

Chemical composition of dust storms in Beijing and implications for the mixing of mineral aerosol with pollution aerosol on the pathway

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[1] Aerosol particle samples collected in spring 2002 in Beijing were analyzed to investigate the impact of transport pathways on chemical composition of Asian dust storms (DSs). The dust storms were divided into two episodes (i.e., DS I and DS II), which were transported along different pathways identified by back-trajectory and PM₁₀ concentrations. The transport pathway from the westerly direction could be seen as the “polluted” pathway and the north-northwesterly direction as the relatively “less-polluted” one. Dust storms not only delivered large amounts of mineral elements but also carried significant quantities of pollutants. The source regions and transport pathways were two vital factors affecting chemical composition of dust storms. Ca/Al could be used as elemental tracer to identify the sources of Asian dust storms owing to the difference in Ca content in different source regions. DS I of the “polluted” pathway carried more pollution elements than DS II of the “less-polluted” one, and the pollution elements were either from dust soil (such as Zn), the mixing of dust soil with pollution aerosol on the pathway (such as As and Pb in DS I), the “pollution” dust resuspended on the pathway and Beijing local area (such as S in DS I, As and Pb in DS II), or the reactions on the surface of dust particles.

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1. Introduction

[2] A dust storm, starting over Gobi deserts in Mongolia and northern China and Taklimakan desert in western China [Sun *et al.*, 2001], spreads rapidly over China, Korea, and Japan [Duce *et al.*, 1980; Uematsu *et al.*, 1983; Hee and Soon, 2002; Uematsu *et al.*, 2002; Chung *et al.*, 2003; Sun *et al.*, 2004], and even to the west coast of North America [Husar *et al.*, 2001; Perry *et al.*, 1999]. During its long-range transport the dust aerosol mixed with pollution

aerosol, such as industrial soot, toxic materials, and acidic gases, on the pathway, and changed the chemical compositions of the aerosol in dust storms. The Aerosol Characterization Experiments-Asia (ACE-Asia) organized by the International Global Atmospheric Chemistry (IGAC) carried out detailed study on the aerosol in dust storms and increased much more knowledge of the effects of Asian dust from China and Mongolia on the Earth’s climate system [Huebert *et al.*, 2003].

[3] Aerosols in dust storms provide surfaces for many chemical and physical processes and serve as carriers of anthropogenic substances. The formation of sulfate and nitrate on the surface of dust particles has been well documented with laboratory simulations, model calculations and individual particle analysis [Underwood *et al.*, 2001; Song and Carmichael, 2001; Zhang and Iwasaka, 1999; Dentener *et al.*, 1996; Okada *et al.*, 1990; Iwasaka *et al.*, 1988] in the last two decades. Iwasaka *et al.* [1988] found that soil particles were coated by solution containing sulfate using Electron microscopy. Okada *et al.* [1990] reported that individual Asian dust particles collected in Japan were mixed with both water-soluble (mainly contained Ca and S) and insoluble materials. Zhou *et al.* [1996] found that S accumulated on the surface of dust particles during its transport from China to Japan. These results suggested that sulfate and nitrate were attached to the dust particles or formed on the surface of dust particles through heteroge-

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neous reactions of acidic gaseous substances such as SO_x and NO_x which would increase the levels of sulfate and nitrate in coarse size fraction [Nishikawa *et al.*, 1991] and lead to their transport and deposition from regional to global scale. Previously studies also pointed out the possible mineral dust sources of nitrate and sulfate [Prospero and Savoie, 1989; Nishikawa *et al.*, 1991]. Dentener *et al.* [1996] pointed out that having a large fraction of sulfate associated with large particles would likely overestimate the climate-cooling effect of sulfate aerosol while the nitrate being present on mineral dust would be transported longer distance and affect on the photochemical oxidant cycle over Pacific Ocean.

[4] It is believed that dust storms not only deliver large amounts of mineral elements but also carry significant quantities of pollutants and nutrients to the remote marine atmosphere and oceans [Gao *et al.*, 1992a; Arimoto *et al.*, 1996; Zhuang *et al.*, 1992a, 1992b]. Zhuang *et al.* [2001] investigated the sources of those pollutants detected in the aerosols in a dust storm on 6 April 2000, the greatest dust storm ever recorded by then in Beijing. The results showed that those pollutants were either from the pollution sources on the pathway which dust storms passed through (As, Se, and Sb) or from Beijing local pollution sources (Zn, Cu, and Pb). Four stages of a dust storm were revealed by examining the $\text{PM}_{10}/\text{SO}_2$, elemental ratios and meteorology during March 2001 and March 2002 in Beijing, and the overlapping of stages was found to be one of the mechanisms of getting high pollution concentrations in dust storms [Guo *et al.*, 2004]. However, the sources of pollutants in dust storms are poorly understood, and the impact of transport pathways on the changes of pollutants' composition is still puzzling. In studies mentioned above, the sources of pollutants were concluded only from the elemental concentrations, enrichment factors and elemental ratios, few researches pay attention to the impacts of source regions and transport pathways on the chemical compositions of the aerosols in dust storms. Two major types of dust storm in spring 2002 in Beijing offered us a starting point of view in studying the impacts of source regions and transport pathways on the composition of the aerosol in Asian dust storms. In this paper, we investigate the impact of the sources of Asian dust storms and the transport pathway on the chemical composition in the aerosols of dust storms by comparison of the two types of Asian dust storms in spring 2002 in Beijing.

2. Experiment

2.1. Sampling

[5] Aerosol samples of TSP and $\text{PM}_{2.5}$ were collected daily in spring of 2002, from February to May, using medium-volume samplers manufactured by Beijing Geological Instrument-Dickel Co., Ltd. (model: TSP/ $\text{PM}_{10}/\text{PM}_{2.5}$ -2; flow rate: 77.59 L/min). All the samples were collected on the roof (~40 m) of the Building of Science & Technology in Beijing Normal University using Whatman[®] 41 filters (Whatman Inc., Maidstone, UK). The filters after sampling were weighed using an analytical balance (model: Sartorius 2004MP) with a reading precision 10 μg after stabilizing in constant temperature ($20 \pm 5\%$) and humidity ($40 \pm 2\%$). All the procedures were strictly quality-

controlled to avoid any possible contamination of the samples. Detailed sampling information was given elsewhere [Sun *et al.*, 2004].

2.2. Chemical Analysis

2.2.1. Element Analysis

[6] The sample filters were digested at 170°C for 4 hours in high-pressure Teflon digestion vessel with 3 mL concentrated HNO_3 , 1 mL concentrated HCl, and 1 mL concentrated HF. After cooling, the solutions were dried, and then diluted to 10 mL with distilled-deionized water. Total 23 elements (Al, Fe, Mn, Mg, Ti, Sc, Na, Eu, Ce, Sr, Ca, Co, Cr, Ni, Cu, Pb, Zn, Cd, V, S, As, Se, and Sb) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Model: ULTIMA, JOBIN-YVON Company, France). The detailed analytical procedures were given elsewhere [Zhuang *et al.*, 2001, 2003].

