

Fig. 1. Sampling locations of 14 Chinese cities (modified from http://www.c-ref.de/gallery/albums/maps/general/China_topo.jpg).

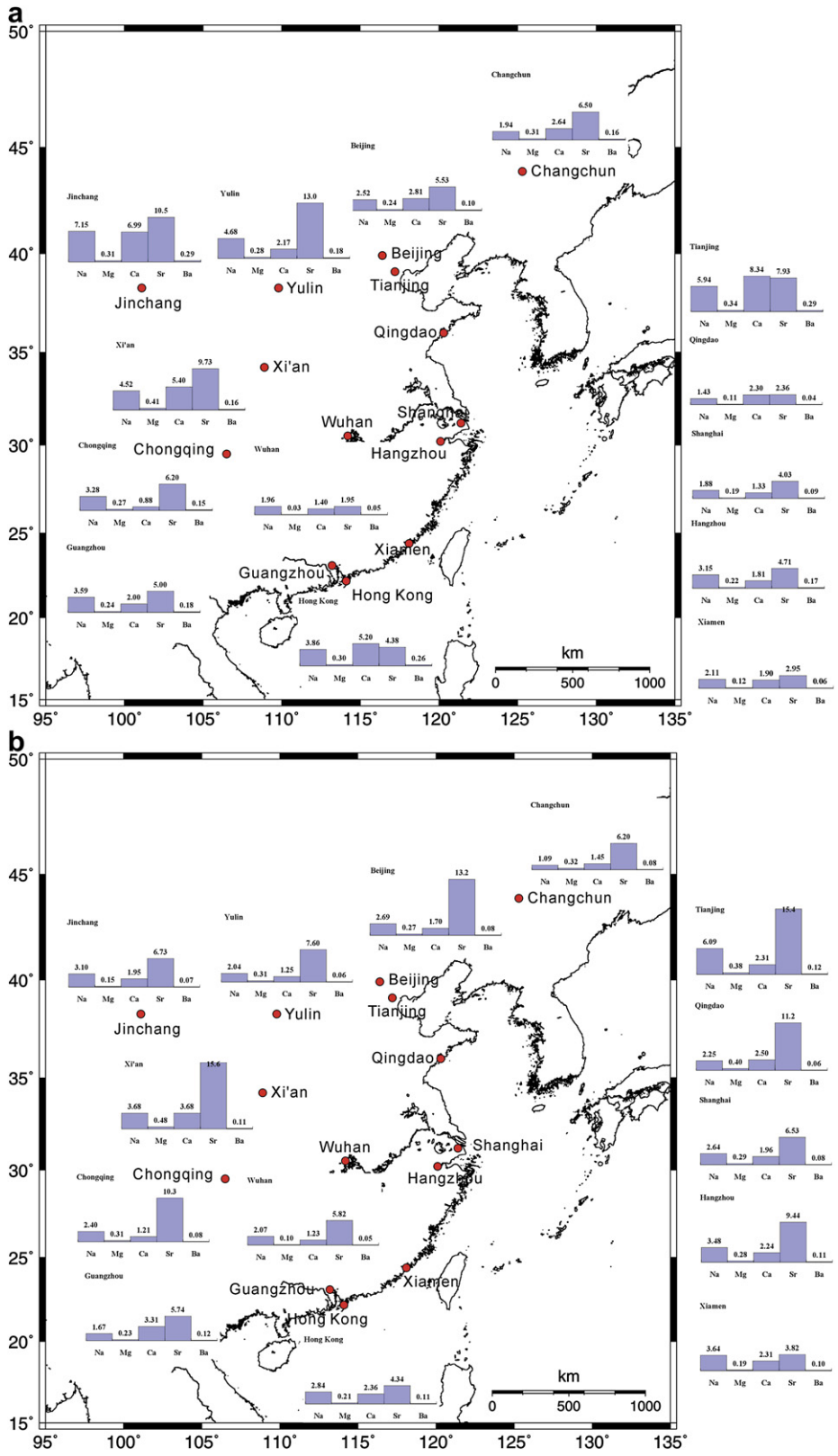

Fig. 2. WS-Na, Mg, Ca, Sr and Ba concentrations in the study area in (a) summer and (b) winter (units for Na, Mg, Ca and Ba are μg m^{-3} and for Sr are ng m^{-3}).

Table 2
Average of water-soluble components in 14 cities over China in summer.

