Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

# The concentration, source apportionment and deposition flux of atmospheric particulate inorganic nitrogen during dust events

Jianhua Qi[1], Ruifeng Zhang[1], Xiaojing Chen[1], Xuehui Lin[2], Huiwang Gao[1], Ruhai Liu[1]

[1]Key Laboratory of Marine Environment and Ecology, Ministry of Education, Ocean University of China, Qingdao, 266100, China
[2]Qingdao Institute of Marine Geology, Qingdao, 266100, China

Correspondence to: Jianhua Qi (qjianhua@ouc.edu.cn)

**Abstract.** To understand the impacts of long-range transport on particulate inorganic nitrogen associated with dust in downwind areas, aerosol samples were collected in the Qingdao coastal region on dust and non-dust (ND) days in spring from 2008 to 2011. The concentrations of water-soluble ions were measured by ion chromatography, with metal elements detected using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Compared to atmospheric aerosols collected on ND days, samples from dust days exhibited higher concentrations of particles and crustal elements. Total aerosol particle concentrations increased by a factor of 5.9 on average dust days. On dust days, the average concentrations of crustal elements (Sc, Al, Fe, Ca and Mg) increased by over a factor of four relative to those on ND days. The inorganic nitrogen content increased 1.2 to 9.2-fold during some dust events in which storms were weak or slow moving and reactions occurred during transport. By contrast, nitrate and ammonium exhibited very low concentrations (<20% of ND samples) or decreased concentrations in some cases as a result of the strong dilution effect of low-nutrient dust particles arising from their rapid transport in a strong dust storm. If air masses traveled faster than 40.5±9.9 km/h, the inorganic nitrogen content of most aerosol samples decreased compared to that of ND samples because of the strong dilution effect. The concentration of atmospheric particulate inorganic nitrogen was related to not only the transport path and speed but also the local emissions and reaction conditions during transport. The positive matrix factorization (PMF) receptor model results showed that the contribution of soil dust dramatically increased from 23% to 36% (90% of the residuals<3.0 and $r^2$=0.97) on dust days, while the contributions of local anthropogenic sources decreased, especially that of secondary aerosols. The dry

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

deposition flux of atmospheric particulates increased from 2800±700 mg/m$^2$/month on ND days to 16,800±15,900 on dust days. The dry deposition flux of particulate inorganic nitrogen increased 1.1 to 5.8-fold under the weak dilution effects of dust events. The dry deposition flux of nitrate decreased by 46%-63%, while that of ammonium decreased by 14% or to ND levels when strong dilution occurred during dust events. The atmospheric input of nitrogen to the ocean was not enhanced by dust events, and dust deposition was an uncertain source of nitrogen to the ocean.

Keywords: aerosols, nitrogen, dust, source apportionment, dry deposition flux

## 1 Introduction

Nitrogen is a key element for marine phytoplankton growth. Nitrogen carried in dust particles can be transported and deposited across vast distances at high wind speeds (Duce et al., 2008; Zhang et al., 2010). Additionally, bioavailable nutrients, via dust particle deposition, may enhance phytoplankton growth in some ocean areas (Shi et al., 2012; Guo et al., 2012; Liu et al., 2013). Tan and Wang (2014) found that chlorophyll concentrations increased four-fold, and a phytoplankton bloom occurred 10-13 days after dust deposition. Banerjee and Kumar (2014) hypothesized that dust-induced episodic phytoplankton blooms are important to the interannual variability of chlorophyll in the Arabian Sea away from active winter convection. Therefore, the atmospheric particulate nitrogen delivered by dust is important for obtaining a better understanding of the effects of dust inputs on marine primary production.

Asian dust, one of the main components of dust worldwide, affects northern China and the eastern area of the China Sea. Asian dust can also affect the northern Pacific Ocean via long-range transport by west winds. During transport, the dust storm particles continually mix with anthropogenic gas and particles from local sources along the pathway to carry desert dust and anthropogenic aerosols to downwind areas. The physical and chemical characteristics of atmospheric particulates downwind of dust weather are remarkably different from those normally present (Yang et al., 2002; Li et al., 2014; Ma et al., 2012). Additionally, the concentrations and characteristics of atmospheric particulate inorganic nitrogen species in downwind areas are greatly affected by dust weather.

Some researchers have found that inorganic nitrogen species in aerosols have high concentrations during Asian dust events. The concentrations of atmospheric particulate $NO_3^-$ and $NH_4^+$ on dust storm

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.



days were 2-5 times higher than those on non-dust storm (ND) days in Beijing (Liu et al., 2014; Liu and Bei, 2016). Xu et al. (2014) found that particulate $SO_4^{2-}$ and $NO_3^-$ simultaneously increased in dust storms on the northern boundary of the Tibetan Plateau because of the enriched dust including more acidic species or anthropogenic aerosols. Compared to those on ND days, higher concentrations of $NO_3^-$ and $NH_4^+$ in aerosol particles were observed on dust storm days in northern China, and $NO_3^-$ and $NH_4^+$ showed lower concentrations during strong dust storm events than during weak dust events (Zhang et al., 2010). Fitzgerald et al. (2015) found that nearly all Asian dust in Korea contains considerable amounts of nitrate because pollution plumes mix with dust from the Gobi and Taklamakan Deserts and are transported over the Asian continent.

However, some studies observed that the concentrations of inorganic nitrogen in aerosols decreased on dust storm days. At Yulin, a rural site near the Asian dust source region, the concentration of $NO_3^-$ significantly decreased in aerosols on dust days as a result of the dilution effect (Wang et al., 2016). The absolute abundances of $NO_3^-$ and $NH_4^+$ were notably lower in dust plumes than in a polluted air parcel because dust plumes are often separated by the arrival of a cold front in Shanghai, China (Wang et al., 2013). Li et al. (2014) found that the concentrations of nitrate and ammonium in downwind aerosol particles decreased on dust storm days, with a decreasing ratio of soluble inorganic ions to $PM_{2.5}$ in the Yellow River Delta, China. When dust is rapidly transported from desert regions without passing through a major urban area and lingers over the Yellow Sea, the concentrations and size distributions of nitrate and ammonium have no significant variation in heavy Asian dust (AD) plumes (Kang et al., 2013). Nitrate and ammonium also exhibited different concentration variations in other desert regions. Jaafar et al. (2014) found that nitrate was more abundant than ammonium, which showed no concentration variation in non-dust aerosol particles during dust episodes originating from both the African and Arabian deserts.

