



Elemental composition of aerosols in Daihai, a rural area in the front boundary of the summer Asian monsoon

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ABSTRACT

TSP and PM_{2.5} were sampled in Daihai, an Asian monsoon-sensitive region in Inner Mongolia, in summer. The aims were to evaluate the characteristics of trace elements and to investigate the influence of the summer monsoon on elemental composition there. Eighteen trace elements, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr and Pb, were determined and their concentrations were evaluated. The TSP/PM_{2.5} ratio of element concentrations showed that crustal elements like K, Ca, Ti and Fe, as well as Pb, Ni and Sr were more abundant in TSP, while other elements predominated in PM_{2.5}. Enrichment factor (EF) calculations revealed that non-crustal trace elements were more enriched in PM_{2.5} than in TSP. Back trajectory analysis indicated that crustal elements such as K, Ca, Ti and Fe had distinctly high concentrations associated with northerly flows, while non-crustal elements showed no clear pattern. However, non-crustal elements showed high EF values related to southeasterly flows. Principal component analysis (PCA) was also applied to the PM_{2.5} data to discuss the source appointment and five factors were determined.

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1. Introduction

Recently, aerosols have received increasing attention due to the roles that they play in many climate and environmental processes (Andreae and Crutzen, 1997). Aerosols can change the energy budget in two ways: directly, by absorbing and dispersing solar radiation, and indirectly, by changing the water cycle through the action of the cloud condensation nuclei (CCN) (Andreae and Crutzen, 1997; IPCC, 2001; Ramanathan et al., 2001). Anthropogenic particles in the atmosphere can also lead to serious environmental and health problems (Mauderly and Chow, 2008; Ramanakumar et al., 2007). The effect of aerosol particles on atmospheric chemistry and physics, as well as on climate and public health, depends on their chemical and physical properties, which vary in response to their origin, source, transformation

mechanism and meteorological condition. Knowledge of their chemical and physical properties is therefore important.

Lake Daihai (1221 m) is situated in a remote mountainous area in Liangcheng County, Inner Mongolia, Northern China (Fig. 1A). It is located in a transitional zone between semi-arid and semi-humid conditions, sensitive to climatic changes related to the East Asian monsoon oscillations and the westerly jet stream (Fig. 1A, Jin et al., 2004; Han et al., 2007, 2008a). The Asian monsoon is an important component of atmospheric circulation and plays a significant role in global hydrologic and energy cycles. During the seasonal transition from winter to summer, the East Asian summer monsoon moves gradually northward as Northern Hemisphere insolation increases, while in winter the East Asian winter monsoon moves southward (An et al., 2000). The monsoon systems vary systematically (An et al., 2000), and thus influence the aerosol chemical composition in the Daihai area. This chemistry can act as a valuable reference for studying and evaluating atmospheric evolution with respect to rapid industrial development (Han et al., 2007; Cong et al., 2007).

In a previous study of sediment cores taken from Lake Daihai, Han et al. (2007) monitored the correlations between

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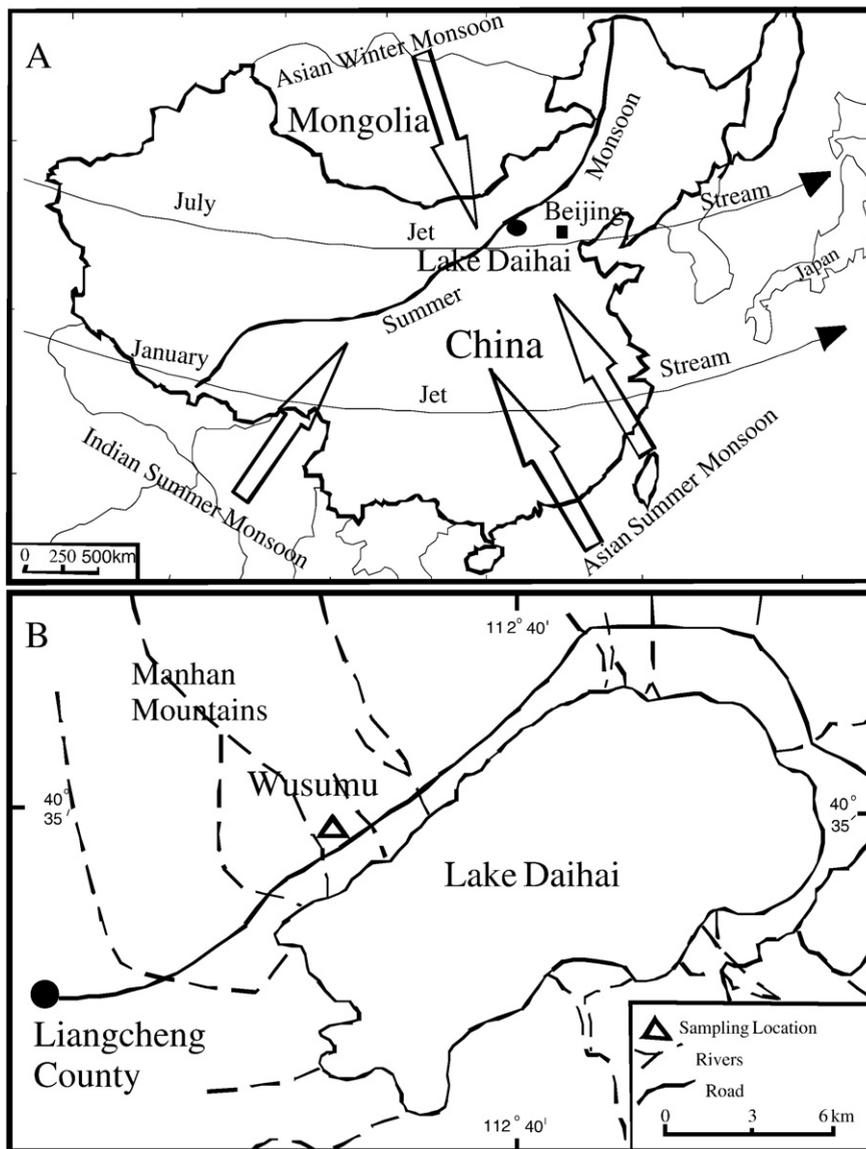