	Na	Mg	Ca	K	Fe	Mn	Zn	Rb	Sr	Ba	Pb	S	Cl	*n*
Beijing	2.52 ± 3.83	0.24 ± 0.13	2.81 ± 1.93	2.16 ± 1.91	109 ± 134	37.3 ± 18.5	0.35 ± 0.30	10.9 ± 9.21	5.53 ± 1.84	0.10 ± 0.05	77.9 ± 151	11.9 ± 6.6	3.60 ± 3.35	4
Changchun	1.94 ± 0.54	0.31 ± 0.30	2.64 ± 2.66	0.58 ± 0.81	76.1 ± 59.2	26.9 ± 30.2	0.30 ± 0.79	2.24 ± 4.08	6.50 ± 8.20	0.16 ± 0.08	17.6 ± 24.0	3.99 ± 2.71	17.9 ± 2.32	3
Jinchang	7.15 ± 3.52	0.31 ± 0.21	6.99 ± 2.27	0.39 ± 0.12	121 ± 80.0	8.69 ± 9.94	0.06 ± 0.19	1.69 ± 1.07	10.5 ± 9.23	0.29 ± 0.27	9.71 ± 12.3	2.85 ± 1.94	24.7 ± 6.61	4
Qingdao	1.43 ± 2.52	0.11 ± 0.30	2.30 ± 2.71	0.15 ± 0.24	28.1 ± 36.5	5.41 ± 5.78	0.03 ± 0.03	0.76 ± 1.43	2.36 ± 3.14	0.04 ± 0.03	0.88 ± 1.20	2.43 ± 2.52	13.2 ± 11.7	4
Tianjin	5.94 ± 5.41	0.34 ± 0.25	8.34 ± 2.63	1.12 ± 0.99	64.0 ± 57.3	28.4 ± 24.3	0.38 ± 0.39	5.63 ± 5.11	7.93 ± 1.90	0.29 ± 0.13	69.5 ± 157	10.6 ± 1.8	31.5 ± 8.32	4
Xi'an	4.52 ± 6.74	0.41 ± 0.47	5.40 ± 10.8	1.51 ± 0.83	86.9 ± 42.2	33.7 ± 32.7	0.70 ± 0.71	6.94 ± 4.15	9.73 ± 11.5	0.16 ± 0.25	120 ± 203	8.24 ± 7.25	14.4 ± 5.63	4
Yulin	4.68 ± 5.88	0.28 ± 0.13	2.17 ± 1.43	0.29 ± 0.51	72.4 ± 144	8.40 ± 10.2	0.03 ± 0.03	n.d.	13.0 ± 36.0	0.18 ± 0.20	3.53 ± 8.00	3.05 ± 3.89	2.65 ± 3.81	4
Chongqing	3.28 ± 2.77	0.27 ± 0.24	0.88 ± 0.75	3.14 ± 1.52	195 ± 209	76.1 ± 129	0.38 ± 0.38	13.3 ± 4.68	6.20 ± 6.25	0.15 ± 0.15	135 ± 108	11.4 ± 6.2	13.9 ± 24.9	4
Guangzhou	3.59 ± 1.29	0.24 ± 0.15	2.00 ± 1.09	1.44 ± 4.69	66.6 ± 59.4	12.4 ± 9.32	0.44 ± 0.36	9.62 ± 37.4	5.00 ± 6.52	0.18 ± 0.15	149 ± 371	4.27 ± 2.55	21.4 ± 2.39	4
Hong Kong	3.86 ± 0.62	0.30 ± 0.19	5.20 ± 0.16	0.35 ± 1.18	51.8 ± 184	45.2 ± 170	0.01 ± 0.01	1.54 ± 0.01	4.38 ± 1.68	0.26 ± 0.48	0.44 ± 1.55	1.27 ± 2.45	4.88 ± 1.86	4
Hangzhou	3.15 ± 2.70	0.22 ± 0.14	1.81 ± 1.24	2.70 ± 4.73	110 ± 98.6	17.7 ± 11.2	0.64 ± 0.57	15.7 ± 25.9	4.71 ± 2.16	0.17 ± 0.14	221 ± 147	7.15 ± 10.4	15.8 ± 5.07	4
Shanghai	1.88 ± 0.54	0.19 ± 0.02	1.33 ± 1.52	1.15 ± 2.68	99.7 ± 74.0	19.3 ± 22.8	0.36 ± 0.24	6.50 ± 15.6	4.03 ± 2.47	0.09 ± 0.04	73.0 ± 81.8	5.70 ± 2.80	15.9 ± 3.42	4
Wuhan	1.96 ± 0.91	0.03 ± 0.03	1.40 ± 0.33	1.05 ± 3.05	29.5 ± 28.0	15.3 ± 15.4	0.30 ± 0.59	8.57 ± 23.8	1.95 ± 1.60	0.05 ± 0.02	49.6 ± 201	2.68 ± 3.61	20.4 ± 1.99	4
Xiamen	2.11 ± 0.43	0.12 ± 0.04	1.90 ± 1.01	0.17 ± 0.11	22.0 ± 27.9	4.75 ± 3.59	0.11 ± 0.14	0.91 ± 0.35	2.95 ± 2.23	0.06 ± 0.02	2.12 ± 4.93	2.89 ± 1.20	4.77 ± 5.78	4
Average	3.33 ± 5.11	0.24 ± 0.30	3.23 ± 6.92	1.16 ± 2.86	80.9 ± 137	24.3 ± 58.4	0.29 ± 0.66	6.48 ± 14.9	6.06 ± 9.68	0.16 ± 0.25	66.4 ± 206	5.80 ± 11.1	15.6 ± 24.3	

Units of Na, Mg, Ca, K, Zn, Ba, S and Cl are μg m^{-3}.
Units of Fe, Mn, Rb, Sr and Pb are ng m^{-3}.
Error bar is 3σ standard deviation.

Table 3
Average water-soluble components in 14 cities over China in winter.