The effect of dust events on the inorganic nitrogen concentration in downwind aerosols is complicated because it involves many factors, such as the mixing state and transport pathway. The effect of AD as a nitrogen source on biogeochemical cycles and marine ecology is not adequately understood. Understanding the variations in the concentration and deposition flux of atmospheric particulate nitrogen on dust days is essential to quantifying the impacts of nutrients on the marine environment and primary production. To understand the influence of dust on atmospheric nitrogen, we collected aerosol samples from the coastal region of the Yellow Sea in spring, when there is a high

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

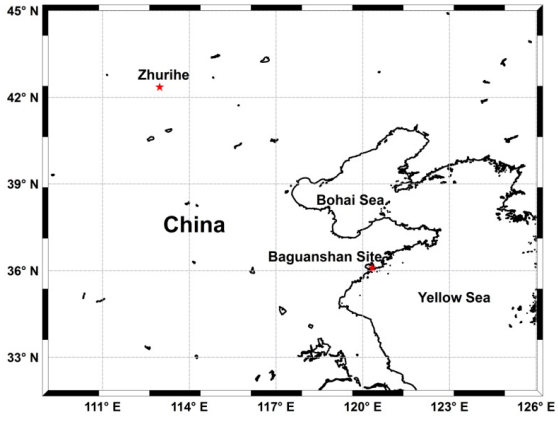


89 frequency of dust storms, from 2008 to 2011. Then, we analyzed the inorganic nitrogen concentrations
90 in the aerosol samples. The concentration, source apportionment and deposition flux of atmospheric
91 particulate inorganic nitrogen in dust events were examined.

92 **2 Materials and methods**

93 **2.1 Sampling**

94 As shown in Fig. 1, total suspended particles (TSP) were collected at the Baguanshan site in the
95 coastal region of the Yellow Sea. The samples were collected with quartz microfiber filters (Whatman
96 QM-A) using a high-volume air sampler (Model KC-1000, Qingdao Laoshan Electronic Instrument
97 Complex Co., Ltd.) with a flow rate of 1 $m^3$/min on the roof of an office building (36° 6' N, 120° 19' E,
98 77 m above sea level) approximately 1.0 km from the shore. The filters were heated at 450°C for 4.5 h
99 to remove organic compounds. Samples were collected on dust days and selected ND days in spring
100 from March 2008 to May 2011, with a sampling duration of 4 h for each sample. We refer to the ND
101 days as sunny and cloudy days before or after dust events in the following discussion.
102 The sand samples were collected at the Zhurihe site (42°22'N, 112°58'E)in the Hunshandake Desert,
103 one of main Chinese sand deserts, in April 2012. After sand samples were packed in clean plastic
104 sample bags, the samples were stored below -20°C.




105
106 **Figure 1.** Location of the aerosol and dust sampling site

107 **2.2 Analysis**

108 The aerosol samples were balanced in a relative humidity- and temperature-controlled chamber until

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

the particle weights remained constant. The mass concentrations of TSP were calculated according to the particle masses and the sampling volume. The sample membranes were then cut into several portions for analysis.

One portion of each aerosol sample and 0.1 g of parallel sand sample were ultrasonically extracted with ultra-pure water in an ice water bath, and the concentration of inorganic water-soluble ions was determined via ICS-3000 ion chromatography (Qi et al., 2011). The parallel sand samples collected from the Hunshandake Desert were analyzed using the same procedure.

One portion of each aerosol filter was cut into 60 $cm^2$ pieces and digested with $HNO_3$+$HClO_4$+HF (5:2:2 in volume) at 160°C using an electric heating plate. A blank membrane was also analyzed using the same procedure to ensure analytical precision. Cu, Zn, Cr, Sc and Pb were measured by inductively coupled plasma-mass spectrometry (Thermo X Series 2), while Al, Ca, Fe, Na and Mg were detected by inductively coupled plasma-atomic emission spectroscopy (IRIS Intrepid II XSP). The metal concentrations were determined by calibrating the measured concentrations of samples using membrane blanks.

**Table 1.** Detection limits, precisions and recoveries of water-soluble ions and metal elements

| Component | Measurement method | Detection limit ($\mu g \cdot L^{-1}$) | Precision (RSD%) | Recovery (%) |
|---|---|---|---|---|
| $NO_3^-$ | IC | 2.72 | 1.54 | 97 |
| $SO_4^{2-}$ | | 1.62 | 1.55 | 98 |
| $NH_4^+$ | | 0.4 | 1.10 | 97 |
| $Ca^{2+}$ | | 0.44 | 0.79 | 94 |
| Cu | ICP-MS (Xin et al., 2012) | 0.006 | 4.0 | 106 |
| Zn | | 0.009 | 2.5 | 102 |
| Cr | | 0.004 | 3.0 | 95 |
| Sc | | 0.002 | 2.4 | 97 |
| Pb | | 0.008 | 3.9 | 104 |
| Al | ICP-AES (Lin et al., 1998) | 7.9 | 0.6 | 103 |
| Ca | | 5.0 | 1.2 | 99 |
| Fe | | 2.6 | 0.7 | 104 |
| Na | | 3.0 | 0.6 | 99 |
| Mg | | 0.6 | 0.6 | 105 |
| Hg | CVAFS | 0.0001 | 6.6 | 105 |
| As | CVAFS | 0.1 | 5.0 | 98 |

One portion of each aerosol sample was digested with $HNO_3$ solution (10% $HNO_3$, 1.6 M) at 160°C for 20 min in a microwave digestion system (CEM, U.S.). Hg and As in sample extracts were analyzed

© Author(s) 2017. CC-BY 3.0 License.



following the U.S. Environmental Protection Agency method 1631E (U.S. EPA, 2002) using cold vapor atomic fluorescence spectrometry (CVAFS).

The detection limits, precisions and recoveries of water-soluble ions and metal elements are listed in Table 1.

### 2.3 Computational modeling

To determine the origins of sampled air masses, the 72 h air mass back trajectories were calculated for each TSP sample using TrajStat software (Wang et al., 2009) and the NOAA GDAS archive data (http:// www.arl.noaa.gov/ready/hysplit4.html). The air mass back trajectories were calculated at an altitude of 1000 m.

The positive matrix factorization (PMF) receptor modeling method (Paatero and Tapper, 1993; Paatero, 1997) was used to obtain the source apportionment of atmospheric particulates on dust and ND days. The correlation coefficient between the predicted and observed concentrations was 0.97.

