



Chemical Composition of Water-soluble Ions and Carbonate Estimation in Spring Aerosol at a Semi-arid Site of Tongyu, China

Zhenxing Shen^{1,2*}, Xin Wang¹, Renjian Zhang³, Kaifai Ho², Junji Cao², Meigeng Zhang⁴

¹ Department of Environmental Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

² SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710075, China

³ Key Laboratory of Regional Climate-Environment Research for Temperate East Asia, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

⁴ LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

ABSTRACT

Fine aerosol samples (PM_{2.5}) were collected daily at Tongyu, a semi-arid site in northeast China from April to June 2006, when Asian dust events occurred frequently. The concentrations of nine water-soluble ions were determined in the filter samples. The results showed that the mean mass level of PM_{2.5} at Tongyu station was 260.9 μg/m³, and the total mass concentration of the nine kinds of water-soluble ions occupied ~17% of the PM_{2.5} mass. Nine dust storm (DS) events were observed during the sampling period with mean concentrations of 528.0 μg/m³ for PM_{2.5} and 39.5 μg/m³ for total ions; during non-dust storm (NDS) periods, these values were 111.7 and 19.6 μg/m³, respectively. The mass concentrations of most of the water-soluble ions in the DS samples were much higher than those in the NDS samples. The ratios of ions to Fe were stable in DS samples, while they were more scattered in NDS samples, suggesting that the anthropogenic influence was significant in NDS samples collected at Tongyu. Moreover, the observed stable values of the K⁺/Fe, Ca²⁺/Fe, Na⁺/Fe, NO₃⁻/Fe, and SO₄²⁻/Fe ratios during the DS events should be associated with the ionic composition characteristics of soil dust in northeastern regions. Ion balance calculations for the NDS samples suggest that those aerosol particles were alkaline while DS samples were strongly alkaline. A deficit of measured anions during DS implies the presence of carbonate, which can be used to evaluate the carbonate concentration. A good relationship between the calculated and detected carbonate concentration was observed, which demonstrates that the ion balance supplies another method for estimating the carbonate content during DS.

Keywords: Tongyu; PM_{2.5}; Water-soluble ions; Carbonate.

INTRODUCTION

Soil dust emitted from arid and semi-arid regions is one of the important atmospheric components, not only because it has a considerable effect on the urban and rural atmospheric environment (Li *et al.*, 1996; Tegen *et al.*, 1996; Arimoto *et al.*, 2001; Wang *et al.*, 2001; Zhuang *et al.*, 2001; Zhang *et al.*, 2004; Cao *et al.*, 2005; Zhang *et al.*, 2005; Arimoto *et al.*, 2006; Hubert *et al.*, 2006; Zhang *et al.*, 2006) but also because soil dust affects the earth's radiative balance by scattering and absorbing incoming solar and outgoing long-wave energy of terrestrial radiation, which can influence the cloud properties by acting as cloud condensation nuclei (CNN) (Charlson *et al.*, 1992; Li *et al.*, 1996; Sokolik and Toon, 1996; Tegen *et al.*, 1996; Haywood and Boucher,

2000). Furthermore, depending on the chemical and mineralogical composition of the aerosol, the physical properties and vertical distribution of the aerosol in the atmosphere, as well as the characteristics of the ground surface, the atmospheric particles can influence tropospheric chemistry through its involvement in various heterogeneous reactions and participation in biogeochemical cycles of trace substances such as iron in the land and the oceans (Young *et al.*, 1991; Dentener *et al.*, 1996; Prospero, J M., 1999; Uematsu *et al.*, 2002; Trochkin *et al.*, 2003; Jickells *et al.*, 2005). Large atmospheric particle loadings degrade air quality and affect human health (Harrison and Yin, 2000; Kim *et al.*, 2001; Zhang *et al.*, 2005). Therefore, more research on the global distribution of dust and its physical, chemical, and mineralogical properties (Duce *et al.*, 1995; Alfaro *et al.*, 2003; Cao *et al.*, 2003; Hubert *et al.*, 2003; Iwasaka *et al.*, 2003; Arimoto *et al.*, 2004; Zhang *et al.*, 2004; Shen *et al.*, 2007; Zhang *et al.*, 2007; Shen *et al.*, 2009) is critical and necessary, as it plays a vital role in identifying the source areas and reducing the uncertainty

* Corresponding author.

E-mail address: zxshen@mail.xjtu.edu.cn

associated with estimating the climatic effect of aerosol.

Dust storm event (DS) is a disastrous weather phenomenon in arid and semi arid areas. A dust storm event can carry considerable eolian dust in atmosphere, which makes air quite turbid and the horizontal visibility lower than 1 km (China Meteorological Agency, CMA). Desert regions in East Asia are considered to be the major sources of Asian dust according to the rain-dust records in Chinese historical documents and present day observations (Merrill *et al.*, 1994; Choi *et al.*, 2001; Zhang *et al.*, 2003; Shen *et al.*, 2007, 2009). The annual input of mineral aerosols into the atmosphere from the arid and semi-arid regions of North China is estimated to be about 800 Tg (Zhang *et al.*, 1997), accounting for about half of the global dust output (Andreae, 1995; Duce *et al.*, 1995). During Asian dust periods, several studies have been made to investigate the physical and chemical properties of dust aerosols from the arid and semi-arid source regions in northern China and their characterization in terms of their spatial and temporal variation in remote marine regions (Zhang *et al.*, 1993; Arimoto *et al.*, 1996; Zhang *et al.*, 1997; Alfaro *et al.*, 2003; Huebert *et al.*, 2003; Iwasaka *et al.*, 2003; Zhang *et al.*, 2003; Arimoto *et al.*, 2004; Xu *et al.*, 2004; Cao *et al.*, 2005; Wang *et al.*, 2005b; Zhang *et al.*, 2005; Zhang *et al.*, 2008). Prior studies showed that water-soluble ions accounted for one-third or more of the aerosol particles' mass in Chinese urban regions (such as: Wang *et al.*, 2005a; Shen *et al.*, 2008). However, there were few studies of water-soluble ion in dust aerosol samples in arid and semi-arid areas. Limited studies showed that ions were valuable indicator for Asian dust storm events and for the surface heterogeneous reaction of dust particles with SO₂ and NO₂ (Choi *et al.*, 2001; Arimoto *et al.*, 2004; Wang *et al.*, 2005a). In this study, fine aerosol particles (PM_{2.5}) were collected at Tongyu during April–June 2006 to determine the chemical composition of water-soluble ions and their sources.