	Na	Mg	Ca	K	Fe	Mn	Zn	Rb	Sr	Ba	Pb	S	Cl	*n*
Beijing	2.69 ± 1.34	0.27 ± 0.08	1.70 ± 0.91	1.82 ± 2.61	192 ± 175	49.0 ± 40.1	0.48 ± 0.89	7.72 ± 10.4	13.2 ± 8.64	0.08 ± 0.03	130 ± 297	12.0 ± 17.0	5.51 ± 8.81	4
Changchun	1.09 ± 0.40	0.32 ± 0.46	1.45 ± 2.46	1.86 ± 1.50	251 ± 402	78.7 ± 138	1.49 ± 3.17	6.53 ± 6.04	6.20 ± 9.93	0.08 ± 0.04	149 ± 190	5.33 ± 2.75	18.2 ± 3.62	4
Jinchang	3.10 ± 3.52	0.15 ± 0.37	1.95 ± 1.18	1.37 ± 2.98	156 ± 148	35.5 ± 79.5	0.29 ± 0.94	7.01 ± 10.6	6.73 ± 3.77	0.07 ± 0.03	132 ± 59.6	9.78 ± 13.3	25.2 ± 3.31	4
Qingdao	2.25 ± 1.18	0.40 ± 1.48	2.50 ± 6.65	2.23 ± 3.16	196 ± 122	57.3 ± 45.9	0.46 ± 0.84	10.4 ± 16.0	11.2 ± 30.0	0.06 ± 0.02	54.0 ± 52.8	6.66 ± 8.45	22.9 ± 4.59	4
Tianjin	6.09 ± 9.16	0.38 ± 0.32	2.31 ± 1.05	5.01 ± 6.18	414 ± 282	151.5 ± 324	1.81 ± 4.82	19.1 ± 34.4	15.5 ± 4.54	0.12 ± 0.03	565 ± 108	17.7 ± 7.80	40.8 ± 12.6	4
Xi'an	3.68 ± 0.97	0.48 ± 0.22	3.68 ± 5.31	6.13 ± 4.58	371 ± 694	57.8 ± 38.5	1.03 ± 1.20	18.4 ± 15.0	15.6 ± 20.4	0.11 ± 0.07	509 ± 127	19.8 ± 30.4	22.1 ± 4.79	3
Yulin	2.04 ± 0.81	0.31 ± 0.47	1.25 ± 0.18	0.84 ± 0.62	122 ± 81.2	13.3 ± 23.4	0.04 ± 0.01	n.d.	7.60 ± 4.17	0.06 ± 0.01	8.38 ± 15.5	4.14 ± 2.24	0.23 ± 0.01	4
Chongqing	2.40 ± 1.02	0.31 ± 0.23	1.21 ± 0.51	6.46 ± 7.37	280 ± 299	91.1 ± 52.4	0.64 ± 0.67	32.3 ± 42.4	10.3 ± 8.97	0.08 ± 0.06	176 ± 267	21.6 ± 15.4	13.2 ± 11.2	4
Guangzhou	1.67 ± 0.68	0.23 ± 0.21	3.31 ± 2.46	4.78 ± 3.68	234 ± 341	65.9 ± 50.2	0.86 ± 0.54	28.5 ± 22.5	5.74 ± 7.00	0.12 ± 0.07	303 ± 121	10.1 ± 8.89	21.5 ± 6.73	4
Hong Kong	2.84 ± 1.42	0.21 ± 0.28	2.36 ± 1.13	1.74 ± 2.49	108 ± 133	24.4 ± 25.4	0.38 ± 0.47	12.5 ± 24.1	4.34 ± 2.92	0.11 ± 0.03	90.7 ± 204	10.8 ± 15.2	5.06 ± 1.71	4
Hangzhou	3.48 ± 1.96	0.28 ± 0.13	2.24 ± 1.63	6.53 ± 5.20	349 ± 348	81.1 ± 74.5	1.27 ± 1.62	34.4 ± 27.9	9.44 ± 11.1	0.11 ± 0.08	353 ± 70.0	11.4 ± 8.78	18.6 ± 2.80	4
Shanghai	2.64 ± 1.58	0.29 ± 0.26	1.96 ± 0.64	5.02 ± 11.6	329 ± 252	108 ± 140	0.95 ± 1.45	20.5 ± 55.2	6.53 ± 7.44	0.08 ± 0.05	231 ± 73.7	12.8 ± 16.8	22.7 ± 9.81	4
Wuhan	2.07 ± 0.67	0.10 ± 0.11	1.23 ± 0.61	2.23 ± 1.35	112 ± 97.1	34.9 ± 16.2	0.46 ± 0.53	3.10 ± 7.47	5.82 ± 7.64	0.05 ± 0.02	123 ± 215	7.69 ± 6.28	20.1 ± 1.35	4
Xiamen	3.64 ± 1.22	0.19 ± 0.09	2.31 ± 0.96	1.23 ± 1.29	200 ± 244	27.8 ± 10.8	0.60 ± 0.85	8.20 ± 10.8	3.82 ± 2.84	0.10 ± 0.01	50.6 ± 49.4	8.61 ± 3.10	7.12 ± 4.28	4
Average	2.90 ± 3.67	0.28 ± 0.30	2.10 ± 2.23	3.38 ± 6.42	237 ± 299	62.6 ± 112	0.77 ± 1.49	16.1 ± 31.3	8.72 ± 11.8	0.09 ± 0.07	205 ± 50.9	11.9 ± 15.0	17.4 ± 31.4	

Units of Na, Mg, Ca, K, Zn, Ba, S and Cl are μg m^{-3}.
Units of Fe, Mn, Rb, Sr and Pb are ng m^{-3}.
Error bar is 3σ standard deviation.