Dry deposition velocities were obtained using Williams' model and accounting for particle growth (Qi et al., 2005). Relative humidity, air temperature and U10 from the National Centers for Environmental Prediction (NCEP)were used in the model as the meteorological inputs. Surface seawater temperature was collected from the European Centre for Medium-Range Weather Forecasts (ECMWF).The climatic and seawater temperature data had a six-hour resolution. According to a previously reported method (Qi et al., 2013), the dry deposition fluxes of the particles and the nitrogen species were calculated for dust and ND days.

### 2.4 Statistical analysis

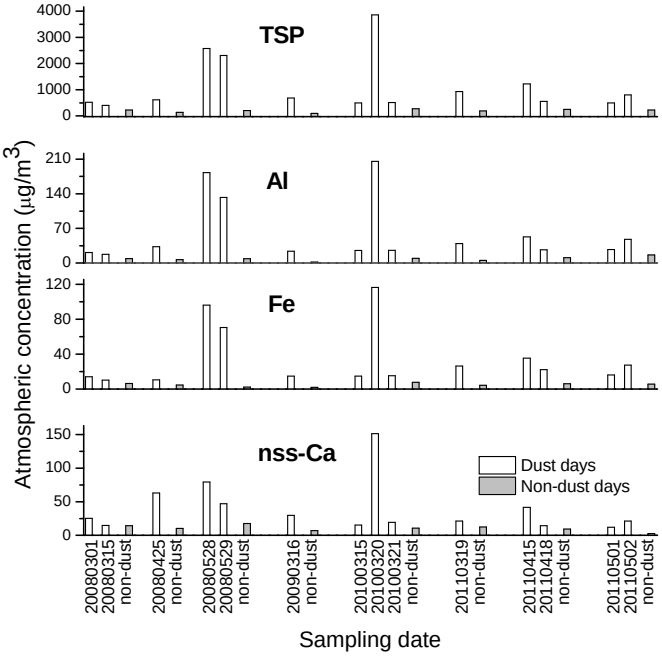
Meteorological data were obtained from the Qingdao Meteorological Administration (http://qdqx.qingdao.gov.cn/zdz/ystj.aspx) and the Meteorological Information Comprehensive Analysis and Process System (MICAPS) of the Meteorological Administration of China. $NO_2$ and air quality index (AQI) data were downloaded from the Qingdao Environmental Protection Bureau (http://www.qepb.gov.cn/m2/). Different weather characteristics, such as sunny days, cloudy days and dust days, were defined according to MICAPS information.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

153 **3 Results and discussion**

154 **3.1 Characterization of aerosol samples collected during dust events**




155

156 **Figure 2.** Concentrations of TSP, Al, Fe and nss-Ca in aerosol samples collected in the coastal region of the Yellow
157 Sea on non-dust and dust days from 2008 to 2011

158 To understand the impact of dust events on atmospheric particulate nitrogen in downwind areas, we
159 collected aerosol samples in the coastal region of the Yellow Sea in the spring from 2008 to 2011.We
160 examined the concentrations of particles and crustal and anthropogenic metals in aerosol samples.
161 Although metal concentrations in aerosols collected on different dust days varied, some
162 characterizations are highlighted below. The concentration of atmospheric particulate increased on dust
163 days. On non-dust (ND) days, aerosol particles varied in the range of 94-275 $\mu g \cdot m^{-3}$, with an average of
164 201 $\mu g \cdot m^{-3}$ (Fig. 2). Particle concentrations increased to 501-3857 $\mu g \cdot m^{-3}$on dust days. The TSP
165 concentration on dust days was 1.8-14.0 times (mean: 5.9) higher than that on ND days. The crustal
166 elements increased considerably with the increasing particle concentrations when dust events occurred.
167 As shown in Table 2, the enrichment factors (EF) of Al, Fe, Ca, and Mg were lower than ten on ND
168 days and decreased to less than three on dust days. These data are indicative of the primarily crustal

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

origins of these elements. We found that the mean concentrations of Sc, Al, Fe, Ca and Mg increased by over a factor of four as compared to those on ND days. Al concentrations in dust weather increased 1.7 to 21.9-fold (mean: 6.9) on ND days. The Al concentration of the "geometric mean×2GSD" (where GSD is the geometric standard deviation) was used as a criterion to define major AD events in areas of East Asia (Hsu et al., 2008). Al concentrations were higher than the criterion level in all dust samples, which indicated that the samples we collected on dust days were truly affected by dust events. Fe was 10.3 times higher on dust days than on ND days. Additionally, nss-Ca, a typical dust index, increased 3.6-fold on dust days (Fig. 2). The EF of the anthropogenic metal elements decreased on dust days. Cu, Pb, Zn, Cr, Hg and As had high EFs, much greater than 10, on ND days, which indicated that these metal elements were mainly from anthropogenic sources. The concentrations of these anthropogenic elements on dust days increased 1.1 to 7.2-fold on average compared to those on ND days. Additionally, the EFs of these anthropogenic elements decreased on dust days. These data are consistent with the very low EFs of these elements in dust particles. Thus, the influence of anthropogenic sources on atmospheric particulates decreased on dust days.

**Table 2.** The average concentrations and EFs of metal elements on dust and non-dust days

| Element | Concentration (ng/m$^3$) | | EF* | |
|---|---|---|---|---|
| | Non-dust days | Dust days | Non-dust days | Dust days |
| Sc | 1.11 | 13.90 | - | - |
| Al | $8.53\times10^3$ | $6.86\times10^4$ | 3.8 | 1.4 |
| Fe | $4.91\times10^3$ | $3.88\times10^4$ | 3. | 1.2 |
| Ca | $1.05\times10^4$ | $4.29\times10^4$ | 14.0 | 2.1 |
| Mg | $1.62\times10^3$ | $1.58\times10^4$ | 3.5 | 1.1 |
| Cu | 50.2 | 124.5 | 36.3 | 6.1 |
| Pb | 127.9 | 221.0 | 389.4 | 56.1 |
| Zn | 340.0 | 457.7 | 248.9 | 20.6 |
| Cr | 33.8 | 244.0 | 44.0 | 11.1 |
| Hg | 0.26 | 0.36 | 176.0 | 13.8 |
| As | 25.5 | 27.4 | 707.2 | 43.9 |

*The EF factor was calculated using Scandium as the reference element (Han et al., 2010).

