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# Seasonal variations and sources of various elements in the atmospheric aerosols in Qingdao, China

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**Abstract**

Seasonal variations and sources of various elements in the atmospheric aerosols of the North China coast were investigated by analyzing aerosol samples collected in Qingdao, China. 23 total suspended particulate (TSP) samples were collected from June 2001 to May 2002, including three samples gathered during Asian dust episodes (20 March and 7–8 April 2002). The concentrations of ten elements including iron (Fe), titanium (Ti), manganese (Mn), vanadium (V), nickel (Ni), copper (Cu), lead (Pb), zinc (Zn), cadmium (Cd) and sulfur (S) were measured by 3000 ICP-OES. All elements measured in the aerosols of Qingdao displayed a strong seasonal variation: the concentrations of Fe, Ti, Mn, V, Ni, Cu, Pb, Zn, Cd were the lowest in summer, and the highest in winter. During the Asian dust episodes, the concentrations of Fe, Ti, Mn, V, Ni, Cu increased remarkably. The concentrations of Pb, Zn, Cu, S also increased greatly during the Asian dust episodes, but they were still lower than those in winter. The enrichment factors (EFs) of all elements (with reference to crustal Fe) indicate that Ti and Mn are mainly from soil sources. V in the Qingdao aerosols is mainly derived from the soil, with a minor contribution from ship emissions. The anthropogenic sources have a relatively higher contribution to Ni and Cu compared with Fe, Ti, and Mn. The S, Pb, Zn and Cd are mainly from anthropogenic sources even during Asian dust episodes. Principal component analysis (PCA), and cluster analysis (CA) indicated that the natural sources contributed about 60% to the sum of measured elements in all samples and anthropogenic sources contributed about 30%, and these elements can be classified into three categories as follow: Fe, Ti, Mn, V, and Ni represent the soil source factor; Cu represents the factor of mixed sources of soil and pollution; and Pb, Zn, Cd and S represents the pollution factor.


*Keywords:* Aerosol; Metals; Seasonal variation; Source; Asian dust episode; Qingdao; China

## 1. Introduction

Aerosols have an important influence on the transmission of atmospheric radiation and the water cycle. Aerosols can change the energy budget of the land–atmosphere system by absorbing and dispersing solar radiation, thus directly affect the climate (Su and Chen, 1997; Qian et al., 1999; Meinrat et al., 1997; Dusek et al., 2006). Anthropogenic particles in the atmosphere can lead to serious environmental problems (Dockery et al., 1993; Schwartz et al., 1996). Heavy metals transported into the oceans by the atmosphere from the polluted areas have an influence on the chemical characteristic of the oceans (Arimoto et al.,

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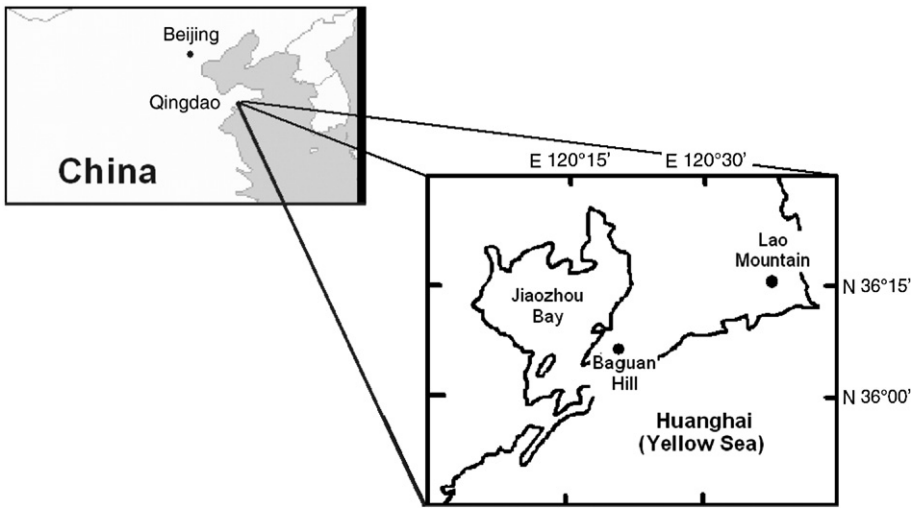


Fig. 1. Sampling site.

1985, 1996). Atmospheric aerosol is an important biogeochemical source (Meinrat et al., 1997), and the concentration of Fe is a limiting factor of the primary productivity in the seawater surface layer in some ocean regions (Cooper et al., 1996; Martin, 1992, 1994; Lefevre and Watson, 1999; Watson, 1999; Watson et al., 2000; Ridgwell et al., 2002), while the Fe is mainly derived from the aerosols (Zhuang et al., 2003) in the open oceans. Large quantities of mineral dust were transported from the Asian continent to the Northern Pacific every year (Duce et al., 1980, 1991). Qingdao is a coastal city situated in the southern tip of the Shandong Peninsula in Northern China (35° 35′ N and 119° 30′ E) with an area of 1102 km$^2$ and a population of 2.346 million (Fig. 1). The major air pollutant in Qingdao is suspended particulate matter. Qingdao is located downwind of the origin of the Asian dust storms in spring when northwesterly winds prevail. Qingdao is in the transport path of the storms as they move to the east and is thus an important exit point of the dust storms to the Pacific, so it is an ideal site to monitor Asian dust storms before dispersion and influx from non-continental sources dilute the air mass.

Many studies on the composition, transportation and deposition of the ions, metals and minerals in the aerosols in Qingdao and its adjacent sea, the Yellow Sea, have been made (Chen et al., 1999, 2003; Fang et al., 1999; In and Park, 2002; Gao et al., 1992; Li and Chen, 1997; Liu and Zhou, 1999; Zhang et al., 2000; Wang and Hu, 2001; Guo et al., 2003; Sheng et al., 2003; Uemastsu et al., 1983; Zhang et al., 1992; Merrill et al., 1989), but about the source and seasonal variation of metals are limited. We collected 23 total suspended particulate (TSP) samples in Qingdao from June 2001 to May 2002 to perform a detailed abundance study of the various elements and discuss their sources on a seasonal basis.