2.2.2. Ion Analysis

[7] Eleven inorganic ions (SO_4^{2-} , NO_3^- , F^- , Cl^- , NO_2^- , PO_4^{3-} , NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and 4 organic acids (acetic, formic, oxalic, and methylsulfonic acid (MSA)) were analyzed by Ion Chromatography (IC, Dionex 600) that consists of a separation column (Dionex Ionpac AS11 for anion and CS12A for cation), a guard column (Dionex Ionpac AG 11 for anion and AG12A for cation), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50) and a gradient pump (Dionex Ionpac GP50). The details were given elsewhere [Yuan *et al.*, 2003; Wang *et al.*, 2005].

3. Results and Discussion

3.1. Dust Episodes

[8] In spring of 2002, a series of dust storms attacked Beijing. The strongest and most intense one ever recorded choked Beijing on 20 March 2002 with peak concentration of TSP 10.9 mg m^{-3} and $\text{PM}_{2.5}$ 1.39 mg m^{-3} [Sun *et al.*, 2004]. Dust storms are normally referred to the weather phenomenon, which leads to the horizontal visibility less than 1000 m due to the dust particles entrained by strong winds. To distinguish quantitatively dust storm from those nondust storm days, we calculated the concentrations of mineral aerosols in TSP and $\text{PM}_{2.5}$ based on Al concentration in the samples collected each day, as Al is usually selected to be an indicator of mineral dust. The average concentration of Al in surface soils collected at Duolun in Inner Mongolia, which was one of the sources of dust storms, and Fengning in Hebei province, which dust storms passed through, is 7.0% (SD = 1.6%, $n = 17$). The result of 7% Al in soil, less than the average crustal abundance of 8% [Taylor and McLennan, 1985; Mason and Moore, 1982] would suggest that the soil samples collected could possibly include somewhat pollution contents. For the consideration of generality, we estimated the concentrations of mineral aerosol in TSP and $\text{PM}_{2.5}$ based on the calculation formula: $\text{Conc.} = [\text{Al}]/8\%$. The concentrations of TSP, $\text{PM}_{2.5}$ and mineral aerosol during March–April 2002 were shown in Figure 1. According to the news reported by Beijing Meteorological Bureau and the mineral concentrations calculated, we found that the threshold of $\sim 500 \mu\text{g m}^{-3}$ for TSP and $\sim 150 \mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$ were reasonable to be used in distinguishing dust storm from nondust storm days

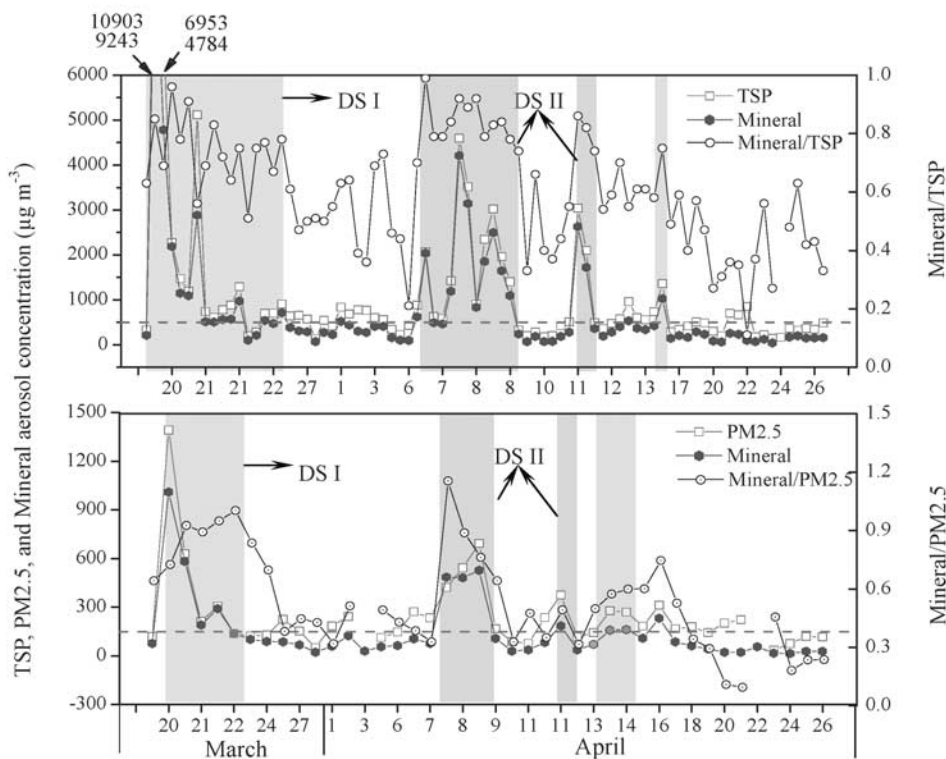


Figure 1. The concentrations of TSP, PM_{2.5} and mineral aerosol during March–April 2002. See color version of this figure in the HTML.

(NDS). From Figure 1, it could be seen clearly that dust storms in 2002 could be divided into two groups: DS I, occurred from 20 to 22 March; DS II, occurred on 6–8 and 11 April. The event of a dust storm on 14 April was ascribed to DS I for they had similar transport pathway (see the next section). The average concentrations of TSP were 2479 and 2121 $\mu\text{g m}^{-3}$ with 9 and 11 samples collected in DS I and DS II, respectively, DS I and DS II were 5.4 and 4.6 times of that in nondust storm days (461 $\mu\text{g m}^{-3}$), respectively. The average concentrations of PM_{2.5}, which the visibility is greatly dependent on, in DS I and DS II were as high as to 492 and 462 $\mu\text{g m}^{-3}$, respectively, both were ~ 8 times higher than the PM_{2.5} daily standard (65 $\mu\text{g m}^{-3}$) of USA National Ambient Air Quality. Mineral aerosol dominated the composition of dust storms, contributing 76% and 85% of TSP, 85% and 77% of PM_{2.5} in DS I and DS II, respectively, while in nondust storm days it only accounted for 51% of TSP and 43% of PM_{2.5}, which indicated the influence of anthropogenic sources in nondust storm days.