Fig. 1. A) Map of the climatic system of China, including the East Asian monsoon, the Westerly wind region, and the Indian monsoon (After Han et al., 2007). B) Sampling location in Wusumu beside Lake Daihai.

trace element enrichments with the East Asian monsoon system and evaluated various human impacts. They revealed that the variation of atmospheric depositions of Cu and Pb corresponded to the East Asian monsoon variations, with high atmospheric deposition coupled with wet, temperate periods when the summer monsoon dominates, and low deposition with dry, cold periods when the winter monsoon dominates. However, there is a lack of evidence from modern observations due to the sparseness of aerosol studies in Daihai. Recently, Han et al. (2008a) studied carbonaceous compositions of total suspended particulate matter (TSP) and $PM_{2.5}$ (particulate matter with an aerodynamic diameter smaller than $2.5 \mu m$) in Daihai from four seasonal observations, revealing the influence of the summer Asian monsoon. As Daihai is located within the front boundary of the summer monsoon (Han et al., 2007), the southerly air masses, which are directly associated

with the summer monsoon, influence this region mainly in summer (Han et al., 2008a). In this study, elemental compositions of summer samples only were therefore determined to gain information on the influence of the summer monsoon in Daihai. Also the possible sources are analyzed using the principal component analysis (PCA), and the possible correlations between element concentrations and monsoon variation are discussed using backward air mass trajectory analysis.

2. Sampling and analysis

2.1. Sampling site description

Wusumu ($112^{\circ}35'E$, $40^{\circ}37'N$) is a small village (Fig. 1B) situated beside Lake Daihai in a remote mountainous area in Liangcheng County, Inner Mongolia (Fig. 1B). It has a population

of less than 500. The annual average temperature in the Daihai region is ~ 5.1 °C and annual average precipitation is 201–653 mm (Ren et al., 1995). Under the influence of the Asian monsoon, rainfall always occurs during summer. Based on the meteorological data obtained from Liangcheng Station in 1988, the annual mean wind velocity is estimated at 2.6 m s^{-1} . The major prevailing wind direction is northwesterly (Ren et al., 1995). The primary bedrock types in the Daihai region are Archean metamorphosed igneous rocks and Tertiary basalt as well as Cenozoic loess (Ren et al., 1995; Han et al., 2007).

2.2. Sampling and PIXE analysis

The sampling procedures have been described previously (Han et al., 2008a). From 12 June to 21 July 2006, TSP and $\text{PM}_{2.5}$ samples were synchronously collected in Wusumu daily. Minival (Airmetrics, USA) inlets operated at 5 l min^{-1} were located 1.5 m above ground level. The samples were acquired on pre-fired, pre-weighed quartz-fiber filters (Whatman, UK) with pore size of $0.4 \mu\text{m}$ and diameter of 47 mm for 24 h from 10:00 A.M. to 10:00 A.M. every day.

Samples were analyzed gravimetrically for mass concentrations using an electronic microbalance with $\pm 1 \mu\text{g}$ sensitivity (Sartorius, Gottingen, Germany) and converted into the standard conditions according to the local air pressure. Since fine particles have a long atmospheric residence time, which facilitates their transportation over long distances, only $\text{PM}_{2.5}$ samples were selected for the discussion of possible long-range transport of pollutants in Daihai. Thus, all $\text{PM}_{2.5}$ samples were analyzed for their elemental composition. For TSP, only about 14 samples (one per every 3 days) were selected for elemental analysis. Elemental composition was analyzed using Proton Induced X-ray Emission (PIXE) spectrometry in the Center of Analytical and Testing, Beijing Normal University. Aerosol elemental composition data from this laboratory is highly regarded for its quality and has been widely recognized (Zhang et al., 1993; Cong et al., 2007).

