June 8, 2017

Dear editor

Here, we submit the revised manuscript (acp-2016-853) entitled, “Limited production of sulfate and nitrate on front-associated dust storm particles moving from desert to distant populated areas in northwestern China” to the special issue of “Anthropogenic dust and its climate impact” of your journal *Atmospheric Chemistry and Physics*. We would like to thank the two referees for their careful and constructive reviews. Based the comments from the referees, we have revised carefully the manuscript.

Attached are the list of all relevant changes made in the manuscript, our point-by-point responses to all review remarks and a marked-up manuscript version in which all changes were marked with underlines.

Thanks for your help.

Yours sincerely,

Daizhou Zhang

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## List of all relevant changes made in the manuscript

1. **In line 12-15 of Page 2:** The sentence **"The significant sulfate and nitrate reported in dust-associated samples in previous studies were more likely produced on locally-emitted and urban mineral particles or from soil-derived sulfate rather than being produced via chemical conversions on desert dust particles."** is changed to **"The significant sulfate and nitrate reported in storm-associated samples in previous studies were more likely from locally-emitted and urban mineral particles or from soil-derived sulfate, because the weather conditions in those studies indicated that the air from which the samples were collected very likely contained a lot of particles from local emissions."**

2. **In line 8 of Page 3:** "RH" was changed to "**relative humidity (RH)**"

3. In line 23-24 of Page 4: The last sentence of the second paragraph of subsection 2 "**This sample collection ensured that mineral particles collected on the filters were dust particles from the desert and there should be no influence of anthropogenic pollutants from the village or the city considered in the samples.**" was modified into **"This sample collection ensured that mineral particles collected on the filters were dominated by dust particles from the desert and possible influence of anthropogenic pollutants from the village or the city was suppressed."**

4. **In line 4 of Page 5:** "April 31" was corrected into "**April 30**".

5. **From line 31 of Page 5 to line 2 of Page 6**: The sentences **"An energy dispersive X-Ray fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V., the Netherlands) was used to quantify elements in the samples of the remained parts of sample filters. Five crustal elements (K, Ca, Ti, Mn, Fe and Ba) and two common anthropogenic trace elements (Zn and Pb), were quantitatively determined. Analytical uncertainties, as checked by parallel analysis of the NIST standard reference material (SRM-2683), were about or less than 10% for the detected elements."** was added to describe how the elements were analyzed.

6. **In line 7-8 of Page 6:** We added "**These values were close to the levels of the relative mass ratios of sulfate in TSP or $PM_{10}$ in samples collected under dust conditions at the Gobi Desert which were reported in previous studies (Table S1).**"

7. **In line 25-26 of Page 6**: The sentence **"although some small-scale mixing might occur in the front"** is added after the sentence **"The cold fronts are the boundaries between the local or regional anthropogenically-polluted air and the long-distance transported air because the movement of air on a synoptic scale is approximately adiabatic, i.e.**

**the air is hardly mixed with thermodynamically-different air it meets."**.

8. **In line 4-7 of Page 7:** We added the sentences "**Zn and Pb are two common anthropogenic trace elements in urban air. Their ratios to Fe in the dust samples in the postfrontal air were much lower than those in the prefrontal air and very close to those in the desert air (Table 3), further suggesting the limited influence of pollution on desert dust particles in the postfrontal air.**"

9. **In line 2 of Page 8: "completely"** was changed to **"mainly"**

10. **In line 10-12 of Page 8:** We added "**These values were close to the levels of the relative mass ratios of nitrate in TSP or $PM_{10}$ in samples collected under dust conditions at the Gobi Desert which were reported in previous studies (Table S1).**"

11. **In line 14 of Page 7**: **"had been"** was revised into **"was likely"**

12. **In line 22-25 of Page 8:** The descriptions **"Note this rate should be the maximum rate because not all the nitrate must have been produced on dust particles and the increase of the relative amount of nitrate during the movement of a dust plume from the desert to Xi'an could have been the consequence of possible different removal rates of dust particles and nitrate-containing particles.**" are added right after the descriptions of the estimated rate values of nitrate production on dust particles.

13. **In line 27 of Page 9:** "**Table 3**" was changed into "**Table 4**"

14. **In line 22 of Page 10:** "mineral/TSP" was changed to "**mineral/TSP (total suspended particulates) ratios**"

15. **In line 21-24 of Page 10:** "**Peak 1**" was removed from the text. **The sentence "…, the mineral/TSP ratios in samples with the highest TSP loading (Peak I described in that study) were significantly lower than those in samples collected after the occurrence of maximum aerosol loading, indicating that the samples around Peak I were not dust particles from desert areas only."** was changed to **"…, the mineral/TSP ratios in samples of the highest TSP loading were significantly lower than those in samples collected after the occurrence of maximum aerosol loading, indicating that the samples at the highest TSP moment were not dust particles from desert areas only."**

16. **In line 21-26 of Page 11**: **"Significant sulfate and nitrate in dust storm periods in China reported in previous studies were likely produced on locally-emitted and urban mineral particles, in addition to soil-derived sulfate, and they were unlikely produced via chemical conversions on dust particles from deserts."** is changed into (as an individual paragraph) **"Significant sulfate and nitrate in dust storm periods in China**

**reported in previous studies were likely from locally-emitted and urban mineral particles, in addition to soil-derived sulfate, and they were unlikely produced via chemical conversions on dust particles from deserts. The major reason is that, in those studies, the air from which the samples were collected had been significantly influenced by local emissions. Without a proper evaluation of the contribution of sulfate and nitrate in the samples by locally-emitted and urban mineral particles, i.e., non-desert mineral particles, it is not safe to attribute the all detected sulfate and nitrate to the production on dust-storm particles."**

17. **In line 26-28 of Page 12: the bibliography of Dong et al. (2016) was included in the reference list.**

18. **In line 1 of Page 17:** The title of Table 1 was changed to **"Summary of weather conditions at the sample collection"**

19. **In Page 19: The table for mass ratios of Ca, Fe, Ti, Mn, Ba, Zn and Pb to Fe in the samples was added in the manuscript as Table 3, and the Table 3 in the last submission was changed into Table 4.**

20. **In the supplementary information: Table S1 was added.**

**Point-by-point response to all review remarks**

***Reviewer# Dr. Barry Huebert***

**The authors greatly appreciate the careful and detailed review by *Dr. Barry Huebert***

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**Introduction:**

**The responses in letter are similar to our responses uploaded on 12 March 2017 to response the comments and questions by Dr. B. Huebert. In this letter, we added the descriptions of the revised parts (the parts in Bold and Underlined) in the manuscript upon the comments.**

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***The authors have made a handful of bulk aerosol composition measurements near source and downwind (urban) of dust storms, separated by several days. (The transit time of air masses between the sites would be about 6 hours.) They use concentration and elemental ratio-differences between these locations to infer the formation or uptake of nitrate and sulfate with time.***

***They undertake a kind of Lagrangian analysis, as if the desert dust they first sampled had moved to Xian by the time they sampled there. (It had in fact moved past the downwind sampling site several days earlier.) The increase in the $NO_3^-$/Ca ratio, in particular, is used to infer a nitrate formation or uptake rate. To compute a trend, one would need more samples and time-coordinated sampling. The uncertainty in the representativeness of the samples is at least as large as the apparent observed upwind/downwind differences. The high natural levels of sulfate in the dust (12%) no doubt vary, adding uncertainty to the inference of a trend.***

**Response:** We want to make clear that (1) the natural level of sulfate we showed in this paper was around 1.2% (Table 2) and was not 12%, and (2) we did not use the $NO_3^-$/Ca ratio to infer a nitrate formation or uptake rate. Please check the contents of the manuscript again. For the formation of sulfate on dust storm particles, the fact we encountered is that the concentration level of sulfate did not increased (the level was 0.91% at the urban site; Table 3). Even if we consider all the sulfate observed at the urban site were produced via surface reactions, the production was still much smaller than that in polluted urban atmosphere. So we considered that sulfate was hardly produced. For the formation of nitrate, we found a small increase (the level was 0.12% at the desert site and 0.22% at the urban site), and then we used the state-of-the-art numerical scheme of nitrate formation on dust particles (Fairlie et al. 2010) to estimate (with the conditions of possible nitric concentration, dust concentration, and the history of the air parcel) if the production of nitrate on dust particles was consistent with the level we observed at the urban site. We found they were in the same order (Page 8 Line 18 – Page 9 Line 8). In fact, similar to sulfate, even if we consider all the nitrate observed at the urban site were produced via surface reactions, the production was still very small than that in polluted urban atmosphere.

***There also aren't enough pieces of data to compute a defendable rate of ion formation on the dust. The experiment was poorly-posed to do so. Since only two sites were involved, it is***

***impossible to infer nitrate increase over the desert vs nitrate picked up upon the dust's arrival in the urban area, based on their observations.***

**Response:** We do not think that data from more or less dust cases at the desert site and at the urban site are the key issue, although data from more cases are better. The key point is if we get the common understandings from the data, no matter the data are more or less. There are a large number of published papers on the formation of sulfate and nitrate on dust particles observed in urban areas in mainland China. To the extent of what we can find, we checked all data in the published literatures on the formation on dust storm particles in post-frontal air. We confirmed the common results as we described in the manuscript: the production of the two salts on dust storm particles in postfrontal air was limited (some results in Table 3). So we think, even we increase the cases of dust observation at the urban site, we will encounter the same results. For the data at the desert site, to the extent of our knowledge, the results reported in this study are the only data from a series samples that were carefully collected at a short time resolution from a dust storm at a desert dust dune all over the world. Yes, more case data will be better. The fact is that we have been there several times and we failed in getting more series of data from dust storms except for some pieces of data due to technique problems, although this is not a scientific reason (*please imagine how can collect a series of dust samples at 2-hour time resolution at a dust dune in a desert area from a severe dust storm without electricity supply*). For compensating this problem, we carefully investigated all published papers of studying nitrate and sulfate in dust from the Gobi Desert at the observation sites in or near this desert area which used samples from routine observation sites near Chinese desert areas, and checked the data from samples that were really obtained under dust conditions or after dust storm arrival (some discussions in section 3.3) of desert dust. We confirmed that the concentration of sulfate and nitrate from the samples under dust conditions in those papers was close to or in the same order as our results in this study (Supplementary Table S1). So we consider our results on sulfate and nitrate at the desert can represent the common level of sulfate and nitrate of natural dust particles at the desert site.

**In the revision, we added that "These values were close to the levels of the relative mass ratios of sulfate in TSP or $PM_{10}$ in samples collected under dust conditions at the Gobi Desert which were reported in previous studies (Table S1)." at the end of 1st paragraph of subsection 3.1, where the concentration of sulfate in dust samples at the desert site was described.**

**For nitrate at the desert site, we added "These values were close to the levels of the relative mass ratios of nitrate in TSP or $PM_{10}$ in samples collected under dust conditions at the Gobi Desert which were reported in previous studies (Table S1)." at the end of 1st paragraph of subsection 3.2, where the concentration of nitrate in dust samples at the desert site was described.**

**In addition, the table mentioned in these descriptions was added in the supplementary information as Table S1. The bibliography of Dong et al. (2016) was also included in the reference list.**

Table S1. The relative mass ratio (%) of nitrate and sulfate in samples collected under dust conditions at the Gobi Desert reported in previous studies.

| Study sites | Size fractions | $NO_3^-$ | $SO_4^{2-}$ | References |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| Ejin Qi, Badain Jaran desert [a] | TSP | 0.04 | 0.63 | Mori et at., 2002 |
| Sonid Youqi-Huade-Zhangbei | TSP | 0.025 | 0.46 | Mori et at., 2003 |
| Gobi desert [b] | $PM_{10}$ | 0.084 | 0.47 | Dong et al., 2016 |
| Tonggunao'er | TSP | 0.12±0.11 | 1.2±0.1 | This study |

[a] Estimated from regressions of aerosol chemical composition on distance from the dust source. [b] Based on the local measurement data reported by Huang et al. (2010).

Mori, I., Nishikawa, M., Quan, H., & Morita, M. (2002). Estimation of the concentration and chemical composition of kosa aerosols at their origin. *Atmos. Environ.*, *36*(29), 4569–4575, doi: 10.1016/S1352-2310(02)00489-2.

Mori, I., Nishikawa, M., Tanimura, T., & Quan, H. (2003). Change in size distribution and chemical composition of kosa (Asian dust) aerosol during long-range transport. *Atmos. Environ.*, *37*(30), 4253–4263, doi: 10.1016/S1352-2310(03)00535-1.

Dong, X., Fu, J. S., Huang, K., Tong, D., and Zhuang, G. (2016). Model development of dust emission and heterogeneous chemistry within the Community Multiscale Air Quality modeling system and its application over East Asia, Atmos. Chem. Phys., 16, 8157-8180, doi:10.5194/acp-16-8157-2016.

***Line 22, Section 2: Here they argue that there should be no pollution in the samples, but in the Conclusions, they suggest otherwise; indeed one cannot sample in an urban area and expect to avoid all pollution.***

**Response:** In this section, we concluded that there should be no pollution in the postfrontal samples of our study. Although the usage of "no" makes the meaning very absolute, this does not contradict the conclusion that significant sulfate and nitrate in dust storm periods in China reported in previous studies were likely produced on locally-emitted and urban mineral particles. The reasons are that the separation of the prefrontal pollutants and the postfrontal dust plume was not considered and/or dust samples were not collected from postfrontal air only in those previous studies.