3.2. Transport Pathways of Asian Dust Storms

[9] The sources of Asian dust storms are mostly concentrated in two regions: Gobi deserts in Mongolia as well as northern China, and Taklimakan deserts in western China [Gao *et al.*, 1992b; Zhang *et al.*, 1997; Sun *et al.*, 2001]. The Loess Plateau appears to be a weak dust source [Xuan and Sokolik, 2002]. Usually, three transport pathways of dust storms (north-northwesterly direction, northwesterly direction, and westerly direction) that passed through Beijing were identified [Zhou *et al.*, 2002; Sun *et al.*, 2001]. Zhang *et al.* [2003] reported that five major transport pathways of Asian dust storms dominated dust transport

in China during spring 2001. We computed the backward isentropic air trajectory of DS I and DS II passed through Beijing using HYSPLIT4 (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model developed by NOAA/Air Resources Laboratory [Draxler and Hess, 1998] and the results were shown in Figures 2 and 3. Clearly, DS I and DS II originated from different sources and were transported along different pathways. DS I originated from Kazakhstan and passed through Xinjiang Autonomous Region (Source region I), and strengthened further in the central/west of Inner Mongolia and Loess Plateau (Source region II), and finally to Beijing along the westerly direction. Comparatively, DS II was mainly from Gobi deserts in Mongolia and passed through the sandy deserts in northern Inner Mongolia and Hebei province (source region III) and finally to Beijing along the northwesterly/north-northwesterly direction. These pathways agreed well with those results based on modeling calculations and surface observations [Shao *et al.*, 2003; Zhang *et al.*, 2005]. PM₁₀ concentrations reported daily in main cities over China could somewhat reflect the pathway of those dust events. When dust storms are transported from source regions to the downwind areas, there must be a time lag of PM₁₀ concentrations between the cities in the west and east of China. If dust storms are not derived from the deserts near the cities or do not pass through the cities, the concentration of PM₁₀ in such cities must be low. Thus we could deduce the sources and the transport pathways of dust storms through the successive order of arrival of PM₁₀ peaks and PM₁₀ concentrations in those cities over China. The concentrations of PM₁₀ in several cities of China (see Figure 4) during March–April 2002 were obtained from air pollution index (API) data,

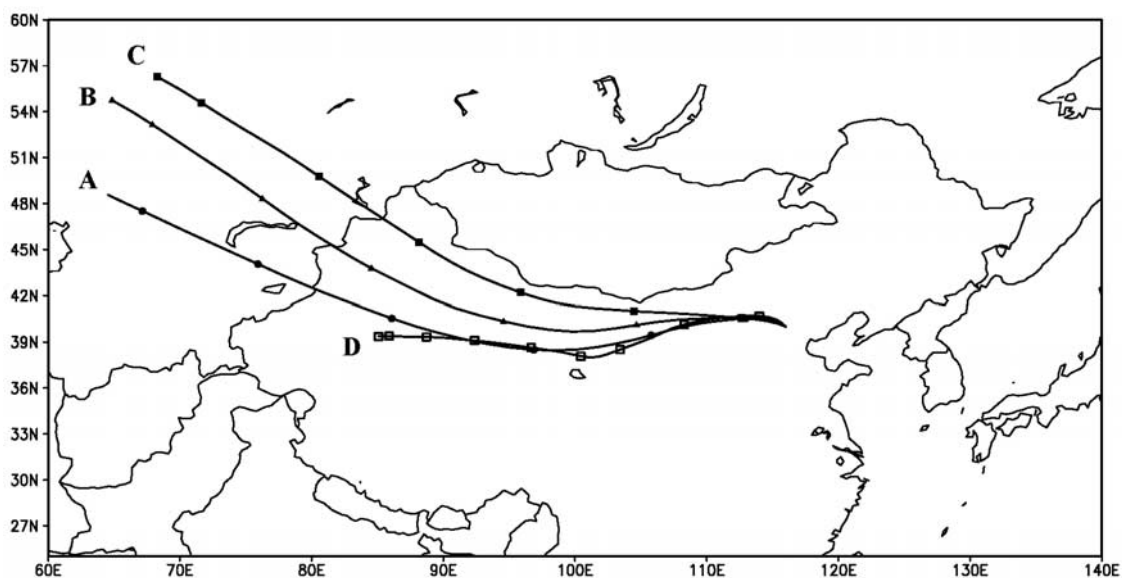


Figure 2. Backward isentropic air trajectory from Beijing (1 km altitude) for DS I: 0300 UTC 20 March (line A), 0500 UTC 20 March (line B), 0700 UTC 20 March (line C), and 0600 UTC 14 April (line D).

which was reported by State Environmental Protection Administration of China (<http://www.zhb.gov.cn/quality/air.php3>). The API data was converted to PM_{10} concentrations according to the following formula:

$$C = C_{low} + [(I - I_{low}) / (I_{high} - I_{low})] \times (C_{high} - C_{low}) \quad (1)$$

where C is the concentration of PM_{10} and I is the API value of PM_{10} . I_{high} and I_{low} , the two values most approaching to value I in the API grading limited value table, stand for the value larger and lower one than I , respectively; C_{high} and C_{low} represent the PM_{10} concentrations corresponding to I_{high} and I_{low} , respectively. For DS I, the PM_{10} peak first

appeared at Urumuchi, located in western part of China (source region D), on 18 March with the concentration of $358 \mu\text{g m}^{-3}$, and then reached at Lanzhou, Xining, Yinchuan, Xi'an, and Hohhot (line 1 in Figure 5), most of which are located in source region II, and then moving eastward and finally to Taiyuan, Beijing, Shijiazhuang, and Qingdao (line 2 in Figure 5). The same procedures were done for DS II. It could be seen that Beijing experienced the highest peak of PM_{10} on 7 April, PM_{10} concentrations on 6–10 April in the cities of Urumuchi, Lanzhou, Xining, and Yinchuan were similar to those in NDS days, and in those cities on transport pathways of western direction, such as Taiyuan, Shijiazhuang and Xi'an, PM_{10} concentrations were only a little higher than NDS days. Hohhot, in the

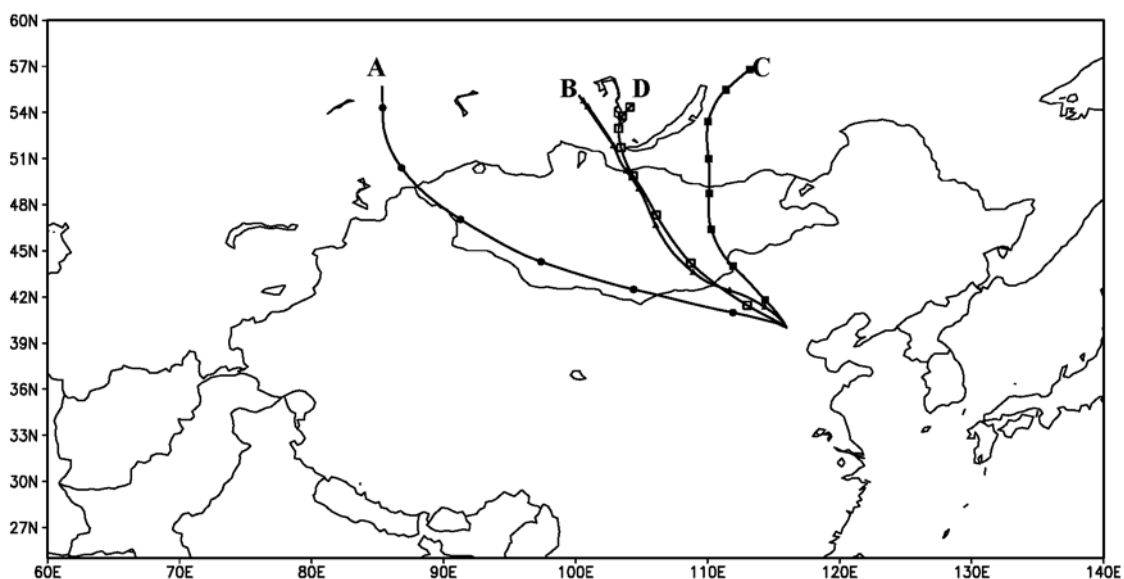


Figure 3. Backward isentropic air trajectory from Beijing (1 km altitude) for DS II: 1000 UTC 7 April (line A), 0400 UTC 8 April (line B), 0700 UTC 8 April (line C), and 1100 UTC 11 April (line D).