MATERIALS AND METHODS

Aerosol Sampling

The Tongyu station for aerosol observation (44°25'E, 122°52'E, 184 m above sea level) is located to the east of the Horqin sand-land, 5 km west of Xinhua downtown, Tongyu County, and the Jilin Province (Liu *et al.*, 2004). The mean annual precipitation is 404 mm in Tongyu. There are no major industrial sources close to the sampling site. The sampling site is on grassland, 3 m above the ground level. A firm Omni Ambient Air Sampler (BGI Inc, Waltham, MA, USA) with solar energy and battery-powered mini-volume samplers operating at flow rates of 5 L/min on 47-mm-diameter Whatman quartz membrane filters was used to collect aerosol samples.

During April 14 to June 21, 2006, particles with aerodynamic diameters $\leq 2.5 \mu\text{m}$ (PM_{2.5}) were collected daily within a 24-h sampling period from 08:00 LST in the morning to 08:00 LST the following morning. A total of 53 aerosol samples were collected in spring 2006 at Tongyu station. During the sampling period, meteorological data,

including ambient temperature, pressure, relative humidity (RH), wind speed, and wind direction, were also recorded by the Tongyu Meteorological Agency.

Mass and Water-soluble Ions Analyses

Aerosol mass loadings were determined gravimetrically using a Sartorius MC5 electronic microbalance ($\pm 1 \mu\text{g}$ sensitivity, Sartorius, Gottingen, Germany). Before weighing, the filters were equilibrated for 24 hours at 20 to 23°C and a relative humidity between 35% and 45% (USEPA, 1997). Each filter was weighed at least three times before and after sampling following the 24-hour equilibration period. The mean net mass for each filter was obtained by subtracting the pre-deployment weight from the average of the post-sampling readings. The precisions of the weight measurements were $< 10 \mu\text{g}$ for blank filters and $< 20 \mu\text{g}$ for filter samples. The uncertainty for PM mass concentration was lower than 5%.

One-fourth of each filter sample was used to determine major ion concentrations following procedures described in detail by Shen *et al.* (2008). That's one-fourth of each filter was put into a separate 20 mL vial containing 10 mL distilled-deionized water (a resistivity of 18 M Ω), and then placed in ultrasonic water bath for 60 min and then shaken by mechanical shaker for 1 hr for complete extraction of the ionic compounds. The extracts were filtered with a 0.45 μm pore size microporous membrane, and the filtrates were stored at 4°C in a clean tube before analysis. Four anions (SO₄²⁻, NO₃⁻, Cl⁻, and F⁻) and five cations (Na⁺, NH₄⁺, K⁺, Mg²⁺, and Ca²⁺) in aerosol samples were determined in aqueous extracts of the filters prepared in three steps using ultrapure (18 M Ω) water. An ion chromatography (IC, Dionex 500, Dionex Corp, Sunnyvale, California, United States) was used for the analysis. The blank values were subtracted from sample concentrations. One sample in each group of ten samples was analyzed twice for quality control purposes. Typical precisions (percent relative standard deviation) for the six pairs of samples were calculated by the equation: $X_i = (C_{i1} - C_{i2})/C_{ia}$. Here, C_{i1} and C_{i2} are the routine and duplicate concentrations, C_{ia} is the mean concentration for measurement pair i, and X_i is the relative difference. The maximum relative precisions were 1.8% for Na⁺, 0.9% for NH₄⁺, 0.6% for K⁺, 4.0% for Ca²⁺, 1.0% for Mg²⁺, 1.2% for SO₄²⁻, 2.6% for NO₃⁻, 0.3% for Cl⁻, and 1.4% for F⁻.

Elemental Fe concentration Analyses

The dust trace element Fe concentration of PM_{2.5} samples were determined directly by a proton induced X-ray emission (PIXE) method using the 2.5 MeV protons with a 50 nA beam current produced by the twin 1.7 MV beams tandem accelerator at the Institute of Low Energy Nuclear Physics, Beijing Normal University. This analysis process was described detailed in Zhang *et al.* (2008).

RESULTS AND DISCUSSION

Temporal Variations of PM_{2.5} Mass Concentrations

The arithmetic mean mass concentration of PM_{2.5} was

260.9 $\mu\text{g}/\text{m}^3$ (range from 22.5 to 1630.1 $\mu\text{g}/\text{m}^3$) during the entire observation period. During sampling period, nine dust storm events (DS) were detected on April 21–23 (DS1), April 28–29 (DS2), May 4–5 (DS3), May 8 (DS4), May 11 (DS5), May 15–19 (DS6), May 22 (DS7), May 29 (DS8), and June 5–7 (DS9), with the corresponding $\text{PM}_{2.5}$ loadings (342.4, 463.1, 637.9, 362.2, 403.0, 805.7, 324.5, 363.0, and 359.9 $\mu\text{g}/\text{m}^3$, respectively) higher than the spring mean value (Table 1). The mean mass concentration of $\text{PM}_{2.5}$ for the nine dust storm events was 527.97 $\mu\text{g}/\text{m}^3$, which is four times the mean mass concentration for non-dust storm (NDS) days. The highest $\text{PM}_{2.5}$ mass concentration observed within a 24-hour period was 1630.1 $\mu\text{g}/\text{m}^3$, which occurred on 17 May (DS6), and it was almost 14 times greater than the daily average concentration of 111.7 $\mu\text{g}/\text{m}^3$ for non-dust storm periods.

Many studies have also reported high $\text{PM}_{2.5}$ mass concentrations during dust storm events. For example, continuous monitoring of airborne particles at chongwan-chongju, in Korea, showed that the average maximum $\text{PM}_{2.5}$ mass concentration during strong dust storms in 2002 was 166.9 $\mu\text{g}/\text{m}^3$ (Chung *et al.*, 2003). On 14 April 2002, a heavy dust storm was observed in Xi'an, a site on the Chinese loess plateau near the Asian dust source regions, and the $\text{PM}_{2.5}$ mass concentration was 740 $\mu\text{g}/\text{m}^3$, which is more than three times the daily average concentration for non-dust storm days observed there (Cao *et al.*, 2005). Shen *et al.* (2007) reported that the highest $\text{PM}_{2.5}$ mass concentration was 399 $\mu\text{g}/\text{m}^3$ on 13 April at Tongliao during a dust storm event in spring 2005. The above comparisons indicate that DS events carry high levels of fine aerosol particles, which lead to poor air quality in the semi-arid regions and downwind regions.

Most of the DS samples at Tongyu were associated with high wind speeds (Table 1). For example, compared with the sampling period average value of 9.5 m/s, the observed wind speeds on 16 May during DS6 were 8.6, 10.7, 10.2, and 12.4 m/s at 02:00, 08:00, 14:00, and 20:00 LST (Local Standard Time), respectively. Low relative humidity levels

(ranging from 10 to 36%) and low barometric pressures were also observed during DS events.

