Anonymous referee #1

This work analyzes the mechanism of haze formation in winter (February) and Summer (July) of 2011 using a regional air quality modeling system, and identifies that higher relative humidity (RH) is an important factor for the haze formation in summer. Considering the serious air pollution and deteriorated air quality in China, this kind of study is important and potentially useful for air pollution controls. This manuscript is in general well written although in some places there are wording issues. I have some general comments that the authors need to address before I recommend its publication in ACP. I suggest that the authors do more in-depth analysis of haze formation mechanisms and also evaluation of models results.

Reply:

We would like to thank the reviewer for his/her constructive comments for the improvement of our manuscript. Our responses to the comments from Reviewer 1 are included in the followings.

Substantial modifications are made on the contents. They are Section 4.2, Section 4.3 and the fourth and fifth point of conclusion and some relevant contents are added. (please check the words with red color in the revised paper). We also modified Fig.1 and Fig. 14, and added Fig. 6, Fig. 8, and Fig. 13. In this way, we hope that the following scientific views can be expressed more explicitly.

Even though the mass concentration of $PM_{2.5}$ is closely inversely correlated with visibility, the influence effect is diversity when the mass concentration of $PM_{2.5}$ locates in different intervals. The analysis of this study showed that the influence of $PM_{2.5}$ mass burden variation on visibility is very weak when its value is relatively high (larger than 100 μg m^{-3}). Only when the mass concentration of $PM_{2.5}$ is cut down to a certain interval can its decrease make the visibility increase rapidly. Therefore, we suggest that it is more reasonably to set a haze occurrence threshold interval (the values of mass concentration of $PM_{2.5}$ when the visibility reaches 10 km in different ambient conditions). Through sensitivity test, we estimated the possible values of haze occurrence threshold in Beijing in different seasons, and discussed the related impact factors.

Detailed statement can refer to the relevant contents in the revised paper. By investigating the characteristics of haze occurrence threshold, one of the important viewpoints of this study is that the atmospheric haze and the atmospheric pollution should be distinguished. Only when the mass concentration of $PM_{2.5}$ is cut down to a threshold interval can its decrease make the visibility increase rapidly, and the haze could be removed. Otherwise, if the mass concentration of $PM_{2.5}$ fails to fall into the

values of this threshold, the improvement of visibility would still be very weak when the emission reduction measures are taken.

We sincerely hope that you can review the modified contents above and give us valuable comments. Thanks again.

(1) In addition to RH, are there other factors affecting the haze formation? Even with in one single month (e.g., February or July) there are huge changes in the visibility, while emissions should not change a lot. The authors briefly touch the stability and convection. I suggest the authors to do more qualitative analysis by calculating the atmospheric stability based on the temperature profiles. I also suggest the authors to plot the surface precipitation as an indicator of wet scavenging of aerosols.

Reply:

Thanks for this comment.

According to the valuable advice of you and other reviewers, substantial modifications are made on the contents. After careful consideration, we finally decide to delete the discussion of this part. The reasons are as follows. First, we could not obtain the observation data of vertical temperature profile right now. The evaluation of the model results is not available here. Second, we kindly think that the main point of this study should focus on investigating the influence mechanism of mass concentration and microphysical properties of aerosols on the haze formation in North China Plain by using the modeling system. To investigate the influence of meteorological field is not the main target of this study. Therefore, in the revised paper, this part is deleted and some more relevant contents are added (including the discussion of microphysical properties of aerosols and haze occurrence threshold, etc.). In addition, we accepted your suggestion, adding the content about verification and discussion of simulated precipitation. Please refer to line 182-188, line 200-204 in the revised paper.

(2) The authors mention that nitrate, sulfate and ammonium are the three major aerosol components in Beijing. How about the contribution of organic carbon (OC) to PM2.5? The model underpredicts OC mass concentration (Figure 8). Are there any aerosol mass spectrometry data available in Beijing in winter and summer to evaluate modeled aerosol components? How about the role of temperature in affecting the secondary formation of these aerosols between winter and summer?

Reply:

Thanks for this comment.