**In the revision, this sentence was modified into "This sample collection ensured that mineral particles collected on the filters were dominated by dust particles from the desert and possible influence of anthropogenic pollutants from the village or the city was suppressed."**

Yes, it is impossible to completely avoid pollution during any sample collection in an urban area. However, the question here is if the pollution is severe enough to lead to a considerable production of sulfate and nitrate on dust particles. The purpose of this study is to answer this question. As we mentioned in the manuscript, if the postfrontal samples were considerably polluted, there should have been some levels of ammonia (a common anthropogenic anion in urban air). The fact is that $NH_4^+$ concentration in the postfrontal air was lower than the detection limit in the first sample and increased slightly in the second and third samples. We also analyzed Zn and Pb, which are usually considered as anthropogenic trace elements in urban air. Their ratios to Fe in the dust in the postfrontal air were significantly lower than those in the prefrontal air and were very close to those in the desert air (Table 3). So there should be unlikely considerable pollution in the samples.

Table 3 Mass ratios of Ca, Fe, Ti, Mn, Ba, Zn and Pb to Fe in the samples at the two sites

| Samples | Ca/Fe | K/Fe | Ti/Fe | Mn/Fe | Ba/Fe | Zn/Fe | Pb/Fe |
|---|---|---|---|---|---|---|---|
| Tengger Desert (April 24, 2014) | | | | | | | |
| T1 | 1.47 | 0.54 | 0.084 | 0.023 | 0.013 | 0.003 | 0.0014 |
| T2 | 1.47 | 0.55 | 0.082 | 0.023 | 0.013 | 0.0023 | 0.0011 |
| T3 | 1.57 | 0.57 | 0.086 | 0.024 | 0.012 | 0.002 | 0.0009 |
| Xi'an (May 1, 2014) | | | | | | | |
| X1[a] | NA | NA | NA | NA | NA | NA | NA |
| X2 | 1.86 | 0.66 | 0.084 | 0.028 | 0.012 | 0.037 | 0.009 |
| X3 | 2.16 | 0.63 | 0.087 | 0.039 | 0.008 | 0.010 | 0.004 |
| X5 | 1.76 | 0.62 | 0.089 | 0.045 | 0.018 | 0.003 | 0.0009 |
| X6 | 1.44 | 0.63 | 0.092 | 0.031 | 0.015 | 0.003 | 0.0008 |
| X7 | 1.80 | 0.68 | 0.089 | 0.024 | 0.022 | 0.003 | 0.0009 |

[a] No enough sample for analysis

**In the revision, the table mentioned in these descriptions was added in the manuscript as Table 3, and Table 3 in the last submission was changed into Table 4.**

**We added the sentences "An energy dispersive X-Ray fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V., the Netherlands) was used to quantify elements in the samples of the remained parts of sample filters. Five crustal elements (K, Ca, Ti, Mn, Fe and Ba) and two common anthropogenic trace elements (Zn and Pb), were quantitatively determined. Analytical uncertainties, as checked by parallel analysis of the NIST standard reference material (SRM-2683), were about or less than 10% for the detected elements." at the end of the last paragraph of subsection 2, to describe how the elements were analyzed.**

**At the end of the fourth paragraph of subsection 3.1, we added the sentences "Zn and Pb are two common anthropogenic trace elements in urban air. Their ratios to Fe in the dust samples in the postfrontal air were much lower than those in the prefrontal air and very close to those in the desert air (Table 3), further suggesting the limited influence of pollution on desert dust particles in the postfrontal air.**"

***Typo: there is no April 31st.***

**Response: It is April 30. We corrected in the revised version.**

***Lines 12-13, P5: Even though I have not seen the supplementary figures, I would in principal disagree that the changes in dust particles during transport would be the same for each event. That would need to be shown.***

**Response:** In the supplements, we show the back-trajectory routes from the desert site and the Xi'an site during two dust storm periods (Figure S2 and Figure S3) and also the vertical thermodynamic structure of postfrontal dust plumes (Figure S6) when the dust samples were collected. The figures show that the two dust storms were really very similar according to their transporting routes and thermodynamic structures. Since these data are from public sites and other simulations, we do not think that it is a good idea to show them in the main body of the manuscript.

Yes, it is not absolutely correct that "the changes in dust particles during transport

would be the same for each event", and every dust storm must be more or less different from other dust storms. However, this does not mean we cannot find new understandings from a single dust storm which are common for dust storms. A single dust storm should have some common characteristics in a number of dust storms from the same desert. For your reference, we show the figures here to illustrate the similarities of the transport and the vertical thermodynamic structures of the two dust storms from which we collected samples.

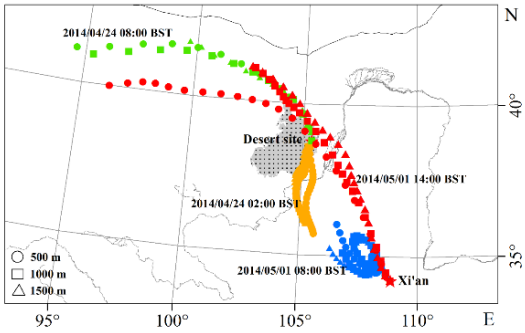


Figure S2: Backward trajectories from the desert site (2014/04/24) and Xi'an site (2014/05/01) from the HYSPLIT model (www.arl.noaa.gov/HYSPLIT.php). (BST = GMT + 08:00)

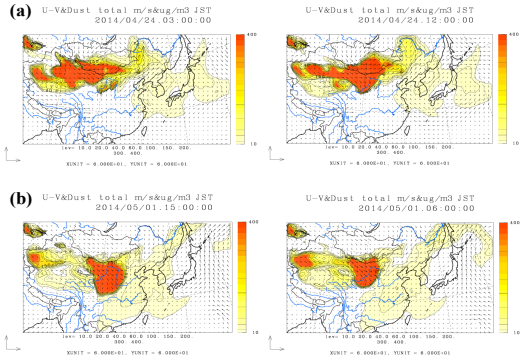


Figure S3: CFORS model output for boundary layer (surface - 1000m) dust concentration (μg/m$^3$, color in log scale) and wind vector at 1000m of East Asia during the sampling periods at desert site (a) and Xi'an (b). (http://www-cfors.nies.go.jp/~cfors/index-j.html) (JST = GMT + 09:00)

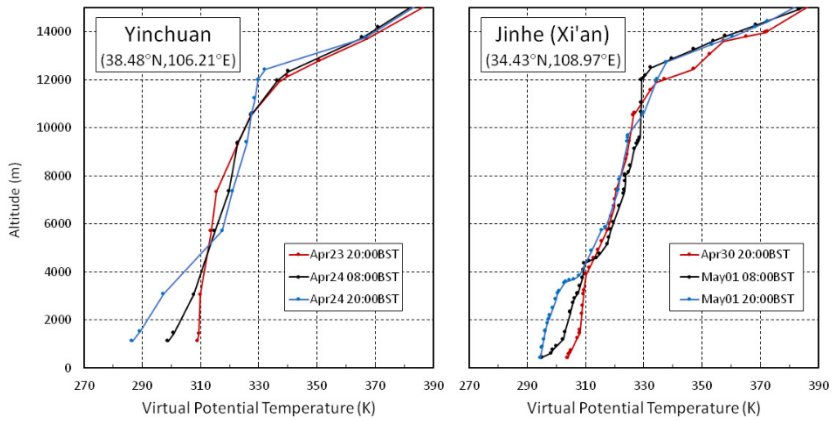


Figure S6: Vertical profiles of virtual potential temperature near the surface at Yinchuan (38.48°N, 106.21°E), the WMO sounding station closest to the desert site, and at Jinhe (34.43°N, 108.97°E), a suburb place of Xi'an, before and after dust occurrence at the two places. The profiles were from the homepage of Atmospheric Soundings of the University of Wyoming (http://weather.uwyo.edu/upperair/sounding.html). Dust occurred at the desert site on the morning of April 24, 2014, and the sample collection was held between 06:30 and 15:00 BST on April 24. Dust occurred at Xi'an site on the morning of May 1, 2014, and the sample collection was held between 07:00 and 19:00 BST on May 1.

***Lines 20-25, page 7: This is one of the fundamental problems with trying to interpret this data. They have no way to distinguish between sulfate from pollution and sulfate in the soil/dust itself.***

**Response:** Yes, it could be absolutely said that there is "no way to distinguish between sulfate from pollution and sulfate in the soil/dust itself". However, what we are discussing here is if the small level of sulfate observed at the urban site (0.9%) was considerably larger than the level at the desert site (1.2%) and if the production of sulfate by surface reactions on dust particles during the particle travel was substantially large and has to be considered. Even the 0.9% of sulfate was totally from anthropogenic pollution, this does not contradict our conclusion that the production was limited. By the way, we do not have a reason to ignore the part of sulfate of mineral origin (1.2% in the present study) in the dust particles.

***Page 9, lines 19-21: "...very different from the conclusions of this study." What evidence is there that this study's "enhanced" (for purposes of discussion) nitrate was collected in transit vs from the populated area near the sampler? I believe this study's Conclusions are unsupported.***

**Response:** Below-detection-limit ammonia and unenriched Zn and Pb (data added in the revised manuscript) relative to mineral dust in the postfrontal air indicate that the nitrate was impossibly explained by possible emissions from the populated area near the sampler. So we consider the nitrate was produced during the transport, although the amount was very limited in comparison with that in polluted urban atmosphere. Even though some of the "enhanced" nitrate was from the populated area near the sampler, the production of nitrate should be very

small in comparison with that in polluted air, which supports our conclusion. Please also see our response to your next comment. In addition, it is very hard for us to believe the limited nitrate was produced in the last moment only before we collected the particles, because the conversion of background-like nitric acid to particle surface in dust air during the transport according to our estimation can, to a large extent, account for the nitrate production.

***Page 9, line 30-31: Yes, prefrontal air is much more polluted than postfrontal air. But that doesn't prove that the postfrontal air is free of contamination. The postfrontal air is still moving across a landscape containing sources, especially near the sampling site in Xian. How rapidly would urban nitrate be formed, relative to the sampling interval in the postfrontal air?***

**Response:** We didn't attempt to show "that the postfrontal air is free of contamination" and we never say that in the manuscript. We show that the production of sulfate and nitrate on dust storm particles were limited. With our data, we estimated the rate of nitrate formation in the postfrontal dust when the particles travelled from the desert area to the urban area, as we show in the manuscript. The adiabatic state of the postfrontal dust plume was kept during the travel. So the rate was very small. Although there should be emissions of anthropogenic pollutants from local areas where the plume passed, the emitted amount was not large enough to influence the dust plume. Otherwise, gaseous pollutants such as $SO_2$ and $NO_2$ would not have decreased to very low levels. The major reason should be that the movement of the postfrontal air was relatively very fast, in comparison with prefrontal air.

***Furthermore, since there was only bulk sampling we don't know for sure that all the nitrate was even on the coarse (dust) mode. Their observations are simply too few and too limited in type to advance our understanding of the uptake of sulfate and nitrate by desert dust.***

**Response:** Currently, we do not have size-differentiated data for the formation of the salts to give a deeper discussion on in what size ranges of dust particles the salts were produced. However, as we mentioned in previous responses, even we consider all nitrate and sulfate were produced on the dust storm particles, the production of the salts was still very limited, which does not contradict our conclusions. Yes, it is true our methods are not advanced and the observations did not provide a lot of samples. Repeatedly, we think that the key point should be if our results support our conclusions, no matter whether the methods are advanced or not, and how many samples we have. To the extent of our knowledge, we did not find data that contradict our data and conclusions. The differences between our data and published data were reasonably explained.

***Page 10, line 4: Briefly explain "Peak 1" or don't mention it.***

**Response:** Peak 1 in the study of Zhao et al. (2007) referred to the period of the highest loading of mass during the dust period.

**In the revision, we removed "Peak 1" from the text.** The sentence **"…, the mineral/TSP ratios in samples with the highest TSP loading (Peak I described in that study) were significantly lower than those in samples collected after the occurrence of maximum aerosol loading, indicating that the samples around Peak I were not dust particles from desert areas only."** was changed to **"…, the mineral/TSP ratios in samples**

**of the highest TSP loading were significantly lower than those in samples collected after the occurrence of maximum aerosol loading, indicating that the samples at the highest TSP moment were not dust particles from desert areas only."**

***I really like most of the discussion on page 10, which addresses a way of identifying urban vs desert influences on dust composition using trace metals. Unfortunately, this study only measured Ca, which is present in both desert and urban dust, so their conclusions can't benefit from this discussion.***

**Response:** In this section, we discussed the indictors of discriminating desert dust from urban aerosols in some previous studies to explain why some studies encountered the result that some "dust samples" contained substantial sulfate and nitrate. We emphasize that $Ca^{2+}$ is present in both desert dust and urban mineral particles and is not as a good indicator for discriminating desert dust from urban aerosols. Dust samples in studies using $Ca^{2+}$ as the indicator of the presence of desert dust could be a mixture of long-distance transported dust particles and locally- and regionally-originated aerosols, which caused the conclusion in some previously published papers that dust particles significantly enhanced the formation of sulfate and nitrate when dust plumes advected over urban areas. So the discussion helps to elucidate the discrepancy between the results of different studies as mentioned in the Introduction.

In our study, we did not use metals as indicators to discriminating desert dust from urban aerosol. We divided the sampling periods into three stages: prefrontal, frontal and postfrontal air. We found that the production of nitrate and sulfate in samples dominated by desert dust particles (in the postfrontal air) was very limited and we explained the results based on the adiabatic movement of the postfrontal dust plume.

In addition, we also measured other metals. In the revised manuscript, we will add the results of two common anthropogenic trace elements Zn and Pb, as mentioned in previous responses. The ratios of them to Fe in postfrontal dust particles were very close to those in the desert air, and much smaller than those in the prefrontal air (Table R2), further suggesting the limited influence of pollution on desert dust particles.