## 2. Experiment

### 2.1. Sampling site

The sampling site was on the rooftop of a three-storey meteorological station on top of Baguan Hill on

Table 1
Meteorological situation on sampling days

| Date | Precipitation (mm) | Mean wind direction | Mean wind speed (km/h) |
|---|---|---|---|
| 11–06–01 | 0 | South | 10 |
| 13–06–01 | 2.5 | Southeast | 5 |
| 11–07–01 | 1.2 | Southeast | 7.5 |
| 12–07–01 | 5 | South | 12 |
| 11–08–01 | 0 | South | 11 |
| 11–09–01 | 0 | North and South | 15 |
| 12–09–01 | 1 | Southeast | 13 |
| 11–10–01 | 0 | North | 18 |
| 16–11–01 | 0 | Northwest | 15 |
| 17–11–01 | 0 | Northwest | 10 |
| 14–12–01 | 0 | Northwest | 25 |
| 15–12–01 | 0 | Northwest | 15 |
| 09–01–02 | 0 | Northwest | 9 |
| 10–01–02 | 0 | South and North | 11 |
| 12–01–02 | 0 | North and Southeast | 10 |
| 21–02–02 | 0.3 | South and North | 13 |
| 07–03–02 | 0 | Southeast | 12 |
| 25–04–02 | 0 | South | 15 |
| 06–05–02 | 22 | Northeast | 15 |
| 26–05–02 | 0 | South and North | 13 |
| 20–03–02 | 10 | Northwest | 16 |
| 07–04–02 | 0 | Northwest | 21 |
| 08–04–02 | 0 | Northwest | 23 |

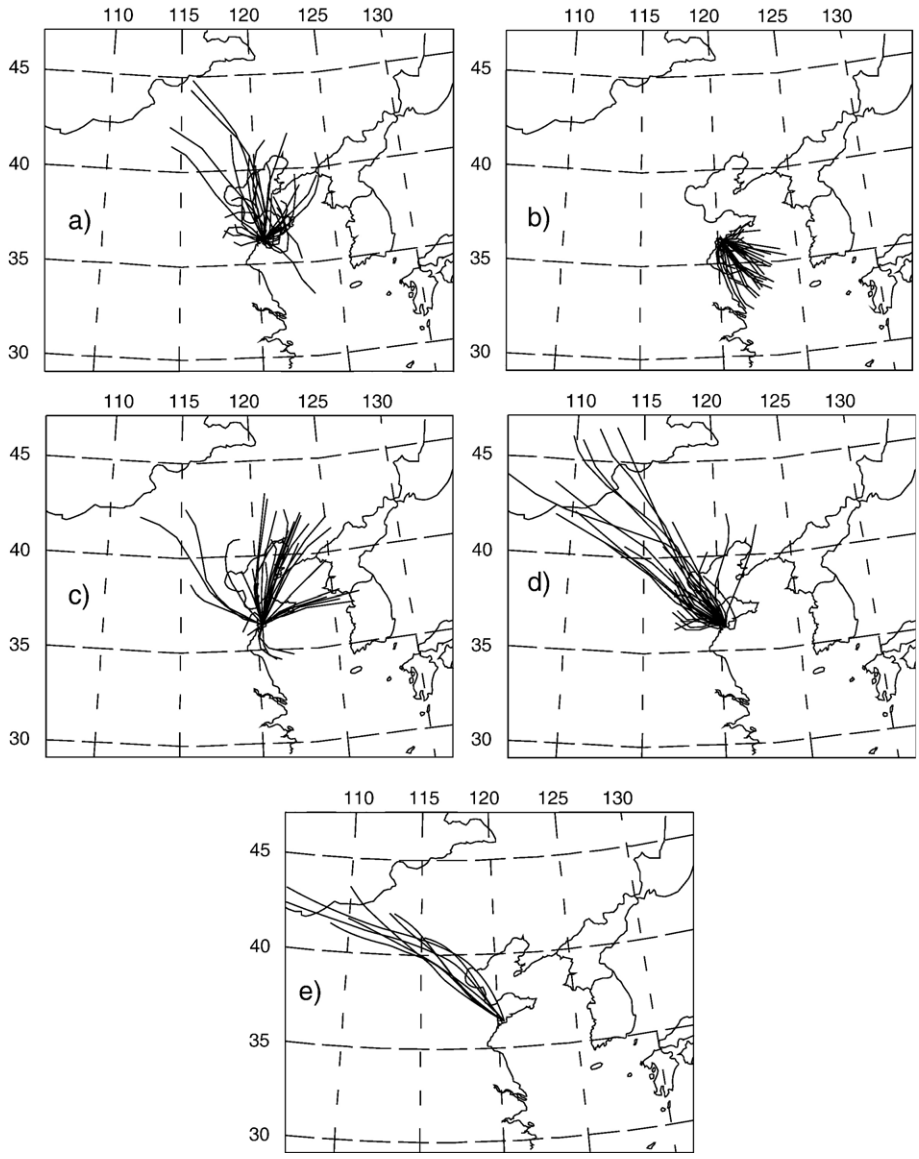


Fig. 2. 24-hour back trajectories of the sampling periods of Qingdao (one trajectory every 8 h): a) spring; b) summer; c) autumn; d) winter; e) dust storm.

the campus of the Ocean University of China (Fig. 1). The elevation of Baguan Hill is 70 m and is about 500 m from the Yellow Sea. The campus is in the midst of a coastal tourist district. There are many restaurants and residential areas in the general area, which has abundant trees and vegetation. The main part of the city is north of the sampling site. About 5 km to the north of the sampling site is Qingdao's industrial district.

### 2.2. Sampling

Total suspended particulate (TSP) samples were collected on quartz fiber filters (Whatman, QM-A 20×25 cm) using a commercial high-volume sampler (Sibata HV-1000F, made in Japan). The flow rate was 1.0 $m^3$ $min^{-1}$ and the sampling time was nominally 24 h. One-eighth of the filter paper was used for elemental measurements.