According to the model simulation results and analysis in our study, the contribution of organic carbon aerosol to the mass concentration of $PM_{2.5}$ was about 5%-15%. However, it is found that the model may underestimate about half of the organic carbon aerosol concentration by comparing with the observation data. According to the related researches, the uncertainty of organic components estimation should be a common problem in model simulations nowadays. Most models underestimate the mass concentration of organic carbon. On one hand, it is because the organic components and emission sources are too complex to recognize. On the other hand, it is difficult to add the simulation schemes of multiple organic components evolution processes, because it needs to modify almost all of the aerosol simulation modules, including the gas-phase chemistry solvers, aqueous-phase solvers, heterogeneous reaction schemes, scavenging schemes, etc. In general, the modeling system in this study can have accurate simulation on the seasonal variation features of organic carbon aerosol at least. However, it is also necessary to improve the accuracy of quantity estimation, which also is one major task of our current study.

We regret that at present the observational data of mass spectrometry could not been collected by our group. Only daily observational data of carbonaceous aerosols which are measured by DRI Model 2001 Thermal/Optical Carbon Analyzer could be obtained. Thus, we cannot provide the evaluation with high time resolution.

The CB05 mechanism was applied to treat the secondary organic aerosol (SOA) formation and its precursors in our modeling system. In the CB05, the SOA formation is modeled by forming semi-volatile products in volatile organic compound (VOC) reactions. The semi-volatile products are partitioned between the gas and aerosol phase according to the ambient conditions, such as temperature, relative humidity, vapor pressure, existing aerosol particles. If we just consider the impact of temperature, the higher temperature should favor the formation of SOA in summer. However, the higher SOA mass burden could also appear in winter because of the stronger emission of its precursors in North China Plain.

(3) The authors discuss the change of aerosol size distribution influencing the threshold of haze occurrence. Are there aerosol size distribution data available for model evaluation?

Reply:

Thanks for this comment.

We regret that the evaluation of modeled aerosol size distribution is not available because the observation data cannot be collected by our group. However, the air quality model CMAQ which was used by this study is one of the widely used regional atmospheric chemistry modeling systems in the world at present. The mechanism of particle coagulation and condensation growth in this modeling system should be reasonable. What's more, the analysis on the aerosol size distribution was just qualitative research (focusing on the decreasing or increasing trend). Therefore, we kindly think that the simulation results can be used by the analysis in this study.

Specific comments:

1. Page 30577. Lines 13-16. Why the mass burden of PM2.5 remain at high levels while SO2 emission has been reduced?

Reply:

Thanks for this comment.

Even though the emission of SO_2 decreases, the related studies showed that the emission loading of nitrate precursors NO_x (Zhang et al., JGR，2007), primary aerosols from anthropogenic activities (including BC, primary organic aerosols, primary $PM_{2.5}$ particles, etc.) (Lei et al., ACP, 2011) obviously increased in recent years. Therefore, the mass burden of $PM_{2.5}$ should be remained at high level.

2. Page 30577. Line 25. Change “the said” to “these” 3. Page 30579. Line 2

Reply:

Thanks for this comment. We have modified the statement (It is in line 65 in the revised paper).

3. Remove “efficiently”

Reply:

Thanks for this comment. We have modified the statement.

4. Page 30580. Add brief description how the model treats SOA.

Reply:

Thanks for this comment. We added the description in line 106-111 in the revised paper. Please see if it is OK.

5. Page 30580. Line 24. Remove “efficiently”

Reply:

Thanks for this comment. We have modified the statement.

6. Page 30582. Line 12. Remove “efficiently”

Reply:

Thanks for this comment. We have modified the statement.

7. Page 30589. Lines 13-15. The authors conclude that the importance of nitrate from the transportation sector as the major sources of secondary particles in Beijing. How does this reconcile with the recent study of Zhang et al. (ACP, 13, 7053-7074) 2013 “Chemical characterizations: : :”. Please add some discussions.

Reply:

Thanks for this comment.

In this study, the conclusion that organic aerosol was higher in winter while inorganic aerosol (sulfate, nitrate, ammonium) was higher in summer in Beijing is consistent with that of Zhang et al. (2013). To investigate the contribution of transport sector to the air pollution in Beijing was not the main point of this study, so it did not discuss in detail. We deduced that the contribution of transport sector to the air pollution should be very important in Beijing because of the high mass burden of nitrate which converted from the precursors NO_x (NO_x is one of the main pollutants emitted from vehicle exhaust). In the study of Zhang et al. (2013), they used positive matrix factorization (PMF) to identify the possible sources of various aerosol components in $PM_{2.5}$ samples in Beijing. There may be great differences on how to apportion the emission sources of $PM_{2.5}$ particles between different source apportionment methods. The nitrate aerosol was identified as “secondary inorganic aerosol" in Zhang et al. (2013), not the pollutant from "traffic source". This shall be the main reason for the inconsistency between the relevant conclusions in this paper and those in Zhang et al., (2013).