***Reviewer# 2***

**The authors greatly appreciate the careful and detailed review by the reviewer 2**

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***General comments:***

*A number of laboratory and field studies have proved that Asian dust particles readily promoted the formation of sulfate and nitrate when the lofted dust plumes transported across urban areas under high RH and elevated levels of reactive trace gases (i.e. $SO_2$, NOx, $O_3$ and OH radicals). This would significantly alter the physical and chemical properties of dust aerosol and subsequent climate change on regional scale.*

*The authors carried out a series of particle samplings at the Tengger desert (06:30–15:00 BST on April 24, 2014) and downwind Xi'an city (07:00–19:00 BST on May 1, 2014) during two independent dust storms. Combination of HYSPLIT backward trajectories model and CFORS simulation, they showed that the two dust events originated from the same source regions and had similar transport routes. They compared the concentrations and mass fraction of chemical components (i.e. sulfate, nitrate, ammonia, and elemental ratios) in dust particles at two sites during the prefrontal, frontal, and postfrontal air parcels, and indicated that the production of sulfate and nitrate on front-associated dust particles was limited when the dust moved from desert sources to populated areas in northwest China. The result of this manuscript seems to be reasonable in spite of limited in-situ sampling data, which is completely different from the other previous studies. Different scientific viewpoints should be encouraged to promote the understanding of interplay between mineral dust and atmospheric chemistry. Therefore, I recommend this manuscript is accepted and published in the journal of ACP after some revisions.*

***Specific comments:***

***1.*** *Abstract, Page 2, lines 12–14: "The significant sulfate and nitrate reported in dust-associated samples in previous studies were more likely produced on locally-emitted and urban mineral particles or from soil-derived sulfate rather than being produced via chemical conversions on desert dust particles."*

*Conclusion, Page 11, lines 2–4: "Significant sulfate and nitrate in dust storm periods in China reported in previous studies were likely produced on locally-emitted and urban mineral particles, in addition to soil-derived sulfate, and they were unlikely produced via chemical conversions on dust particles from deserts."*

***Comment:*** *I think there is no enough evidence for the manuscript to demonstrate this conclusion. Because the dry condition (RH<40%) and low mass concentrations of trace gases (i.e. $SO_2$ and $NO_2$) were observed in Xi'an during the dust-storm episode, which didn't favor the formation of sulfate and nitrate on the surface of mineral particles. However, these are only a few cases. The authors didn't show the results when dust storm transported across the other polluted areas with high RH conditions and high levels of trace gases.*

**Responses**: The mentioned conclusion is not derived from our data. It is from the careful investigation of the sample collection records in published literature where significant sulfate and nitrate in so-called dust samples (Section 3.3) were reported. We checked all papers that we can find on the formation of sulfate and nitrate on Asian dust particles by field measurement data. Unfortunately, most of the papers did not give the details of the dust conditions and the evolution of

weather conditions at the start and stop time of sample collection. To the extent that we can confirm the dust and weather conditions at the start and stop time of samples collection, results from the samples that were really collected under dust storm conditions are all similar to the results we reported in this study, as described in Section 3.3.

We do not intend to show that dust storm particles cannot enhance the production of sulfate and nitrate via chemical conversions on their surface. We want to report that dust storm particles did not enhance the production in postfrontal air within the Asian continent. The reason is the adiabatic state of the air parcels loading the dust particles, which is the reason for the low RH and less $SO_2$ and NOx. We totally agree that the absence of the sulfate and nitrate in the samples of dust storm particles of ours were due to the dry conditions and the low concentration of $SO_2$ and NOx. In case when dust particles are put into an environment with high RH and high concentrations $SO_2$ and NOx, sulfate and nitrate can be produced efficiently. However, this is not the case of long-distance transport of dust storm plumes following cold front within the Asian continent. In cases of cyclone with cold fronts, the postfrontal air is always dry and its arrival is always accompanied with a rapid decrease of anthropogenic pollutants including $SO_2$ and NOx. There are a lot of papers on this point for dust arrival in East China and we cited some, such as Hu et al (2016), to mention this. Please see section 3.3.

We prefer to remain the explanation for the difference of our results with some previous studies, although we do not have evidence from our data. The reasons are: (1) to the extent of our knowledge, we can give such an instant explanation; (2) the explanation is referentially meaningful for further studies of the formation of nitrate and sulfate on dust particles being transported within the Asian continent in postfrontal air; and (3) if we do not provide a possible explanation, readers will have a question "how do the authors explain/consider the previously-published results?" after reading the abstract.

To avoid the misunderstanding, we made some revisions in the Abstract and Conclusion:

In the abstract,

**"The significant sulfate and nitrate reported in dust-associated samples in previous studies were more likely produced on locally-emitted and urban mineral particles or from soil-derived sulfate rather than being produced via chemical conversions on desert dust particles."**

is changed to

**"The significant sulfate and nitrate reported in dust storm-associated samples in previous studies were more likely from locally-emitted and urban mineral particles or from soil-derived sulfate, because the weather conditions in those studies indicated that the air from which the samples were collected very likely contained a lot of particles from local emissions."**

In the revision of Conclusion, in addition to make the above point more clear, we also mention the need of an effort to quantify the contribution of non-desert mineral particles to the sulfate and nitrate in future studies.

**In the revision, the description of "Significant sulfate and nitrate in dust storm periods in China reported in previous studies were likely produced on locally-emitted and urban mineral particles, in addition to soil-derived sulfate, and they were unlikely produced via chemical conversions on dust particles from deserts."**

is changed into (as an individual paragraph)

**"Significant sulfate and nitrate in dust storm periods in China reported in previous studies were likely from locally-emitted and urban mineral particles, in addition to soil-derived sulfate, and they were unlikely produced via chemical conversions on dust particles from deserts. The major reason is that, in those studies, the air from which the samples were collected had been significantly influenced by local emissions. Without a proper evaluation of the contribution of sulfate and nitrate in the samples by locally-emitted and urban mineral particles, i.e., non-desert mineral particles, it is not safe to attribute all the detected sulfate and nitrate to the production on dust-storm particles."**

***2.*** *Page 4, lines 21–22: "This sample collection ensured that mineral particles collected on the filters were dust particles from the desert and there should be no influence of anthropogenic pollutants from the village or the city considered in the samples."*
***Comment:*** *The evidence provided by this manuscript could not fully support this sentence. Please reconsider again.*
**Response:** As we described in the manuscript, we collected the samples carefully with a proper time resolution for describing the variation with weather change. We chose the samples as dust storm samples when the air was from the desert and the same direction. We consider that possible influence from the village and the city was avoided when the wind was from the desert direction.
In the revision, the descriptions were revised into **"This sample collection ensured that mineral particles collected on the filters were dominated by dust particles from the desert and possible influence of anthropogenic pollutants from the village or the city was suppressed."**

***3.*** *Page 6, lines 15–17: "The cold fronts are the boundaries between the local or regional anthropogenic-polluted air and the long-distance transported air because the movement of air on a synoptic scale is approximately adiabatic, i.e. the air is hardly mixed with thermodynamically-different air it meets."*
***Comment:*** *I don't agree with this viewpoint about "the air is hardly mixed with thermodynamically-different air it meets". In terms of meteorology, the warm and humid air mass is readily lifted and the weather process (e.g., strong wind and cooling weather, rainfall or snow) often changes dramatically on the border of frontal system when a cold front passes over. As shown in Figure 2a, the RH increased sharply from 40% at 13:00 BST to 100% at 16:00 BST, which indicated clearly that a rainfall or snow process took place at Tengger desert (also see Page 4, line 15 and Table 1). The cold fronts are dominated and accompanied strong winds intensify the diffusions of local air pollutants.*

**Response:** We totally agree that "the weather process (e.g., strong wind and cooling weather, rainfall or snow) often changes dramatically on the border of frontal system when a cold front passes over." However, this occurs only in the front. In the case of the presence of a cold front, the cold and dry postfrontal air did not mix with the prefrontal air in the viewpoint of air movement on synoptic scales, which is the reason of the presence of the front. We also totally agree that "the cold fronts are dominated and accompanied strong winds intensify the diffusions of local air pollutants." However, the major part of accumulated pollutants in prefrontal air is usually pushed by the front, move northeastward and separately from postfrontal dust storm plumes, and transported out of the Asian continent. Only a small part of the pollutants close to the front might be mixed with dust-

loading air in the front. In addition, this is very different from dust particles in marine atmosphere. In our previous studies in the downwind marine atmosphere of the Asian continent (in southwestern Japan), we have confirmed the mixture, that is likely due to the vertical mixing in the marine atmosphere between China coast and Japanese islands.

On the RH=100% at 16:00 BST in Figure 2a, the dust storm has finished at that time and the weather was recovering with the increase of temperature and RH. The high RH was caused by the arrival of another air parcel which was dryer and much colder than the previous air, leading to snowing.

In the revision, **"although some small-scale mixing might occur in the front"** is added after the mentioned sentence.

***4.*** *Page 7, lines 26–33: "At the desert site, $NO_3^-$ concentration in dust samples was 4-6 μg $m^{-3}$ and the average was 5 μg$m^{-3}$. The relative amount of $NO_3^-$ range between 0.11% and 0.12%, and the average was 0.12%. ...Right after the passage of the cold front (the first sample in the postfrontal air), the concentration of $NO_3^-$ was 0.9 μg$m^{-3}$ and it occupied 0.2% of the aerosol mass. The relative amount in this sample was about twice of that in the desert samples although it was the lowest in the samples at Xi'an site, indicating that nitrate had been produced on dust particles during their travel to Xi'an."*

***Comment:*** *At the Tengger desert site, $NO_3^-$ concentration in dust samples was 4-6 μg $m^{-3}$ (with the average value and fraction of 5 μg $m^{-3}$ and 0.12%), which were much larger than that at Xi'an after the cold front (~0.9 μg$m^{-3}$, with the mass fraction ~0.2%). The higher mass fraction of $NO_3^-$ at Xi'an was ascribed to the low concentration of TSP (total suspended particulates, ~420 μg $m^{-3}$), and the TSP concentration in Tengger desert site was about 5000 μg $m^{-3}$. Although the relative amount of $NO_3^-$ at Xi'an was about twice of that in the desert samples, it couldn't indicate that nitrate had been produced on dust particles during their travel to Xi'an. Please explain this.*

**Response:** Yes, we agree that "Although the relative amount of $NO_3^-$ at Xi'an was about twice of that in the desert samples, it couldn't indicate that nitrate had been produced on dust particles during their travel to Xi'an". A possibility we did not consider is that the increase was caused by possible difference of removal rate of dust particles and nitrate (or nitrate-containing particles). If this possibility were the fact, it means that part of the nitrate, similar to sulfate, was not produced in the dust-loading plumes, or the production rate was smaller than our estimation, both of which do not conflict with our conclusion that the production of nitrate was limited.

**In the revision,**

**(1) "indicating that nitrate had been produced on dust particles during their travel to Xi'an"** was revised into **"indicating that nitrate was likely produced on dust particles during their travel to Xi'an."**

(2) The following descriptions are added right after the descriptions of the estimated rate values of nitrate production on dust particles: **"Note this rate should be the maximum rate because not all the nitrate must have been produced on dust particles and the increase of the relative amount of nitrate during the movement of a dust plume from the desert to Xi'an could have been the consequence of possible difference of removal rates of dust particles and nitrate-containing particles.**"

***5.*** *Page 18, Table 2; Page 19, Table 3: The authors sampled the concentrations of TSP (total suspended particulates) and analyzed the chemical components (i.e. sulfate, nitrate, and ammonia) in TSP at the Tengger desert and Xi'an sites.*

***Comment:*** *Please explain why did you sample the concentrations of TSP, instead of $PM_{10}$ or $PM_{2.5}$. It is well known that most of the coarse-size dust particles (radii > 10 μm) generally settle near the source region on account of large gravitational deposition velocity, whereas the finer dust particles (radii < 10 μm) are transported more efficiently to the downstream areas. And the concentrations of TSP (meaning coarse-size particle with radii>10 μm) in Xi'an city should include the local source emissions (e.g., engines of vehicles, road dust, and construction dust; Page 4, lines 27-29) that increases the TSP concentrations, but may decrease the relative mass fraction of sulfate, nitrate, and ammonia. Inferred from Page 6, Lines 1-7, the mass concentrations of TSP and sulfate are about 425 μg $m^{-3}$ and 17 μg $m^{-3}$ at Xi'an before the dust arrival (i.e. prefrontal air). In the postfrontal air, the mass concentrations of sulfate are 3.8, 3.5, and 3.4 μg $m^{-3}$, respectively, right after, two hour after, and four hours after the passage of cold front (means slight variations), whereas the corresponding TSP concentrations are 422, 318, and 189 μg $m^{-3}$ (shows large variations). Clearly, relative mass fractions of sulfate reduce.*

**Response:** Size-differentiated sulfate and nitrate can give a deeper understanding on the variation of the sulfate and nitrate on dust particles. Samples of different size fractions are always collected using Anderson sampler. Unfortunately, the sampling site in the desert was located at an active sand dune and we did not have an electricity power to support such sample collections. Moreover, it is difficult to collect enough samples of different size fractions for water-soluble ions analysis using the Anderson sampler within 1-2 hours. So we collected TSP (total suspended particulates) samples. It is possible that the content of mineral sulfate in dust particles is a size matter and the size dependence must have large influence on the soil-derived sulfate in downstream areas, which is an important subject in future studies.

At Xi'an, the relative mass fractions of sulfate increased gradually with the decrease (the leaving of the front) of TSP. This result is consistent with previous studies demonstrating the passage of cold fronts, including on-line instrument measurements such as Wang et al. (2014) at Xi'an, and Niu et al (2016) and Hu et al. (2016) at Beijing. It is because the gradual increase of the influence of local emissions as the front leaves away. Anyway, the concentration of sulfate in postfrontal dust air was very low, in comparison with usual urban polluted air. Even we consider part of the sulfate we encountered at Xi'an was produced on desert dust particles via surface reactions, the production was still very low, which is consistent with the major conclusion of this study.