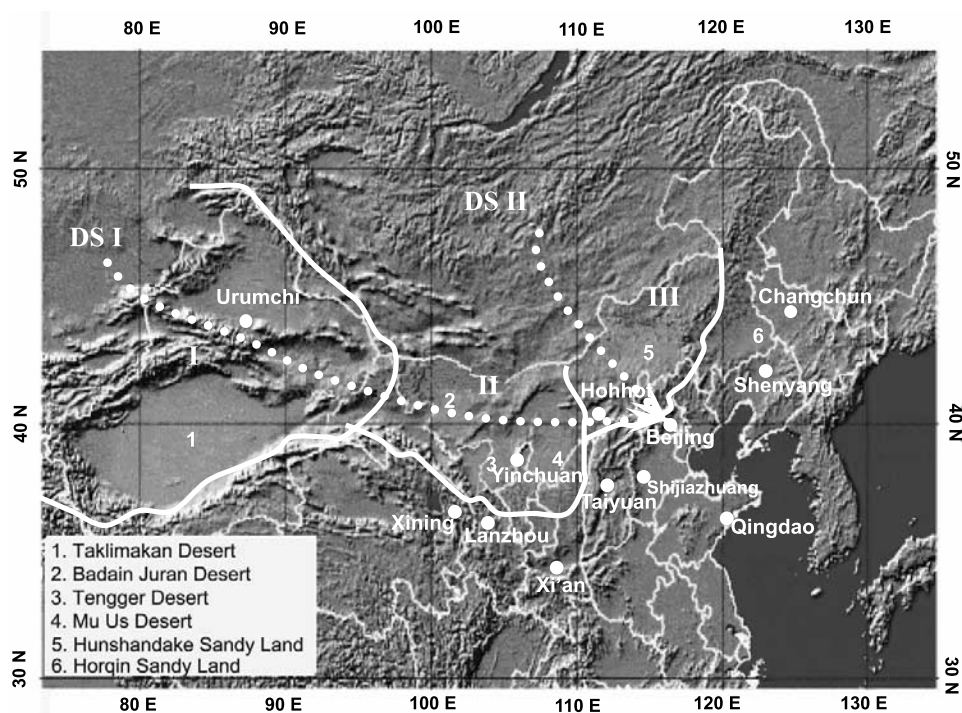


Figure 4. Transport pathways of DS I and DS II. See color version of this figure in the HTML.

west-northwesterly direction of Beijing first showed relatively high concentration of PM_{10} , and then Beijing, Changchun, Shenyang appeared PM_{10} peaks (line 3 in Figure 5). This dust storm went on moving eastward and

reached Qingdao finally (line 4 in Figure 5). It could be concluded that DS II most likely originated from source region III, and then was transported along the north-northwesterly direction.

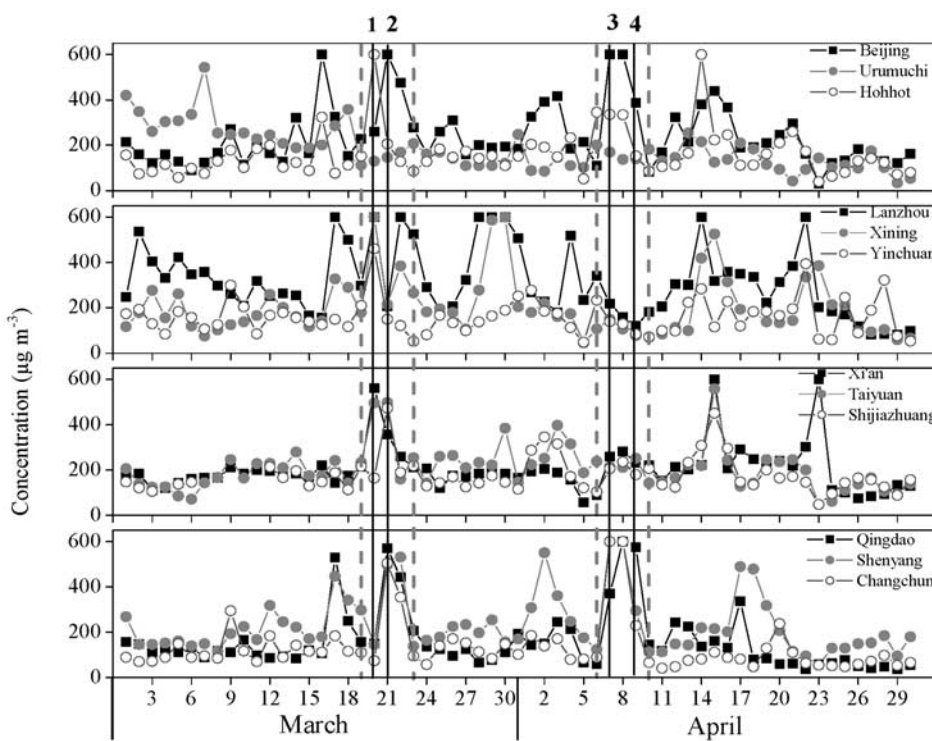


Figure 5. PM_{10} concentrations ($\mu\text{g m}^{-3}$) in the cities of China from March to April in 2002. See color version of this figure in the HTML.