Compared with the dust storm events, the background aerosol loading for the entire spring, represented by the NDS samples, was 111.7 $\mu\text{g}/\text{m}^3$, which is much lower than that of the DS events. To put these values in context, the NDS $\text{PM}_{2.5}$ value is higher than the 24-hour U.S. National Ambient Air Quality Standards (NAAQS) of 35 $\mu\text{g}/\text{m}^3$ and the yearly mean value of 15 $\mu\text{g}/\text{m}^3$ (USEPA, 2004). China currently has no national $\text{PM}_{2.5}$ standard. The high background levels of $\text{PM}_{2.5}$ at Tongyu reveal that fine particle pollution is a serious problem even in semi-arid regions in North China.

Water-Soluble Ion Compositions

In Table 2, the average concentrations and standard deviations of water-soluble ions in $\text{PM}_{2.5}$ are given for two cases. The total ion concentration during DS was 39.0 $\mu\text{g}/\text{m}^3$, which is two-fold greater than the concentration of 18.8 $\mu\text{g}/\text{m}^3$ during NDS. However, the mass fractions of the sums of the total ions in $\text{PM}_{2.5}$ during DS and NDS were 7.51% and 17.54%, respectively, which reveals that water-soluble ions were much more abundant in NDS aerosols than in DS samples. On the basis of the percentages of the total cations and total anions, $\text{PM}_{2.5}$ particle acidity is mainly due to SO_4^{2-} and NO_3^- , whereas Ca^{2+} and Na^+ tend to buffer the acidity. The Ca^{2+} concentration was the highest in DS samples, followed by $\text{SO}_4^{2-} > \text{NO}_3^- > \text{Na}^+ > \text{K}^+ > \text{Cl}^- > \text{Mg}^{2+} > \text{F}^- > \text{NH}_4^+$. In NDS samples, the concentrations of ionic species followed a decreasing order as: $\text{SO}_4^{2-} > \text{Ca}^{2+} > \text{Na}^+ > \text{NO}_3^- > \text{Cl}^- > \text{K}^+ > \text{Mg}^{2+} > \text{F}^- > \text{NH}_4^+$.

As summarized in Table 2, during the dust storm period, the mean concentration of Ca^{2+} was 12.5 $\mu\text{g}/\text{m}^3$ which was almost three times greater than that during the NDS, indicating that Ca^{2+} was entrained along with the Asian dust. Arimoto *et al.* (2004) also observed high Ca^{2+} concentrations during DS near a desert source region site. Such chemical specie can provide another indication of the

Table 1. Summary of statistics for the concentration of $\text{pm}_{2.5}$, water-soluble ions, and wind speed for nine dust storm events in spring 2006 at Tongyu (units: $\mu\text{g}/\text{m}^3$).

Dust storm Events	DS1 21–23 April	DS2 28–29 April	DS3 4–5 May	DS4 8 May	DS5 11 May	DS6 15–19 May	DS7 22 May	DS8 29 May	DS9 5–7 June
$\text{PM}_{2.5}$	342.4	463.1	637.9	362.2	403.0	805.7	324.5	363.0	359.9
Fe	7.4	7.1	8.4	7.9	5.7	10.3	3.8	1.6	5.1
Na^+	3.7	4.2	5.1	5.4	6.8	4.7	3.5	3.3	4.1
NH_4^+	0.3	0.4	0.6	nd	1.4	1.5	0.0	nd	3.1
K^+	1.3	1.6	2.4	1.0	1.6	2.1	0.8	0.8	1.8
Mg^{2+}	0.8	1.0	1.1	0.7	1.0	1.3	0.7	0.5	0.9
Ca^{2+}	8.8	13.2	13.9	8.6	11.7	16.4	9.0	5.0	10.4
F^-	0.5	0.9	0.7	0.7	1.1	0.8	0.6	0.4	0.6
Cl^-	1.5	1.9	1.9	1.6	2.0	1.7	1.1	1.0	1.5
NO_3^-	4.3	3.5	6.5	3.4	7.9	5.3	2.4	2.4	4.6
SO_4^{2-}	8.7	8.8	12.6	7.4	21.1	16.1	5.4	4.2	12.1
WS m/s	10.9	11.7	10.3	5.8	10.1	12.4	7.1	7.5	9.3

^a DS: dust storm period; PM: particulate matter; WS: wind speed

Table 2. Concentrations of the major chemical species in PM_{2.5} and their ratio to Fe.

Species	DS ^a (n ^b = 19)			NDS ^c (n = 34)		
	Concentration, µg/m ³ Mean	SD ^d	Ratio to Fe	Concentration, µg/m ³ Mean	SD	Ratio to Fe
PM _{2.5}	528.0	311.0		111.7	64.3	
Fe	7.3	4.0	1.00	1.4	1.1	1.00
Na ⁺	4.5	1.0	0.62	3.3	0.9	2.40
NH ₄ ⁺	1.2	1.0	0.16	0.6	0.6	0.41
K ⁺	1.7	1.0	0.24	0.8	0.5	0.57
Mg ²⁺	1.0	0.4	0.14	0.3	0.2	0.25
Ca ²⁺	12.5	5.9	1.71	4.5	4.6	3.24
F ⁻	0.7	0.3	0.10	0.4	0.2	0.27
Cl ⁻	1.5	0.4	1.22	1.1	0.5	0.16
NO ₃ ⁻	4.6	2.5	0.63	3.0	1.4	2.15
SO ₄ ²⁻	11.8	7.8	1.62	5.7	3.2	4.11

^a DS: dust storm; ^bn: sample numbers; ^cNDS: non-dust-storm days; ^dSD: standard deviation.

occurrence and intensity of Asian dust events in downwind regions. For example, Choi *et al.* (2001) detected high Ca²⁺ and Mg²⁺ concentrations in Seoul during Asian dust storm events, and they indicated that high Ca²⁺ and Mg²⁺ concentrations can be taken as good indicators for Asian dust events and the intensity of dust events. The concentration of water-soluble Ca²⁺ was highly correlated with Fe concentration ($R = 0.62$, $N = 53$, $P < 0.0001$), which demonstrates that soluble Ca²⁺ originates primarily from the crustal material. Water-soluble Ca²⁺ in eolian dust is commonly associated with the minerals calcite, anhydrite, and gypsum (Claquin *et al.*, 1999).