Details of the analytical procedures are given elsewhere (Zhang et al., 1993). Eighteen elements (S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Sr, Zr and Pb) were determined. As quartz filters were used in order to obtain organic and elemental carbon concentrations as well (Han et al., 2008a), Si, Mg and Al concentrations were not retrieved in this study. The detection limit and the % error were also obtained, for each particle and element, by the spectrum fitting software GUPIX. The detection limits ranged from 2 to 17 ng m^{-3} for these different elements, except for S, which had a detection limit of about 50 ng m^{-3} . The % error was smaller than 10% for 8 elements (S, Cl, K, Ca, Ti, Mn, Fe, and Zn), and 10–20% for the other 10 elements. All elemental concentrations were corrected from blank filters and then converted into the standard conditions according to the local air pressure.

3. Results and discussion

3.1. Elemental composition

Statistical results for the element concentrations of $\text{PM}_{2.5}$ and TSP in summer 2006 are shown in Table 1. Element concentrations of $\text{PM}_{2.5}$ from urban areas in East Asia are listed for comparison. In general, the decreasing order of average element concentration in $\text{PM}_{2.5}$ was S, Ca, Fe, K, Mn, Cl, Zn, Zr, Pb, Sr and Ti. The remaining seven elements varied slightly from 6.1 to 9.4 ng m^{-3} . In TSP, the decreasing order of element concentration was Ca, Fe, S, K, Ti, Mn, Cl, Pb, Sr, Zr, Ni, Zn, As and Br, with the remaining four elements being lower than 10 ng m^{-3} . S, Ca, and Fe were the major elements in $\text{PM}_{2.5}$, while Ca, Fe, S, and K were the major elements in TSP. Crustal elements Ti, K, Fe and Ca, as well as Pb, Ni and Sr showed average TSP/ $\text{PM}_{2.5}$ ratios (calculated with synchronously collected samples) higher than 2, indicating that they were predominant in TSP. Pb and Ni, as anthropogenic elements, were also in this group, which may be mainly associated with the similar directional flows of crustal

Table 1

Element concentrations (ng m^{-3}) of $\text{PM}_{2.5}$ and TSP in Daihai in summer ($\text{PM}_{2.5}$ from 40 samples; TSP from 14 samples), as well as some $\text{PM}_{2.5}$ element concentrations from urban cities in East Asia for comparison

Elements	$\text{PM}_{2.5}$				TSP				Beijing		Shanghai		Taiwan	Seoul, Korea
	Aver	S.D.	Min	Max	Aver	S.D.	Min	Max	Chegong Zhuang	Tsinghua University	Hanan Road	Tongji University	Taichung	
S	924.2	820.6	114.7	3704.7	880.0	632.5	114.7	2123.5	6570	6930				2270
Cl	37.0	15.7	8.0	91.1	53.9	44.2	8.0	156.4	2050	2450	1810	1450		
K	98.0	151.1	2.3	817.0	599.6	263.2	2.3	963.4	2830	3050	1980	1660		500
Ca	618.4	445.7	2.4	2134.0	2757.5	1001.6	2.4	4346.1	1230	1210	550	540		200
Ti	11.1	21.7	3.5	135.2	95.0	55.1	3.5	183.0						7.0
V	6.8	2.2	1.5	18.0	6.7	0.4	0.4	7.6						6.3
Cr	6.1	3.7	0.4	15.3	6.6	5.0	0.4	20.7					33.5	2.0
Mn	63.9	94.4	10.2	517.4	72.0	40.8	10.2	178.7	97	93				14.4
Fe	385.8	412.7	3.5	2329.4	1824.0	583.4	3.5	2675.2	1140	1130	900	820	162.8	260
Ni	7.0	5.5	0.7	24.6	16.5	8.0	0.7	27.3	15	12			11.8	4.0
Cu	7.3	4.9	0.3	33.1	8.5	3.1	0.3	17.9	35	39			11.5	20.9
Zn	27.8	36.8	3.2	195.7	12.4	13.7	3.2	44.4	480	570			177.8	160
As	7.4	3.6	0.9	21.3	10.3	2.0	0.9	12.2						8.7
Se	8.3	5.3	0.2	23.3	7.8	3.9	0.2	11.9	9	10				1.4
Br	9.4	6.7	0.8	29.3	10.2	5.2	0.8	23.7	17	23				
Sr	14.0	9.4	0.4	38.1	29.2	17.5	0.4	56.7						
Zr	24.1	12.8	3.4	58.3	20.4	11.7	3.4	37.5						
Pb	20.4	20.4	1.8	100.3	44.3	33.6	1.8	116.0	304	335	280	270	283.1	86.6
Reference	This study								He et al. (2001)		Ye et al. (2003)		Fang et al. (2003)	Park and Kim (2005)

elements, which also entrained Pb and Ni in the coarse fraction (see section 3.3 and 3.4). The other elements showed average TSP/PM_{2.5} ratios lower than 2.0, indicating that they were predominant in PM_{2.5}.