Table 1. Concentrations, Enrichment Factors, and Percentages of Major Mineral Elements to the Mass of the Aerosols in NDS, DS I, and DS II (Co, Cd, and Sc as ng m^{-3} , Others as $\mu\text{g m}^{-3}$)

| Species | NDS | | | DS I | | | DS II | | |
|-------------------------------|---------------|------|---------------|---------------|-----|---------------|---------------|-----|---------------|
| | Concentration | EF | Percentage, % | Concentration | EF | Percentage, % | Concentration | EF | Percentage, % |
| Mass | 461 | | | 2497 | | | 2121 | | |
| As | 0.033 | 93 | 0.0072 | 0.12 | 39 | 0.0050 | 0.037 | 12 | 0.0018 |
| Cr | 0.048 | 2.2 | 0.011 | 0.23 | 1.3 | 0.010 | 0.14 | 0.8 | 0.0070 |
| Zn | 0.57 | 39 | 0.12 | 0.31 | 3.1 | 0.016 | 0.28 | 2.5 | 0.014 |
| Sr | 0.12 | 1.4 | 0.025 | 0.61 | 0.9 | 0.026 | 0.44 | 0.7 | 0.022 |
| Pb | 0.25 | 104 | 0.054 | 0.26 | 20 | 0.019 | 0.16 | 8.4 | 0.0090 |
| Ni | 0.19 | 12.1 | 0.039 | 0.13 | 1.3 | 0.0070 | 0.20 | 1.7 | 0.011 |
| Co | 7.1 | 1.1 | 0.0014 | 58 | 1.3 | 0.0026 | 37 | 0.8 | 0.0017 |
| Cd | 16 | 609 | 0.0048 | 5.8 | 26 | 0.00040 | 3.0 | 9.9 | 0.00016 |
| Fe | 12 | 1.0 | 2.4 | 89 | 1.0 | 3.6 | 80 | 0.9 | 3.8 |
| Mn | 0.23 | 1.0 | 0.047 | 1.37 | 0.8 | 0.053 | 1.33 | 0.8 | 0.063 |
| Mg | 5.8 | 1.2 | 1.2 | 34 | 0.9 | 1.4 | 29 | 0.8 | 1.2 |
| V | 0.034 | 1.3 | 0.0077 | 0.26 | 0.9 | 0.0089 | 0.22 | 0.9 | 0.010 |
| Ca | 27 | 3.2 | 5.7 | 178 | 2.9 | 7.7 | 58 | 0.9 | 2.9 |
| Cu | 0.17 | 12 | 0.032 | 0.10 | 1.3 | 0.0054 | 0.17 | 2.0 | 0.0095 |
| Ti | 1.1 | 1.1 | 0.24 | 10 | 1.2 | 0.38 | 8.8 | 1.1 | 0.41 |
| Sc | 2.5 | 0.9 | 0.00051 | 24 | 1.1 | 0.00094 | 18 | 0.9 | 0.00084 |
| Al | 19 | 1.0 | 4.1 | 151 | 1.0 | 6.0 | 146 | 1.0 | 6.8 |
| Na | 4.4 | 0.7 | 0.88 | 37 | 0.5 | 1.0 | 39 | 0.7 | 1.7 |
| S | 7.6 | 175 | 1.7 | 12 | 29 | 0.53 | 6.6 | 18 | 0.39 |
| NO ₃ ⁻ | 20 | | 3.9 | 2.9 | | 0.19 | 9 | | 0.63 |
| SO ₄ ²⁻ | 19 | | 4.0 | 18 | | 0.74 | 18 | | 1.1 |

[10] The source area and the transport pathway are two vital factors affecting the composition of dust storms. The transported dust with the mixing process on the pathway will be sure to change the composition of the aerosols in dust storms. The following discussion will focus on the differences of DS I and DS II and the impact of the transport pathways on the chemical composition of dust storms.

3.3. Mineral Elements

[11] The concentrations, enrichment factors, and percentages of major mineral elements to the mass of the aerosols in NDS, DS I, and DS II were presented in Table 1. The average concentrations of Al, Ca, Fe, Mg, and Na were 151, 178, 89, 34, and 37 $\mu\text{g m}^{-3}$ in DS I and 146, 58, 80, 29, and 39 $\mu\text{g m}^{-3}$ in DS II, respectively, which were 5~8 times higher than those in NDS days. Although the loadings of these elements were highly elevated, their mass percentages and ratios to Al were basically unchanged. For example, in the case of Fe, the mass percentages were 2.4% in NDS, 3.6% in DS I, and 3.8% in DS II, all were close to the value of 3.5% in crust [Taylor and McLennan, 1985]. In addition, the ratios of Fe/Al in NDS, DS I, and DS II were 0.60, 0.60 and 0.55 respectively, all close to that in crust (0.62), as shown in Figure 6a. The results above clearly indicated the crustal origin of Fe. The enrichment factor of Fe, using Al as a reference element ($\text{EF}_{\text{crust}} = (\text{X}/\text{Al})_{\text{aerosol}}/(\text{X}/\text{Al})_{\text{crust}}$), was close to unit in NDS, DS I, and DS II, demonstrating further the crustal origin of Fe. Additionally, the ratio of Fe/Al was relatively similar to that (0.55) in deserts of northern China [Zhang *et al.*, 1997, 2003], but much lower than that (1.02) in western deserts [Zhang *et al.*, 1997, Table 2], indicating that, to some extent, DS I and DS II during March–April 2002 were less influenced by western deserts. In the case of Mg and Sc, the ratio of Mg/Al in DS I and DS II were 0.24 and 0.21, of Sc/Al were 0.15 and 0.12, respectively, which were similar to those in Earth's upper continental crust (0.26 for Mg/Al and 0.14 for Sc/Al). These results indicated that different source regions and transport

pathways would not bring much difference for most of the crustal elements.

[12] However, Ca was much different from those crustal elements mentioned above. The strong correlations between Ca and Al in both DS I and DS II were observed (The correlation coefficient $r = 0.99$ for DS I and 0.96 for DS II), as it is shown in Figure 6b, indicating the crustal origin of Ca. However, Ca showed relatively weaker correlation with Al ($r = 0.71$) in NDS, indicating that Ca could possibly have other pollution sources, e.g., the local construction dust. The most important finding was that there was much difference for Ca between DS I and DS II. The average ratio of Ca/Al in DS I (1.31) was much higher than that in crust (Ca/Al = 0.45), while in DS II the average ratio of Ca/Al (0.42) was close to the value in crust. The average mass percentages of Ca in DS I was 7.7%, ~1.5 times higher than 3.0% in Earth's crust, while in DS II it was 2.9%, close to the background value of soil in northern China [Zhang, 1994]. Zhang *et al.* [2003] reported the mass percentages of 7% of Ca at northern high-dust sources and 8% at loess area, which were both close to that in DS I. However, the Ca percentages in DS I and DS II were both much different from the Western High-Dust Sources, which were characterized by high content of Ca (12%) [Zhang *et al.*, 2003]. All of these results indicated that: (1) DS from the north-northwesterly direction brought the aerosols with much lower concentration of Ca than the westerly direction; (2) DS I originated mainly from source region II and DS II from source region III, which agreed well with the results from backward trajectories and PM₁₀ concentrations; (3) Ca/Al could be used as elemental tracer to identify the sources of dust storms, as different source regions showed much different Ca content.