CC and TJ and TJ. The lowest concentrations of Na, Ca, Zn, Pb and Cl were measured in CC, CQ, YL, YL and YL (Tables 2 and 3).

The results show that concentrations of WS-major ions in decreasing order was: Cl > S > Na > Ca > K > Mg, and the WS-metal with the highest concentration was Fe. Most of the WS-ions (K, Fe, Mn, Zn, Rb, Pb, S and Cl) showed higher concentrations in winter and lower concentrations in summer. However, the seasonal pattern for WS-Na, Ca, Ba, Mg and Sr showed no clear seasonal variation.

3.2. Principal component analysis (PCA)

In the discussion, we focused our attention on identifying sources of WS-ions in fine aerosols particles during different seasons. We used principal component analysis (PCA) to generally separate anthropogenic or seawater sources and to group the WS-concentrations by season. The dominant variables in PCA, their factor loadings and the variances after varimax raw rotation are summarized in Tables 4 and 5.

In summer, factor 1 (F1) had the highest variance (37.0%) and high loadings for Zn, Pb and K (>0.7), and moderate loadings for S (>0.5). Dissolved K may be derived from seasalts, silicates, calcareous soils, agricultural fertilizer and biogenic aerosols (Andreae, 1983). Some studies have used measurements of excess K to trace aerosols derived from biomass and coal combustion (Duvall et al., 2008; Zhang et al., 2011). Dissolved Zn in aerosols results from metal processing and dissolved Pb originates from multiple anthropogenic sources including high-temperature metal combustion, fossil fuel burning, and other primary sources (Scudlark et al., 1994). Dissolved S is derived mainly from sea spray, biogenic emission, fossil fuel combustion and other anthropogenic sources (Xiao et al., 2008; Zhang et al., 2011). As a consequence, F1 should be related to anthropogenic activities such as metal processing, and biomass and fossil fuel combustion.

Factor 2 (F2) had 26.3% variance and showed high loadings for Mg, Na, Ca and Ba (>0.7), and moderate loadings for Sr (>0.5). F2 possibly reflected inputs associated with seasalts. Factor 3 (F3) had 13.6% variance and showed a high loading for Rb (>0.7). Factor 4 (F4) had 7.5% variance and showed a high loading for Mn (>0.7) and a moderate loading for Fe (>0.5). The loadings associated with Fe may indicate potential anthropogenic sources, but differed from the loadings for F1. This seems to indicate that either anthropogenic or seawater sources are important in summer.

In winter, F1 had the highest variance of 53.3% and showed high loadings for Cl (>0.7). This factor was also correlated with Mn and Pb, and weakly correlated with Zn and Fe. Although Cl is derived mostly from seasalts, coal combustion is also a source of Cl in aerosols (Yao et al., 2002; Zhang et al., 2011). Sources of aerosol Mn might include construction activity, industrial sources and crustal materials (Allen et al., 2001; Fang et al., 2005; Zheng et al., 2005). Heal et al. (2005) also reported a similar correlation between Mn, Fe, Zn and Pb in aerosol water-soluble concentrations. In winter, F1 is related to anthropogenic activity, in particular black carbon and particles generated from industrial, combustion or traffic sources (Heal et al., 2005). F2 and F3 showed similar variances of 10.7% and 10.3%, respectively and had high loadings for Mg vs. Sr and Ca vs. Ba.

Overall, the PCA results suggest that main sources of WS-ions in $PM_{2.5}$ were metallic, biomass burning and fossil fuels from anthropogenic activities, and seasalts in summer. In winter, the main sources of WS-ions in aerosols were industrial, combustion emission and crustal sources.

Table 4
Factor loadings and eigenvalues after varimax rotated normalization in water-soluble contents in 14 cities over China in summer.

	Factor			
	1	2	3	4
Mn	0.20	0.09	−0.11	**0.93**
Zn	**0.90**	0.00	−0.10	0.05
Mg	0.17	**0.77**	0.14	0.26
Ca	−0.20	**0.90**	−0.19	−0.06
Rb	−0.15	0.07	**0.92**	−0.09
Sr	−0.01	*0.64*	*0.63*	−0.01
Ba	0.02	**0.93**	0.08	0.14
Pb	**0.97**	−0.01	−0.08	0.09
Na	−0.02	**0.91**	0.21	−0.04
S	*0.53*	0.11	−0.03	0.39
Cl	0.17	0.30	−0.21	−0.11
K	**0.79**	−0.12	−0.06	0.43
Fe	0.36	0.12	0.10	*0.51*
Cumul. (%)	37.01	63.32	76.92	84.46
Eigenval.	5.55	3.95	2.04	1.13
Expl. Var.	3.07	3.99	1.63	1.62
Prp. Totl.	0.20	0.27	0.11	0.11

Table 5
Factor loadings after varimax rotated normalization in water-soluble contents14 cities over China in winter.

