Point-by-point responses to referee comments

Reviewer#2

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.

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, $NO3^-$ concentration in dust samples was 4-6 μg m^{-3} and the average was 5 μgm^{-3}. The relative amount of $NO3^-$ 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 $NO3^-$ was 0.9 μgm^{-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, $NO3^-$ 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 μgm^{-3}, with the mass fraction ~0.2%). The higher mass fraction of $NO3^-$ 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 $NO3^-$ 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 $NO3^-$ 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.

Thank you very much for your careful review and helpful comments and suggestions. Your any comments are appreciated.