During the dust storm period, the concentrations of SO₄²⁻ and NO₃⁻ were also maintained at high levels in comparison with NDS samples. In contrast, the percentages of SO₄²⁻ and NO₃⁻ among the total ion concentration were higher in NDS than in DS. As Fe is the typical crustal origin element, here the relationships between Fe with SO₄²⁻ and NO₃⁻ were calculated to identify their origin. Good correlations for Fe with SO₄²⁻ and NO₃⁻ were observed in 19 DS samples ($R = 0.71$ and 0.70 , respectively), but poor relationships occurred in 34 NDS samples ($R = 0.22$ and 0.03 , respectively). Such results aimed at inferring the origin of SO₄²⁻ and NO₃⁻ were remarkably different between DS and NDS. Salt in arid and semi-arid regions should be the main source for SO₄²⁻ and NO₃⁻ during DS, while these ions originated mainly from anthropogenic sources during NDS, probably as secondary aerosol species.

Prior studies have shown that biomass burning is a significant source of water-soluble K⁺ (Andreae, 1983; Duan *et al.*, 2004). In this study, K⁺ accounted for 34% of the total K during DS, while the percentage increased to 54% during NDS. These results reveal that anthropogenic sources heavily influence the K⁺ concentration during NDS. In fact, wheat straw and maize stalks are burned for cooking in all seasons and for heat during winter and early spring (from November to April) in rural areas of North China.

Source Identification of Ionic Species

The ratios of nine water-soluble ions to Fe were

calculated to identify the origin of the ions. As shown in Table 2, the ratios of ions to Fe were remarkably different between DS and NDS samples. In general, these ratios increased from DS to NDS samples, suggesting that the typical water-soluble ions were influenced by the non-crustal sources, possibly anthropogenic sources during NDS conditions. The ratio of Ca²⁺/Fe in PM_{2.5} samples at Tongyu was 1.7 during the dust storms compared with 3.2 for the NDS samples. This enrichment of Ca²⁺ in the NDS samples suggests an influence from local pollution sources that were richer in Ca²⁺ than desert dusts, and cement particles released from construction sites were likely candidates. This water-soluble Ca²⁺ enrichment on non-dust days was also observed at Zhenbeitai, Yulin by Alfaro *et al.* (2003). The ratio of K⁺ to Fe during NDS is double than that in DS samples, which reflects the contribution of biomass burning during NDS. High SO₄²⁻/Fe and NO₃⁻/Fe ratios during NDS also demonstrate the important influence of anthropogenic sources on spring fine particles at Tongyu. To further evaluate the origin of the major ions in spring aerosol particles, mass ratios of water-soluble ions to Fe versus Fe were plotted as shown in Fig. 1.

The ratios of water-soluble ions to Fe remained stable at low values for the DS samples, suggesting that they also originated from the crustal source during dust storm events. Such values reflect the characteristics of the ionic composition of soil dust on a regional scale. In contrast, the ratios of water-soluble ions to Fe showed more scatter in the NDS samples, which reveals that these ions are heavily influenced by local anthropogenic sources. Arimoto *et al.* (2004) also observed the mixing of mineral dust and pollution aerosol in spring near a desert source region site of ZBT. Previous studies of Asian dust by Mori *et al.* (2003), Wang *et al.* (2005a) and Shen *et al.* (2007) also showed that the mixing of mineral dust with pollution aerosol occurred evenly in dust source regions. In this study, the following equation was used to estimate the contribution of anthropogenic sources to ionic species during NDS periods:

$$C_{\text{non}} = C_{\text{NDS}} - C_{\text{Fe-NDS}} \times (C/C_{\text{Fe}})_{\text{DS}} \quad (1)$$

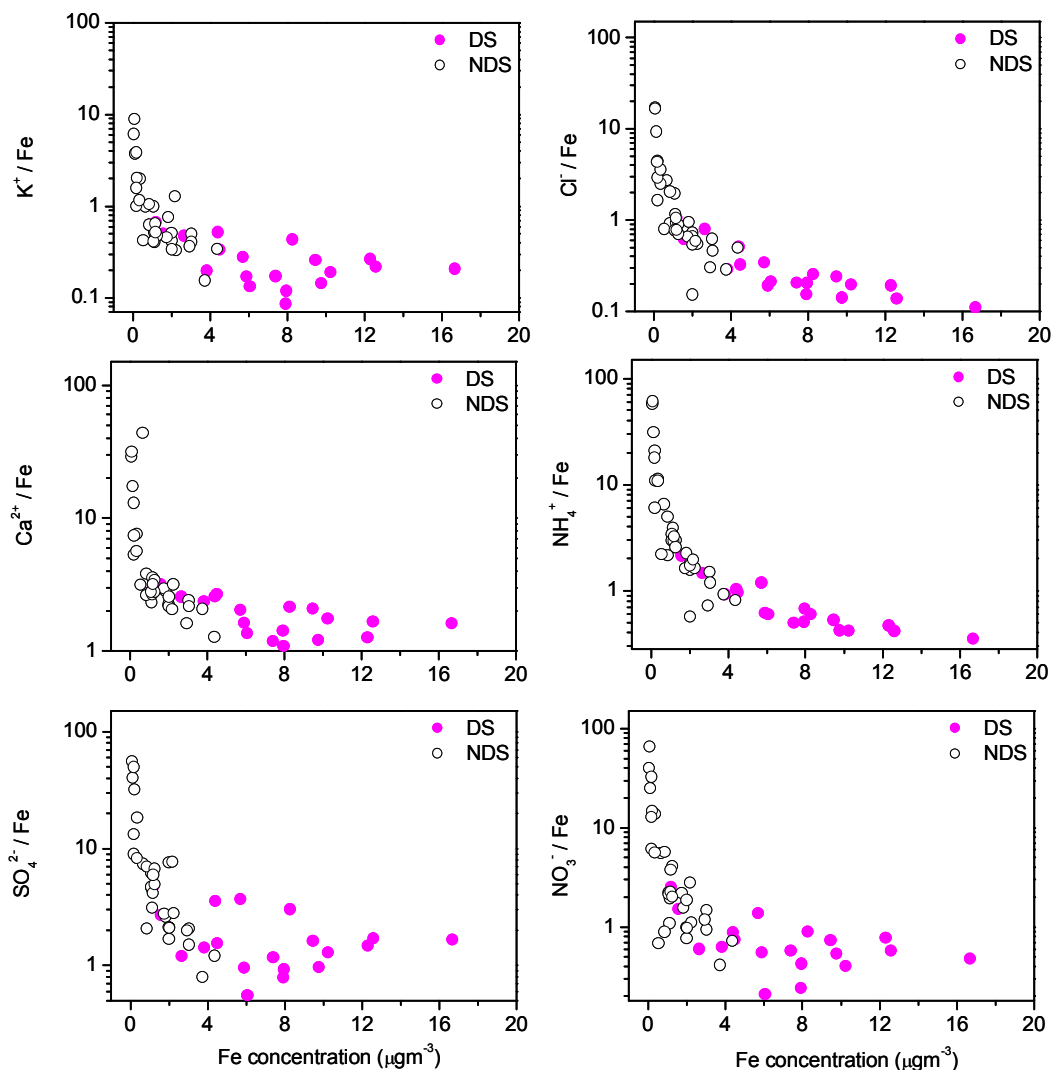


Fig. 1. Scatter plots of water-soluble ions/Fe ratios against Fe at Tongyu.