Hu, W., Niu, H., Zhang, D., Wu, Z., Chen, C., Wu, Y., Shang, D. and Hu, M.: Insights into a dust event transported through Beijing in spring 2012: Morphology, chemical composition and impact on surface aerosols, Sci. Total Environ., 565, 287–298, doi:10.1016/j.scitotenv.2016.04.175, 2016.

Niu, H., Hu, W., Zhang, D., Wu, Z., Guo, S., Pian, W., Cheng, W., Hu, M., 2016. Variations of fine particle physiochemical properties during a heavy haze episode in the winter of Beijing. Sci. Total Environ. 571, 103–109. doi:10.1016/j.scitotenv.2016.07.147

Wang, G. H., Cheng, C. L., Huang, Y., Tao, J., Ren, Y. Q., Wu, F., Meng, J. J., Li, J. J., Cheng, Y. T.,

Cao, J. J., Liu, S. X., Zhang, T., Zhang, R. and Chen, Y. B.: Evolution of aerosol chemistry in Xi'an, inland China, during the dust storm period of 2013—Part 1: Sources, chemical forms and formation mechanisms of nitrate and sulfate, Atmos. Chem. Phys., 14(21), 11571–11585, doi:10.5194/acp-14-11571-2014, 2014.

**Minor comments:**

***1.*** *Abstract, Page 2, lines 3–4: "but the production was very inefficient in other studies."*
***Comment:*** *Please give the quoted literature.*
**Response:** The literature is given in the second paragraph of the Introduction. Since this part is abstract, we prefer not to list references here.

***2.*** *Page 3, line 8: "RH"*
***Comment:*** *Change to "relative humidity (RH)"*
**Response:** Corrected in the revision.

***3.*** *Page 10, line 4: "mineral/TSP ratios"*
***Comment:*** *Change to "mineral/TSP (total suspended particulates) ratios"*
**Response:** Corrected in the revision.

# Limited production of sulfate and nitrate on front-associated dust storm particles moving from desert to distant populated areas in northwestern China

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**Abstract.** Sulfate and nitrate compounds can greatly increase the hygroscopicity of mineral particles in the atmosphere and, consequently, alter the particles' physical and chemical properties. Their uptake on long-distance transported Asian dust particles within mainland China has been reported to be substantial in previous studies, but the production was very inefficient in other studies. We compared these two salts in particles collected from a synoptic scale, mid-latitude cyclone-induced dust storm plume at the Tengger desert (38.79º N, 105.38º E) and in particles collected in a postfrontal dust plume at an urban site in Xi'an (34.22º N, 108.87º E) when a front-associated dust storm from the Tengger desert arrived there approximately 700 km downwind. Results showed that sulfate concentration was not considerably different at the two sites while nitrate concentration was slightly larger at the urban site than that at the desert site. The estimated nitrate production rate was 4-5 ng per μg mineral dust per day, which was much less than that in polluted urban air. These results indicate that the production of nitrate and sulfate on dust particles following cold fronts was limited when the particles moved from the desert to populated areas. The adiabatic process of the dust-loading air was suggested to be the reason for the absence of sulfate formation and the uptake of background $HNO_3$ to be the reason for the small nitrate production. The significant sulfate and nitrate reported in storm-associated samples in previous studies were more likely from locally-emitted and urban mineral particles or from soil-derived sulfate, because the weather conditions in those studies indicated that the air from which the samples were collected very likely contained a lot of particles from local emissions.

**Keywords**: Asian dust, Tengger desert, long-distance transport, chemical conversion, background $HNO_3$

## 1 Introduction

Mineral dust particles constitute a substantial fraction of atmospheric aerosol mass and plays various roles in atmospheric physics and chemistry (Dentener et al., 1996; Sokolik and Toon, 1996; Tegen et al., 1996). Dust particles at their source areas are mainly composed of quartz, clays, micas, feldspars, carbonates (primarily calcite, $CaCO_3$), and other minor minerals (Usher et al., 2003). While suspended, they may be altered by uptake of gases and smaller particles and surface reactions. Laboratory studies have demonstrated the formation of sulfate and nitrate on dust particles upon exposure to reactive gases such as $NO_x$, $HNO_3$, $NO_3$, $N_2O_5$ and $SO_2$ (Usher et al., 2003). The formation of salts on the particles can enhance the solubility of the particles, lower their effective deliquescence relative humidity (RH), and alter their size and physical state in association with atmospheric conditions (Semeniuk et al., 2007). These changes in turn feed back into the activities of dust particles in various chemical and physical processes in the atmosphere (Bauer and Koch, 2005), such as the enhancement of bioavailable iron (Meskhidze, 2003) and the removal of acidic gases in the atmosphere (Dentener et al., 1996; Zhang and Carmichael, 1999).

Field studies have shown different results regarding the formation of sulfate and nitrate on dust particles and some results are contradictory. Many studies reported substantial sulfate and nitrate on the surface of Asian dust particles after the particles were transported over long distances in the atmosphere (Cao et al., 2003; Huang et al., 2010; Li and Shao, 2009; Mori, 2003; Nie et al., 2012; Nishikawa et al., 1991; Qi et al., 2006; Ro et al., 2005; Sun et al., 2010; 2004; Wang et al., 2005b; 2007; Wu and Okada, 1994; Zhao et al., 2011). In contrast, an early study of Zhang and Iwasaka (1999) found that sulfate and nitrate were rarely formed on Asian dust particles which had been transported over a long distance in inland China after about two days. A study at the Taklimakan desert pointed out that in some cases the content of sulfate in dust particles might not change even when the particles traveled over a long distance. The dust particles contained substantial sulfate (~4% by mass) which was from the surface soil (Wu et al., 2012). It was also found that, for a dust plume lofted from the surface by a synoptic mid-latitude cyclone, the plume did not mix significantly with adjacent air parcels polluted by anthropogenic sources; the dust plume and the polluted air were separated as two air parcels by the cold front associated with the cyclone (Bates et al., 2004; Tsai et al., 2014; Wang et al., 2013; Zhang et al., 2005). Some measurements of chemical composition of long-distance transported dust particles have also shown that most of the dust particles were not altered chemically and were externally mixed with species produced in the air via gas-to-particle reactions, such as sulfate and nitrate (Denjean et al., 2015; Song et al., 2005). These results leave a question: what are the reasons for the discrepancy between the results of those studies?

In April 2014, we collected a series of atmospheric particle samples during a cyclone-induced dust storm at the eastern edge of the Tengger desert, which is one of the most significant sources of Asian dust (Zhang et al., 2003). We also collected a series of samples at Xi'an, a large city in northwestern China when a dust storm from the Tengger desert passed there after travelling about 6 hours following a cold front. In this study, we compare the concentrations and mass fractions of sulfate and nitrate in the samples at the two sites, examine the production of nitrate and sulfate on desert dust particles after the particles

were transported from the desert to the populated area, and discuss possible reasons for the difference in previously reported results.

## 2 Particle Collection and Analysis

The observation site at the Tengger desert was located at an active sand dune at a location called Tonggunao'er along the northeastern rim of the desert (38.79ºN, 105.38ºE; Fig. 1). The closest village, with a population less than 200, is about 5 km to the east of the site and the nearest city is Bayan Hot (Inner Mongolia Autonomous Region, China) about 35 km to the east of the site (Fig. S1). Anthropogenic pollutants from the village and the city may arrive at the site if the wind direction is from the east. Backward trajectories of air masses (Fig. S2) and the simulation (Fig. S3a) of the on-line Chemical Weather Forecasting System (CFORS, developed and open on-line by NIES and Kyushu University, Japan: http://www-cfors.nies.go.jp/~cfors/index-j.html) showed that a dust storm was induced by a synoptic scale, mid-latitude cyclone in the southwest part of the Mongolia on April 23, 2014. The resulting dust plume was then transported southeastward and passed the sampling site on the morning of April 24 (Fig. S3a).

Observations were carried out between 06:30 BST (Beijing standard time: GMT + 08:00) and 15:00 BST on April 24, 2014. Particles were collected using a homemade filter pack sampling system, which consisted of one Teflon front filter for collecting particulate matter and one back filter for the collection of gas-phase species. The flow rate of 16.7 litres per minute was controlled with a mass flow controller (SmartTrak 50, Sierra). The filters were changed every 2 hours, and the collection of the fourth sample was stopped when it started to snow (Table 1). Field blank filters were prepared and obtained by mounting filters in a sampling system in a similar way to the particle collection for 2 hours without pumping air. Meteorological conditions including surface pressure, temperature, relative humidity, wind speed, and wind direction were monitored with a weather tracker (Kestrel 4500, Kestrelmeters). The cold front passed the site between 04:00 and 04:30 BST on 24 April, which was characterized by the rapid decrease of relative humidity, the sudden change of wind direction from south to north, the growth of wind speed, and the gradual increase of pressure (Fig. 2a). Therefore, all samples were collected after the passage of the cold front. This sample collection ensured that mineral particles collected on the filters were dominated by dust particles from the desert, and possible influence of anthropogenic pollutants from the village or the city was suppressed.

Xi'an (34.22ºN, 108.87ºE) lies in central China, approximately 700 km from the Tengger desert (Fig. 1). The observation in Xi'an was carried out on the roof of a building (10 m above ground) on the campus of the Institute of Earth Environment. The institute is located in the southwest area of the city, and its surroundings are residences, streets and office buildings. There are no large, continuous sources of anthropogenic pollutants such as factories or agriculture fields near the institute. Previous studies at this site have revealed that the local pollutants are mainly from traffic and the particulate pollutants mainly include particles from engines of vehicles, road dust, and construction dust, all of which have been characterized by contents of crustal elements, sulfate, organic matter, nitrate, and ammonium (Huang et al., 2014a; Zhang et al., 2011).

Particles were collected on May 1, 2014 when dust-loading air passed Xi'an. Backward trajectories of air masses (Fig. S2) and the CFORS simulation (Fig. S3b) showed that, similar to the dust storm observed at the Tengger desert, this dust storm was also induced by a cyclone in the southwest part of the Mongolia and moved southeastward (Fig. S3b). It passed the site of the Tengger desert on the evening of April 30 and arrived at Xi'an on the morning of May 1. Particle collection was carried out between 07:00 BST and 19:00 BST on May 1. The same sampling system and the same type filters as those used for the particle collection at the desert site were used. Samples were collected at a time interval of 1 or 2 hours. In total, 7 samples were obtained from the dust-storm approach to its dissipation (Table 1). Meteorological conditions were monitored by the Kestrel 4500 weather tracker. The sudden decrease of relative humidity showed that the arrival of the cold front of the cyclone occurred between 9:30 and 11:30 BST (Fig. 2b). Therefore, the first sample was collected before the arrival of the cold front, the second and third samples were collected in the frontal air and the fourth, fifth, and sixth samples were collected after the passage of the cold front. Unfortunately, the fourth sample was not available for analysis because the collection system was blown down by wind when this sample was collected. The concentrations of $SO_2$ and $NO_2$ were measured by an UV fluorescence analyzer (Ecotech, model EC9850) and a chemiluminescence analyzer (Thermo, model 42i) and were recorded in units of ppb at a time intervals of 5 minutes. The lowest detection limit was approximately 0.04 ppb for $SO_2$ and 0.4 ppb for $NO_2$. Since the dust occurring in Xi'an had the source same as and a transport route similar to that at the desert site (Fig.S2, Fig.S3), the comparisons between the samples collected at the desert site and the Xi'an site can show changes of dust particles during the transport although the samples were not from the same dust event.

Teflon-membrane filter samples were equilibrated in a temperature and relative humidity controlled environment (20–23°C and 35–45% RH, respectively) before gravimetric analysis to minimize particle volatilization and aerosol liquid water interferences. Filters were weighed before and after sampling using a ME 5-F electronic microbalance (Sartorius, GOTTINGEN, Germany) with a sensitivity of ± 0.001 mg. The precision of multiple weighings for unexposed and exposed filters was smaller than ± 0.010 and ± 0.015 mg, respectively. Filters were exposed to a low-level radioactive source (500 pCi of polonium-210) before sample weighing to remove static charge. Mass concentrations were calculated with the difference of weight before and after sampling and the volume of sampled air. Half of each filter was analyzed to quantify water-soluble components in particles. Each sampled filter was initially wetted with 200 µl ethanol. Water-soluble components were extracted by ultrasonic agitation in 10 mL distilled water. The extraction solution was filtered with 0.45 mm pore size microporous membranes, and then the filtrate solution was stored at 4°C until subsequent analyses. An ion chromatograph (Dionex DX-600) was used to quantify sulfate ($SO_4^{2-}$), nitrate ($NO_3^-$), chloride ($Cl^-$), sodium ($Na^+$), potassium ($K^+$), ammonium ($NH_4^+$), calcium ($Ca^{2+}$), and magnesium ($Mg^{2+}$) in the solution. Calibration curves were constructed from the peak areas of the chromatograms which were produced from a series of mixed standards.

An energy dispersive X-Ray fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V., the Netherlands) was used to quantify elements in the samples of the remained parts of sample filters. Five crustal elements (K, Ca, Ti, Mn, Fe and Ba) and two common anthropogenic trace elements (Zn and Pb) were quantitatively determined. Analytical

uncertainties, as checked by parallel analysis of the NIST standard reference material (SRM-2683), were about or less than 10% for the detected elements.

## 3 Results and discussion

### 3.1 Sulfate

In the dust plume at the Tengger desert, the concentration of sulfate ranged from 39 to 59 μg $m^{-3}$. The relative amount of sulfate in the dust samples, i.e. the mass fraction of sulfate in the samples, was between 1.1% and 1.2% and the average was 1.2% (Table 2). These values were close to the levels of the relative mass ratios of sulfate in TSP or $PM_{10}$ in samples collected under dust conditions at the Gobi Desert which were reported in previous studies (Table S1).