Comparing PM_{2.5} element concentrations in Daihai with those from urban cities in East Asia such as Beijing (He et al., 2001), Shanghai (Ye et al., 2003), Taiwan (Fang et al., 2003), and Seoul (Park and Kim, 2005) showed that anthropogenic elements such as S, Cl, Cu, Zn and Pb were lower in Daihai by a factor of at least five, whereas crustal elements such as Ca, Ti and Fe had similar levels in the different areas. In the case of K, which is generally thought to be of mixed origin such as crustal material as well as biomass and fossil fuel combustion (Ho et al., 2003; Kocak et al., 2007), the concentration was much lower than in the above cities. In an area as remote as Daihai it seems that crustal material was the predominant source of K.

3.2. Enrichment factor (EF)

EF is often used to differentiate between elements originating from human activities and those from nature (Al-Momani et al., 2005; Han et al., 2006; Ragosta et al., 2008) and is generally defined as follows:

$$EF_X = (C_X/C_R)_{\text{aerosol}} / (C_X/C_R)_{\text{reference}}$$

where X represents the element of interest; C_X is the concentration of X, and C_R is the concentration of a reference element, which was commonly used as Al, Si, Ti, and Fe, etc. In this study we selected Fe as the reference element. The aerosol

and reference subscripts refer to particles in the aerosol samples and in reference materials. Generally both local soils and the crustal material can be selected as the reference materials (Ragosta et al., 2008), and crustal composition is more often being used as it needs no further measurements for the composition of local soils. However this may produce biases since it might be not representative of the local background. Daihai is located within the Loess Plateau of China, and loess is mainly from wind dust accumulation and has trace element concentration generally similar with or close to those of the Upper Continental Crust (Wen, 1989; Han et al., 2008b). Comparing the sediments in the margin of the Lake Daihai (Jin et al., 2006; Han et al., 2007), which were thought to have little sedimentary sorting and catchment weathering (Jin et al., 2006), to the Upper Continental Crust (Wedepohl, 1995) revealed small differences in their element concentrations. Thus in this study the Earth's crust (Wedepohl, 1995) was selected as the reference material.

Fig. 2 shows the EFs of 18 elements in PM_{2.5} and TSP, respectively, in decreasing order of PM_{2.5} elements. It has been well established that elements with EF less than 10 are due to crustal emission while elements with EF greater than 10 are considered highly enriched and originate from non crustal sources (Finlayson-Pitts and Pitts, 2000; Al-Momani et al., 2005). Overall, all elements, except K and Ti, showed higher enrichment in PM_{2.5} than TSP. Elements such as Br, As, S and Pb, showed strong enrichment both in PM_{2.5} (>266) and in TSP (>30), indicating that they originated from anthropogenic sources. For the other group of elements, including Zn, Cu, Zr, Ni, Mn, Cl, Se, V and Cr, the EF values ranged from 10 to 100 in PM_{2.5}, while in TSP they were less than 10. Elements Sr, Ca, K, Ti

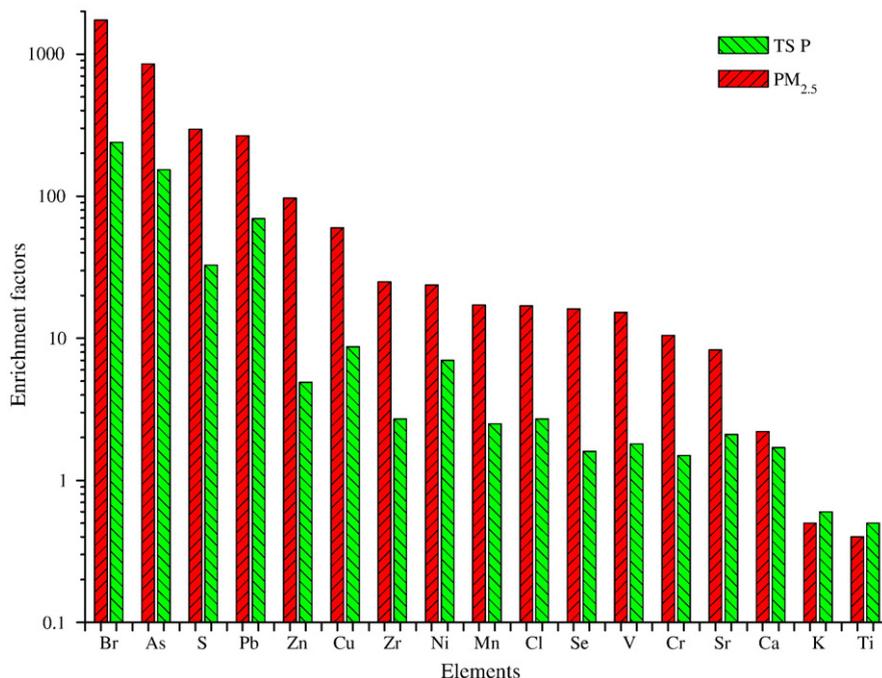


Fig. 2. Comparison of the enrichment factors of trace elements in TSP and PM_{2.5}. Br, As, S and Pb showed EFs higher than 200 in PM_{2.5} and higher than 30 in TSP; Zn, Cu, Zr, Ni, Mn, Cl, Se, V and Cr had EF values higher than 10 in PM_{2.5}, but lower than 10 in TSP; Sr, Ca, K and Ti had EFs lower than 10 in both TSP and PM_{2.5}.