Here, C_{non} represents ion concentration from non-crustal sources, C_{NDS} is the ion concentration during the NDS period, $C_{\text{Fe-NDS}}$ is the elemental Fe concentration during NDS, and $(C/C_{\text{Fe}})_{\text{DS}}$ is the ratio of ions to Fe during the DS period. The concentrations of five major soluble ions derived from anthropogenic activities were calculated and are presented in Table 3. The results reveal that the influence of anthropogenic activities was significant for NDS samples. The percentage of non-crustal Ca^{2+} accounted for almost 47.2% of its total mass, while the concentrations of sulfate and nitrate generated from anthropogenic sources increased to 58.1% and 70.7%, respectively. The high sulfate in terms of both mass concentration and fraction implies the large contribution of coal combustion during the NDS period.

Table 3. Ion concentrations from non-crustal sources (C_{non}) and percentages of ion mass during NDS periods ($C_{\text{non}}/C_{\text{NDS}}$).

	Na^+	K^+	Ca^{2+}	NO_3^-	SO_4^{2-}
$C_{\text{non}}, \mu\text{g}/\text{m}^3$	2.5	0.4	2.1	2.1	3.1
$C_{\text{non}}/C_{\text{NDS}}, \%$	74.2	55.2	47.2	70.7	58.1

Ion Balance and the Alkalinity of $\text{PM}_{2.5}$: Evidence for the Importance of Carbonate in Mineral Dust

Ion balance calculations can be used as an approach for studying the acid-base balance of ions measured in aerosol particle samples. To evaluate the cation and anion balances of aerosol samples, mass concentrations were converted to ion microequivalents in $\text{PM}_{2.5}$ samples based on the following equations:

$$C \text{ (cation microequivalents } 1/\text{m}^3) = \text{Na}^+/23 + \text{NH}_4^+/18 + \text{K}^+/39 + \text{Mg}^{2+}/12 + \text{Ca}^{2+}/20 \quad (2)$$

$$A \text{ (anion microequivalents } 1/\text{m}^3) = \text{F}^-/19 + \text{Cl}^-/35.5 + \text{NO}_3^-/62 + \text{SO}_4^{2-}/48 \quad (3)$$

A strong correlation between cation and anion equivalents for all samples (Fig. 2(a)) indicates that the determined five cations and four anions are the major ionic species. Ion balance calculations stratified by DS and NDS (Fig. 2(b)) show that most of the samples collected were positioned lower than a 1:1 anion:cation (A:C) line, implying a deficiency in anions. Fifteen of the nineteen DS

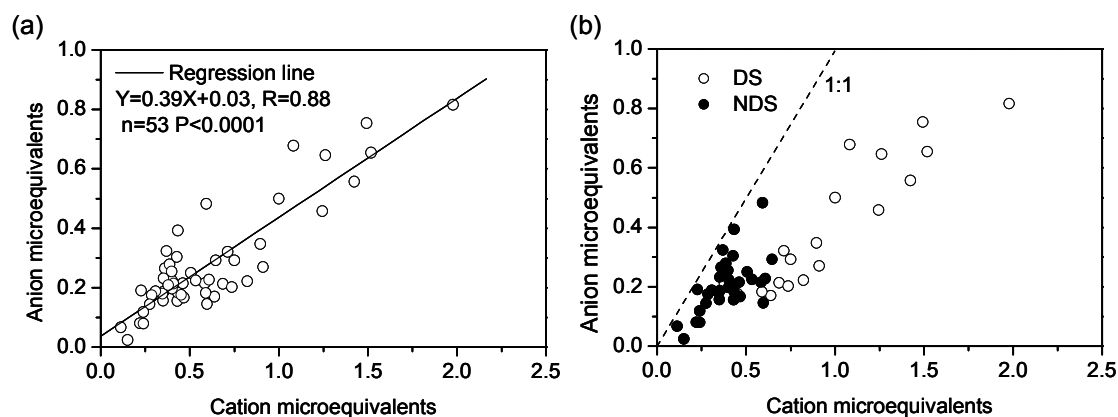


Fig. 2. Total anion microequivalents versus total cation microequivalents.

samples lay farther below the 1:1 line, while a certain number of the NDS samples were positioned slightly below or near the unity line. Moreover, the average ratios of total cation to anion equivalents (C/A) for the DS and NDS samples were 2.6 and 2.1, respectively. These results reveal that the DS samples were more alkaline than the NDS samples, and both of them were strongly alkaline.

Plumes of alkaline dust particles may be important for other chemical cycles because they can buffer atmospheric acidity as the dust transports to the downwind regions (Shen *et al.*, 2007). The DS data indicated an apparent deficit of anions. This was more than likely due to carbonate (CO_3^{2-}), which was measured as described below, and possibly other anions, such as CH_3COO^- , HCOO^- , $\text{C}_2\text{O}_4^{2-}$, and PO_4^{3-} that also were not investigated in this study. Prior studies have actually observed the occurrence of carbonate in Asian dust (Xu *et al.*, 2004; Cao *et al.*, 2005; Wang *et al.*, 2005b; Shen *et al.*, 2007), and its presence would be significant because it would provide sites for heterogeneous reactions with SO_2 and NO_x . The molar concentrations of CO_3^{2-} were calculated as the deficit values of measured anions, and CO_3^{2-} concentrations were then determined by multiplying the molar concentration values by 30. A good correlation was observed between estimated CO_3^{2-} and Ca^{2+} (Fig. 3), and the molar ratios of CO_3^{2-} to Ca^{2+} were nearly uniform, with an average value of 0.96. These results imply that this simple method supplies another method with which to obtain the carbonate content.