Anonymous referee #3

General Comments:

This paper presents a model study upon the haze formation in Beijing, China. It concluded that high PM2.5 loading was the main cause of haze events in Beijing, and that water uptake by aerosols resulted in the frequent formation of haze in Beijing, particularly during summertime. In general, this paper is well organized except some technical defects. However, my major concern is that this paper did not provide new concept or scientific findings relevant to haze. Coupling RAMS-CMAQ with an aerosol optical scheme is not a new idea as a similar study from the same group has been published in another Journal (Atmospheric Environment, 2013, 72: 177-191). Moreover, It is well known in atmospheric physics that high levels of aerosol concentration will resulted in cases of low visibility, and hygroscopic growth of aerosols will enhance the light scat-tering capability, or mass-specific light extinction efficiency of aerosol particles. The case of Beijing is interesting because the microphysical properties of aerosols could be different from those observed in US or Europe. Unfortunately, the authors stopped at a general description of the phenomena of haze formation and did not advance further into the details of aerosol chemistry and/or physics. Therefore, I suggest reject this paper from ACP because lack of scientific merits.

Reply:

We would like to thank the reviewer for his/her constructive comments for the improvement of our manuscript. Our responses to the comments from Reviewer 1 are included in the followings.

In general, besides the routine analysis of simulation results, this study also wants to provide some further research about the mechanism of haze formation and how to efficiently decrease the possibility of haze occurrence over NCP by using the modeling system. Due to the improper structure arrangement and descriptive approach of the paper, the main scientific view may not be well expressed. Therefore, we adjusted the paper structure and made substantial modification. Section 4.2, Section 4.3 and the fourth and fifth point of conclusion are modified, and some relevant contents are added (please check the words with red color in the revised paper). We also modified Fig.1 and Fig. 14, and added Fig. 6, Fig. 8, and Fig. 13. In this way, we hope that the following two scientific views can be expressed more explicitly.

(1) The mechanism of haze formation in Beijing in winter is obviously different from that in summer. The mass concentration of $PM_{2.5}$ is relatively higher, and the ratios of inorganic salts and carbonaceous components are generally balanced in winter. Therefore, the high mass concentration of $PM_{2.5}$ and diverse aerosol components should be the major reasons of the serious haze occurrence in winter. While the mass

concentration of $PM_{2.5}$ in summer was relatively lower, but the ratio of hygroscopic inorganic salts, including sulfate, nitrate and ammonium, increased and their mass concentrations were even higher than those in winter. With obviously higher relative humidity, it could still form more serious haze even the mass concentration of $PM_{2.5}$ is lower than that in winter. The water uptake of hygroscopic components played a key role in it. This indicated that it is important to apply emission reduction measures based on the specific pollution and meteorological characteristics in different seasons. In this way, the possibility of haze occurrence can be effectively decreased.

(2) Even though the mass concentration of $PM_{2.5}$ is closely inversely correlated with visibility, the influence effect is diversity when the mass concentration of $PM_{2.5}$ locates in different intervals. The analysis of this study showed that the influence of $PM_{2.5}$ mass burden variation on visibility is very weak when its value is relatively high (larger than 100 $\mu g\ m^{-3}$). Only when the mass concentration of $PM_{2.5}$ is cut down to a certain interval can its decrease make the visibility increase rapidly. Therefore, we suggest that it is more reasonably to set a haze occurrence threshold interval (the values of mass concentration of $PM_{2.5}$ when the visibility reaches 10 km in different ambient conditions). Through sensitivity test, we estimated the possible values of haze occurrence threshold in Beijing in different seasons, and discussed the related impact factors. Detailed statement can refer to the relevant contents in this paper. By investigating the characteristics of haze occurrence threshold, one of the important viewpoints of this study is that the atmospheric haze and the atmospheric pollution should be distinguished. Only when the mass concentration of $PM_{2.5}$ is cut down to a threshold interval can its decrease make the visibility increase rapidly, and the haze could be removed. Otherwise, if the mass concentration of $PM_{2.5}$ fails to fall into the values of this threshold, the improvement of visibility would still be very weak when the emission reduction measures are taken.