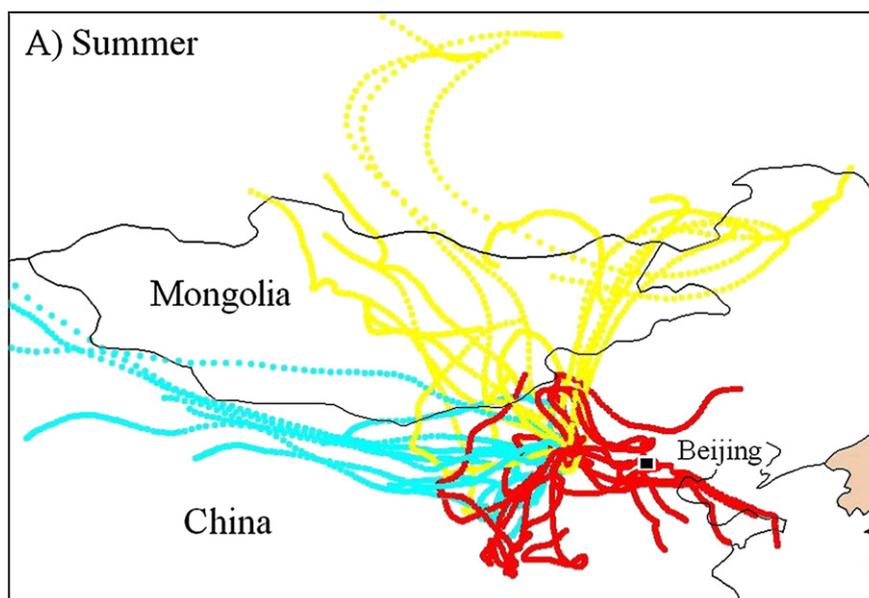


Fig. 3. 120-h backward air mass trajectories passing over Daihai in summer during the sampling time (produced using NOAA ARL Website: www.arl.noaa.gov/ready/, after Han et al., 2008a). The trajectories were divided into southward air mass inflow (red) from central China, northward inflow (yellow) from Mongolia, and westward inflow (blue) from Middle Asia. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and Fe showed low EFs (<10) in both sizes of particles. Therefore, Br, As, S and Pb were considered to be indicators of anthropogenic sources, Sr, Ca, K, Ti and Fe to be indicators of natural sources, and all other elements of pollution sources found only in $PM_{2.5}$.

3.3. Back trajectory analyses on $PM_{2.5}$ elements

Lagrangian integrated back trajectories (HYSPLIT, Draxler and Hess, 1998) have been made by Han et al. (2008a). The trajectories were classified into three directional groups; that is, northerly transport from Mongolia, southeasterly transport from central China, and westerly transport from Middle Asia (Fig. 3). The element concentrations in $PM_{2.5}$ that correspond to each trajectory direction are summarized in Table 2. The highest average concentrations of crustal elements such as K, Ca, Ti and Fe were linked to the northerly flows, indicating that the dust sources in Daihai arise mainly from the Mongolia Gobi desert. For the non-crustal elements, the correlation between the average element concentrations and trajectory was not clear. For example, S and Zn as indicators of industrial-induced elements distinctly showed the highest average concentration in association with southeasterly

flows, exceeding the corresponding concentrations associated with the remaining two directional flows by a factor of about 2. The remaining elements showed small differences in their average concentrations with respect to the three directional flows by a factor of less than 1.5. Pb, Ni, and Br, which had higher TSP/ $PM_{2.5}$, showed higher concentrations associated with the northerly flows.

Using concentration variations from different trajectory directions, it was not easy to differentiate the human-induced sources resulting from long-range transport from those of natural origins. Thus, average EFs corresponding to each trajectory direction were also calculated as listed in Table 2. Crustal elements such as K, Ca, Ti and Fe showed low EF values and small differences between the three directional flows. The remaining elements, S, Cl, V, Cr, Mn, Ni, Cu, Zn, As, Br, Sr, Se and Pb, all showed highest average EFs associated with southeasterly flows and lowest average EFs with westerly flows, indicating the highest intensity of human sources was from central China. The elements of Cl, V, Mn, Ni and Se showed EFs associated with westerly flows less than or close to 10, indicating small or little human sources. This is in good agreement with the characteristics of the Daihai location. Daihai is bordered to the south and southeast by industrialized