### 2.3. Elemental analysis

The method of measurement for elements was according to Zheng et al. (2005). Briefly, the elemental composition of the samples was quantified using a Perkin Elmer 3000 ICP-OES of the Center for Atmospheric and Coastal Research, Hong Kong University of Science and Technology (HKUST). Sample

Table 2
The concentrations of various elements in aerosols in Qingdao (ng $m^{-3}$)

| Sample | Fe | Ti | Mn | Pb | Cu | Zn | V | Ni | Cd | S |
|---|---|---|---|---|---|---|---|---|---|---|
| 11/06/01 | 421.4 | 63.2 | 11.4 | 27.1 | 5.4 | 80.7 | 5.8 | 1.6 | 0.5 | 6178.6 |
| 13/06/01 | 628.4 | 63.9 | 20.0 | 28.8 | 11.7 | 72.3 | 13.2 | 3.9 | 0.6 | 4889.4 |
| 11/07/01 | 1895.3 | 132.5 | 46.4 | 87.6 | 24.8 | 269.7 | 12.3 | 8.7 | 1.4 | 5202.4 |
| 12/07/01 | 601.7 | 79.9 | 15.5 | 20.6 | 7.0 | 204.6 | 7.7 | 1.1 | 0.1 | 2307.0 |
| 11/08/01 | 4159.5 | 205.3 | 128.9 | 155.6 | 22.1 | 393.1 | 12.9 | 16.3 | 3.9 | 6353.0 |
| Average (summer) | 1541.3 | 109.0 | 44.4 | 63.9 | 14.2 | 204.1 | 10.4 | 6.3 | 1.3 | 4986.1 |
| 11/09/01 | 2004.7 | 122.7 | 38.6 | 69.5 | 38.3 | 135.0 | 4.6 | 1.1 | 0.3 | 2071.7 |
| 12/09/01 | 1234.5 | 103.5 | 30.0 | 47.3 | 14.3 | 88.6 | 4.9 | 3.1 | 0.3 | 1657.3 |
| 11/10/01 | 5751.3 | 262.1 | 147.5 | 382.1 | 22.3 | 376.2 | 12.9 | 26.2 | 4.4 | 5290.8 |
| Average (fall) | 2996.8 | 162.8 | 72.0 | 166.3 | 25.0 | 199.9 | 7.5 | 10.1 | 1.7 | 3006.6 |
| 16/11/01 | 3525.4 | 313.5 | 210.5 | 407.4 | 42.4 | 543.0 | 16.6 | 8.0 | 3.4 | 8354.4 |
| 17/11/01 | 3849.3 | 395.5 | 204.1 | 701.6 | 47.3 | 701.8 | 16.2 | 10.7 | 10.0 | 11,459.0 |
| 14/12/01 | 2408.5 | 277.6 | 84.1 | 149.9 | 28.7 | 200.2 | 10.4 | 5.9 | 1.2 | 2924.9 |
| 15/12/01 | 2981.6 | 248.2 | 61.2 | 104.2 | 20.2 | 294.3 | 13.7 | 8.0 | 1.2 | 4468.5 |
| 9/01/02 | 4204.5 | 471.5 | 163.0 | 367.3 | 72.7 | 605.1 | 21.7 | 11.5 | 5.6 | 9072.5 |
| 10/01/02 | 3145.7 | 362.9 | 95.2 | 249.2 | 24.3 | 323.1 | 13.3 | 3.7 | 4.7 | 7744.8 |
| 12/01/02 | 2722.8 | 289.1 | 93.3 | 260.4 | 36.4 | 469.9 | 14.1 | 5.6 | 6.4 | 10,262.1 |
| 21/02/02 | 7466.7 | 643.5 | 156.7 | 276.0 | 33.3 | 477.8 | 23.8 | 15.6 | 8.6 | 11,370.9 |
| Average (winter) | 3788.1 | 375.2 | 133.5 | 314.5 | 38.2 | 451.9 | 16.2 | 8.6 | 5.1 | 8207.1 |
| 7/03/02 | 5291.7 | 531.9 | 120.3 | 230.3 | 61.7 | 464.1 | 23.0 | 14.4 | 7.2 | 10,590.5 |
| 25/04/02 | 1848.0 | 210.3 | 48.5 | 65.7 | 8.7 | 87.9 | 6.2 | 3.2 | 3.9 | 2157.6 |
| 6/05/02 | 802.4 | 61.9 | 16.2 | 34.5 | 5.3 | 68.4 | 6.3 | 1.3 | 0.5 | 995.8 |
| 26/05/02 | 3578.1 | 322.9 | 78.4 | 72.3 | 33.0 | 198.4 | 20.0 | 13.6 | 1.4 | 3570.5 |
| Average (spring) | 2880.0 | 281.8 | 65.8 | 100.7 | 27.2 | 204.7 | 13.9 | 8.1 | 3.2 | 4328.6 |
| 20/03/02 | 43,057.3 | 5818.4 | 1221.0 | 226.4 | 87.6 | 522.1 | 146.7 | 64.1 | 1.8 | 12,439.3 |
| 7/04/02 | 30,001.0 | 3721.9 | 813.5 | 144.6 | 40.0 | 231.8 | 92.8 | 34.8 | 0.7 | 5496.0 |
| 8/04/02 | 26,549.1 | 3331.8 | 695.7 | 182.8 | 44.2 | 268.1 | 76.9 | 31.8 | 1.6 | 4770.4 |
| Average (dust) | 33,202.5 | 4290.7 | 910.1 | 184.6 | 57.3 | 340.7 | 105.4 | 43.6 | 1.4 | 7568.6 |

pre- and post-processing were performed in the HKUST Institute for Environment and Sustainable Development Clean Room's Class 100 booths. All plastic ware was acid-cleaned prior to use. Filters were digested in a 5 ml mixture of HCl, $HNO_3$ and HF on a hot plate at 110 °C for 4 h. After digestion, the samples were evaporated to dryness at 60 °C, redissolved in 2% nitric acid and filtered before ICP-OES analysis. Quantification was carried out by the external calibration technique using a set of external calibration standards at concentration levels close to that of the samples. Procedural and field blanks were also determined and were subtracted from the samples. Recoveries derived from the analysis of SRM1648 (Standard Reference Material 1648, urban suspended particulates) were in the range of 89% for Fe to 103% for Ti. The error for analysis is less than 5%.