The concentration of $SO_4^{2-}$ at Xi'an varied in a large range as the front of the dust-loading cyclone was approaching, passing and leaving (Fig. 3). It was 17 μg $m^{-3}$, contributing 4% of aerosol mass, in the prefrontal air, i.e. before the dust arrival. As the front was passing, the concentration decreased rapidly. In the postfrontal air, the concentration was 3.8 μg $m^{-3}$ right after the front passage, 3.5 μg $m^{-3}$ two hours after the passage, 3.4 μg $m^{-3}$ four hours after the passage. The average in the postfrontal air was 3.5 μg $m^{-3}$. The relative amounts of sulfate in these samples were 0.9%, 1.1%, and 1.8%, respectively, and the average was about 1.3 %. In comparison with that in the prefrontal air, the concentration in the postfrontal air was very small and approximately constant, although the relative amount increased gradually as the front left.

In cyclones moving eastward across northern China, the source and consequently, the compositions of major particles in the air before and after cold fronts are different although they are in the same cyclones (Hu et al., 2016; Niu et al., 2011). Prefrontal air usually moves slowly from the south or southwest directions toward the north or northeast, and is usually warm and humid. Particles in prefrontal air are originated mainly from local or regional areas and they are usually dominated by anthropogenic pollutants (Li et al., 2012). The postfrontal air moves more rapidly from north or northwest direction and is usually cold and dry. Particles in postfrontal air are those lifted by cold fronts of the cyclones at the places they pass, and long-distance transported dust particles are usually the majority if the cyclones have caused dust storms at the arid and semi-arid areas in northwestern China (Wang et al., 2005a). The cold fronts are the boundaries between the local or regional anthropogenically-polluted air and the long-distance transported air because the movement of air on a synoptic scale is approximately adiabatic, i.e. the air is hardly mixed with thermodynamically-different air it meets, although some small-scale mixing might occur in the front. Aerosol particles at the time period of front passage should be dominated by both locally originated and long-distance transported ones. The rapid decrease of sulfate with the passage of the cold front at Xi'an was consistent with the increase of long-distance transported dust.

$NH_4^+$ is one of the major water-soluble species in aerosol particles, and can be remarkably enhanced by anthropogenic emissions. We found that its concentration was close to the lowest detection limit in dust samples at the desert site. This fact makes $NH_4^+$ a good indicator for examining the influence of local or regional anthropogenic particles on the samples observed at Xi'an. The variation of $NH_4^+$ during the sampling period is also shown in Fig. 3. With the increase of long-distance

transported dust particles, $NH_4^+$ decreased remarkably as the front was passing the site, and was very low in the frontal air. In the postfrontal air, $NH_4^+$ concentration was lower than the detection limit in the first sample and increased slightly in the second and third samples. These results indicate that the composition of particles in the postfrontal air was close to the state of dust particles at the desert areas, whereas the composition was gradually affected by local emissions afterwards. Zn and Pb are two common anthropogenic trace elements in urban air. Their ratios to Fe in the dust samples in the postfrontal air were much lower than those in the prefrontal air and very close to those in the desert air (Table 3), further suggesting the limited influence of pollution on desert dust particles in the postfrontal air.

The relative amount of $SO_4^{2-}$ in dust samples at the desert, 1.1 to 1.2% in mass, was similar to or even larger than the relative amount at Xi'an (the relative amount in the first sample in the postfrontal air was 0.9%). This result indicates that sulfate was rarely produced on dust particles during the particles travelled from the desert to the distant urban area. Heterogeneous reactions involving $SO_2$ on mineral particles was the major processes for sulfate production on the particles. The conversion of $SO_2$ to sulfate by heterogeneous reactions on particles is much more efficient under humid conditions than under dry conditions (Usher et al., 2003). The relative humidity was less than 40% during the dust-storm episode in Xi'an (Fig. 2b), which did not favor the formation of sulfate on the surface of mineral components (Huang et al., 2014b). Moreover, the cold air lofting the dust-storm particles was from arid or semi-arid areas in the southwest part of the Mongolia, where $SO_2$ emission is usually weak (Fig. S4). The concentration of $SO_2$ in the postfrontal air was nearly close to the detection limit (Fig. S5), which was much smaller than the concentration in the prefrontal air (~ 20 ppb). Therefore, sulfate was hardly formed on the dust particles due to the lack of $SO_2$ and the dry condition. The postfrontal air had passed some populated areas between the desert and Xi'an, where anthropogenic $SO_2$ emission was usually observed due to human activities (Wang et al., 2011). However, the postfrontal air did not pick up any accumulated air pollutants on the way. Anthropogenic pollutants that might have been taken into the air were those freshly emitted at the moment of the air passage. Such pollutants should not have a considerable influence on the dust. Otherwise, (1) the movement of the dust-loading air should not have been an adiabatic process, the reason for the cold front occurrence when arriving at Xi'an; (2) the front should have disappeared; (3) some $NH_4^+$ should have been present; and (4) sulfate content in the samples at Xi'an should be larger than the desert-sample level. The vertical thermodynamic structure near the surface at the two sites became more stable when dust occurred (Fig.S6: from the homepage of Atmospheric Soundings of the University of Wyoming, http://weather.uwyo.edu/upperair/sounding.html), indicating that the dust plume layer established at the dust source was not mixed with air of different chemical (gas and particulate phase) composition from above during the advection.

There was a small amount of sulfate in the dust samples at Xi'an. The concentration was much smaller than that in the dust samples at the desert area. However, the relative level of sulfate in total aerosol mass in the postfrontal air samples (0.91-1.75%) was close to and even smaller than that at the desert area (1.19% on average). This result means that the sulfate in the dust samples at Xi'an was very likely one of the original components of the dust particles, i.e., the so-called soil-derived sulfate in desert dust. It has been found that dust at desert areas contained substantial soil-derived sulfate (Abuduwaili et al., 2008; Sun et al., 2010; Wang et al., 2012; Wu et al., 2012; Yabuki et al., 2005; Zhang et al., 2009) and the sulfate was confirmed in

long-distance transported dust in the downstream areas in a small number of studies (Wang et al., 2014; 2016b; 2007; Wu et al., 2012). For these reasons, we consider that the sulfate detected in the dust samples right after the cold front was mainly from the desert areas as soil-derived one, rather than the sulfate produced by chemical conversions on the particle surface when the particles floated in the air.

### 3.2 Nitrate

At the desert site, $NO_3^-$ concentration in dust samples was 4-6 μg $m^{-3}$ and the average was 5 μg $m^{-3}$. The relative amount of $NO_3^-$ ranged between 0.11% and 0.12%, and the average was 0.12%. At Xi'an site, similar to $SO_4^{2-}$, the concentration of $NO_3^-$ varied in a large range as the dust-loading cyclone passed, with the concentration high in the prefrontal air and low in the postfrontal air. Right after the passage of the cold front (the first sample in the postfrontal air), the concentration of $NO_3^-$ was 0.9 μg $m^{-3}$ and it occupied 0.2% of the aerosol mass. These values were close to the levels of the relative mass ratios of nitrate in TSP or $PM_{10}$ in samples collected under dust conditions at the Gobi Desert which were reported in previous studies (Table S1).

The relative amount in this sample was about twice of that in the desert samples although it was the lowest in the samples at Xi'an site, indicating that nitrate was likely produced on dust particles during their travel to Xi'an. We assume that the removal of dust particles from the dust plume was independent from the chemical components of dust particles. This assumption is reasonable because the dust plume was relatively dry during its movement from the desert area to the urban area and the settling of dust particles under such conditions depends on particles' size only (Zhang, 2008). The concentration of nitrate in dust samples at the desert site was used as the referential value of the part of nitrate originating from the desert areas in the samples at Xi'an areas. The results show that nitrate production on the dust particles was 1.0-1.1 ng per μg dust (approximately 0.1-0.11% in mass) during the dust movement from the desert to Xi'an. Since the dust plume took approximately six hours to move from the desert to Xi'an, this increase of nitrate was equivalent to a production rate of 4-5 ng nitrate per μg dust per day. Note this rate should be the maximum rate because not all the nitrate must have been produced on dust particles and the increase of the relative amount of nitrate during the movement of a dust plume from the desert to Xi'an could have been the consequence of possible difference of removal rates of dust particles and nitrate-containing particles. Anyway, the estimated rate is much smaller than that in polluted urban air, where secondary nitrate usually accounts for 2-6% of aerosol loading (Wang et al., 2003) and the production rate is 20~60 ng nitrate per μg aerosol per day, if we consider the residence time of particles in polluted air is 24 hours.

In general, nitrate on dust particles is produced on the surface via heterogeneous conversions, or the uptake of $HNO_3$ which is formed via homogeneous reactions in the atmosphere. Model studies have shown that the latter one is the major route for nitrate formation on dust particles, and the contribution of the former route, in particular under dry conditions, is very small (Fairlie et al., 2010; Song and Carmichael, 2001). Desert soil hosts the premier natural nitrate minerals on the earth (Walvoord, 2003). Nitrate in desert soil can be reduced to $NO_x$ through microbiological denitrification (Hartley and Schlesinger, 2000) and abiotic thermal decomposition (McCalley and Sparks, 2009). A background-like nitrate, which is about 2-8 μg $m^{-3}$ and

supposed to be in the form of nitric acid, has been found in desert air (Wu et al., 2014). Such $HNO_3$ could be absorbed and transformed into nitrate on dust particles during the dust movement from the source region to Xi'an.

A first-order chemical kinetic equation was used to estimate the uptake of $HNO_3$ during the transport.

$$c_t = c_0\, e^{-kt}, \quad (1)$$

where $c_t$ is the concentration of $HNO_3$ at transport time $t$, $c_0$ is the initial concentration of $HNO_3$ in the air mass, and $k$ is the first order rate at which the gaseous precursor is taken up by dust. The reaction rate can be calculated as below:

$$k = \frac{1}{4} v_{HNO_3} \gamma_{HNO_3} A_P, \quad (2)$$

where $v_{HNO_3}$ is the mean molecular speed of $HNO_3$ and is taken as $3.0\times10^4$ cm $s^{-1}$ (Fairlie et al., 2010). $\gamma_{HNO_3}$ is the reactive uptake coefficient for $HNO_3$ on dust particles. Measurements in laboratory experiments showed the uptake coefficient of $HNO_3$ on mineral dust ranged from $5.2\times10^{-5}$ (Underwood et al., 2001) to $5\times10^{-3}$ (Song et al., 2007). The coefficient was a function of relative humidity (Vlasenko et al., 2006), and estimated to be ~$2\times10^{-4}$ under experimental conditions of 30~40% relative humidity (Fairlie et al., 2010). $A_P$ ($cm^2\ cm^{-3}$) is the total surface area of dust particles and is determined by the loading of dust particles and its specific surface area. Surface area analysis has shown the specific area of Gobi dust to be approximately 110 $cm^2\ mg^{-1}$ (Underwood et al., 2001). The dust load by mass (in $\mu g\ m^{-3}$) initially at the Tengger desert for the dust plume observed at Xi'an is estimated to be 1187 $\mu g\ m^{-3}$, based on the dust load of the first sample of postfrontal air (415.4 $\mu g\ m^{-3}$) and the relationship between dust concentration and its transport distance suggested by Mori et al. (2002).

The reaction rate for $HNO_3$ gas uptake on mineral dust was $1.96\times10^{-4}$ $s^{-1}$. The concentration of $HNO_3$ after 6 hours reduced to ~1% of the initial concentration, indicating that almost all $HNO_3$ could be transformed into nitrate on the dust particles during their transport. As described above, nitrate produced on the dust samples was 0.1-0.11%, indicating the concentration of $NO_3^-$ increased by 1.2-1.3 $\mu g\ m^{-3}$. To produce this amount of nitrate, the $HNO_3$ concentration in the dust-loading air should be approximately 1.2-1.3 $\mu g\ m^{-3}$ on average. Unfortunately, there are no data on nitric acid in the air over the Tengger desert for further comparison. The concentration of nitrate (including particulate and gaseous phases) at Taklimakan desert in northwestern China was 2~8 $\mu g\ m^{-3}$ (Wu et al., 2014), which was in the same range as found for the nitrate concentration in the dust at our Xi'an site.

### 3.3 Inter-comparisons and implication

There have been studies on dust-associated sulfate and nitrate in aerosol particles downwind of areas in mainland China (in Table 4). Zhao et al. (2007) investigated the evolution of air pollutants when an extremely strong dust storm from Gobi Desert near China-Mongolia border passed Beijing and confirmed the rapid decrease of sulfate and nitrate after the passage of the dust-associated cold front. The relative amounts of sulfate and nitrate in the postfrontal air were 0.77% and 0.08%, respectively, which were close to the relative amounts of the salts we observed at the desert site and Xi'an site in this study. Wang et al. (2014) reported hourly sulfate and nitrate in aerosols at Xi'an during a dust storm period on March 9, 2013. The

dust storm originated also from the Gobi Desert in the southwest part of the Mongolia, similar to the dust cases in this study. After the passage of the cold front, the relative amounts of sulfate and nitrate were 1.05% and 0.21%, respectively, which were also very close to the results of this study.