	Factor		
	1	2	3
Mn	0.29	0.22	−0.05
Zn	0.11	0.20	0.21
Mg	−0.02	**0.90**	0.19
Ca	0.18	0.28	**0.91**
Rb	−0.13	0.03	−0.17
Sr	0.08	**0.82**	0.01
Ba	−0.14	−0.05	**0.81**
Pb	0.27	0.32	0.45
Na	0.14	0.17	0.19
S	−0.03	0.30	0.13
Cl	**0.76**	0.19	0.11
K	0.17	0.23	0.24
Fe	0.13	0.40	0.23
Cumul. (%)	53.30	63.98	74.26
Eigenval.	8.00	1.60	1.54
Expl. Var.	1.01	2.80	2.00
Prp. Totl.	0.07	0.19	0.13

4. Discussion

4.1. Spatial and seasonal variations in WS-elements

4.1.1. Na, Mg, Ca, Sr and Ba

The spatial and seasonal distributions of WS-Na, Mg, Ca, Sr and Ba concentration in the 14 Chinese cities are shown in Fig. 2. WS-Na is mainly derived from seasalts (Al-Momani et al., 1995); however, the influence of loess particles cannot be ruled out as Na is one of the main contents in aerosols originating from Chinese Losses Plateau (Yokoo et al., 2004; Zhang et al., 2011). The sampling site, TJ, is located near the coastal area and had higher WS-Na in summer (Fig. 2a). However, we did not find other elevated WS-Na concentrations in coastal sampling sites. The highest WS-Na concentrations were in JC, with Na concentrations decreasing from inland station to the coastal region. JC is located within an Asian dust source region and is a developing city which lied in Asian dust source region. Besides, due to the industrial develop and sky-high buildings in JC, it suffers serious heat island effects. These characteristics in JC have caused high WS-Na contents in summer. Several stations (TJ, XM, HZ, JC and XA) showed the highest WS-Na concentrations (>3.0 μg m^{-3}) in winter (Fig. 2b). Three of these cities (TJ, XM and HZ) are located in coastal region and the latter two (JC and XA) are situated in the inland area. This pattern indicates that WS-Na in fine particles was influenced by seasalt. Other possible sources include coal combustion and eolian particles.

WS-Mg is derived mainly from seasalt and particulates such as eroded soil particles (Mouli et al., 2005). We did not find any significant seasonal and spatial variation in concentrations of WS-Mg in study area (Fig. 2). WS-Ca originates from seasalt, eroded and airborne soil particles, traffic dust and long distance transported aerosols (Mouli et al., 2005). Sampling sites TJ, HK, JC and XA had high WS-Ca contents in summer (Fig. 2a). Two cities (TJ and HK) are located near the coastal areas and the other two (JC and XA)