Quartz fiber filters contain high Na, Al, Ca and Mg background and therefore will not yield accurate enough results for our purpose. On the other hand, filter blanks of Fe, S, Ti, Mn, Pb, Cu, Zn and V are low and the average respective concentrations of these metals in the samples are 3 to 10 times higher than the filter blank, making the results usable.

## 3. Results and discussion

### 3.1. Climatic conditions and back trajectory analysis

Qingdao is in the temperate zone and is influenced by the East Asian Monsoon. The climate is maritime in characteristics with relatively small variation in daily and annual temperature. The meteorological situation during the sampling periods was listed in Table 1. Average ambient temperature was 12.3 °C in spring, 23.9 °C in summer, 19.7 °C in autumn and 4.5 °C in winter. Summer is the rainy season (http://www.stats-qd.gov.cn/).

Back trajectories for the sampling periods (one trajectory every 8 h) are given in Fig. 2 and agreed well with the East Asian Monsoon system. The wind directions were relatively steady in summer and winter but varied in spring and autumn. In summer, air parcels arriving at Qingdao were mainly from the sea and clean. The winter air parcels were from the land in the northwest direction. In spring and autumn, air parcels were mainly from the northwest to north and some from southwest to south. Qingdao is thus impacted by the pollutants from surrounding regions, and the dust storms

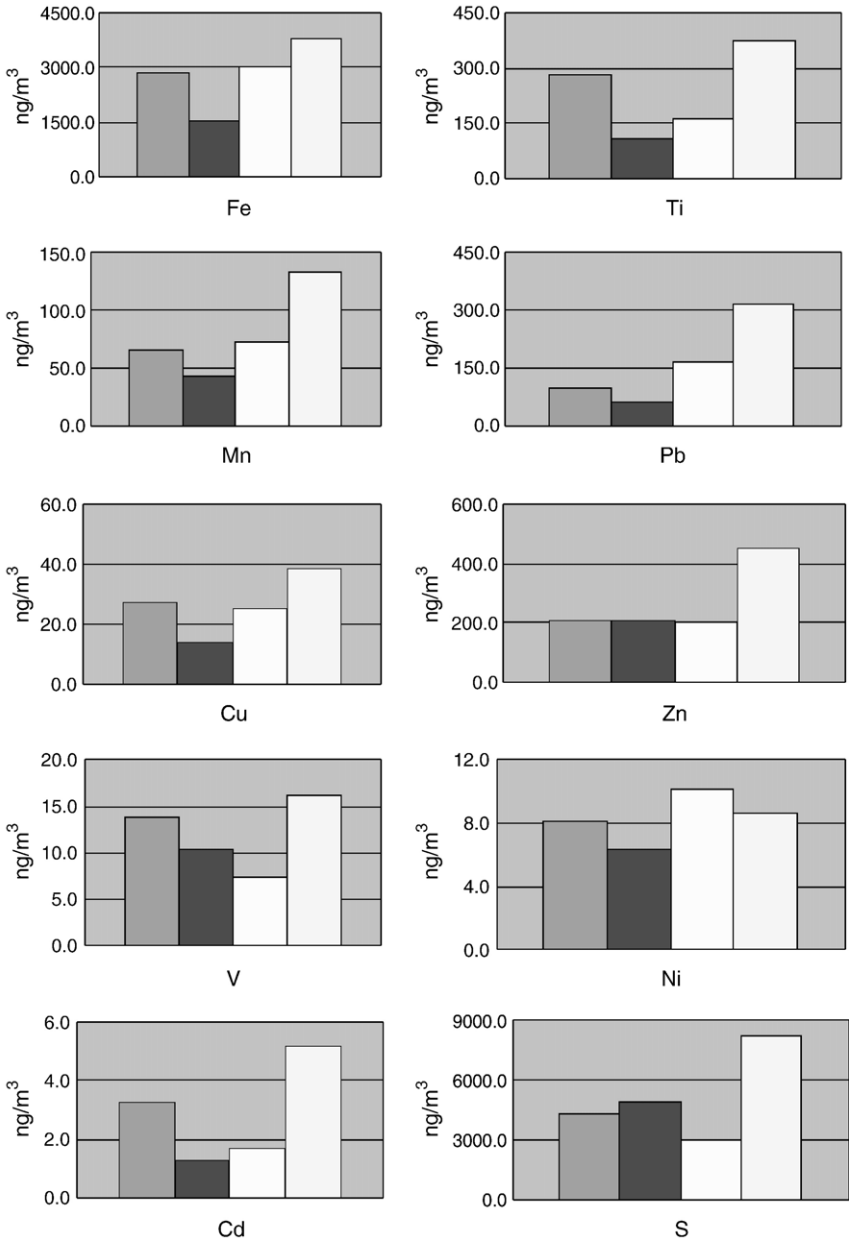


Fig. 3. The variation of various elements in seasonal average in aerosols in Qingdao (ng $m^{-3}$). Averages in spring, summer, fall and winter.

are mainly from the north western region (Fig. 2) across Beijing–Tianjin industrial region, and the outflow of continental pollutants to the East China Seas and the Pacific Ocean is mainly in winter, spring, and autumn. Samples on 16/11/01, 17/11/01, 14/12/01, 15/12/01, 9/01/02, when the wind was northwest, were impacted by the anthropogenic source, including industrial emission; samples on 11/06/01, 13/06/01, 11/07/01, 12/07/01, 11/08/01, when the wind was mainly from the sea, the influence from industrial regions should be limited.