A number of studies in China reported that dust particles significantly enhanced the formation of sulfate and nitrate when dust plumes advected over urban areas (Li and Shao, 2009; Li et al., 2014; Nie et al., 2012; Qi et al., 2006; Sheng et al., 2003; Wang et al., 2013; Zhao et al., 2011; 2007), which are very different from the conclusions of this study. We carefully examined the available meteorological records for the dust episodes in those studies. In cases of cold-front associated dust (Li et al., 2014; Qi et al., 2006; Sheng et al., 2003; Zhao et al., 2007), the samples used in those studies were collected repeatedly in pre-fixed time periods without a careful consideration of the time of dust arrival. That means the samples were not separately collected from well defined prefrontal air and postfrontal air masses and some samples used for analysis included particles from both prefrontal air and postfrontal air. The results from such samples would show the presence of substantial sulfate and nitrate. But the sulfate and nitrate were from the particles originating from the local and regional areas and they were not produced on dust particles from desert areas. A recent publication about the passage of a dust storm passing Beijing with high-time resolution, on-line records demonstrated clearly the separation of the prefrontal pollutants and the postfrontal dust plume (Hu et al., 2016), further indicating the necessity of separating particles in prefrontal air and postfrontal air for an accurate description of salt origin in dust samples.

In addition, mineral ions or crustal elements (e.g. $Ca^{2+}$ ion, or elemental Al) have been frequently applied as the indicators of mineral dust in studies (Nie et al., 2012; Zhao et al., 2007). Samples with the highest loading of mass or crustal compositions (e.g. $Ca^{2+}$, Al) were frequently regarded as the samples of long-distance transported dust. However, the samples in those studies were actually collected from the front air as we described above and were a mixture of long-distance transported dust particles and locally- and regionally-originated aerosols. For example, in the study of Zhao et al. (2007), the mineral/TSP (total suspended particulate matters) ratios in samples of the highest TSP loading were significantly lower than those in samples collected after the occurrence of maximum aerosol loading, indicating that the samples at the highest TSP moment were not dust particles from desert areas only. The indicators of mineral crustal ions or elements (e.g. $Ca^{2+}$ ion, or elemental Al) may actually cause large uncertainties in the explanation of the origins and sometimes even misunderstandings on the origins of aerosol particles. The reason is that, besides road dust and construction dust, coal burning is a major source of mineral components in aerosols in China, and emits particulate matter that is abundant in mineral elements such as Si, Al, Ca and Fe (Chen et al., 2012). Coal burning emissions have been proven to cause significant air pollution in China (Cao et al., 2005; Wang et al., 2015; 2016a). Anthropogenic pollutants are usually present in prefrontal air. If only the presence of substantial mineral elements such as Ca, Al or Si is used as the indicator of the occurrence of mineral dust particles from desert areas, anthropogenic pollutants such as road dust and particles emitted from coal burning would have been categorized as desert dust particles. Such an examination would lead to a result of the occurrence of substantial sulfate- and nitrate-containing dust particles in samples.

In many cases, dust was observed in cyclonic disturbances with weak fronts or without fronts (Cao et al., 2003; Nie et al., 2012; Wang et al., 2013). Cold fronts could not be confirmed clearly at places of dust arrival in those studies. The cases usually occur in the south parts of China after the cold and dry air from the north lose their adiabatic state, and the postfrontal air arriving at such places has, to an extent, mixed with the local and regional air. Samples of aerosol particles after dust arrival at such places contain both long-distance transported dust particles and locally or regionally emitted pollutants. For example, Wang et al. (2013) reported the occurrence of nitrate and sulfate in particles during two extreme dust storms in Shanghai, a megacity in eastern China, from 20 to 22 March 2010 and from 26 to 27 April 2010. Weather charts (see Fig. 8 in the paper) showed the consecutive transport of anthropogenic air masses and dust storm plumes to Shanghai during the dust periods either with a cold front arrival (the previous case; equivalent to dust case with front in this study) or by the stimulation of a cold front event even though the front did not extend to Shanghai (the latter case; dust case without front). The relative amounts of sulfate and nitrate in samples at Shanghai during this period were 2.7% and 1.4% in the previous case and 9% and 5.9% in the latter case. Anthropogenic sulfate and nitrate in particles from the local and regional areas in the latter case would have appeared in the samples although they were not produced on dust particles from desert areas.

## 4 Conclusion

Dust particles were collected at the Tengger desert and Xi'an during two dust storm periods. Meteorological records showed these two dust storms originated from the same source region and had similar transport routes. The comparison of sulfate and nitrate of dust aerosol at the two places indicated that the production of sulfate and nitrate on dust particles following cold fronts was limited when the dust moved from the desert to the populated area. The adiabatic process of the dust-loading air movement was most likely the reason for the absence of sulfate formation, and the uptake of $HNO_3$ was for the small nitrate production.

Significant sulfate and nitrate in dust storm periods in China reported in previous studies were likely from locally-emitted and urban mineral particles, in addition to soil-derived sulfate, and they were unlikely produced via chemical conversions on dust particles from deserts. The major reason is that, in those studies, the air from which the samples were collected had been significantly influenced by local emissions. Without a proper evaluation of the contribution of sulfate and nitrate in the samples by locally-emitted and urban mineral particles, i.e., non-desert mineral particles, it is not safe to attribute all the detected sulfate and nitrate to the production on dust-storm particles.

**Author contribution**: Feng Wu and Daizhou Zhang designed the experiments; Xiao Guo, Yao Xia and Ting Zhang collected the samples and analyzed them. Juji Cao, Yan Cheng and Hui Lu reviewed and commented on the paper; Feng Wu and Daizhou Zhang prepared the manuscript with contributions from all co-authors.

**Competing interests**: The authors declare that they have no conflict of interest.

**Acknowledgments**

This work was supported by the "Strategic Priority Research Program" of the Chinese Academy of Sciences (Grant No. XDB05000000), the NNSF of China (Grant No. 40872211). It was also partly funded by the Grant-in-Aid for Scientific Research (B) of JSPS (No.16H02942). The authors thank Prof. Jay Melton and Prof. Morrow Stewart for their reviewing of grammar and language. We also thank Dr. Shuyu Zhao for her providing the figure of $SO_2$ emission distributions.

**References**

Abuduwaili, J., Gabchenko, M. V. and Junrong, X.: Eolian transport of salts—A case study in the area of Lake Ebinur (Xinjiang, Northwest China), Journal of Arid Environments, 72(10), 1843–1852, doi:10.1016/j.jaridenv.2008.05.006, 2008.

Bates, T. S., Quinn, P. K., Coffman, D. J. and Covert, D. S.: Marine boundary layer dust and pollutant transport associated with the passage of a frontal system over eastern Asia, J. Geophys. Res., 109(D19), D19S19, doi:10.1029/2003jd004094, 2004.

Bauer, S. E. and Koch, D.: Impact of heterogeneous sulfate formation at mineral dust surfaces on aerosol loads and radiative forcing in the Goddard Institute for Space Studies general circulation model, J. Geophys. Res., 110(D17), D17202, doi:10.1029/2005JD005870, 2005.

Cao, J. J., Wu, F., Chow, J. C., Lee, S. C., Li, Y., Chen, S. W., An, Z. S., Fung, K. K., Watson, J. G., Zhu, C. S. and Liu, S. X.: Characterization and source apportionment of atmospheric organic and elemental carbon during fall and winter of 2003 in Xi'an, China, Atmos. Chem. Phys., 5(11), 3127–3137, doi:10.5194/acp-5-3127-2005, 2005.

Cao, J., Lee, S., Zheng, X., Ho, K., Xiaoye Zhang, Guo, H., Chow, J. C. and Wang, H.: Characterization of dust storms to Hong Kong in April 1998, Water Air Soil Pollut: Focus, 3(2), 213–229, 2003.

Chen, H., Laskin, A., Baltrusaitis, J., Gorski, C. A., Scherer, M. M. and Grassian, V. H.: Coal fly ash as a source of iron in atmospheric dust, Environ. Sci. Technol., 46(4), 2112–2120, doi:10.1021/es204102f, 2012.

Denjean, C., Caquineau, S., Desboeufs, K., Laurent, B., Maille, M., Quiñones Rosado, M., Vallejo, P., Mayol-Bracero, O. L. and Formenti, P.: Long-range transport across the Atlantic in summertime does not enhance the hygroscopicity of African mineral dust, Geophys. Res. Lett., 42(18), 7835–7843, doi:10.1002/2015GL065693, 2015.

Dentener, F. J., Carmichael, G. R., Zhang, Y., Lelieveld, J. and Crutzen, P. J.: Role of mineral aerosol as a reactive surface in the global troposphere, J. Geophys. Res., 101(D17), 22869–22889, doi:10.1029/96JD01818, 1996.

Dong, X., Fu, J. S., Huang, K., Tong, D., and Zhuang, G. (2016). Model development of dust emission and heterogeneous chemistry within the Community Multiscale Air Quality modeling system and its application over East Asia, Atmos. Chem. Phys., 16, 8157-8180, doi:10.5194/acp-16-8157-2016.

Fairlie, T. D., Jacob, D. J., Dibb, J. E., Alexander, B., Avery, M. A., van Donkelaar, A. and Zhang, L.: Impact of mineral dust on nitrate, sulfate, and ozone in transpacific Asian pollution plumes, Atmos. Chem. Phys., 10(8), 3999–4012, doi:10.5194/acp-10-3999-2010, 2010.

Hartley, A. E. and Schlesinger, W. H.: Environmental controls on nitric oxide emission from northern Chihuahuan desert soils, Biogeochemistry, 50, 279–300, 2000.

Hu, W., Niu, H., Zhang, D., Wu, Z., Chen, C., Wu, Y., Shang, D. and Hu, M.: Insights into a dust event transported through Beijing in spring 2012: Morphology, chemical composition and impact on surface aerosols, Sci. Total Environ., 565, 287–298, doi:10.1016/j.scitotenv.2016.04.175, 2016.

Huang, K., Zhuang, G., Li, J., Wang, Q., Sun, Y., Lin, Y. and Fu, J. S.: Mixing of Asian dust with pollution aerosol and the transformation of aerosol components during the dust storm over China in spring 2007, J. Geophys. Res., 115, D00K13, doi:10.1029/2009JD013145, 2010.

Huang, R.-J., Zhang, Y., Bozzetti, C., Ho, K.-F., Cao, J.-J., Han, Y., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z., Szidat, S., Baltensperger, U., Haddad, I. E. and Prevot, A. S. H.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, doi:10.1038/nature13774, 2014a.

Huang, X., Song, Y., Zhao, C., Li, M., Zhu, T., Zhang, Q. and Zhang, X.: Pathways of sulfate enhancement by natural and anthropogenic mineral aerosols in China, J. Geophys. Res. Atmos., 119(24), 14,165–14,179, doi:10.1002/2014JD022301, 2014b.

Li, J., Wang Z., Zhuang, G., Luo, G., Sun, Y. and Wang, Q.: Mixing of Asian mineral dust with anthropogenic pollutants over East Asia: a model case study of a super-duststorm in March 2010, Atmos. Chem. Phys., 12(16), 7591–7607, doi:10.5194/acp-12-7591-2012, 2012.

Li, W. J. and Shao, L. Y.: Observation of nitrate coatings on atmospheric mineral dust particles, Atmos. Chem. Phys., 9(6), 1863–1871, doi:10.5194/acp-9-1863-2009, 2009.

Li, W., Shao, L., Shi, Z., Chen, J., Yang, L., Yuan, Q., Yan, C., Zhang, X., Wang, Y., Sun, J., Zhang, Y., Shen, X., Wang, Z. and Wang, W.: Mixing state and hygroscopicity of dust and haze particles before leaving Asian continent, J. Geophys. Res. Atmos., 119(2), 1044–1059, doi:10.1002/2013JD021003, 2014.

McCalley, C. K. and Sparks, J. P.: Abiotic gas formation drives nitrogen loss from a desert ecosystem, Science, 326(5954), 837–840, doi:10.1126/science.1178984, 2009.

Meskhidze, N.: Iron mobilization in mineral dust: Can anthropogenic $SO_2$ emissions affect ocean productivity? Geophys. Res. Lett., 30(21), doi:10.1029/2003gl018035, 2003.

Mori, I.: Change in size distribution and chemical composition of kosa (Asian dust) aerosol during long-range transport, Atmos. Environ., 37(30), 4253–4263, doi:10.1016/S1352-2310(03)00535-1, 2003.

Mori, I., Nishikawa, M., Quan, H. and Morita, M.: Estimation of the concentration and chemical composition of kosa aerosols at their origin, Atmos. Environ., 36(29), 4569–4575, doi:10.1016/s1352-2310(02)00489-2, 2002.

Nie, W., Wang, T., Xue, L. K., Ding, A. J., Wang, X. F., Gao, X. M., Xu, Z., Yu, Y. C., Yuan, C., Zhou, Z. S., Gao, R., Liu, X. H., Wang, Y., Fan, S. J., Poon, S., Zhang, Q. Z. and Wang, W. X.: Asian dust storm observed at a rural mountain site in

southern China: chemical evolution and heterogeneous photochemistry, Atmos. Chem. Phys., 12(24), 11985–11995, doi:10.5194/acp-12-11985-2012, 2012.

Nishikawa, M., Kanamori, S., Kanamori, N. and Mizoguchi, T.: Kosa aerosol as eolian carrier of anthropogenic material, Sci. Total Environ., 107, 13–27, doi:10.1016/0048-9697(91)90247-C, 1991.

Niu, H., Shao, L. and Zhang, D.: Aged status of soot particles during the passage of a weak cyclone in Beijing, Atmos. Environ., 45(16), 2699–2703, doi:10.1016/j.atmosenv.2011.02.056, 2011.

Qi, J., Li, X., Feng, L. and Zhang, M.: Characterization of dust and non-dust aerosols with SEM/EDX, J. Ocean Univ. China, 5(1), 85–90, doi:10.1007/BF02919381, 2006.

Ro, C.-U., Hwang, H., Kim, H., Chun, Y. and Van Grieken, R.: Single-Particle Characterization of Four "Asian Dust" Samples Collected in Korea, Using Low- ZParticle Electron Probe X-ray Microanalysis, Environ. Sci. Technol., 39(6), 1409–1419, doi:10.1021/es049772b, 2005.