Table 2

Element concentrations and enrichment factors (Fe as the reference element) associated with different air masses in Daihai in summer; Fe was used as the reference element

Direction		S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	As	Se	Br	Sr	Zr	Pb
Northerly	Concentration	673.8	40.6	145.9	816.4	19.4	6.6	6.4	65.9	562.6	7.8	9.6	17.7	7.5	9.7	10.5	13.8	31.3	25.4
	EF	189.0	16.4	0.5	2.6	0.4	14.1	10.3	13.9	1.0	20.6	61.0	49.9	734.9	19.2	1419.6	7.7	32.5	280.7
Westerly	Concentration	664.1	29.4	67.3	674.2	5.7	6.1	5.4	31.7	419.7	6.5	5.3	13.7	6.3	7.0	7.8	16.3	21.0	18.0
	EF	116.0	7.5	0.3	1.8	0.2	7.7	4.6	6.3	1.0	12.9	28.0	27.4	431.6	7.4	904.1	5.9	12.0	158.8
Southeasterly	Concentration	1281.3	39.4	83.3	436.0	8.7	7.4	6.4	83.9	233.7	6.8	7.0	44.5	8.1	8.2	9.5	12.5	20.8	18.3
	EF	494.0	23.6	0.7	2.1	0.5	20.9	14.6	26.8	1.0	33.2	79.9	178.3	1220.5	19.5	2519.6	10.3	28.1	327.1

The directions correspond to the results of the back trajectory analysis (Fig. 3).

Table 3
Rotated component matrix for PM_{2.5} elements in Daihai

Compositions	Principal components					Extraction
	1	2	3	4	5	
S	-0.148	0.650	0.493	0.302	-0.102	0.789
Cl	0.264	0.699	0.226	0.096	0.082	0.625
K	0.891	0.071	0.357	-0.031	0.134	0.945
Ca	0.797	0.104	-0.243	0.008	0.321	0.807
Ti	0.911	0.080	0.093	0.185	-0.084	0.887
V	-0.389	0.806	-0.120	0.202	0.143	0.877
Cr	0.046	0.467	0.026	-0.008	-0.406	0.386
Mn	0.109	0.160	0.851	-0.062	0.010	0.765
Fe	0.965	0.041	-0.066	0.022	0.078	0.943
Ni	0.669	0.008	-0.170	-0.227	-0.453	0.733
Cu	0.101	0.171	-0.043	-0.044	0.804	0.690
Zn	-0.189	0.701	0.392	0.374	0.028	0.821
As	0.275	0.793	0.095	-0.103	0.068	0.729
Se	-0.029	0.049	-0.074	0.873	-0.058	0.775
Br	0.484	0.140	0.182	0.677	0.091	0.754
Zr	0.174	0.684	-0.388	-0.175	0.127	0.695
Pb	0.660	-0.116	0.476	0.177	-0.256	0.773
Initial Eigenvalue	4.716	3.481	1.842	1.668	1.287	
% of variance	27.741	20.477	10.834	9.812	7.572	
Cumulative%	27.741	48.218	59.051	68.863	76.435	

PCA loadings >0.4 are shown in bold. Factor loadings >0.71 are typically regarded as excellent and <0.32 as very poor (Han et al., 2006).

continental areas of China, Shanxi province, the base of coal mining industry in China. To the north, industrial regions such as Huhhot city, the capital of Inner Mongolia, and Baotou city can be found, while to the east, desert belts of Mu Us and Kubuqi are located. Thus, it is to be expected that more human contaminants are associated with the southeasterly flows and less with the westerly flows. This is also in agreement with a previous study examining Cu and Pb history using sediment cores obtained in Daihai (Han et al., 2007).

Interestingly, Zr showed a different EF pattern from all other elements. The average EF of Zr influenced by northerly flows was higher than that associated with southeasterly flows. Although the average EFs were higher than 10 in all three directional flows, Zr is generally thought to be a lithogenic element (Shotyk et al., 2001). The high EFs may be attributable to the source of primary bedrock in the Daihai region, which is characterized by Archean metamorphosed igneous rocks and Tertiary basalt (Han et al., 2007), both of which contain high Zr (Shotyk et al., 2001; Jin et al., 2006).

3.4. Determination of the main origin of the elements in PM_{2.5}

Principal component analysis (PCA) with Varimax rotation (eigenvalues >1) was applied to the PM_{2.5} data to obtain groups containing species with similar behavior and to identify their possible sources. Sr was excluded from the PCA analysis because its extraction was lower than 0.6. Table 3 displays the factor loadings with a VARIMAX rotation as well as the eigenvalues. Five principal factors were obtained, accounting for 76.44% of the total variance. The first factor was dominated by K, Ca, Ti, Fe, Ni, Br and Pb, accounting for 27.74% of the total variance. Ni, Pb and Br loadings were lower than 0.7, which may imply a quasi-independent behavior within the group (Han et al., 2006). This group was attributable to mineral dusts from northerly flows, especially with regard to K, Ca, Ti and Fe. Ni, Pb and Br, which are

generally thought to be anthropogenic elements, are also incorporated in this group. This may be attributed to the northern flows associated with these elements. From the back trajectory analyses, higher concentrations of Pb, Ni and Br can be found to be associated with the northerly flows than with the other two directional flows (Table 2). Huhhot city is located less than 100 km from Daihai to the northwest, possibly contributing to the high loadings of anthropogenic elements in this group. This is also in good agreement with the TSP/PM_{2.5} ratio, which showed that Pb is more abundant in TSP.