### 3.2. Seasonal variation of various elements

The concentrations of various elements in aerosols of Qingdao are listed in Table 2, and the seasonal variation of various elements in aerosols of Qingdao is shown in Fig. 3. From Table 2 and Fig. 3, we can see that all measured elements in the aerosols (except the samples during Asian dust storm) of Qingdao showed a strong seasonal variation in yield: the average concentrations of Fe, Ti, Mn, V, Ni, Cu, Pb, Zn, Cd were the lowest in

Table 3
Enrichment factors of various elements in aerosols in Qingdao (with reference to crustal Fe after Taylor, 1964)

| Sample | Ti | Mn | Pb | Cu | Zn | V | Ni | Cd | S |
|---|---|---|---|---|---|---|---|---|---|
| 11/06/01 | 1.5 | 1.6 | 289.3 | 13.1 | 154.1 | 5.8 | 28.5 | 308.6 | 3174.8 |
| 13/06/01 | 1.1 | 1.9 | 332.8 | 10.4 | 120.1 | 4.6 | 35.8 | 342.2 | 1589.1 |
| 11/07/01 | 0.7 | 1.5 | 208.2 | 13.4 | 114.4 | 2.7 | 34.5 | 212.8 | 594.4 |
| 12/07/01 | 1.3 | 1.5 | 154.3 | 11.9 | 273.4 | 5.3 | 13.4 | 46.8 | 830.3 |
| 11/08/01 | 0.5 | 1.8 | 168.5 | 5.4 | 76.0 | 1.3 | 29.4 | 265.7 | 330.7 |
| Average (summer) | 1.0 | 1.7 | 230.6 | 10.8 | 147.6 | 3.9 | 28.3 | 235.2 | 1303.9 |
| 11/09/01 | 0.6 | 1.1 | 156.1 | 19.6 | 54.2 | 1.0 | 4.0 | 42.2 | 223.8 |
| 12/09/01 | 0.8 | 1.4 | 172.7 | 11.8 | 57.7 | 1.7 | 18.7 | 74.0 | 290.7 |
| 11/10/01 | 0.5 | 1.5 | 299.2 | 4.0 | 52.6 | 0.9 | 34.2 | 215.4 | 199.2 |
| Average (fall) | 0.6 | 1.3 | 209.3 | 11.8 | 54.8 | 1.2 | 19.0 | 110.5 | 237.9 |
| 16/11/01 | 0.9 | 3.5 | 520.5 | 12.3 | 123.9 | 2.0 | 17.0 | 273.1 | 513.1 |
| 17/11/01 | 1.0 | 3.1 | 820.9 | 12.6 | 146.6 | 1.8 | 20.9 | 732.8 | 644.6 |
| 14/12/01 | 1.1 | 2.1 | 280.3 | 12.2 | 66.9 | 1.8 | 18.4 | 143.8 | 263.0 |
| 15/12/01 | 0.8 | 1.2 | 157.3 | 6.9 | 79.4 | 1.9 | 20.2 | 117.4 | 324.5 |
| 9/01/02 | 1.1 | 2.3 | 393.4 | 17.7 | 115.8 | 2.1 | 20.4 | 372.8 | 467.2 |
| 10/01/02 | 1.1 | 1.8 | 356.8 | 7.9 | 82.6 | 1.8 | 8.8 | 420.4 | 533.1 |
| 12/01/02 | 1.0 | 2.0 | 430.8 | 13.7 | 138.8 | 2.2 | 15.6 | 656.7 | 816.1 |
| 21/02/02 | 0.9 | 1.2 | 166.5 | 4.6 | 51.5 | 1.3 | 15.7 | 325.8 | 329.8 |
| Average (winter) | 1.0 | 2.2 | 390.8 | 11.0 | 100.7 | 1.9 | 17.1 | 380.4 | 486.4 |
| 7/03/02 | 1.0 | 1.3 | 196.0 | 11.9 | 70.5 | 1.8 | 20.4 | 381.7 | 433.4 |
| 25/04/02 | 1.1 | 1.6 | 160.1 | 4.8 | 38.3 | 1.4 | 13.0 | 597.5 | 252.8 |
| 6/05/02 | 0.8 | 1.2 | 193.9 | 6.8 | 68.6 | 3.3 | 12.1 | 171.7 | 268.7 |
| 26/05/02 | 0.9 | 1.3 | 90.9 | 9.4 | 44.6 | 2.3 | 28.6 | 107.1 | 216.1 |
| Average (spring) | 0.9 | 1.3 | 160.2 | 8.2 | 55.5 | 2.2 | 18.5 | 314.5 | 292.7 |
| 20/03/02 | 1.3 | 1.7 | 23.7 | 2.1 | 9.8 | 1.4 | 11.2 | 12.1 | 62.6 |
| 7/04/02 | 1.2 | 1.6 | 21.7 | 1.4 | 6.2 | 1.3 | 8.7 | 7.0 | 39.7 |
| 8/04/02 | 1.2 | 1.6 | 31.0 | 1.7 | 8.1 | 1.2 | 9.0 | 17.0 | 38.9 |
| Average (dust) | 1.2 | 1.6 | 25.5 | 1.7 | 8.0 | 1.3 | 9.6 | 12 | 47 |

summer, and the highest in winter. The highest concentrations of Fe, Ti, Mn, V, Cu, Pb, Zn, Cd are all in winter, but the highest concentration of Ni is on October 11 in fall. The highest concentrations of Fe, Ti, Mn, V, Ni, Cu, Pb, Zn, Cd are respectively 7466.7, 643.5, 210.5, 23.8, 26.2, 72.7, 701.6, 701.8, 10 ng $m^{-3}$. The lowest concentrations of Fe, Mn, Ni, Pb, Cd are all in summer. The lowest concentrations of Ti, Cu, Zn, S are all in spring except for Asian dust periods. The lowest concentration of V is in fall.

There are four possible reasons for the lowest average concentration of the airborne elements in summer in Qingdao (Fig. 3): (1). Summer is the wet season in Qingdao (Table 1 and Fig. 2.) so the wet deposition of aerosol is strong. (2). The vegetation is flourishing, so the soil source is relatively reduced. (3). Southeast wind from the sea prevails in Qingdao, thus dispersion and influx of clean sea air dilute the local air mass (Fig. 2). (4). Pollutant emission to the atmosphere in summer is less than that in winter, the space-heating season.