3.4. Pollution Elements

[13] Dust storms not only deliver large amounts of mineral aerosols but also carry significant quantities of pollution aerosols. The concentration of pollution elements,

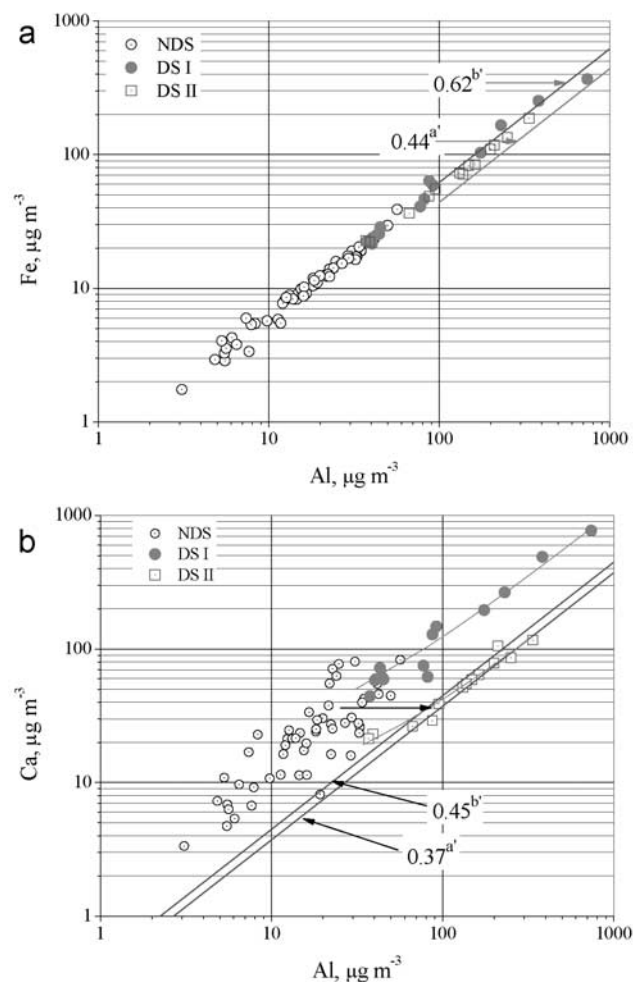


Figure 6. (a) Fe versus Al and (b) Ca versus Al in TSP samples collected from 19 March to 27 April in 2002. Superscript “a” denotes the Earth’s average crust composition from *Taylor and McLennan* [1985], and superscript “b” denotes Earth’s average crust composition from *Mason and Moore* [1982]. See color version of this figure in the HTML.

such as Zn, Pb, As, and S, in DS I increased 3–14 times as Al rose from $38 \mu\text{g m}^{-3}$ to $739 \mu\text{g m}^{-3}$, while they were elevated 2–9 times in DS II as Al ranged from $37 \mu\text{g m}^{-3}$ to $337 \mu\text{g m}^{-3}$. It could be seen clearly that the pollution elements increased while Al increased. Were the increases of the pollution elements from pollution sources, either Beijing local pollution sources or the mixing with pollutants emitted by pollution sources on the pathway, or from dust soils, either the natural dust carried by dust storms or resuspended dust from Beijing local area? We are trying to address this question by comparison of the differences between DS I and DS II. The pollution elements were divided into three groups based on their correlations to element, Al. Zn could be the representative of the first group. The average concentration of Zn in DS I was $0.31 \mu\text{g m}^{-3}$, a little higher than that in DS II ($0.28 \mu\text{g m}^{-3}$). Zn was closely related with Al in both DS I ($r = 0.98$) and DS II ($r = 0.78$) and Zn/Al ratio was within factors of 2–4 of its crustal ratio (Figure 7a). This indicated the crustal origin of

Zn in both DS I and DS II. The crustal contribution accounted for 36% of Zn in DS I and 48% in DS II, which were calculated with a simple formula ($X_{\text{crustal}} = (Al/X) \cdot (X/Al)_{\text{crust}}$), where $(X/Al)_{\text{crust}}$ is the average concentration ratio of X to Al in crust [*Taylor and McLennan*, 1985], while in NDS the crustal Zn accounted for only 7% of the total Zn. The enrichment factors of only 3.1 and 2.5 of Zn in both DS I and DS II, respectively, confirmed further the crustal origin of “pollution” element Zn. The different original source areas and the different transport pathways appeared not to bring much difference of Zn in these two types of dusts storm except that Zn from westerly direction seemed to be a little more polluted than that from north-northwesterly direction.

[14] As and Pb could be the representatives of the second group. In DS II, As and Pb showed good correlations with Al ($r = 0.97$ for As and $r = 0.64$ for Pb, see Figures 7b and 7c), and As/Al and Pb/Al ratios varied within a factor of 1–3 throughout the dust events. The enrichment factors of As and Pb in DS II in average were 13 and 8.4, respectively. Both As and Pb did not show strong correlations with Al in DS I, and the ratios of As/Al and Pb/Al varied from 1.3×10^{-4} to 2.2×10^{-3} and from 6.3×10^{-4} to 9.8×10^{-3} , with the variation factors of 17 and 15, respectively. The enrichment factors of As and Pb in DS I in average were 39 and 20, respectively.

[15] The high enrichments of As and Pb indicated their dominant pollution sources in both DS I and DS II. However, the good correlations of As and Pb with Al, the reference of crust, in DS II would indicate that part of As and Pb could be from the crustal source or from the resuspended “polluted” crustal dust. As mentioned above in section 3.2 and 3.3, DS II from the north-northwesterly direction passed through relatively “less-polluted” areas of China, it was less influenced by pollution aerosols on the pathway as manifested by the lower enrichment factors of As and Pb in DS II than DS I. The concentrations of pollution elements would be greatly dependent on the emission rates of pollution sources and the distance to the sources. DS I from the westerly direction passed through a lot of industrial city zones, such as coal mine regions, metal mine regions, as well as those high polluted cities, and then mixed with large amounts of pollutants emitted from coal burning, vehicles, and industries on the pathway and finally carried them to Beijing. Thus the concentrations of pollution elements varied significantly for the different source emissions in different regions and/or at different time, which was

Table 2. Ratios of Elements to Al for Chinese Deserts Regions and Beijing Aerosol

| Type | Fe/Al | Mg/Al | Sc/Al | Ca/Al | References |
|-----------------------------|-------|-------|-------------------|-----------------|-------------------------------|
| Crust | 0.62 | 0.26 | 0.14 ^a | 0.45 | <i>Mason and Moore</i> [1982] |
| Western desert ^b | 1.02 | 0.21 | 0.23 ^c | ND ^d | <i>Zhang et al.</i> [1997] |
| Taklimakan desert | 1.34 | ND | ND | 3.07 | <i>Makra et al.</i> [2002] |
| Northern desert | 0.55 | 0.25 | 0.34 ^c | ND | <i>Zhang et al.</i> [1997] |
| NDS | 0.60 | 0.30 | 0.13 | 1.44 | This study |
| DS I | 0.60 | 0.24 | 0.16 | 1.31 | This study |
| DS II | 0.55 | 0.21 | 0.12 | 0.42 | This study |

^a*Taylor and McLennan* [1985].