To further evaluate the anion deficit method for estimating the CO_3^{2-} content, the carbonate carbon (CC) concentrations during DS events were also determined using a DRI Model 2001 Thermal/Optical Carbon Analyzer following the procedure of Ho *et al.* (2010). The equivalent CO_3^{2-} concentrations were then determined by multiplying the CC values by five (Shen *et al.*, 2007). Calculated in this way, the arithmetic mean mass concentration of CO_3^{2-} during DS periods was $12.9 \mu\text{g}/\text{m}^3$, which would account for 2.4% of the total $\text{PM}_{2.5}$ mass (corresponding to 8.4% of calcite). The measured carbonate concentrations were consistent with the results estimated using the ion balance method (Fig. 4), which demonstrates that ion balance difference supplies another simple method for directly calculating the mass concentration of CO_3^{2-} for DS samples.

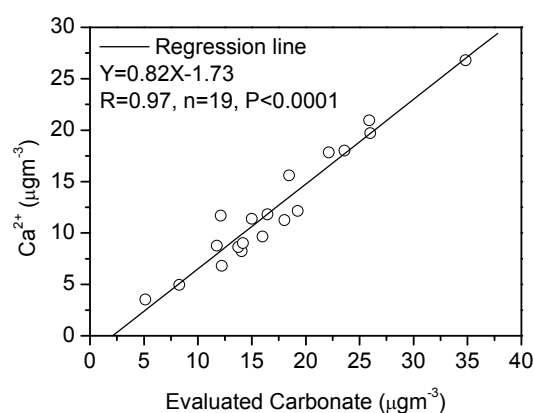


Fig. 3. Correlations of mass concentration between Ca^{2+} and carbonate concentrations determined by the ionic balance difference method.

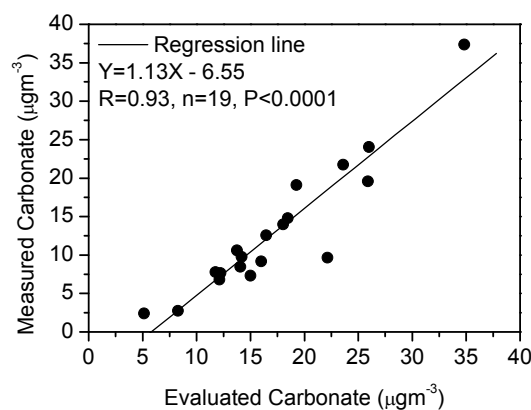


Fig. 4. Correlations of carbonate concentrations determined between measured carbonate and evaluated carbonate using the ionic balance difference method.

Chinese loess is characteristically richer in calcite than dolomite (Wen, 1989). The weak correlation observed between Ca^{2+} and SO_4^{2-} concentrations further reveals that calcite was the major form of CO_3^{2-} in the aerosol samples. Compared with other samples of Asian dust, the apparent carbonate mass fractions calculated here were much lower. For example, Cao *et al.* (2005) documented strong dust storm events at Xi'an and showed that the CO_3^{2-} was 8% of

the Asian dust mass in the PM_{2.5} fraction, while Xu *et al.* (2004) found that the carbonate content during DS at ZBT was 11%. The lower carbonate content in Tongyu can also compare to the 3.6% in Tongliao (Shen *et al.*, 2007, 2009). Wang *et al.* (2005b) reported that the carbonate content in eolian dust decreases from west to east in northern China, which is inversely with mean annual precipitation pattern. And this is mainly for calcium carbonate rapidly precipitates during drought conditions. Because of the contribution to climatic and environmental effects at local, regional, and even global scales, research on soil-derived carbonate is significant (Dentener *et al.*, 1996).

CONCLUSIONS

The chemical characteristics of Asian dust were investigated in aerosol particles (PM_{2.5}) collected at Tongyu in northeastern China during the spring of 2006. High aerosol loadings in the area are serious concerns. The mean mass concentration of PM_{2.5} at Tongyu during spring 2006 was over 260.0 µg/m³, and even on non-dust storm days the average mass concentration of PM_{2.5} (111.7 µg/m³) exceeded the 24-hour air quality standard in the United States.

The mass fractions of the sums of the total ions in PM_{2.5} during DS and NDS were 7.51% and 17.54%, respectively (Table 3), revealing that water-soluble ions were much more abundant in NDS aerosols than in DS samples. The ratios of water-soluble ions to Fe remained stable in the DS samples, while they were more variant during NDS, suggesting that the anthropogenic influence was significant on ionic species during normal days even at arid and semi-arid regions. The contributions from anthropogenic sources for the six major ions exceed 50%. Ion balance calculations for the NDS samples suggest that those aerosol particles were alkaline, while DS samples were strongly alkaline. The ion balance deficit supplies another simple method for estimating the CO₃²⁻ concentration during the DS period, which was demonstrated to be more valuable.

ACKNOWLEDGEMENTS

This research is supported by the Pilot Project of Knowledge Innovation Program of the Chinese Academy of Sciences (KZCX2-YW-Q11-03, IAP09315), and the SKLLQG, Chinese Academy of Sciences (grant SKLLQG1010).