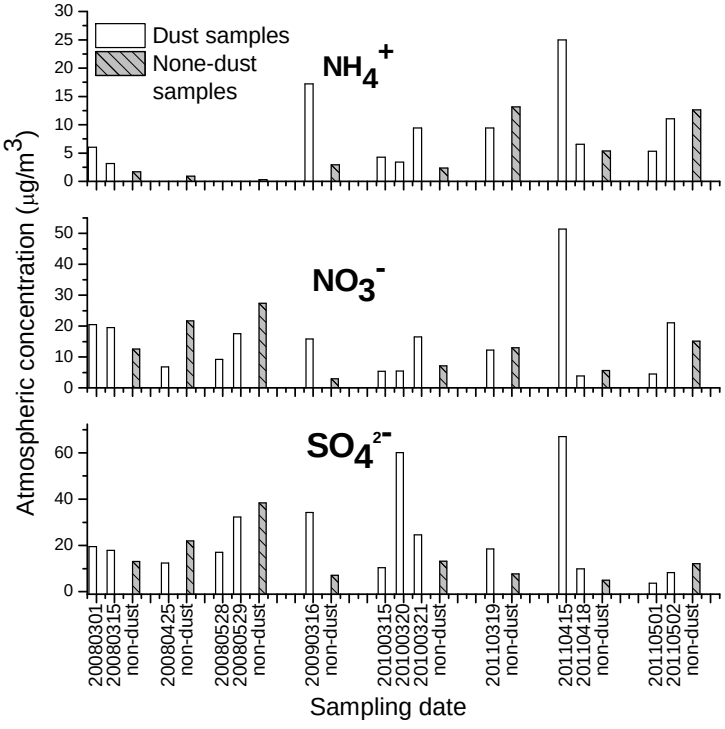
### 3.2 Concentration distribution of inorganic nitrogen in dust events

As discussed above, the concentrations of TSP and metal elements increased on dust days compared to those on ND days. However, the concentrations of inorganic nitrogen species $NH_4^+$ and $NO_3^-$ exhibited different variations in particles and crustal metal elements. The concentration of ammonium

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

189 increased by a factor of 1.2-5.7 on some dust days and decreased or had a very low concentration (less
190 than 20% of that on ND days) on other dust days (Fig. 3). Similar to ammonium, nitrate displayed two
191 different concentration variations on dust days. Nitrate concentrations increased by a factor of 1.4-9.2
192 on some dust days and decreased on other dust days. The secondary inorganic ion $SO_4^{2-}$ exhibited
193 concentration variations that were similar to those of nitrate. Therefore, the influence of dust on these
194 secondary ions was different from that on crustal metal elements, and the effect of dust on inorganic
195 nitrogen differed during different types of dust events.




196

197 **Figure 3.** $NH_4^+$, $NO_3^-$ and $SO_4^{2-}$ in aerosol samples collected in the coastal region of the Yellow Sea on non-dust
198 and dust days from 2008 to 2011

199 When we focused on inorganic nitrogen (IN), we found that IN concentrations could be grouped into
200 three cases (Table 3). IN concentrations were higher on dust days than on ND days for Case 1, while IN
201 was lower on dust days for Case 2. For Case 3, nitrate concentrations on dust days were less than on
202 ND days, while ammonium concentrations on dust days were slightly higher than those on ND days. To
203 understand the influence of dust on the nitrogen concentration, we compared the IN content in aerosols

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

from the coastal region of the Yellow Sea with sand particles and atmospheric aerosols from Duolun, a site very close to the Zhurihe Sand Desert. The Yellow Sea is mainly affected by dust storms from this sand source (Zhang and Gao, 2007). From Table 4, we found that nitrate and ammonium concentrations in the source sand particles were very low (less than 50 μg/g). Therefore, the dust particles in this source area that affect the Yellow Sea are nutrient poor. Although the IN content in aerosols at Duolun was higher than that in sand particles, the nitrate and ammonium concentrations were much lower than in the coastal region of the Yellow Sea. Therefore, we believe that the dust particles from the source have a dilution effect on atmospheric particulate nitrogen because of the low IN concentration in sand particles. When dust events occurred, the content of nitrogen per particle mass decreased because of the dilution of particulate nitrogen resulting from the increased number of nutrient-poor dust particles rapidly leaving the source area. The dilution effect depends on the intensity of dust events and the distance from the dust source. The stronger a dust storm is and the closer to the source, the stronger the dilution effect is.

**Table 3.** Average concentrations of inorganic nitrogen, TSP, NOx, Relative Humidity (RH) and T for each case in aerosol samples in the coastal region of the Yellow Sea

| | Sample numbers | TSP $\mu g \cdot m^{-3}$ | $NO_3^-$ $\mu g \cdot m^{-3}$ | $NH_4^+$ $\mu g \cdot m^{-3}$ | RH % | T ℃ | NOx $\mu g \cdot m^{-3}$ | Summary |
|---|---|---|---|---|---|---|---|---|
| Case 1 | 080301, 080315, 090316, 100321, 110415, 110502 | 696 | 24.1 | 14.9 | 46.6 | 13.8 | 62.7 | IN>ND |
| Case 2 | 080425, 080528, 080529, 110319, 110501 | 1199 | 3.1 | 2.6 | 29.2 | 19.8 | 52.3 | IN<ND |
| Case 3 | 100315, 100320, 110418 | 1639 | 4.9 | 4.7 | 10.1 | 10.1 | 70.7 | $NO_3^-$<ND $NH_4^+$≅ND |
| Non-dust | | 212 | 5.5 | 4.6 | 42.2 | 13.7 | 59.7 | |

During transport, the concentration of IN will increase by reacting with gas emitted into the air under

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.



appropriate reaction conditions or by mixing with polluted aerosol particles from a local source. Therefore, IN concentrations will increase in aerosols in downwind areas because of reactions on the dust surfaces or mixing with anthropogenic particles along the transport path. If no effective emission or absorption and reaction occur during transport, the IN content per particle mass (μg/g) will decrease in atmospheric aerosols in the downwind area. In Case 1, the particle concentration in the dust events was less than 700 $\mu g/m^3$, and the IN concentration in atmospheric aerosols increased by a factor of more than three in dust events in the coastal region of the Yellow Sea, which might be a result of slow transport or a weak dilution effect. High relative humidity (RH), low temperature and high $NO_X$ transport over a long distance and at a low speed are beneficial to the formation of nitrate and ammonium. In Cases 2 and 3, the particle concentrations were very high, with an average higher than 1100 $\mu g \cdot m^{-3}$, which indicated that the samples were affected by a strong dust storm or that the dust might be transported quickly. Concentrations of IN in aerosols in dust events decreased at the downwind site in Case 2 because the low RH, high temperature and low NOx during rapid transport were not advantageous to the formation of IN. In Case 3, the low IN content was a result of a strong dilution effect and low RH. In addition, the transport path affected the IN content of aerosol particles in the downwind area, and this influence will be discussed in Section 3.3.