^bAksu and Qira.

^cModal value.

^dNo data.

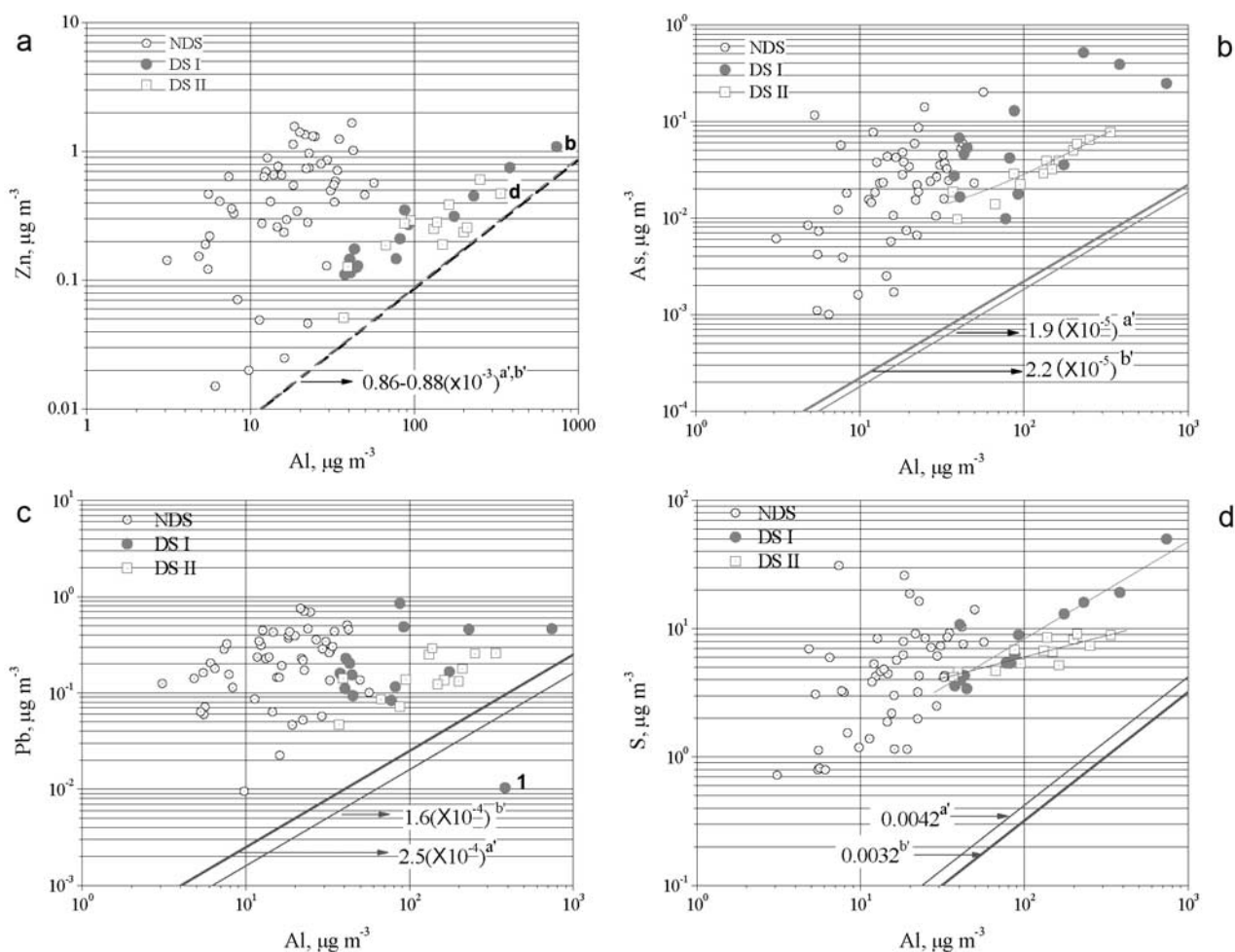


Figure 7. X ((a) Zn, (b) As, (c) Pb, and (d) S) versus Al in TSP samples collected from 19 March to 27 April in 2002. Superscript “a” denotes the Earth’s average crust composition from *Taylor and McLennan* [1985], and superscript “b” denotes Earth’s average crust composition from *Mason and Moore* [1982]. See color version of this figure in the HTML.

in consistent with the strong variations of As/Al and Pb/Al ratios in DS I. Overall, the pollution elements As and Pb could be from the emission at the local Beijing area or the mixing with the pollution aerosols on the pathway.

[16] Element S could be the representative of the third group of the pollution elements. S in both DS I and DS II showed strong correlations with Al ($r = 0.97$ in DS I, $r = 0.78$ in DS II), indicating that there must be a crustal source of S. However, the average ratio of S/Al in DS I and DS II was 0.093 and 0.059, respectively, ~ 28 and ~ 17 times higher than its crustal ratio of 0.0032 (Figure 7d). This would indicate further that there also must be a pollution source of S in both DS I and DS II. Significant difference of S between DS I and DS II were observed. The concentration of S in DS I was $12 \mu\text{g m}^{-3}$, nearly a factor of 2 of that in DS II ($6.6 \mu\text{g m}^{-3}$) and the enrichment factor of S in DS I was 29, much higher than 18 in DS II. The results clearly indicated that DS I was more influenced by anthropogenic sources than DS II, although they were both much from the anthropogenic sources.

[17] Dust storms carried large amounts of pollution elements during its long-range transport, and these pollution

elements were partly from crustal source and partly from the mixing of dust with pollutants on the pathway, and partly from the reactions on the surface of dust particles. The difference between DS I and DS II showed that DS I was more influenced by pollution sources and carried more pollutants, while DS II was accompanied with more clean air with fewer pollutants, i.e., the transport pathway from westerly direction delivered more pollutants than that from north-northwesterly direction. Thus the route of DS I and DS II could be seen as “polluted” and relatively “less-polluted” transport pathway, respectively.