The average concentration of most elements is the highest in winter, which indicates the poor air quality in Qingdao in winter (Fig. 3). Four possible reasons for this are listed: (1). Because a lot of coal is burnt for space-heating in Qingdao, more pollutants such as sulfur oxides, nitric oxides, dusts and so on are emitted to the atmosphere. (2). It is the convergence period of the cool and warm airflows in winter. Due to the existence of a temperature inversion in Qingdao, the airflow diffusion is not direct (Wang et al., 2003). (3). It is very dry in winter in Qingdao, so wet deposition is weak. (4). With little vegetation and relatively more powerful northwest wind, more contribution from soil source aerosols can be expected in winter.

Among the measured elements, it is special that the average concentration of S is the highest in winter, but the average concentration of S in summer is higher than that in spring and autumn (Fig. 3). The main reasons for this should be due to the dissolving of sulfur oxides in water and changing quickly into sulfate by in-cloud processes in the wet summer (Yao et al., 2003); thus the concentration of S in the aerosols is increased distinctly. (2). The Fe–S coupling process that promotes the dissolving of sulfur oxides in the aerosol is also important (Zhuang et al., 2003).

Because of the wet deposition and the vegetation cover, the dust concentration in the atmosphere from May

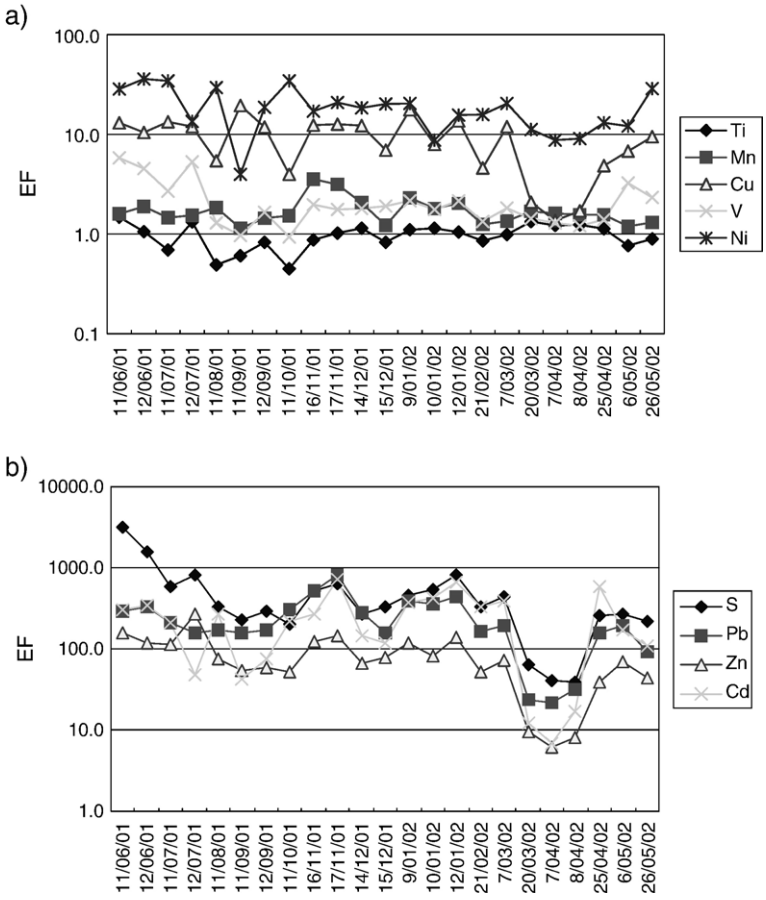


Fig. 4. a. Seasonal variation of enrichment factors of S, Pb, Zn and Cd. b. Seasonal variation of enrichment factors of Ti, Mn, Cu, V and Ni.

to August, is very low, but the average concentration of Vanadium in summer is higher than that in autumn (Fig. 3); this is different from other elements. Besides a soil source, V can also be derived from the combustion of heavy residual oil typically used in ships (Nriagu and Pacyna, 1988), therefore, as a famous port, the higher V in Qingdao's atmosphere in spring and summer should not be a surprise.

A very heavy dust episode occurred in Qingdao during March 20–21st, and a relatively heavy dust episode occurred during April 7–8th. During these dust episodes, the concentrations of Fe, Ti, Mn, V, Ni, Cu increased remarkably compared with the non-dust episodes in spring. The concentrations of Fe, Ti and Mn in the dust episode samples were 10 times more than those in non-dust episode samples. Compared with the non-dust episodes in spring, the concentrations of Pb, Zn, Cu, S in the dust episode samples also had a remarkable increase, but they were obviously lower than those in winter samples.

### *3.3. Source of various elements in TSP in Qingdao*

#### *3.3.1 Seasonal variation of enrichment factors (EFs) of various elements*

The concentrations of Fe, S, Ti, Mn, Pb, Cu, Zn, Cd and V of the 23 samples analyzed are listed in Table 2, and the EFs (with reference to crustal Fe) are listed in Table 3. The abundance of the targeted crustal elements is from the report of Taylor (Taylor, 1964). The EFs are calculated with the following formula:

$$\mathrm{EF} = (X/\mathrm{Fe})_{\mathrm{Atmosphere}}/(X/\mathrm{Fe})_{\mathrm{Crust}}$$

Seasonal variation of EFs of various elements is showed in Fig. 4a and b. Fig. 4a shows that the seasonal variation of EFs of the elements Ti, Mn are very small, and are basically close to 1, suggesting that the two elements have the similar origin, i.e. the soil source.