Semeniuk, T. A., Wise, M. E., Martin, S. T., Russell, L. M. and Buseck, P. R.: Water uptake characteristics of individual atmospheric particles having coatings, Atmos. Environ., 41(29), 6225–6235, doi:10.1016/j.atmosenv.2007.04.001, 2007.

Sheng, L., Geng, M., Wang, Y., Gao, H., Shi, G. and Yu, P.: Effects of dust storms on atmospheric aerosols in Qingdao in spring 2002, Research of Environmental Sciences (in Chinese), 16(5), 11–13, 2003.

Sokolik, I. N. and Toon, O. B.: Direct radiative forcing by anthropogenic airborne mineral aerosols, Nature, 381(6584), 681–683, doi:10.1038/381681a0, 1996.

Song, C. H. and Carmichael, G. R.: A three-dimensional modelling investigation of the evolution processes of dust and sea-salt particles in east Asia, J. Geophys. Res., 106(D16), 18131–18154, doi:10.1029/2000JD900352, 2001.

Song, C. H., Kim, C. M., Lee, Y. J., Carmichael, G. R., Lee, B. K. and Lee, D. S.: An evaluation of reaction probabilities of sulfate and nitrate precursors onto East Asian dust particles, J. Geophys. Res., 112(D18), D18206, doi:10.1029/2006JD008092, 2007.

Song, C. H., Maxwell-Meier, K., Weber, R. J., Kapustin, V. and Clarke, A.: Dust composition and mixing state inferred from airborne composition measurements during ACE-Asia C130 Flight #6, Atmos. Environ., 39(2), 359–369, doi:10.1016/j.atmosenv.2004.08.046, 2005.

Sun, Y., Zhuang, G., Huang, K., Li, J., Wang, Q., Wang, Y., Lin, Y., Fu, J. S., Zhang, W., Tang, A. and Zhao, X.: Asian dust over northern China and its impact on the downstream aerosol chemistry in 2004, J. Geophys. Res., 115, D00K09, doi:10.1029/2009JD012757, 2010.

Sun, Y., Zhuang, G., Yuan, H., Zhang, X. and Guo, J.: Characteristics and sources of 2002 super dust storm in Beijing, Chinese Sci Bull, 49(7), 698–705, doi:10.1007/BF03184268, 2004.

Tegen, I., Lacis, A. A. and Fung, I.: The influence on climate forcing of mineral aerosols from disturbed soils, Nature, 380(6573), 419–422, doi:10.1038/380419a0, 1996.

Tsai, F., Tu, J.-Y., Hsu, S.-C. and Chen, W. N.: Case study of the Asian dust and pollutant event in spring 2006: Source, transport, and contribution to Taiwan, Sci. Total Environ., 478, 163–174, doi:10.1016/j.scitotenv.2014.01.072, 2014.

Underwood, G. M., Li, P., Al-Abadleh, H. and Grassian, V. H.: A Knudsen Cell Study of the Heterogeneous Reactivity of Nitric Acid on Oxide and Mineral Dust Particles, J. Phys. Chem. A, 105(27), 6609–6620, doi:10.1021/jp002223h, 2001.

Usher, C. R., Michel, A. E. and Grassian, V. H.: Reactions on mineral dust, Chem. Rev., 103(12), 4883–4940, doi:10.1021/cr020657y, 2003.

Vlasenko, A., Sjogren, S., Weingartner, E., Stemmler, K., Gäggeler, H. W. and Ammann, M.: Effect of humidity on nitric acid uptake to mineral dust aerosol particles, Atmos. Chem. Phys., 6(8), 2147–2160, doi:10.5194/acp-6-2147-2006, 2006.

Walvoord, M. A.: A reservoir of nitrate beneath desert soils, Science, 302(5647), 1021–1024, doi:10.1126/science.1086435, 2003.

Wang, F., Xu, D., Shi, J. and Chen, X.: Numerical analysis of interaction of $SO_2$ emission among 19 cities along the Middle-up stream of Yellow River and their contribution to Beijing city, Sci. Technol. Rev., 29(11), 25–29, 2011.

Wang, G. H., Cheng, C. L., Huang, Y., Tao, J., Ren, Y. Q., Wu, F., Meng, J. J., Li, J. J., Cheng, Y. T., Cao, J. J., Liu, S. X., Zhang, T., Zhang, R. and Chen, Y. B.: Evolution of aerosol chemistry in Xi'an, inland China, during the dust storm period of 2013—Part 1: Sources, chemical forms and formation mechanisms of nitrate and sulfate, Atmos. Chem. Phys., 14(21), 11571–11585, doi:10.5194/acp-14-11571-2014, 2014.

Wang, G., Cheng, S., Li, J., Lang, J., Wen, W., Yang, X. and Tian, L.: Source apportionment and seasonal variation of $PM_{2.5}$ carbonaceous aerosol in the Beijing-Tianjin-Hebei Region of China, Environ Monit Assess, 187(3), 143, doi:10.1007/s10661-015-4288-x, 2015.

Wang, G., Wang, H., Yu, Y., Gao, S., Feng, J., Gao, S. and Wang, L.: Chemical characterization of water-soluble components of $PM_{10}$ and $PM_{2.5}$ atmospheric aerosols in five locations of Nanjing, China, Atmos. Environ., 37(21), 2893–2902, doi:10.1016/S1352-2310(03)00271-1, 2003.

Wang, H., An, J., Cheng, M., Shen, L., Zhu, B., Li, Y., Wang, Y., Duan, Q., Sullivan, A. and Xia, L.: One year online measurements of water-soluble ions at the industrially polluted town of Nanjing, China: Sources, seasonal and diurnal variations, Chemosphere, 148, 526–536, doi:10.1016/j.chemosphere.2016.01.066, 2016a.

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, Atmos. Res., 127, 22–33, doi:10.1016/j.atmosres.2013.02.011, 2013.

Wang, Q., Zhuang, G., Huang, K., Liu, T., Lin, Y., Deng, C., Fu, Q., Fu, J. S., Chen, J., Zhang, W. and Yiming, M.: Evolution of particulate sulfate and nitrate along the Asian dust pathway: Secondary transformation and primary pollutants via long-range transport, Atmos. Res., 169, 86–95, doi:10.1016/j.atmosres.2015.09.013, 2016b.

Wang, S., Wang, J., Zhou, Z. and Shang, K.: Regional characteristics of three kinds of dust storm events in China, Atmos. Environ., 39(3), 509–520, doi:10.1016/j.atmosenv.2004.09.033, 2005a.

Wang, X., Hua, T., Zhang, C., Lang, L. and Wang, H.: Aeolian salts in Gobi deserts of the western region of Inner Mongolia: Gone with the dust aerosols, Atmos. Res., 118, 1–9, doi:10.1016/j.atmosres.2012.06.003, 2012.

Wang, Y., Zhuang, G., Sun, Y. and An, Z.: Water-soluble part of the aerosol in the dust storm season—evidence of the mixing between mineral and pollution aerosols, Atmos. Environ., 39(37), 7020–7029, doi:10.1016/j.atmosenv.2005.08.005, 2005b.

Wang, Y., Zhuang, G., Tang, A., Zhang, W., Sun, Y., Wang, Z. and An, Z.: The evolution of chemical components of aerosols at five monitoring sites of China during dust storms, Atmos. Environ., 41(5), 1091–1106, doi:10.1016/j.atmosenv.2006.09.015, 2007.

Wu, F., Zhang, D., Cao, J., Xu, H. and An, Z.: Soil-derived sulfate in atmospheric dust particles at Taklimakan desert, Geophys. Res. Lett., 39(24), L24802, doi:10.1029/2012GL054406, 2012.

Wu, F., Zhang, D., Cao, J., Zhang, T. and An, Z.: Background-like nitrate in desert air, Atmos. Environ., 84, 39–43, doi:10.1016/j.atmosenv.2013.11.043, 2014.

Wu, P.-M. and Okada, K.: Nature of coarse nitrate particles in the atmosphere—A single particle approach, Atmos. Environ., 28(12), 2053–2060, doi:10.1016/1352-2310(94)90473-1, 1994.

Yabuki, S., Mikami, M., Nakamura, Y., Kanayama, S., Fu, F., Liu, M. and Zhou, H.: The characteristics of atmospheric aerosol at Aksu, an Asian dust-source region of North-West China: A summary of observations over the three years from March 2001 to April 2004, J. Meteor. Soc. Japan, 83A, 45–72, doi:10.2151/jmsj.83A.45, 2005.

Zhang, D.: Effect of sea salt on dust settling to the ocean. Tellus 68B, 641-646, doi:10.1111/j.1600-0889.2008.00358.x, 2008.

Zhang, D. and Iwasaka, Y.: Nitrate and sulfate in individual Asian dust-storm particles in Beijing, China in Spring of 1995 and 1996, Atmos. Environ., 33(19), 3213–3223, doi:10.1016/S1352-2310(99)00116-8, 1999.

Zhang, D., Iwasaka, Y., Shi, G., Zang, J., Hu, M. and Li, C.: Separated status of the natural dust plume and polluted air masses in an Asian dust storm event at coastal areas of China, J. Geophys. Res., 110(D6), D06302, doi:10.1029/2004JD005305, 2005.

Zhang, T., Cao, J. J., Tie, X. X., Shen, Z. X., Liu, S. X., Ding, H., Han, Y. M., Wang, G. H., Ho, K. F., Qiang, J. and Li, W. T.: Water-soluble ions in atmospheric aerosols measured in Xi'an, China: Seasonal variations and sources, Atmos. Res., 102(1-2), 110–119, doi:10.1016/j.atmosres.2011.06.014, 2011.

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.: Characterization of soil dust aerosol in China and its transport and distribution during 2001 ACE-Asia: 1. Network observations, J. Geophys. Res., 108(D9), 4261, doi:10.1029/2002JD002632, 2003.

Zhang, X., Zhuang, G., Yuan, H., Rahn, K. A., Wang, Z. and An, Z.: Aerosol particles from dried salt-lakes and saline soils carried on dust storms over Beijing, Terr. Atmos. Ocean. Sci., 20(4), 619, doi:10.3319/TAO.2008.07.11.03(A), 2009.

Zhang, Y. and Carmichael, G. R.: The role of mineral aerosol in tropospheric chemistry in East Asia — A model study, J. Appl. Meteor., 38(3), 353–366, doi:10.1175/1520-0450(1999)038<0353:tromai>2.0.co;2, 1999.

Zhao, J., Zhang, F., Xu, Y., Chen, J., Yin, L., Shang, X. and Xu, L.: Chemical characteristics of particulate matter during a heavy dust episode in a coastal city, Xiamen, 2010, Aerosol Air Qual. Res., doi:10.4209/aaqr.2010.09.0073, 2011.

Zhao, X., Zhuang, G., Wang, Z., Sun, Y., Wang, Y. and Yuan, H.: Variation of sources and mixing mechanism of mineral dust with pollution aerosol—revealed by the two peaks of a super dust storm in Beijing, Atmos. Res., 84(3), 265–279, doi:10.1016/j.atmosres.2006.08.005, 2007.

Table 1: Summary of weather conditions at the sample collection

| Samples ID | Sampling time (BST[c]) | Pressure (hPa) | Temperature (℃) | RH (%) | Wind | |
|---|---|---|---|---|---|---|
| | | | | | Direction | Speed (m $s^{-1}$) |
| Tengger Desert (April 24, 2014) | | | | | | |
| T1 | 06:32-08:32 | 870.2-872.5 | 9.5-11.0 | 30-35 | NW | 5.7-13.6 |
| T2 | 08:42-10:42 | 872.4-874.7 | 8.0-9.4 | 31-37 | NW | 5.6-11.4 |
| T3 | 10:51-12:51 | 875.2-876.7 | 5.5-7.7 | 31-39 | NW | 6.0-14.6 |
| T4[a] | 13:02-15:03 | 876.2-878.1 | -1.4-4.8 | 40-97 | NW | 5.8-12.3 |
| Xi'an (May 1, 2014) | | | | | | |
| X1 | 07:16-09:16 | 965.6-968.1 | 17.6-19.6 | 63-72 | W | 0-1.8 |
| X2 | 09:20-10:20 | 968.2-969.7 | 19.5-21.7 | 45-67 | NW | 0-2.5 |
| X3 | 10:22-11:22 | 970-971.7 | 21.2-22.2 | 39-50 | NW | 0.5-3.2 |
| X4[b] | 11:27-12:27 | 971.7-972.7 | 20.1-21.3 | 40-43 | NW | 0.6-3.4 |
| X5 | 12:28-14:28 | 972.7-973.5 | 20.0-20.7 | 38-42 | NW | 0.4-2.9 |
| X6 | 14:38-16:38 | 972.4-973.2 | 19.0-21.6 | 38-47 | NW | 0-5.4 |
| X7 | 16:43-19:43 | 972.5-973.1 | 18-21.8 | 38-48 | NW | 0-3.0 |

[a] Not suitable for comparison because of snow and results from this sample were excluded for further analysis.
[b] Not available for analysis because the collection system was blown down by wind.
[c] Beijing standard time (8 hours prior to GMT).