**Table 4.** Comparison of the IN content in dust particles according to the dust source region (unit: μg/g)

| Sands sampled in Zhurihe | | Aerosols in Duolun* | | Aerosols in the coastal region of the Yellow Sea | |
|---|---|---|---|---|---|
| $NO_3^-$ | $NH_4^+$ | $NO_3^-$ | $NH_4^+$ | $NO_3^-$ | $NH_4^+$ |
| 25.46±22.87 | 4.21±1.03 | 1200 | 900 | Non-dust: 28,200±24,819 | Non-dust: 24,063±21,515 |
| | | | | Case 1: 34,892±9570 | Case 1: 22,571±7016 |
| | | | | Case 2: 5542±5117 | Case 2: 4758±5698 |
| | | | | Case 3: 6359±4697 | Case 3: 7059±5591 |

* Adapted from Cui (2009)

### 3.3 Influence of transport on particulate inorganic nitrogen

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

239 To understand the influence of transport on atmospheric particulate IN, we analyzed the air mass
240 trajectory of each sample (Fig. 4). The results showed that all dust samples were collected from north
241 or northwest air masses. The reported threshold of wind speed for dust mobilization in the Gobi Desert
242 ranges from 10-12 m/s (Choi and Zhang, 2008). We estimated 40.5±9.9 km/h as the average wind
243 speed during a dust storm according to Asia dust observations (He et al., 2008; Li et al., 2006;
244 Natsagdorjaet al., 2003; Zhan et al., 2009). If air masses were transported faster than 40.5 km/h, we
245 found that the IN content in most atmospheric aerosol samples was lower on dust days than on ND
246 days because of the strong dilution effect. This effect was observed in samples 080528, 080529,
247 110319 and 100315 (Table 5). If an air mass was transported over the ocean for some distance (ratio of
248 oversea to total distance of at least 10%), no matter how fast the transport velocity, the IN content
249 decreased because of the input of clean marine air, such as in samples 080425, 100320, 110418 and
250 110501. If the air mass was transported slowly (less than 42.4 km/h) or transported only a short
251 distance over the sea, with an oversea to total distance ratio of less than 10%, the IN content increased
252 in samples collected in the downwind area, such as in samples 080301, 090316, 100321 and 110502.
253 However, there were exceptions, such as samples 080315 and 110415, which had high transport speeds
254 and passed over the sea. Therefore, the IN content is related to not only the transport path and speed but
255 also local emissions and reaction conditions during transport.

256 **Table 5.** IN content, RH, NOx, transport speed and transport distance over the sea for atmospheric aerosol samples
257 on dust days

| Group | Sample number | TSP ($\mu g/m^3$) | $NO_3^-$ ($\mu g/g$) | $NH_4^+$ ($\mu g/g$) | Speed (km/h) | Distance over the sea (km) | Ratio of the distance over the sea to the total distance (%) |
|---|---|---|---|---|---|---|---|
| Case 1 IN>ND | 080301 | 527 | 38984 | 24107 | 35.1 | 0 | 0 |
| | 080315 | 410 | 47611 | 34130 | 53.4 | 262 | 6.8 |
| | 090316 | 688 | 23050 | 25012 | 59.5 | 0 | 0 |
| | 100321 | 519 | 31741 | 18155 | 49.2 | 0 | 0 |
| | 110415 | 1225 | 41970 | 20390 | 57.0 | 258 | 6.3 |
| | 110502 | 810 | 25995 | 13632 | 31.2 | 121 | 5.4 |
| Case 2 IN<ND | 080425 | 256 | 4089 | 372 | 29.3 | 253 | 12.0 |
| | 080528 | 2579 | 232 | 72 | 79.8 | 259 | 4.5 |

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.



| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 080529 | 2314 | 26 | 166 | 78.0 | 229 | 4.1 |
| | 110319 | 939 | 13088 | 10067 | 55.4 | 404 | 10.1 |
| | 110501 | 502 | 8924 | 10631 | 30.6 | 298 | 13.5 |
| Case 3 | 100315 | 501 | 10767 | 8515 | 58.7 | 183 | 4.3 |
| $NO_3^-$<ND | 100320 | 3857 | 1418 | 884 | 38.0 | 254 | 9.3 |
| $NH_4^+$≅ND | 110418 | 558 | 6891 | 11778 | 23.0 | 380 | 22.9 |

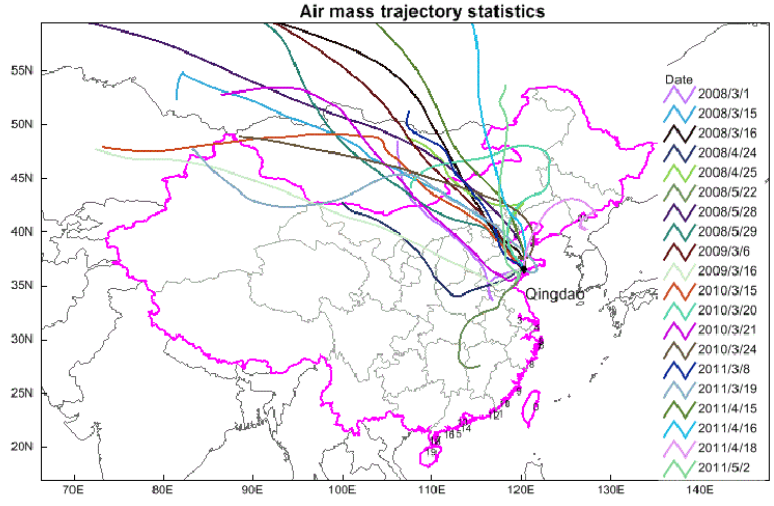
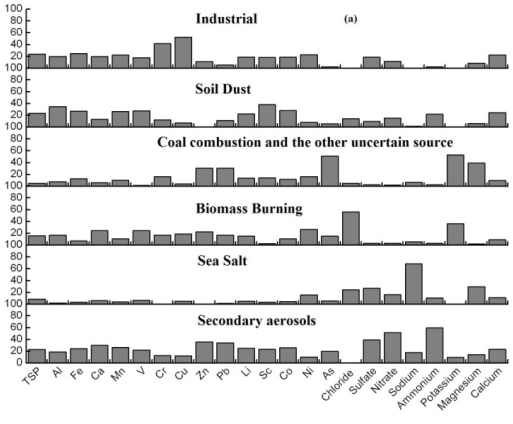