3.5. Sulfate and Nitrate

[18] As shown in Figure 8, sulfate had strong correlation with Al ($r = 0.98$) and nitrate had relatively good correlations with Al ($r = 0.71$) in DS I, indicating that both sulfate and nitrate could be partially from the sources of dust soils. However, the average ratios of $[\text{SO}_4^{2-}]/\text{Al}$ and $[\text{NO}_3^-]/\text{Al}$ were 0.12 and 0.016 respectively, which was significantly higher than that in surface soils of Gobi Desert and Loess Plateau (0.002 for $[\text{SO}_4^{2-}]/\text{Al}$ and <0.002 for $[\text{NO}_3^-]/\text{Al}$) [*Nishikawa et al.*, 1991]. The mass percentage of 0.66 and

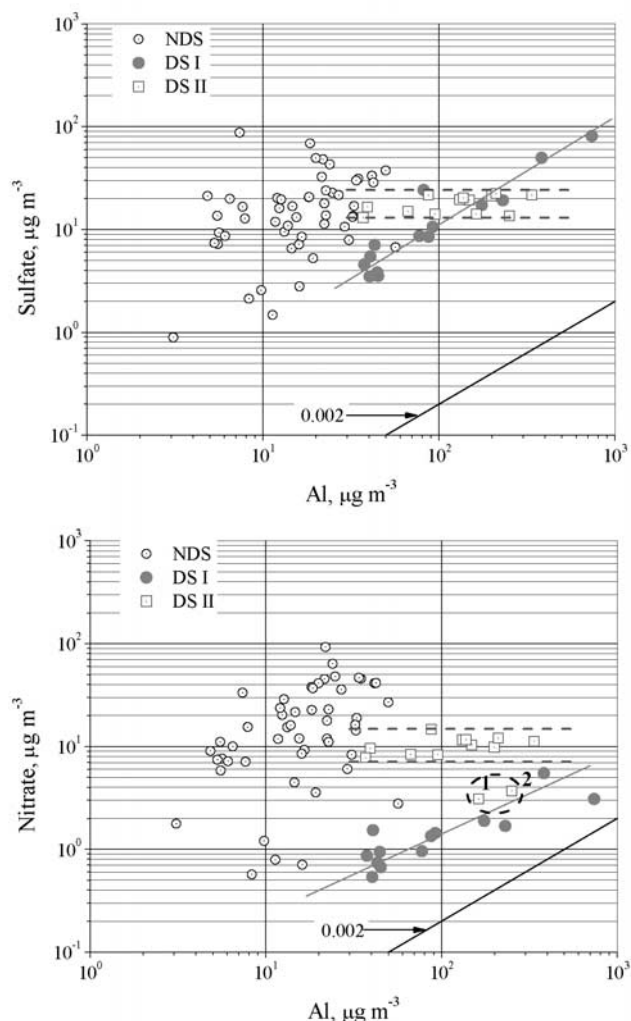


Figure 8. Sulfate versus Al and nitrate versus Al in TSP samples collected from 19 March to 27 April 2002. See color version of this figure in the HTML.

0.095% for sulfate and nitrate in DS I was also much higher than those in surface soils (0.01% for sulfate and <0.01% for nitrate) [Nishikawa *et al.*, 1991]. These results clearly indicated that besides the dust source there must be other sources of sulfate and nitrate in DS I, either from the reactions of SO_2 , NO_x , sulfuric acid, and nitric acid on the surface of dust particles or the sulfate and nitrate resuspended on the pathway to be attached to the dust particles during the long-range transport. There were a positive correlations between S and Ca ($r = 0.95$ in DS I and 0.82 in DS II). The alkalinity of dust aerosols, mainly determined by the calcium carbonate content greatly benefits the uptake of pollution gases, such as SO_2 , NO_x . Thus the strong correlations between S and Ca in both DS I and DS II indicated the possible reactions of SO_2 or sulfuric acid on the surface of mineral aerosols or the mixing of sulfate aerosol with mineral aerosol on the pathway [Arimoto *et al.*, 2004]. As mentioned above DS I passed through many coalmine regions and “polluted” cities, where high sulfur emission was observed [Akimoto and Narita, 1994]. Clearly, the high SO_2 concentration plus the

alkalinity of dust aerosols greatly benefit the uptake and conversion of SO_2 .

[19] In DS II, however, there was no correlation between sulfate/nitrate and Al. As Al varied nearly 10 times from $37 \mu\text{g m}^{-3}$ to $336 \mu\text{g m}^{-3}$, the concentrations of sulfate and nitrate varied with a small factor of ~ 2 (see Figure 8). DS II was transported along the relatively “less-polluted” pathway where the amounts of SO_2 and NO_x emission could be small. Consequently, there must be less reaction and uptakes of SO_2 and NO_x on the surface of the dust particles. Additionally, as the intensity of DS II was much weaker than DS I, the two stages of “clear-out pollutants” and “addition of pure dust” could overlap [Guo *et al.*, 2004], therefore, the “less-polluted” dust storms from north-northwesterly direction would mix more pollutants from the local pollution aerosol in Beijing. The similar concentrations of sulfate between DS II ($18 \mu\text{g m}^{-3}$) and NDS days ($19 \mu\text{g m}^{-3}$) confirmed this. However, the average nitrate concentration of $9 \mu\text{g m}^{-3}$ in DS II was lower than that in NDS days of $20 \mu\text{g m}^{-3}$. HNO_3 can react with aqueous carbonates on soil particles to form coarse mode nitrate through the following reaction [Mamane and Gottlieb, 1992] that could represent a significant sink for NO_x .



The lower concentration of nitrate in DS II should be ascribed to the dry deposition of coarse mode nitrate. The two samples (1 and 2 in Figure 8) with lowest concentration of nitrate were both collected at night, when the reaction of nitric acid with carbonates was more effective, and the nitrate formed in coarse mode would be removed more rapidly by dry deposition with the gravitational sedimentation of large particles and showed lower concentration.

[20] The difference of sulfate and nitrate in DS I and DS II suggested that the transport pathways would greatly affect the chemical processes and, in turn, the composition of the aerosols during the long-range transport of dust storms. Dust storms could be served as surface carrier for the formation of sulfate and nitrate. The sulfate present on the mineral dust particles probably implied that the assumption that sulfate aerosol follows an accumulation mode size distribution is likely to overestimate the climate-cooling effect of sulfate aerosol [Dentener *et al.*, 1996], and the nitrate associated with mineral aerosol will enhance its transport distance, and the long transported nitrate in the open Pacific Ocean would react with sea-salt aerosols to yield chlorine atoms in the marine boundary layer [Elliott *et al.*, 1997], which would have significant effect on the global photochemical cycle.

4. Conclusions

[21] A series of dust storms attacked Beijing in spring of 2002, which could be divided into two episodes, i.e., DS I and DS II, which were transported along different pathways identified by back-trajectory and PM_{10} concentrations. DS I mainly originated from the central/west deserts in Inner Mongolia and Loess Plateau, and DS II from the Gobi Deserts in Mongolia and sandy deserts in northern Inner Mongolia. The transport pathway from the westerly direction could be seen as “polluted” pathway and the north-

northwesterly direction as relatively “less-polluted” one. Dust storms not only delivered large amounts of mineral elements but also carried significant quantities of pollutants. The source regions and transport pathways were two vital factors affecting chemical compositions of dust storms. Ca/Al could be used as elemental tracers to identify the sources of dust storms, as there was much difference in Ca content in different source regions. DS I of “polluted” pathway carried more pollution elements than DS II of “less-polluted” one, and the pollution elements were either from dust soil or from the mixing of dust soil with pollution aerosol on the pathway or the “pollution” dust resuspended on the pathway and Beijing local area or the reactions on the surface of dust particles.

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