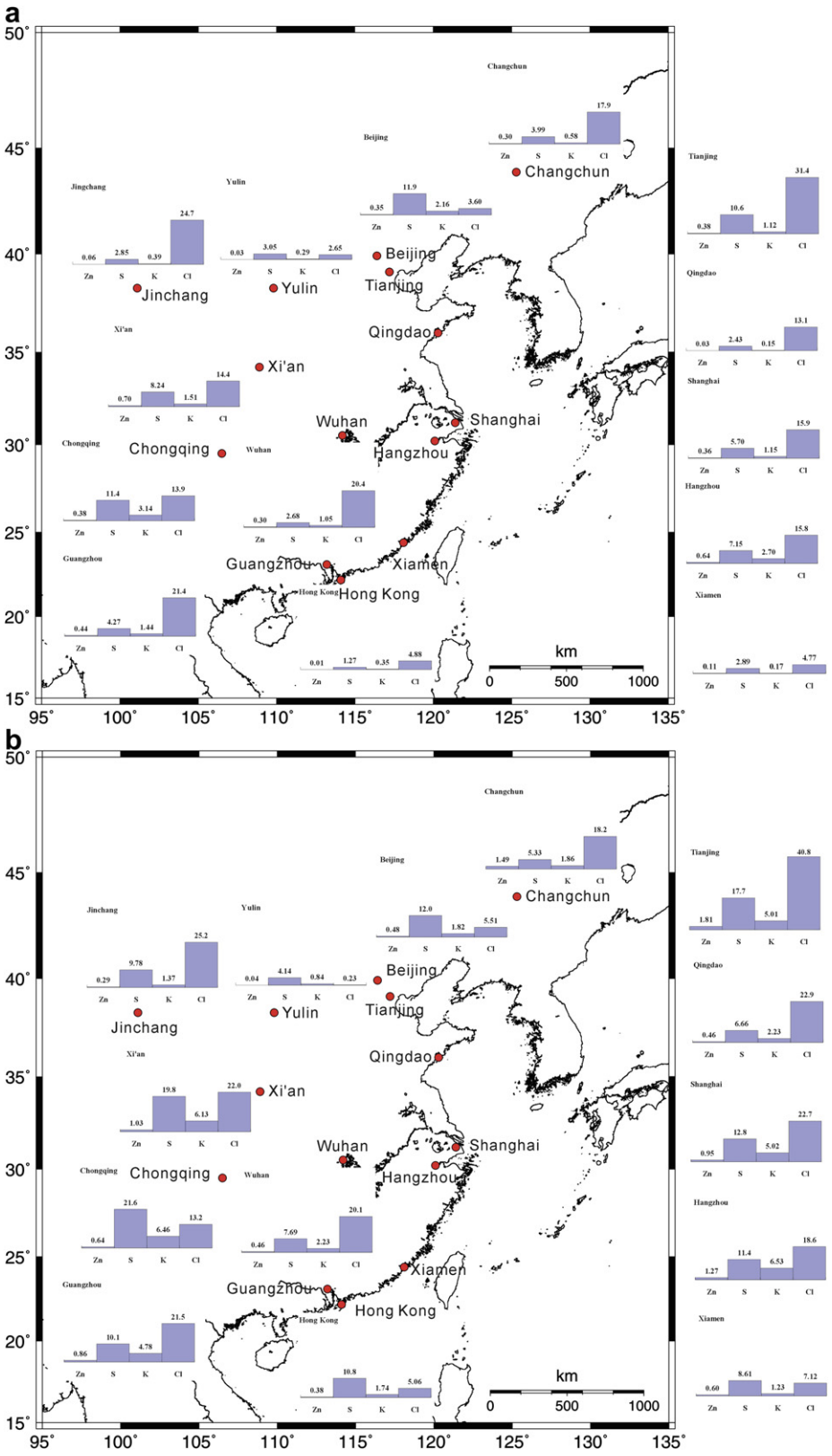

Fig. 3. WS-Zn, S, K and Cl concentrations in the study area (a) summer (b) winter (units for Cl, S, K and Zn are in μg m^{-3}).

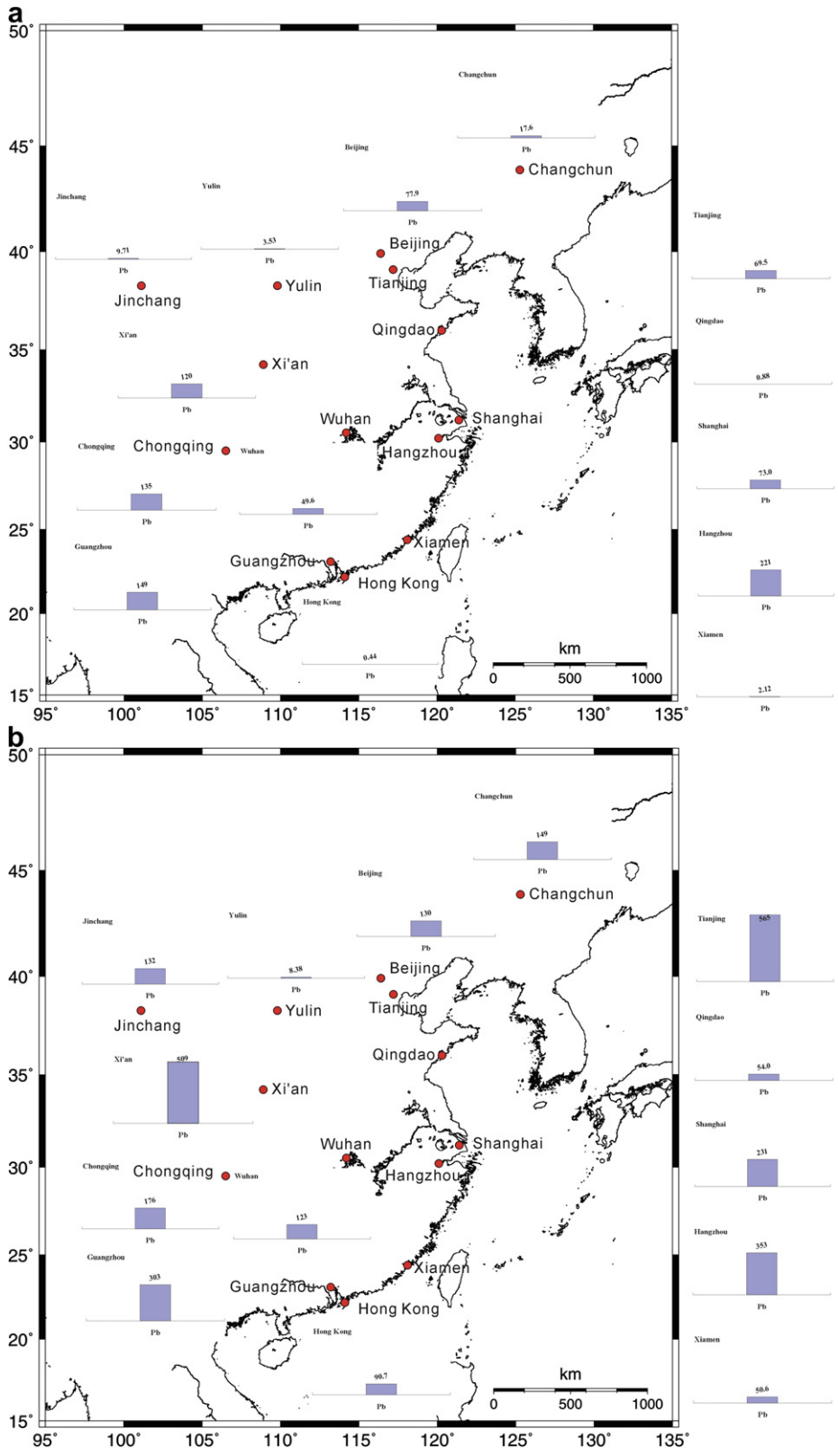

Fig. 4. WS-Pb concentrations (a) summer and (b) winter (units for Pb are ng m^{-3}).