The EFs of V are very close to one in most months, which indicates that the main origin of V in Qingdao is

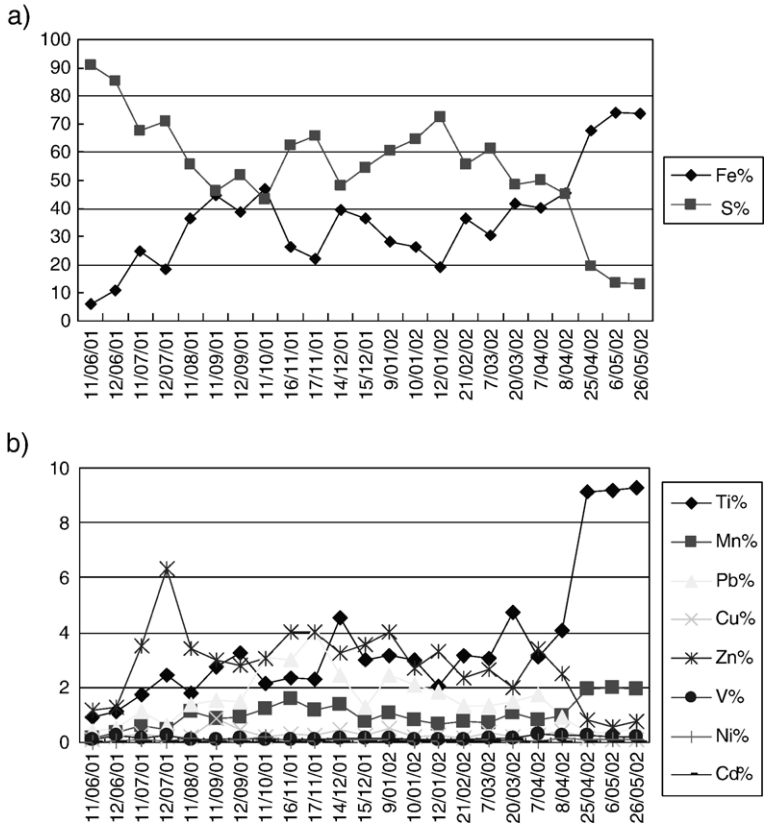


Fig. 5. a. % of Fe, S in sum of elements. b. % of Ti, Mn, Pb, Cu, Zn, V, Ni, Cd in sum of elements.

soil. The relatively higher EFs of samples collected in May, June, July, and August indicate that part of the V is derived from anthropogenic sources from May to August (explained in Section 3.3.1).

The EFs of Ni and Cu are relatively higher than Ti, Mn and V, which indicates that anthropogenic sources have a relatively higher contribution to Ni, Cu. The EFs of Cu decreased remarkably to near one during the dust episodes, showing that Cu during the dust episodes is mainly from soil source, and the anthropogenic source is minor.

The EFs of S, Pb, Zn and Cd share the similar seasonal variation pattern, though the EFs of S, Pb are significantly higher than those of Zn and Cd. During

Table 4
Total variance explained

| Component | Initial Eigenvalues | | | Extraction sums of squared loadings | | | Rotation sums of squared loadings | | |
|---|---|---|---|---|---|---|---|---|---|
| | Total | % of Variance | Cumulative % | Total | % of Variance | Cumulative % | Total | % of Variance | Cumulative % |
| 1 | 6.023 | 60.227 | 60.227 | 6.023 | 60.227 | 60.227 | 5.357 | 53.570 | 53.570 |
| 2 | 3.042 | 30.417 | 90.644 | 3.042 | 30.417 | 90.644 | 3.614 | 36.137 | 89.706 |
| 3 | 0.328 | 3.282 | 93.926 | 0.328 | 3.282 | 93.926 | 0.422 | 4.220 | 93.926 |
| 4 | 0.299 | 2.992 | 96.918 | | | | | | |
| 5 | 0.157 | 1.565 | 98.483 | | | | | | |
| 6 | 0.095 | 0.947 | 99.431 | | | | | | |
| 7 | 0.049 | 0.491 | 99.921 | | | | | | |
| 8 | 0.004 | 0.045 | 99.966 | | | | | | |
| 9 | 0.002 | 0.022 | 99.988 | | | | | | |
| 10 | 0.001 | 0.012 | 100.000 | | | | | | |

Extraction method: principal component analysis.

Table 5
Fuels used in 2001 in Qingdao

| Name | Unit | Total | Industrial usage | Other usage (heating and others) |
|---|---|---|---|---|
| Raw coal | Ton | 7,931,900 | 7,686,400 | 245,500 |
| Coke | Ton | 816,827 | 816,411 | 416 |
| Crude oil | Ton | 2,452,413 | 2,452,389 | 24 |
| Gasoline | Ton | 37,888 | 24,703 | 13,185 |
| Kerosene | Ton | 3996 | 2825 | 1171 |
| Diesel oil | Ton | 86,365 | 67,483 | 18,882 |

the dust episodes, the EFs of S, Pb, Zn and Cd have a distinct decrease, but are still higher than 10, and the EFs of Zn, Cd still higher than 7, which indicates that the S, Pb, Zn and Cd are mainly derived from anthropogenic sources. Sulfur is mainly derived from the combustion of fossil fuels (Zhang and Friedlander, 2000), and the average concentration of S in winter is the highest, so coal burning for heating in winter is an important source. Zn can come from industrial sources and the abrasion of rubber tires on roads (Rogge et al., 1993). Lead is a known component in automobile emissions (Nriagu and Pacyna, 1988).

*3.3.2 Seasonal variation of the percentage of an element in the sum of elements*

The percentage of an element in the sum of elements was calculated and the formula is: percentage of $X = X$ / (sum of all elements) * 100%.

From Fig. 5a and b, we can see that the percentage of Fe increased remarkably in the samples of the dust storm, and the percentage of Pb increased in winter distinctly. The increase of the percentage of Fe in the dust storm samples indicated that the proportion of natural source increased, and the increase of the percentage of Pb increase in winter was caused by emissions from space-heating.