**Figure 4.** The 72-h backward trajectories for non-dust and dust samples from 2008 to 2011

### 3.4 Source apportionment of aerosols from dust and non-dust events



Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

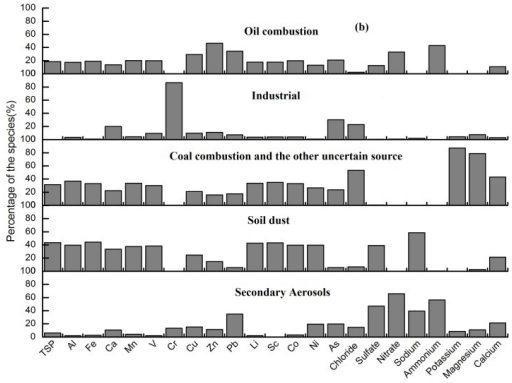



**Figure 5.** Source profiles of atmospheric aerosol samples collected on non-dust (a) and dust (b) days using the PMF model

The sources of atmospheric aerosols on dust and ND days were determined by running the PMF model (Paatero and Tapper, 1993; Paatero, 1997). As shown in Fig. 5,atmospheric aerosols on ND days were mainly from six sources: industry, soil dust, secondary aerosols, sea salt, biomass burning, coal combustion and the other uncertain sources (90% of the scaled residuals between -3 and +3; $r^2$=0.97). On dust days, the sources of aerosols differed from those on ND days, mainly including oil combustion, industry, soil dust, secondary aerosols, coal combustion and other uncertain sources. We compared the contributions of aerosol sources in dust and ND periods. As shown in Table 6, the contribution of soil dust increased from 23% to 36% on dust days, which is consistent with the high concentrations of TSP and crustal metals observed on dust days. Liu et al. (2014) also found that the contributions of dust aerosols to $PM_{10}$ increased by 31%-40% on dust days, which is greater than the 10%-20% contribution of local soil dust on ND days. The contributions of local anthropogenic sources decreased, especially those of secondary aerosols, which verified that the influence of anthropogenic sources on atmospheric particulates decreased on dust days. Coal combustion emissions were mainly a mixture of coal combustion and other pollutants emitted along the transmission path on dust days. Therefore, the sources of aerosol particles changed on dust days. Dust events had a great impact on aerosol sources in the downwind area. The influence of soil dust on aerosols and IN-loaded particles was greater than that on local sources on dust days. In fact, the contribution of soil dust to aerosols was related to the intensity of the dust storm and the transport path. However, we could not determine the contributions of dust to aerosols for the different dust cases because of the limited number of samples.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

286 **Table 6.** Sources and source contributions (expressed as %) calculated for aerosol samples collected during dust
287 and non-dust events

| Dust event | | Non-dust event | |
|---|---|---|---|
| Source | % of TSP | Source | % of TSP |
| Soil dust | 36 | Soil dust | 23 |
| Industrial | 21 | Industrial | 24 |
| Secondary aerosol | 6 | Secondary aerosol | 23 |
| Oil combustion | 6 | Biomass burning | 16 |
| Coal combustion and other uncertain sources | 31 | Coal combustion | 5 |
| | | Sea salt | 9 |

288 **3.5 Dry deposition fluxes of aerosol particles, particulate inorganic nitrogen and metals**

289 Dust events increased the concentration and deposition of aerosol particles during long-range
290 transport along the transport path. Fu et al. (2014) found that the long-range transport of dust particles
291 increased the dry deposition of $PM_{10}$ in the Yangtze River Delta region by 2398%. Some studies
292 observed enhancements in chlorophyll αfollowing a dust storm event (Tan and Wang, 2014; Banerjee
293 and Kumar, 2014). The deposition magnitude of dust varied greatly among dust storms, and only some
294 dust episodes were followed by increases in chlorophyll (Banerjee and Kumar, 2014). The role of dust
295 deposition as a nutrient source leading to an increase in algal blooms has not been adequately
296 addressed. To understand the influence of dust weather on the nitrogen deposition flux, we calculated
297 the dry deposition fluxes of aerosols particles, IN and metal elements during dust and ND periods using
298 the measured component concentrations and modeled dry deposition velocities obtained from Williams'
299 model (Qi et al., 2005)(Table 7).

300 Compared to that on ND days, the dry deposition flux of atmospheric particulate increased on dust
301 days. On ND days, the dry deposition flux of particles was 2800±700 mg/m$^2$/month in the coastal
302 region of the Yellow Sea, and the particle flux varied over a wide range from 5,200-65,000
303 mg/m$^2$/month under different dust conditions, with an average of 16,800 mg/m$^2$/month. The results
304 verified that dust events enhanced the dry deposition flux of atmospheric particulates. However, the dry
305 deposition flux of IN showed variations with particles. In Case 1, the dry deposition flux of IN
306 increased by a factor of 1.1-5.8, and the flux of atmospheric particles increased by a factor of 1.8-6.3.
307 In Cases 2 and 3, the dry deposition flux increased 2.3 to 23.2-fold compared to that on ND days.
308 Except for ammonium in Case 3, the dry deposition flux of particulate IN decreased by an average of

© Author(s) 2017. CC-BY 3.0 License.



41% in the case of high particle concentrations. The concentration of nitrate decreased 63% and 46% in Cases 2 and 3, respectively. Additionally, the ammonium flux decreased by 14% in Case 2, while in Case 3, ammonium was higher than that on ND days. We found that dust events sometimes led to an increase in the nitrogen input to the ocean relative to that during ND events, but it did not always occur depending on the chemical composition of the dust particles. As discussed, dust particles may carry abundant reactive nitrogen when they travel through polluted continental atmosphere. However, the relatively pure dust particles may be transported when no air pollution occurs along the dust transport route to oceans.

The dry deposition flux of Fe in atmospheric particulates increased by a factor of 2-25 on dust days compared to that on ND days. Atmospheric inputs of iron to the ocean can enhance primary production in high-nutrient, low-chlorophyll regions (HNLC) (Jickells et al., 2005). However, except for Pb and Zn in Case 2, the dry deposition fluxes of Cu, Pb and Zn increased with nitrogen and iron on dust days. These trace metals were found to have a toxic effect on marine phytoplankton and inhibit their growth (Bielmyer et al., 2006; Echeveste et al., 2012). In Case 3, dust was deposited in the ocean, the atmospheric supply of nitrogen decreased, and the atmospheric inputs of Fe and some toxic metals increased. Moreover, phytoplankton growth was affected by the addition of nutrient elements and toxic elements. The overall effect of dust deposition on primary productivity was a combination of these two effects. This is likely the reason why inhibition coexisted with the promotion of some phytoplankton species in incubation experiments using additions of AD in the southern Yellow Sea in the spring of 2011 (Liu et al., 2013).