are situated inland. In general, the average concentration of winter WS-Ca was lower than the summer average. Concentrations of WS-Ca were higher at all inland, coastal and industrial cities, probably influenced by dusts from construction activity in urban cities (Zhang et al., 2011). WS-Sr and Ba are derived mainly from crustal sources (Fang et al., 2005; Zheng et al., 2005), and we measured higher concentrations in inland sites and generally lower concentrations at XA, a coastal city, in summer (Fig. 2).

4.1.2. Zn, Pb, K, S and Cl

The spatial and seasonal variation in concentrations of WS-Zn, Pb, S, K and Cl concentrations are shown in Figs. 3 and 4. The average WS-Zn and Pb concentrations in summer are much lower than those in winter. The high WS-Zn and Pb specimens are mainly appeared in some highly industrial cities, no matter situated in inland or near the coast. The industrial cities have shown high WS-Pb in summer, no correlation with the distance from the ocean. In winter, much higher WS-Zn and Pb concentrations appear in the highly industrialized cities, compared with those in summer. More interestingly, the average WS-Pb in coastal cities is much higher than the inland ones. These results suggest that WS-Zn and Pb were rather high both in summer and winter, due to anthropogenic activities in the highly industrialized and high population cities.

The WS-K can be derived from seasalt, silicates, calcareous soils, agricultural fertilizer and biogenic aerosols, as well as biomass burning (Andreae, 1983; Duvall et al., 2008) and coal combustion and traffic emissions (Zhang et al., 2011). The average WS-K is higher in winter (Fig. 3a) than in summer (Fig. 3b) and shows good correlation with WS-Pb, Zn and S (Fig. 4). These results suggest that anthropogenic WS-K, Pb, and Zn are presented both in winter and summer.

There are high WS-S contents in two highly industrialized cities, BJ and CQ, in summer (Fig. 3a). In contrast, much lower WS-S concentrations were measured in similar industrialized coastal cities (i.e., HK). This pattern is possible due to air-mass dilution from the ocean. For instance, the much higher S observed in the XA aerosols supports the argument that extensive coal burning, gas or oil combustion for household warming are important S sources in the air in winter (Xiao et al., 2008; Zhang et al., 2011). The average WS-S in winter is much higher than in summer, partly caused by fossil fuels combustion in winter (Xiao et al., 2008). WS-S concentrations are likely related to fossil fuel combustion and possibly other industrial sources (Cao et al., 2007; Zhang et al., 2011).

Atmospheric Cl is mainly derived from seasalts, coal combustion and industrial emissions (Al-Momani et al., 1995; Han et al., 2007; Li et al., 2010; Zhang et al., 2011). There were 4 sampling stations (TJ, GZ, JC and WH) with elevated WS-Cl concentrations in summer (Fig. 3a). Only two coastal cities (TJ and GZ) showed similar high WS-Cl contents in summer. Others (BJ, HK and XM) had lower WS-Cl concentrations. High WS-Cl concentrations were found in inland cities (JC and WH). This might imply that in addition to seasalts, industrial emissions also make a contribution to aerosol WS-Cl in summer.

If seasalt was the main source of WS-Cl during winter, all coastal cities would have similar elevated concentrations of WS-Cl. The low WS-Cl concentrations we found in HK and XM seem to counter this argument. The prevailing winds during winter monsoon are from Mongolia, carrying little Cl-bearing seasalt (Fig. 1). Thus anthropogenic sources in industrialized cities could be related to WS-Cl concentrations in winter. Furthermore, high WS-Cl specimens were presented in both coastal and industrial cities in winter. These results suggest that important point sources of WS-Cl are associated with coal combustion in the region.

The East-Asia monsoon system is an important factor regulating atmospheric circulation and pollutant transport in Northern Hemisphere (Han et al., 2009). This monsoon system moves southward and carries pollutants from northern China in winter. The summer monsoon moves northward to bring clean air from ocean and potentially to dilute pollutants in the atmosphere, especially in coastal zones, such as XM, HK, QD and HZ. The summer monsoon, with its heavy rainfall and high mixing heights would reduce concentrations of anthropogenic aerosols in summer (Han et al., 2009). Heal et al. (2005) found higher aerosol WS-metal concentrations, with higher anthropogenic contribution than crust-derived particulates.