REFERENCES

- Alfaro, S.C., Gomes, L., Rajot, J.L., Lafon, S., Gaudichet, A., Chatenet, B., Maille, M., Cautenet, G., Lasserre, F., Cachier, H. and Zhang, X.Y. (2003). Chemical and Optical Characterization of Aerosols Measured in Spring 2002 at the ACE-Asia Supersite, Zhenbeitai, China. *J. Geophys. Res.* 108: 8641, doi: 10.1029/2002JD003214.
- Andreae, M.O. (1983). Soot Carbon and Excess Fine Potassium: Long-range Transport of Combustion-derived Aerosols. *Science* 220: 1148–1151.
- Andreae, M.O. (1995). In *Future Climates of the World*, Climate Effects of Changing Atmospheric Aerosol Levels, in World Survey of Climatology, Henderson-sellers, A. (Ed.), Elsevier Science, New York, p. 41–392.
- Arimoto, R., Duce, R.A., Ray, B.J., Ellis Jr., W.G., Cullen, J.D. and Merrill, J.T. (1995). Relationships among Aerosol Constituents from Asia and the North Pacific during Pem-West A. *J. Geophys. Res.* 101: 2011–23.
- Arimoto, R. (2001). Eolian Dust and Climate: Relationships to Sources, Tropospheric Chemistry, Transport and Deposition. *Earth Sci. Rev.* 54: 29–42.
- Arimoto, R., Zhang, X.Y., Huebert, B.J., Kang, C.H., Savoie, D.L., Prospero, J.M., Sage, S.K., Schloesslin, C.A., M.Khaing, H. and Oh, S.N. (2004). Chemical Composition of Atmospheric Aerosols from Zhenbeitai, China, and Gosan, South Korea, during ACE-Asia. *J. Geophys. Res.* 109: D19S04, doi: 10.1029/2003JD004323.
- Arimoto, R., Kim, Y.J., Kim, Y.P., Quinn, P.K., Bates, T.S., Anderson, T.L., Gong, S., Uno, I., Chin, M., Huebert, B.J., Clarke, A.D., Shinozuka, Y., Weber, R.J., Anderson, J.R., Guazzotti, S.A., Sullivan, R.C., Sodeman, D.A., Prather, K.A. and Sokolik, I.N. (2006). Characterization of Asian Dust during ACE-Asia. *Global Planet. Change* 52: 23–56.
- Cao, J.J., Lee, S.C., Zheng, X.D., Ho, K.F., Zhang, X.Y., Guo, H., Chow, J.C. and Wang, H.B. (2003). Characteristics of Hong Kong Aerosols during the Dust Storm in April 1998. *Water Air Soil Pollut. Focus* 3: 213–229.
- Cao, J.J., Lee, S.C., Zhang, X.Y., Chow, J.C., An, Z.S., Ho, K.F., Watson, J.G., Fung, K., Wang, Y.Q. and Shen, Z.X. (2005). Characterization of Airborne Carbonate over a Site near Asian Dust Source Regions during Spring 2002 and its Climatic and Environmental Significance. *J. Geophys. Res.* 110: D03203, doi: 10.1029/2004JD005244.
- Charlson, R.J., Schwartz, S.E., Hales, J.M., Cess, R.D., Coakley Jr., J.A., Hansen, J.E. and Hofmann, D.J. (1992). Climate Forcing by Anthropogenic Aerosols. *Science* 255: 423–430.
- Choi, J.C., Lee, M.H., Chun, Y.S., Kim, J.Y., Oh, S.N. (2001). Chemical Composition and Source Signature of Spring Aerosol in Seoul, Korea. *J. Geophys. Res.* 106: 18067–18074.
- Chung, Y.S., Kim, H.S., Dulama, J. and Harris, J. (2003). On Heavy Dustfall Observed with Explosive Sandstorms in Chongwon-Chongju, Korea in 2002. *Atmos. Environ.* 37: 3425–3433.
- Claquin, T., Schulz, M. and Balkanski, Y.J. (1999). Modeling the Mineralogy of Atmospheric Dust Sources. *J. Geophys. Res.* 104: 22243–22256.
- Dentener, F.J., Carmichael, G.R., Zhang, Y., Lelieveld, J. and Crutzen, P.J. (1996). Role of Mineral Aerosol as a Reactive Surface in the Global Troposphere. *J. Geophys. Res.* 101: 22869–22890.
- Duce, R.A. (1995). In *Aerosol Forcing of Climate*, Sources, Distributions and Fluxes of Mineral Aerosols and their Relationship to Climate. Charlson, R., Heintzenberg, J. (Eds.), John Wiley, New York p. 43–72.
- Duan, F., Liu, X., Yu, T. and Cachier, H. (2004). Identification