The second factor had high loadings of S, Cl, V, Zn, Zr, and As, as well as a proportion of Cr, accounting for 20.48% of the total variance. This source was interpreted as a miscellaneous industrial factor. Overall, back trajectory analyses demonstrated higher concentrations of S, V, Zn, As and Cr associated with the southeasterly flows (Table 2). Cl, which is generally regarded as of sea salt origin, was incorporated in this group, and may also be attributed to the long-range transport of pollutants from southeasterly flows. The third factor was characterized by Mn, S and Pb, reflecting the effect of traffic resuspension. Mn is generally thought to be a crustal component (Han et al., 2006; Kocak et al., 2007). This group may be affected by a road located about 500 m away from the sampling location. The fourth factor was loaded mainly by Se and Br. Se is typically associated with coal combustion (Pekney et al., 2006), and indeed a coal-fired power plant is present to the south of Daihai that was performing test at the end of 2005. The last factor presented high loading of Cu. Ni and Cr had lower loadings (<0.5) and were negatively correlated with Cu in this group. It is not easy to target their sources. Since Cu, Ni, and Cr all have industrial contributions, copper metallurgy may be the main source.

4. Conclusion

In this study, monitoring of trace elements in TSP and PM_{2.5} was performed in Daihai, a monsoon-sensitive region. S, Ca, and Fe were found to be the major elements in PM_{2.5}, whereas Ca, Fe, S, and K were the major elements in TSP. Compared with the concentrations in PM_{2.5} from urban cities in East Asia, anthropogenic elements were much lower in Daihai, while crustal elements such as Ca, Fe and Ti showed similar levels. EF analysis revealed that Br, As, S and Pb were indicators of anthropogenic sources, while Ca, K, Ti, Sr and Fe of natural sources. Other elements were regarded as marker elements of pollution sources only in PM_{2.5}. Back trajectory analyses associated with the element concentrations indicated that crustal elements such as K, Ca, Ti and Fe had distinctly higher concentrations under the influence of northerly flows than that of the remaining two directional flows, while anthropogenic elements showed no clear pattern. High EF values of non-crustal elements were related to the southeasterly flows. This suggests that long-range transport of pollutants from central China under the summer monsoon may be the most important factor affecting air pollution in Daihai. As a result of PCA analysis, five factors were revealed, explaining about 76.4% of the elemental compositions. Source apportionment showed that crustal elements such as K, Ca, Ti and Fe may be linked to the northerly flows, which also influenced Pb, Ni, and Br loadings.

Miscellaneous industries were associated with high loadings of S, Cl, V, Zn and As, as well as a proportion of Cr, Se and Br are of coal combustion origin.