Table 2: Concentration (Conc., in μg $m^{-3}$) of TSP ([M]), sulfate ($[SO_4^{2-}]$), nitrate ($[NO_3^-]$) and ammonia ($[NH_4^+]$) at the desert site in the dust episode. Also included are the relative amount (R. M., in %) of the three ions in TSP

| Samples | [M] | $[SO_4^{2-}]$ | | $[NO_3^-]$ | | $[NH_4^+]$ | |
|---|---|---|---|---|---|---|---|
| | | Conc. | R. M. | Conc. | R. M. | Conc. | R. M. |
| T1 | 4754 | 59 | 1.2 | 5.9 | 0.12 | 0.27 | <0.01 |
| T2 | 4487 | 54 | 1.2 | 5.1 | 0.11 | 0.22 | <0.01 |
| T3 | 3481 | 39 | 1.1 | 3.8 | 0.11 | ND[a] | ND |
| Ave. | 4241±672 | 51±10 | 1.2±0.1 | 5.0±1.1 | 0.12±0.11 | 0.16±0.14 | <0.01 |

[a] Not detected

Table 3: Mass ratios of Ca, Fe, Ti, Mn, Ba, Zn and Pb to Fe in the samples at the two sites

| Samples | Ca/Fe | K/Fe | Ti/Fe | Mn/Fe | Ba/Fe | Zn/Fe | Pb/Fe |
|---|---|---|---|---|---|---|---|
| Tengger Desert (April 24, 2014) | | | | | | | |
| T1 | 1.47 | 0.54 | 0.084 | 0.023 | 0.013 | 0.003 | 0.0014 |
| T2 | 1.47 | 0.55 | 0.082 | 0.023 | 0.013 | 0.0023 | 0.0011 |
| T3 | 1.57 | 0.57 | 0.086 | 0.024 | 0.012 | 0.002 | 0.0009 |
| Xi'an (May 1, 2014) | | | | | | | |
| X1[a] | NA | NA | NA | NA | NA | NA | NA |
| X2 | 1.86 | 0.66 | 0.084 | 0.028 | 0.012 | 0.037 | 0.009 |
| X3 | 2.16 | 0.63 | 0.087 | 0.039 | 0.008 | 0.010 | 0.004 |
| X5 | 1.76 | 0.62 | 0.089 | 0.045 | 0.018 | 0.003 | 0.0009 |
| X6 | 1.44 | 0.63 | 0.092 | 0.031 | 0.015 | 0.003 | 0.0008 |
| X7 | 1.80 | 0.68 | 0.089 | 0.024 | 0.022 | 0.003 | 0.0009 |

[a] No enough sample for analysis

Table 4: The relative amounts (%) of nitrate, sulfate and ammonia in TSP or $PM_{2.5}$ in postfrontal air during dust storms at dust downwind Chinese cities.

| Site | $SO_4^{2-}$ | $NO_3^-$ | $NH_4^+$ | Remarks | References |
|---|---|---|---|---|---|
| Xi'an | 0.91 | 0.22 | NA | TSP (May 1, 2014) | This study |
| Xi'an | 1.05 | 0.21 | 0.09 | TSP (March 9, 2013) | Wang et al. (2014) |
| Beijing | 0.75 | 0.08 | 0.05 | TSP (March 22, 2002) | Zhao et al. (2007) |
| Shanghai | 2.7 | 1.4 | 0.7 | $PM_{2.5}$ (March 20-21, 2010) | Wang et al. (2013) |

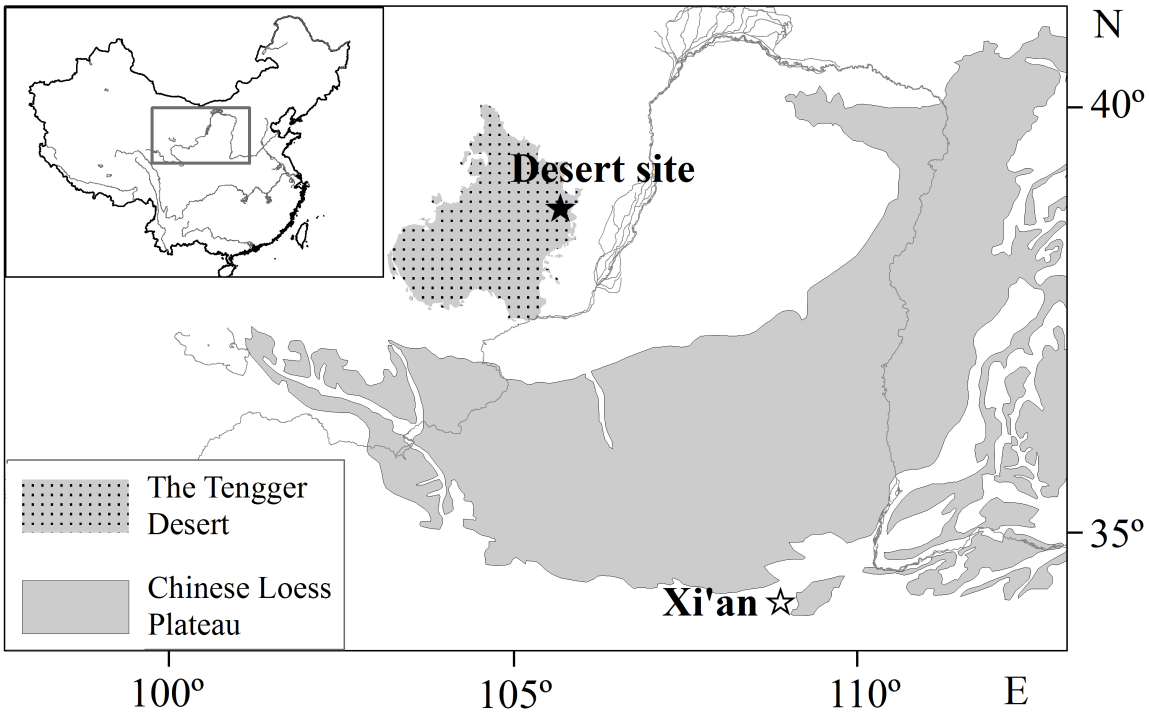


Figure 1: Location of the sampling sites. Also shown is the Chinese Loess Plateau.

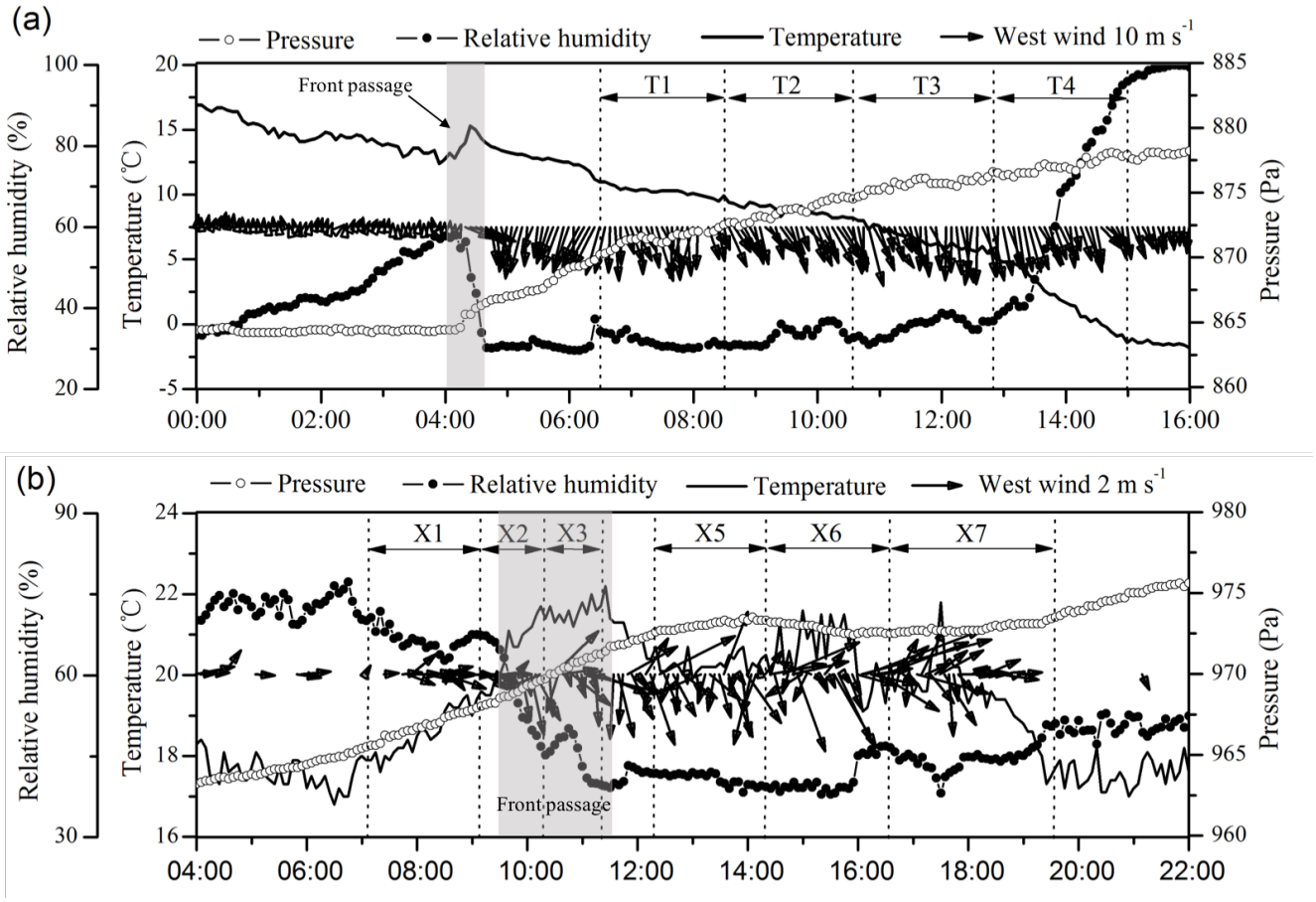


Figure 2: Surface pressure, temperature, relative humidity (RH), and wind during the sampling periods at the desert site (a: 2014/04/24 04:00-15:00 BST) and at Xi'an site (b: 2014/05/01 04:00-12:00 BST). Also shown are the front passage (shaded bars) and the durations of sample collections (Table 1).

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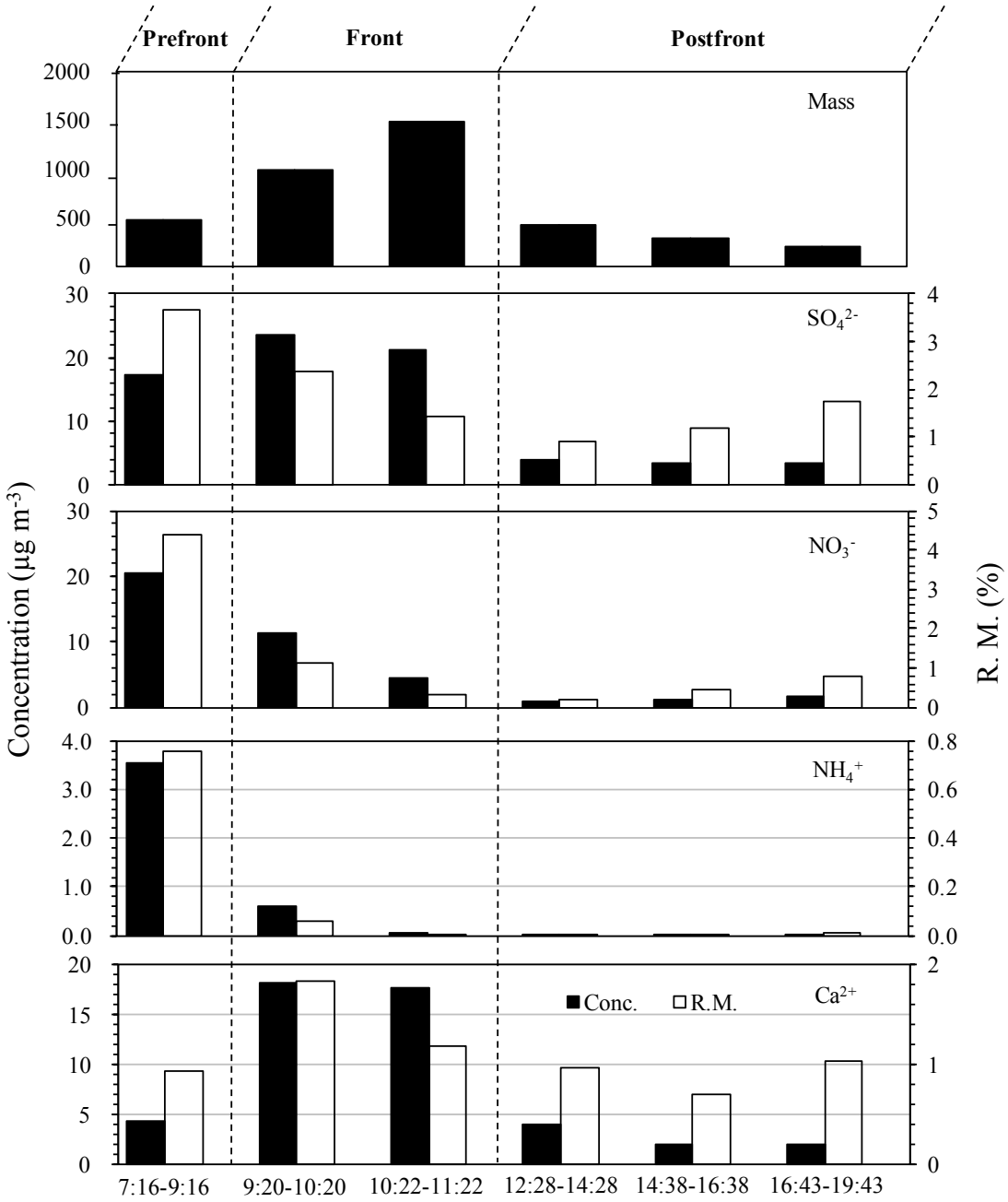


Figure 3: Concentrations of mass, $SO_4^{2-}$, $NO_3^-$, $NH_4^+$ and $Ca^{2+}$ at Xi'an site during the dust passage. Data for samples between 11:27 and 12:27 BST are not included since the sampler was blown down by wind. The relative amounts (R. M.: the ratios of the ion concentrations to the total mass concentration in percentage) of these ions are also illustrated.