- and Estimate of Biomass Burning Contribution to the Urban Aerosol Organic Carbon Concentrations in Beijing. *Atmos. Environ.* 38: 1275–1282.
- Harrison, R.M., and Yin, J. (2000). Particulate Matter in the Atmosphere: Which Particle Properties are Important for its Effects on Health. *Sci. Total Environ.* 249: 85–101.
- Haywood, J.M., and Boucher, O. (2000). Estimates of the Direct and Indirect Radiative Forcing Due to Tropospheric Aerosols: A Review. *Rev. Geophys.* 38: 513–543.
- Ho, S.H., Ho, K.F., Lee, S.C., Liu, S.X., Liu, W.D., Fung, K.K., Zhang, R.J. and Cao, J.J. (2011). Conventional Quantification of Carbonate Carbon in Aerosol Samples with Modification of a Thermal Optical Carbon Analyzer. *Aerosol Sci. Technol.* (submitted).
- Huebert, B.J., Bates, T., Russell, P.B., Shi, G., Kim, Y.J., Kawamura, K., Carmichael, G. and Nakajima, T. (2003). An Overview of ACE-Asia: Strategies for Quantifying the Relationships between Asian Aerosols and their Climatic Impacts. *J. Geophys. Res.* 108: 8633, doi: 10.1029/2003JD003550.
- Iwasaka, Y., Shi, G. Y., Matsuki, A., Trochkin, D., Kim, Y. S., Zhang, D., Nagatani, T., Shibata, T., Nagatani, M., Nakata, H., Shen, Z.B., Li, G. and Chen, B. (2003). Importance of Dust Particles in the Free Troposphere over the Taklamakan Desert: Electron Microscopic Experiments of Particles Collected with a Balloon Borne Particle Impactor at Dunhuang, China. *J. Geophys. Res.* 108: 8644, doi: 10.1029/2002JD003270.
- Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A., Kawahata, H., Kubilay, N., laRoche, J., Liss, P.S., Mahowald, N., Prospero, J.M. Ridgwell, A.J., Tegen, I. and Torres, R. (2005). Global Iron Connections between Desert Dust, Ocean Biogeochemistry, and Climate. *Science* 308: 67–71.
- Kim, K.W., Kim, Y.J. and Oh, S.J. (2001). Visibility Impairment during Yellow Sand Periods in the Urban Atmosphere of Kwangju, Korea. *Atmos. Environ.* 35: 5157–5167.
- Li, X., Maring, H., Savole, D., Voss, K., and Prospero, J.M. (1996). Dominance of Mineral Dust in Aerosol Light-scattering in the North Atlantic Trade Winds. *Nature* 380:416–419.
- Merrill, J., Arnold, E., Margaret, L. and Weaver, C. (1994). Mineralogy of Aeolian Dust Reaching the North Pacific Ocean 2, Relationship of Mineral Assemblages to Atmospheric Transport Patterns. *J. Geophys. Res.* 99: 21025–21032.
- Mori, I., Nishikawa, M., Tanimura, T., and Quan, H. (2003). Change in the Size Distribution and Chemical Composition of Kosa (Asian Dust) Aerosol during Long-range Transport. *Atmos. Environ.* 37: 4253–4263.
- Prospero, J.M. (1999). Long-range Transport of Mineral Dust in the Global Atmosphere: Impact of African Dust on the Environment of the Southeastern United States. *Proc. Nat. Acad. Sci. U.S.A.* 96: 3396–3403.
- Shen, Z.X., Cao, J.J., Arimoto, R., Zhang, R.J., Jie, D.M., and Liu, S.X. (2007). Chemical Composition and Source Characterization of Spring Aerosol over Horqin sand Land in Northeastern China. *J. Geophys. Res.* 112: D14315, doi: 10.1029/2006JD007991.
- Shen, Z.X., Arimoto, R., Okuda, T., Cao, J.J., Zhang, R. J., Li, X.X., Du, N., Nakao, S., Tanaka, S. (2008). Seasonal Variations and Evidence for the Effectiveness of Pollution Controls on Water-soluble Inorganic Species in Total Suspended Particulates and Fine Particulate Matter from Xi'an, China. *J. Air Waste Manage. Assoc.* 58: 1560–70.
- Shen, Z.X., Sandrine, C., Cao, J.J., Zhang, X.Y., Han, Y.M., Annie, G. and Laurent, G. (2009). Mineralogical Characteristics of Soil Dust from Source Regions in Northern China. *Particuology* 7: 507–512.
- Sokolik, I.N. and Toon, O.B. (1996). Direct Radiative Forcing by Anthropogenic Airborne Mineral Aerosols. *Nature* 380: 681–683.
- Tegen, I., Andrew, A.L., Fung, I. (1996). The Influence on Climate Forcing of Mineral Aerosols from Disturbed Soils. *Nature* 380: 419–422.
- Trochkin, D., Iwasaka, Y., Matsuki, A., Yamada, M., Kim, Y.S., Nagatani, T., Zhang, D., Shi, G.Y. and Shen, Z. (2003). Mineral Aerosol Particles Collected in Dunhuang, China, and their Comparison with Chemically Modified Particles Collected over Japan. *J. Geophys. Res.* 108: 8642, doi: 10.1029/2002JD003268.
- Uematsu, M., Yoshikawa, A., Muraki, H., Arao, K. and Uno, I. (2002). Transport of Mineral and Anthropogenic Aerosols during a Kosa Event over East Asia. *J. Geophys. Res.* 107: 4059, doi: 10.1029/2001JD000333.
- U.S. Environmental Protection Agency (USEPA). (1996). National Ambient Air Quality Standards for Particulate Matter: Final rule, Fed. Register. Research Triangle Park N. C; 62(138). p. 38651–38701.
- U.S. Environmental Protection Agency (USEPA). (2004). Air Quality Criteria for Particulate Matter. Research Triangle Park, NC: National Center for Environmental Assessment-RTP Office. Report No. EPA/600/P-99/OO a2F.
- Wang, M.X., Zhang, R.J. and Pu, Y.F. (2001). Recent Researches on Aerosol in China. *Adv. Atmos. Sci.* 18: 576–586.
- Wang, Y., Zhuang, G.S., Sun, Y.L. and An, Z.S. (2005a). Water-soluble Part of the Aerosol in the Dust Storm Season: Evidence of the Mixing between Mineral and Pollution Aerosols. *Atmos. Environ.* 39: 7020–7029.
- Wang Y.Q., Zhang X.Y., Arimoto, R., Cao, J.J. and Shen, Z.X. (2005b). Characteristics of Carbonate Content and Carbon and Oxygen Isotopic Composition of Northern China Soil and Dust Aerosol and its Application to Tracing Dust Sources. *Atmos. Environ.* 39: 2631–2642.
- Wen, Q.Z. (1989). Chinese loess Geochemistry (in Chinese). Beijing: *Sci. Press.* p. 115–158.
- Xu, J., Bergin, M.H., Greenwald, R., Schauer, J.J. Shafer, M.M., Jaffrezo, J.L., and Aymoz, G. (2004). Aerosol Chemical, Physical, and Radiative Characteristics near a Desert Source Region of Northwest China during ACE-Asia. *J. Geophys. Res.* 109: D19S03, doi: 10.1029/2003JD004239.
- Young, R.W., Karder, K.L., Betzer, P.R., Costello, D.K., Duce, R.A., Tindale, N.W., Laws, E.A., Uematsu, M.,

- and Feely, R.A. (1991). Atmospheric Iron Inputs and Primary Productivity: Phytoplankton Responses in the North Pacific. *Global Biogeochem. Cycles*. 5: 119–134.
- Zhang, M., Uno, I., Yoshida, Y., Xu, Y., Wang, Z., Akimoto, H., Bates, T., Quinn, T., Bandy, A., and Blomquist, B. (2004). Transport and Transformation of Sulfur Compounds over East Asia during the TRACE-P and ACE-Asia Campaigns. *Atmos. Environ.* 38: 6947–6959.
- Zhang, R., Arimoto, R., An, J., Yabuki, S. and Sun, J. (2005). Ground Observations of a Strong Dust Storm in Beijing in March 2002. *J. Geophys. Res.* 110: D18S06, doi: 10.1029/2004JD004589.
- Zhang, M.G., Pu, Y., Zhang, R.J. and Han, Z.W. (2006). Simulation of Sulfur Transport and Transformation in East Asia with a Comprehensive Chemical Transport Model. *Environ. Modell. Softw.* 21: 812–820.
- Zhang, R.J, Fu, C.B., Han, Z.W., and Zhu, C.S. (2008). Characteristics of Elemental Composition of PM_{2.5} in the Spring Period at Tongyu in the Semi-arid Region of Northeast China. *Adv. Atmos. Sci.* 25: 922–930.
- Zhang, X.Y., Arimoto, R. and An, Z.S. (1997). Dust Emission from Chinese Desert Sources Linked to Variations in Atmospheric Circulation. *J. Geophys. Res.* 102: 28041–28047.
- Zhang, X.Y., Arimoto, R., An, Z.S., Chen, T., Zhang, G.Y., Wang, X. (1993). Atmospheric Trace Elements over Source Regions for Chinese Dust: Concentrations, Sources and Atmospheric Deposition on the Loess Plateau. *Atmos. Environ.* 27: 2051–2067.
- Zhang, X.Y., Gong, S.L., Shen, Z.X., Mei, F.M., Xi, X.X., Liu, L.C., Zhou, Z.J., Wang, D., Wang, Y.Q. and Cheng, Y. (2003). Characterization of Soil Dust Aerosol in China and its Transport and Distribution during 2001 ACE-Asia: 1. Network Observations. *J. Geophys. Res.* 108: 4261, doi: 10.1029/2002JD002632.
- Zhuang, G.S., Guo, J.H., Yuan, H., and Zhao, C.Y. (2001). The Compositions, Sources, and Size Distribution of the Dust Storm from China in Spring of 2000 and its Impact on the Global Environment. *Chin. Sci. Bull.* 46: 895–901.

Received for review, February 17, 2011

Accepted, April 18, 2011