The contribution of dust events to marine nitrogen input and primary production will be overestimated if the nutrient flux simply considers dust concentrations and a constant ratio of nutrients to particles. The atmospheric input of nitrogen to the ocean on dust days depends on the 'dilution effect' of a dust event. Dust subjected to long-range transport does not always increase the atmospheric input of nitrogen. Long-term observations of dust events must be performed to evaluate the contributions of dust to the biogeochemistry of nitrogen and primary production in oceans.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1183, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 28 February 2017
© Author(s) 2017. CC-BY 3.0 License.

Atmospheric Chemistry and Physics Discussions

**Table 7.** Dry deposition of aerosol particles (mg/m$^2$/month), particulate inorganic nitrogen (mg N/m$^2$/month) and some toxic trace metals (mg/m$^2$/month) on dust and non-dust days

| | Dry deposition flux | | | | | | |
|---|---|---|---|---|---|---|---|
| | Particles | $NO_3^-$-N | $NH_4^+$-N | Fe | Cu | Pb | Zn |
| Case 1 IN>ND | 9600± 4300 | 87±53 | 25±13 | 650±340 | 2±1 | 0.3±0.2 | 6±3 |
| Case 2 IN<ND | 18000± 11,000 | 13±18 | 5±7 | 1300±1000 | 3±2 | 0.08±0.04 | 4±1 |
| Case 3 $NO_3^-$<ND $NH_4^+$≅ND | 29,000± 31,000 | 26±6 | 17±8 | 2100±2200 | 6±1 | 0.20±0.02 | 5±3 |
| Non-dust | 2800± 700 | 48±33 | 8±8 | 190±110 | 1±1 | 0.09±0.1 | 5±4 |

## 4 Conclusion

The concentration of particulate IN exhibited a large variation from event to event on dust days, and a dust event did not simply increase nutrient concentrations. The effect of dust events on particulate nitrogen in the downwind region was determined by the dilution effect of a dust event, which depends on many factors, such as the dust storm intensity, transport speed and path, local source emissions during transport, meteorological state and atmospheric reactions. Dust events affect the source apportionment of aerosols. The contribution of soil dust to aerosols increased, while local anthropogenic sources decreased during a dust event. The contribution of dust to aerosols must be studied further under different IN conditions. Dust events enhance the input of atmospheric particulates via dry deposition. However, the influence of dust events on the input of nitrogen to the ocean is still uncertain. The dry deposition flux of IN on dust days decreased when a strong dilution effect was present. The contribution of dust events to marine nitrogen inputs and primary production could be overestimated if the dry deposition flux of nutrients is estimated using only particulate concentrations on dust days.

*Acknowledgments.* This work was supported by the Department of Science and Technology of the P. R. China through the State Key Basic Research & Development Program under Grant No. 2014CB953701 and the National

© Author(s) 2017. CC-BY 3.0 License.



Natural Science Foundation of China (No. 41375143).We thank Prof. Xiaohong Yao for the valuable discussion regarding this research. We also express our appreciation to Tianran Zhang for help with sand sampling.

## References

Banerjee, P., and Prasanna Kumar, S.: Dust-induced episodic phytoplankton blooms in the Arabian Sea during winter monsoon, Journal of Geophysical Research Oceans, 119, 7123-7138, 2014.

Bielmyer, G. K., Grosell, M., and Brix, K. V.: Toxicity of silver, zinc, copper, and nickel to the copepod Acartiatonsa exposed via a phytoplankton diet, Environmental science & technology, 40, 2063-2068, 2006.

Choi H., Zhang Y. H. : Predicting duststorm evolution with the vorticity theory, Atmospheric Research, 89, 338–350, 2008.

Cui W. L.: Chemical transformation of dust components and mixing mechanisms of dust with pollution aerosols during the long range transport from north to south China, M.S. thesis, Department of Environmental Science and Engineering, Fudan University, 32-38 pp., 2009.

Duce, R. A., and Zamora, L.: Impacts of atmospheric anthropogenic nitrogen on the open ocean, Science, 320, 893-897, 2008.

Echeveste, P., Agustí, S., and Tovar-Sánchez, A.: Toxic thresholds of cadmium and lead to oceanic phytoplankton: cell size and ocean basin-dependent effects, Environmental Toxicology and Chemistry, 31, 1887–1894, 2012.

EPA, U.: Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry, US Environmental Protection Agency Washington, DC, 2002.

Fitzgerald, E., Ault, A. P., Zauscher, M. D., Mayol-Bracero, O. L., and Prather, K. A.: Comparison of the mixing state of long-range transported Asian and African mineral dust, Atmospheric Environment, 115, 19-25, 2015.

Fu, X., Wang, S. X., Cheng, Z., Xing, J., Zhao, B., Wang, J. D., and Hao, J. M.: Source, transport and impacts of a heavy dust event in the Yangtze River Delta, China, in 2011, Atmospheric Chemistry & Physics, 14, 1239-1254, 2014.

Guo, C., Yu, J., Ho, T. Y., Wang, L., Song, S., Kong, L., and Liu, H.: Dynamics of phytoplankton community structure in the South China Sea in response to the East Asian aerosol input, Biogeosciences, 9, 1519-1536, 2012.

Han, X.: Air Quality Modeling for of a Strong Dust Event in East Asia in March 2010, Aerosol & Air Quality Research, 12, 615-628, 2012.

He Q., Wei W., Li X., Aili M., Li S.: Profile Characteristics of Wind Velocity, Temperature andHumidity in the Surface Layer during a Sandstorm Passing Taklimakan Desert Hinterland, Desert and Oasis Meteorology, 2(6), 6-11, 2008.

Hsu, S. C., Liu, S. C., Huang, Y. T., Lung, S. C. C., Tsai, F., Tu, J. Y., and Kao, S. J.: A criterion for identifying Asian dust events based on Al concentration data collected from northern Taiwan between 2002 and early 2007, Journal of Geophysical Research Atmospheres, 113, 1044-1044, 2008.

Jaafar, M., Baalbaki, R., Mrad, R., Daher, N., Shihadeh, A., Sioutas, C., and Saliba, N. A.: Dust episodes in Beirut and their effect on the chemical composition of coarse and fine particulate matter, Science of the Total Environment, 496C, 75-83, 2014.

Jickells, T., An, Z., Andersen, K. K., Baker, A., Bergametti, G., Brooks, N., Cao, J., Boyd, P., Duce, R., and Hunter, K.: Global iron connections between desert dust, ocean biogeochemistry, and climate,

© Author(s) 2017. CC-BY 3.0 License.



science, 308, 67-71, 2005.

