Point-by-point responses to the comments by Prof. B. Huebert

March 11, 2017

Dear Prof. B. Huebert,

Thank you very much for your review of our submission. It is likely we could not receive the comments of other reviewers on our submission soon, here we would like to answer your comments and questions first. The revision of the manuscript will be finished after getting comments from other reviewers.

Our point-by-point responses to your comments and questions are attached to this letter. They are a little long. Please do us a favor to read them patiently.

With best regards.

Daizhou Zhang
(On behalf of authors)

Interactive comment on "Limited production of sulfate and nitrate on front-associated dust storm particles moving from desert to distant populated areas in northwestern China" by Feng Wu et al.
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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 show 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 result we observed was that the concentration levels of sulfate were similar at the two site (the level was 0.91% at the urban site; Table 3).

Even if we consider all the sulfate observed at the urban site was produced via reactions on particle surface, the production was still much smaller than that in polluted urban atmosphere. So we consider 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 recent 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 during the dust travel was consistent with the level we observed at the urban site. We found the estimated one and the observed one were in the same order (Page 8 Line 18 – Page 9 Line 8). In fact, similar to sulfate, even though we consider all the nitrate observed at the urban site was produced via surface reactions, the production was still very smaller than that in polluted urban atmosphere.

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.

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 issues, although data from more cases are better. The key point is whether 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 have carefully checked all data in published literatures on the formation in dust storm particles in postfrontal air. We confirmed the common result as we describe in the manuscript: the production of the two salts on dust storm particles in postfrontal air was limited (some reference results in Table 3). So we think, even we increase the cases of dust observation at the urban site, we will encounter similar 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. Unfortunately, we failed in getting more high quality series of data from dust storms as we show in the manuscript, except for some pieces of data, due to technique problems.

For compensating this lack, we have carefully checked all published papers of studying nitrate and sulfate in dust from the Chinese Gobi Desert at observational sites in or close to the Tengger desert, and checked the data from samples that were considered to be dust storm particles with no anthropogenic pollution. We confirmed that the nitrate concentration from any dust storm samples in those papers was always very small and not very different from we encountered in this study (Table R1). So we consider our result on nitrate we observed at the desert can represent the common level of nitrate there. In the revision, we will add the range of nitrate concentration in desert dust plumes which were reported in published literatures to show

this point.

Table R1. The relative amounts (%) of nitrate and sulfate in dust samples from the Gobi Desert

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 kosa source. [b] Developed based on local measurement data collected 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 too absolute (we will decrease the tone in the revision), 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.

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 R2), indicating that there should not be considerable pollutants in the samples.

Table R2 The ratios of Ca, Fe, Ti, Mn, Ba, Zn and Pb to Fe in aerosol samples at two sampling 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

Typo: there is no April 31st.

Response: It is April 30th. We will correct it 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 another dust storm. 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 convenience to read them, 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. Please do us a favor to check the similarities between the two dust storms.

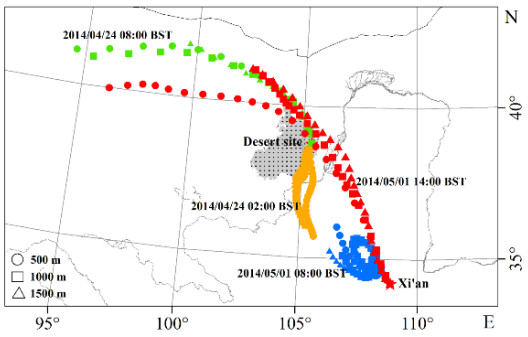

Figure S2: Backward trajectories from the desert site (2014/04/24) and Xi'an site (2014/05/01) from the HYSPLIT model (www.arl.noaa.gov/HYSPLIT.php). (BST = GMT + 08:00)

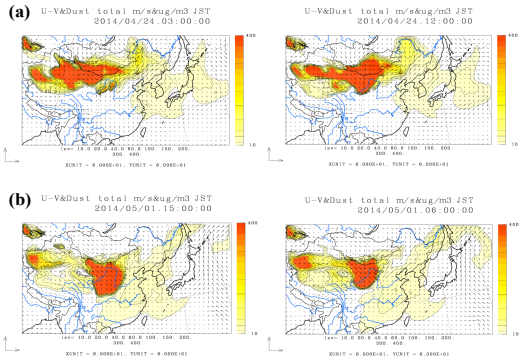

Figure S3: CFORS model output for boundary layer (surface - 1000m) dust concentration (μg/m^3, color in log scale) and wind vector at 1000m of East Asia during the sampling periods at desert site (a) and Xi'an (b). (http://www-cfors.nies.go.jp/~cfors/index-j.html) (JST = GMT + 09:00)

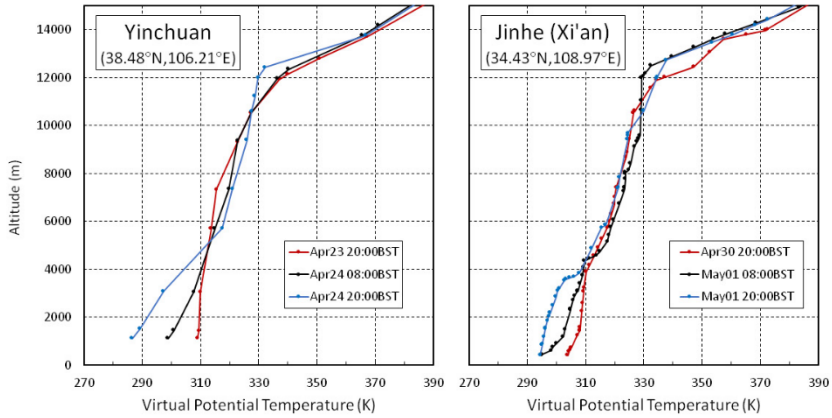

Figure S6: Vertical profiles of virtual potential temperature near the surface at Yinchuan (38.48°N, 106.21°E), the WMO sounding station closest to the desert site, and at Jinhe (34.43°N, 108.97°E), a suburb place of Xi'an, before and after dust occurrence at the two places. The profiles were from the 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. 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 (we will add the data in the revision) 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. Would you mind to give more details on why you disagree our conclusions, in order for us to understand accurately why you believe "the conclusions are unsupported".

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 have many case data. 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 in the discussion of the manuscript.

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 will remove "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." will be revised in the revision

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: Thank you very much for your encouragement. 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. The mixture 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.

Thank you very much again for our careful review of our submission. Your any further comments are welcome.