Table 6
Rotated component matrix

| | Component | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| Ti | 0.992 | 0.026 | 0.047 |
| Fe | 0.991 | 0.056 | 0.032 |
| V | 0.991 | 0.064 | 0.094 |
| Mn | 0.985 | 0.125 | 0.004 |
| Ni | 0.938 | 0.200 | 0.049 |
| Cu | 0.632 | 0.630 | −0.039 |
| Pb | 0.074 | 0.949 | −0.145 |
| Zn | 0.222 | 0.945 | 0.057 |
| Cd | −0.158 | 0.892 | 0.227 |
| S | 0.280 | 0.751 | 0.574 |

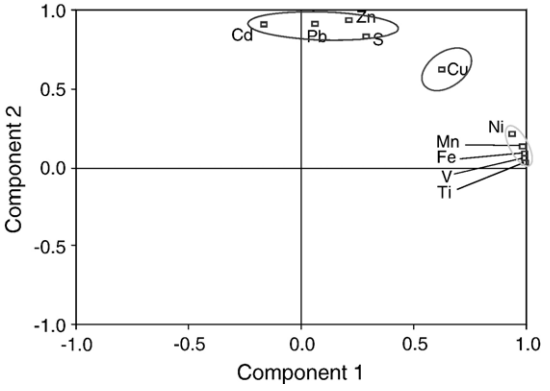


Fig. 6. PCA results in the two-dimensional space: plot of loadings of the first two principal components.

*3.3.3 Principal component analysis (PCA)*

Principal component analysis (PCA) is used to identify the main sources of all elements (Tokalioğlu and Kartal, 2006; Singh, 2006). Total variance was listed in Table 4. Three principal components were identified based on the loading of various elements and accounted for 60%, 30% and 3%, respectively of the total variance (Table 4), which indicated that the natural source contributed to about 60% of all samples and the anthropogenic source contributed to about 30%. The three initial factor's percentage of variance contributed 94% of the total variance, which indicates that the selected three components included most initial information of the various elements. The information of fuel used in 2001 in Qingdao is listed in Table 5 (http://www.stats-qd.gov.cn/). The industrial usage of all fuel was the most important, and the usage for heating was the second, so there were two main anthropogenic sources: industrial emission which was the most important

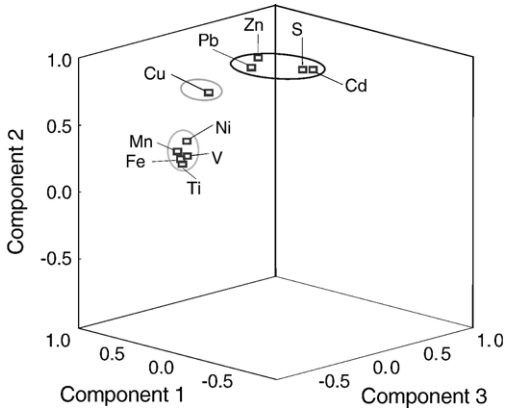


Fig. 7. PCA results in the three-dimensional space: plot of loadings of the first three principal components.

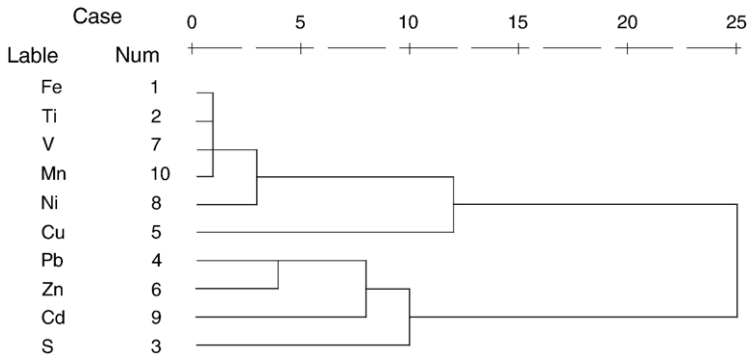


Fig. 8. Cluster analysis.

source, and the emission for space-heating especially in winter.

The rotated component matrix of all elements is shown in Table 6. Component 1 loading of Fe, Ti, V, Mn, Ni is separately 0.991, 0.992, 0.991, 0.985, 0.938, while Pb, Zn, Cd, S is separately 0.074, 0.222, − 0.158, 0.280, indicating that component 1 is the most important character of Fe, Ti, V, Mn, Ni. The component 2 loading of Fe, Ti, V, Mn, Ni is separately 0.056, 0.026, 0.064, 0.125, 0.200, while Pb, Zn, Cd, S is separately 0.949, 0.945, 0.892, 0.751, indicating that component 2 is the most important character of Pb, Zn, Cd, S. The component 1 and 2 loading of Cu is separately 0.632 and 0.630, indicating that Cu is not only derived from component 1 but also from component 2.

All elements distribute in three different areas in a component plot of two-dimensional and three-dimensional space (Figs. 6 and 7), so dividing all elements into three categories in the cluster analysis is reasonable too.

*3.3.4 Cluster analysis (CA)*

Cluster analysis (CA) is applied to classify measured elements into different groups. We normalized the variables into the range (0, 1), adopted the methods of between-groups linkage, and the Squared Euclidean Distance. The variables were found to be in three categories as shown in Fig. 8.

From Fig. 8, we can see the number (0–25) of the Squared Euclidean Distance. According to the result of the cluster analysis (CA), we choose the number 11 as the dividing number, and all variables are divided into three categories: the first category including Fe, Ti, Mn, V, Ni represents the soil source component; the second category including Cu represents the component of mixed sources from soil and pollution; and the third category including Pb, Zn, Cd and S represents the pollution component. The result of the clustering is similar to the result of the correlation analysis.

## 4. Conclusion

All the analyzed elements in the aerosols of Qingdao displayed strong seasonal variations: the concentration of Fe, Ti, Mn, V, Ni, Cu, Pb, Zn, Cd was the lowest in the summer, and the highest in winter. As an exception, the concentration of S in summer is higher than that in spring and autumn. During the dust episode, the concentration of Fe, Ti, Mn, V, Ni, Cu increased remarkably, while the concentrations of Pb, Zn, Cd, S were obviously lower than those in winter though they also increased remarkably. Ti, Mn are mainly derived from soil sources. V in the atmosphere is mainly derived from soil with a minor contribution from ship emissions. The anthropogenic source has a relatively higher contribution to Ni and Cu in the non-dust samples, while Cu is mainly from soil sources during the dust episode. The S, Pb, Zn and Cd are mainly derived from anthropogenic sources, even during dust episodes. Natural sources contributed about 60% to the sum of the measured elements and anthropogenic sources contributed about 30%.

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