KaiZhang, ZK., and Gao, H.: The characteristics of Asian-dust storms during 2000–2002: From the source to the sea, Atmospheric Environment, 41, 9136-9145, 2007.

Kang, E., Han, J., Lee, M., Lee, G., and Kim, J. C.: Chemical characteristics of size-resolved aerosols from Asian dust and haze episode in Seoul Metropolitan City, Atmospheric Research, 127, 34-46, 2013.

Li N., Liu Z. , Yang H., Wu J., Lei Y. : Change of wind speed and soil moisture during occurrence of dust storms, Journal of Natural Disasters, 15(6), 28-32, 2006.

Li, W., Shao, L., Shi, Z., Chen, J., Yang, L., Yuan, Q., Yan, C., Zhang, X., Wang, Y., and Sun, J.: Mixing state and hygroscopicity of dust and haze particles before leaving Asian continent, Journal of Geophysical Research Atmospheres, 119, 1044–1059, 2014.

Lin, X., Liu, C., and Zhang, H.: Determination of Metal Elements in Aerosol by ICP-AES, Rock & Mineral Analysis, 1998, 17(2): 143-146.

Liu, Q., and Bei, Y.: Impacts of crystal metal on secondary aliphatic amine aerosol formation during dust storm episodes in Beijing, Atmospheric Environment, 128, 227-334, 2016.

Liu, Q., Liu, Y., Yin, J., Zhang, M., and Zhang, T.: Chemical characteristics and source apportionment of PM 10 during Asian dust storm and non-dust storm days in Beijing, Atmospheric Environment, 91, 85-94, 2014.

Liu, Y., Zhang, T. R., Shi, J. H., Gao, H. W., and Yao, X. H.: Responses of chlorophyll a to added nutrients, Asian dust, and rainwater in an oligotrophic zone of the Yellow Sea: Implications for promotion and inhibition effects in an incubation experiment, Journal of Geophysical Research Biogeosciences, 118, 1763–1772, 2013.

Ma, Q., Liu, Y., Liu, C., Ma, J., and He, H.: A case study of Asian dust storm particles: Chemical composition, reactivity to SO 2 and hygroscopic properties, Journal of Environmental Sciences, 24, 62-71, 2012.

Natsagdorj L., Jugder D., Chung Y. S.: Analysis of dust storms observed in Mongolia during1937–1999, Atmospheric Environment, 37, 1401–1411, 2003.

Paatero, P., and Tapper, U.: Analysis of different modes of factor analysis as least squares fit problems, Chemometrics and Intelligent Laboratory Systems, 18, 183-194, 1993.

Paatero, P.: Least squares formulation of robust non-negative factor analysis, Chemometrics& Intelligent Laboratory Systems, 37, 23-35, 1997.

Qi, J. H., Gao, H. W., Yu, L. M., and Qiao, J. J.: Distribution of inorganic nitrogen-containing species in atmospheric particles from an island in the Yellow Sea, Atmospheric Research, 101, 938-955, 2011.

Qi, J. H., Shi, J. H., Gao, H. W., and Sun, Z.: Atmospheric dry and wet deposition of nitrogen species and its implication for primary productivity in coastal region of the Yellow Sea, China, Atmospheric Environment, 81, 600-608, 2013.

Qi, J., Li, P., Li, X., Feng, L., and Zhang, M.: Estimation of dry deposition fluxes of particulate species to the water surface in the Qingdao area, using a model and surrogate surfaces, Atmospheric Environment, 39, 2081-2088, 2005.

Shi, J. H., Gao, H. W., Zhang, J., Tan, S. C., Ren, J. L., Liu, C. G., Liu, Y., and Yao, X.: Examination of causative link between a spring bloom and dry/wet deposition of Asian dust in the Yellow Sea, China, Journal of Geophysical Research Atmospheres, 117, 127-135, 2012.

Tan, S. C., and Wang, H.: The transport and deposition of dust and its impact on phytoplankton growth

© Author(s) 2017. CC-BY 3.0 License.

in the Yellow Sea, Atmospheric Environment, 99, 491-499, 2014.

Wang, L., Du, H., Chen, J., Zhang, M., Huang, X., Tan, H., Kong, L., and Geng, F.: Consecutive transport of anthropogenic air masses and dust storm plume: Two case events at Shanghai, China, Atmospheric Research, 127, 22–33, 2013.

Wang, Q., Zhuang, G., Huang, K., Liu, T., Lin, Y., Deng, C., Fu, Q., Fu, J. S., Chen, J., and Zhang, W.: Evolution of particulate sulfate and nitrate along the Asian dust pathway: Secondary transformation and primary pollutants via long-range transport, Atmospheric Research, 169, 86-95, 2015.

Wang, Y. Q., Zhang, X. Y., and Draxler, R. R.: TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data, Environmental Modelling& Software, 24, 938-939, 2009.

XIN, W.-c., LIN, X.-h., and XU, L.: ICP-MS Determination of 34 Trace Elements in Marine Sediments [J], Physical Testing and Chemical Analysis (Part B: Chemical Analysis), 4, 029, 2012.

Xu, J., Wang, Z., Yu, G., Qin, X., Ren, J., and Qin, D.: Characteristics of water soluble ionic species in fine particles from a high altitude site on the northern boundary of Tibetan Plateau: Mixture of mineral dust and anthropogenic aerosol, Atmospheric Research, 143, 43-56, 2014.

Yang, D., Yan, P., and Xu, X.: Characteristics of aerosols under dust and sand weather in Beijing, Quarterly Journal of Applied Meteorology Meteorlolgy, 2002S1, 185-194, 2002.

Zhan, K., Zhao, M., Fang, E., Yang, Z., Zhang, Y., Guo, S., Zhang, J., Wang, Q., and Wang, D.: The wind speed characteristics of near-surface vertical gradient of 50m in sandstorm process in 2006, Journal of Arid Land Resources & Environment, 23, 100-105, 2009.

Zhang, W., Zhuang, G., Huang, K., Li, J., Zhang, R., Wang, Q., Sun, Y., Fu, J. S., Chen, Y., and Xu, D.: Mixing and transformation of Asian dust with pollution in the two dust storms over the northern China in 2006, Atmospheric Environment, 44, 3394-3403, 2010.

Zhang, Y., Yu, Q., Ma, W., and Chen, L.: Atmospheric deposition of inorganic nitrogen to the eastern China seas and its implications to marine biogeochemistry, Journal of Geophysical Research Atmospheres, 115, 3421-3423, 2010.