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References

- Al-Momani, I.F., Daradkeh, A.S., Haj-Hussein, Amin T., Yousef, Y.A., Jaradat, Q.M., Momani, K.A., 2005. Trace elements in daily collected aerosols in Al-Hashimya, central Jordan. *Atmos. Res.* 73, 87–100.
- An, Z., Porter, S.C., Kutzbach, J.E., Wu, X., Wang, S., Liu, X., Li, X., Zhou, W., 2000. Asynchronous Holocene optimum of the East Asian monsoon. *Quat. Sci. Rev.* 19, 743–762.
- Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosol: biogeochemical sources and role in atmospheric chemistry. *Science* 276, 1052–1058.
- Cong, Z., Kang, S., Liu, X., Wang, G., 2007. Elemental composition of aerosol in the Nam Co region, Tibetan Plateau, during summer monsoon season. *Atmos. Environ.* 41, 1180–1187.
- Draxler, R.R., Hess, G.D., 1998. An overview of the HYSPLIT-4 modeling system for trajectories, description, and deposition. *Aust. Meteorol. Mag.* 47, 295–308.
- Fang, G.-F., Chang, C.-N., Chu, C.-C., Wu, Y.-S., Fu, P.P.-C., Yang, I.-L., Chen, M.-H., 2003. Characterization of particulate, metallic elements of TSP, PM_{2.5} and PM_{2.5-10} aerosols at a farm sampling site in Taiwan, Taichung. *Sci. Total Environ.* 308, 157–166.
- Finlayson-Pitts, B.J., Pitts, J.N.J., 2000. Chemistry of the Upper and Lower Atmosphere. Academic Press, San Diego.
- Han, Y.M., Du, P.X., Cao, J.J., Posmentier, E.S., 2006. Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. *Sci. Total Environ.* 355, 176–186.
- Han, Y.M., Jin, Z.D., Cao, J.J., Posmentier, E.S., An, Z.S., 2007. Atmospheric Cu and Pb deposition and transport in lake sediments in a remote mountain area, Northern China. *Water Air Soil Pollut.* 179, 167–181.
- Han, Y.M., Han, Z.W., Cao, J.J., Chow, J.C., Watson, J.G., An, Z.S., Liu, S.X., Zhang, R.J., 2008a. Distribution and origin of carbonaceous aerosol over a rural high-mountain lake area, Northern China and its transport significance. *Atmos. Environ.* 42, 2405–2414.
- Han, Y.M., Cao, J.J., Posmentier, E.S., Fung, K., Tian, H., An, Z.S., 2008b. Particulate-associated potentially harmful elements in urban road dusts in Xi'an, China. *Appl. Geochem.* 23, 835–845.
- He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X., Chan, C.K., Cadle, S., Chan, T., Mulawa, P., 2001. The characteristics of PM_{2.5} in Beijing, China. *Atmos. Environ.* 35, 4959–4970.
- Ho, K.F., Lee, S.C., Chan, C.K., Yu, J.C., Chow, J.C., Yao, X.H., 2003. Characterization of chemical species in PM_{2.5} and PM₁₀ aerosols in Hong Kong. *Atmos. Environ.* 37, 31–39.
- IPCC, 2001. In: Watson, R.T., et al. (Ed.), Intergovernmental Panel on Climate Change, Climate Change. Cambridge University Press, New York.
- Jin, Z., Wu, J., Cao, J., Wang, S., Shen, J., Gao, N., Zou, C., 2004. Holocene chemical weathering and climatic oscillations in north China: evidence from lacustrine sediments. *Boreas* 33, 260–266.
- Jin, Z., Li, F., Cao, J., Wang, S., Yu, J., 2006. Geochemistry of Daihai Lake sediments, Inner Mongolia, north China: implication for provenance, sedimentary sorting, and catchment weathering. *Geomorphology* 80, 147–163.
- Kocak, M., Mihalopoulos, N., Kubilay, N., 2007. Chemical composition of the fine and coarse fraction of aerosols in the northeastern Mediterranean. *Atmos. Environ.* 41, 7351–7368.
- Mauderly, J.J. and Chow, J.C., 2008. Health effects of organic aerosols. *Inhal. Toxicol.* 20, 257–288.
- Park, S.S., Kim, Y.J., 2005. Source contributions to fine particulate matter in an urban atmosphere. *Chemosphere* 59, 217–226.
- Pekney, N.J., Davidson, C.I., Bein, K.J., Wexler, A.S., Johnston, M.V., 2006. Identification of sources of atmospheric PM at the Pittsburgh Supersite, Part I: single particle analysis and filter-based positive matrix factorization. *Atmos. Environ.* 40, S411–S423.
- Ragosta, M., Caggiano, R., Macchiato, M., Sabia, S., Trippetta, S., 2008. Trace elements in daily collected aerosol: level characterization and source identification in a four-year study. *Atmos. Res.* 89, 206–217.
- Ramanakumar, A.V., Parent, M.-E., Siemiatycki, J., 2007. Risk of lung cancer from residential heating and cooking fuels in Montreal, Canada. *Am. J. Epidemiol.* 165, 634–642.
- Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D., 2001. Aerosols, climate, and the hydrological cycle. *Science* 294, 2119–2124.
- Ren, T.J., Ma, Y.R., Duan, L.H., 1995. Daihai Lake in Inner Mongolia. In: Jin, X.C. (Ed.), Lakes in China—Research of Their Environment. Haiyang Press, Beijing, China, pp. 531–559. In Chinese.
- Shotyk, W., Weiss, D., Kramers, J.D., Frei, R., Cheburkin, A.K., Cloor, M., Reese, S., 2001. Geochemistry of peat bog at Etang de la Gruere, Jura mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace elements (Sc, Ti, Y, Zr, and REE) since 12,370 ¹⁴C yr BP. *Geochim. Cosmochim. Acta* 65, 2337–2360.
- Wedepohl, H.K., 1995. The composition of the continental crust. *Geochim. Cosmochim. Acta* 59, 1217–1232.
- Wen, Q.Z., 1989. Loess Geochemistry in China. Science Press, Beijing. In Chinese.
- Ye, B., Ji, X., Yang, H., Yao, X., Chan, C.K., Cadle, S.H., Chan, T., Mulawa, P.A., 2003. Concentration and chemical composition of PM_{2.5} in Shanghai for a 1-year period. *Atmos. Environ.* 37, 499–510.
- Zhang, X.Y., Arimoto, R., An, Z.S., Chen, T., Zhang, G.Y., Zhu, G.H., Wang, X.F., 1993. Atmospheric trace-elements over source regions for Chinese dust-concentrations, sources and atmospheric deposition on the Loess Plateau. *Atmos. Environ.* 27 (13), 2051–2067.