4.2. City properties and topography influence

The distribution of S, Zn and Pb at XA, CQ, TJ, BJ, HZ, SH and GZ stations indicate important anthropogenic pollutant sources occurred mainly in winter (Fig. 3). Among these cities, the Tianjing–Beijing (TJ and BJ) and the Xi'an–Chongqing (XA and CQ) are the two most important regional sources of air pollutants. XA and CQ belong to the Guanzhong Plain and the Sichuan Basin, respectively. Both cities are rather continental and industrialized located at inland regions (Table 1). Petrochemical and aeronautical industries are found in XA, whereas the main industries in CQ are metallurgy and automobile production. BJ and TJ are belonging to the Beijing–Tianjin–Tanggu industrial zone with many diversified heavy industries. The elevated WS-Pb concentrations in GZ, HZ and SH is consistent with the heavily industrial and commercial development found there (Table 1). Although HZ was not described as an industrialized city (Table 1), it is located in the same industrial zone as SH and located close to the Hangzhou Bay. It is interesting to note that concentrations of WS-Pb and Zn were lower in QD, HK and XM in both summer and winter. These cities are located near the coast where fresh air masses dilute concentrations of anthropogenic pollutants.

Mountain systems in northern China can affect the distribution and transport of WS-elements in aerosols as depicted in the topographic map (Fig. 1). Mountain systems may interrupt potential

Table 6
The calculated pH values influenced by sulfur addition in air.

	Sulfur (mM) (summer average)	Calculated $[H^+]$ increase (mM)	Calculated pH (summer)	Sulfur (mM) (winter average)	Calculated $[H^+]$ increase (mM)	Calculated pH (winter)
Xiamen	1.28	2.56	2.59	1.93	3.86	2.41
Hong Kong	0.29	0.57	3.23	2.43	4.86	2.31
Beijing	2.56	5.11	2.29	2.70	5.39	2.27
Chongqing	3.07	6.13	2.21	4.57	9.13	2.04
Yulin	0.66	1.32	2.88	0.93	1.86	2.73
Tianjin	2.35	4.69	2.33	3.94	7.88	2.10
Jinchang	0.64	1.28	2.89	2.17	4.35	2.36
Qingdao	0.87	1.75	2.75	1.49	2.99	2.52
Wuhan	0.60	1.21	2.91	1.72	3.45	2.46
Guangzhou	0.96	1.92	2.71	2.27	4.53	2.34
Changchun	0.89	1.78	2.75	1.21	2.43	2.61
Shanghai	1.26	2.53	2.60	2.78	5.55	2.25
Hangzhou	1.48	2.96	2.53	2.55	5.10	2.29
Xi'an	1.89	3.78	2.42	3.82	7.65	2.12

We assume that the pH of normal rain is 5 and the hydrogen ions is 10^{-5} M.

pollutants transport pathways or cause local deposition of airborne pollutants (Fig. 1). Concentrations of WS-S, Zn and Pb in XA and CQ in western China, as well as others of TJ and BJ in eastern China, are partly influenced by morphological relief. Low WS-S, Zn and Pb concentrations were found along the mountain belts to form a saddle-like distribution.

4.3. Contribution of WS-soluble components to acid precipitation

SO_2 Emissions directly impact patterns of acid deposition in Asia (Larssen et al., 2006). Extensive use of coal and oil is the cause of acid precipitation in China (Larssen et al., 2006). High concentrations of particulates and SO_2 have been found in many areas in China (Larssen et al., 2006).

Sulfur is readily oxidized to H_2SO_4 in the atmosphere, where one molecule of S consumed can produce two H^+ molecules. We used the measured WS-S concentrations in fine particles to calculate $[H^+]$ in Table 6. The assumed pH values were calculated using formulas 1 and 2:

$$[\text{Sulfur}]*2 = \text{calculated } \left[H^+\right] \text{ increase} \quad (1)$$

$$\text{calculated pH value} = -\log\left(\text{calculated } \left[H^+\right] \text{ increase} + 10^{-5}\right) \quad (2)$$

Here we assumed that pH of normal rain is 5 (hydrogen ion concentration of 10^{-5} M).

The results show that WS-S can increase the $[H^+]$ concentration and decrease the pH of precipitation (Table 6). It is clear that greater increases in $[H^+]$ occurred in winter than in summer in the study area. This agrees with a scenario where coal combustion leads to increased concentrations of sulfur dioxide and lower precipitation pH in winter compared to summer. In summer, the pH of precipitation in coastal cities (such as XA, HK, QD, and GZ) is higher than those of inland and industrial cities (such as CQ and BJ). Some precipitation with elevated pHs have been neutralized by alkaline particles in the atmosphere.

5. Conclusions

$PM_{2.5}$ samples in 14 major cities in China were collected in 2003 and analyzed for WS-Na, Mg, Ca, K, Fe, Mn, Zn, Rb, Sr, Ba, Pb, S and Cl concentrations to examine the spatial and seasonal variation. The major findings of this study are:

1, The PCA results show that anthropogenic materials are the most important sources of WS-ions contents in $PM_{2.5}$ aerosols both in summer and in winter.
2, The WS-Zn, Pb and S concentrations in aerosols are mainly influenced by anthropogenic inputs in summer and in winter. However, the high concentrations of these in winter are related to coal combustion in northern China.
3, Distribution of WS-S, Zn and Pb in $PM_{2.5}$ aerosols is highly correlated with the locations of major industrial zones and topography relief in China.
4, Our results demonstrate that WS-S in $PM_{2.5}$ aerosols increases H concentration (lower pH).

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