We sincerely hope that you can review the modified paper and give us valuable comments. Thanks again.

Specific Comments:

1. Method Sec: Calculation of light extinction coefficient of aerosols is the key component of this task. In addition to citing references, it is worth a detailed description in this Sec, so that readers know what parameters were used in the model and thereby can make judgment.

Reply:

Thanks for this comment.

We are sorry we did not give a clear description of the modeling system. We have modified the related description of the modeling system in the manuscript. Please see the statement from line 132 to line 141.

2. Model evaluation: it was indicated that the model performed well as shown in the figures. However, there were indeed some cases where the model value was inconsistent with the observation. To perform a model validation, I suggest make the comparison in terms of statistics and refer to Eder and Yu (AE, 2006) and Appel et al. (AE, 2012).

Reply:

Thanks for this comment.

We have added some relevant content into the manuscript. Please see the statement in line 192-205. Here we just calculated the statistic parameters of $PM_{2.5}$, O_3, NO_2, and visibility comparisons. For other variables, including the meteorological factors and aerosol components, the statistic samples are relatively small, so we did not provide the statistic parameters of their comparisons.

3. Sec 4.1: It was indicated that "the heavy mass burden of PM2.5 was mainly concentrated in four urban areas...". However, the urban hot spots were not shown in the figures. Actually, the pattern shown in those figures are more likely caused by a regional pollution event.

Reply:

Thanks for this comment.

We have added the district areas of Beijing, Tianjin, Shijiazhuang, and Jinan in Fig. 1, and modified the description in section 4.1. We think that your advice is correct. The high mass burden of $PM_{2.5}$ generally covered Beijing, Tianjin, the whole area of Hebei province and northwest part of Shandong province, not just the urban areas. Please see the modified statement in line 236-240.

4. Sec 4.1: It was indicated that "the distribution patterns of visibility broadly followed those of PM2.5...". Don't you think this is a result as expected and is determined by the calculation of visibility in model (i.e. EQ1)?

Reply:

Thanks for this comment.

Actually, except the mass concentration of aerosols, the calculation method used in this study also considers the influences of aerosol microphysical properties, including water uptake of soluble particles (by Kohler theory), internal mixing state (by Maxwell-Garnett mixing rule), and particle size distribution (the change of lognormal distribution parameters of three modes) as explained in line 132-141. Therefore, the mass burden of $PM_{2.5}$ was not the only impact factor of visibility variation in our model. Even though the distribution patterns of visibility broadly followed those of $PM_{2.5}$ mass burden, we can also see that the extinction was obviously enhanced by the higher relative humidity in July. Anyway, we are sorry that the description about the aerosol optical properties calculation is not clear, and hope the modified content is suitable.

5. Sec 4.2: Decline in pollution caused by the enhanced vertical convection is a classical case in PBL dynamics. I suggest move forward to investigate factors that were controlling the convection and, in turn, influencing air quality.

Reply:

Thanks for this comment.

On second thoughts, we kindly think this part of analysis is not quite necessary for this study. The reasons are as follows. First one is that the vertical structure of modeled temperature was not evaluated by any observation data. Second one is that we would like to focus on the influence of aerosol characteristic (such as the particle components and microphysical properties) and related meteorological factors that can change the particle optical properties (such as the relative humidity which changes the water uptake of soluble particles). The impact mechanism of meteorological conditions on haze formation is not the main point of this study. Therefore, we kindly chose to delete this part of analysis, and added other content which is more suitable for the subject of this paper, including the discussion of microphysical properties of aerosols and haze occurrence threshold, etc.

6. Sec 4.3: The method for “contribution ratio” calculation is unclear. Are you turning off the formation of a specific compound in the model to investigate the corresponding effects? In that case, there could be some bias in the results. For instance, if you turn off the formation of ammonium sulfate then the ammonia will go to nitrate and change the partition and fate of N-containing species in the atmosphere.

Reply:

Thanks for this comment.

Actually, the input data of each specific aerosol component was just ignored when calculated the extinction coefficient by using the aerosol optical property module. The aerosol chemical and physical processes in the air quality modeling system was not modified or turned off. So the bias should not be existed in this method. Sorry we did not give a clear explanation. The statement in line 288-289 has been modified. Please check if it is OK.

7. Sec 4.3: Regarding the case study of size distribution, the mass fraction of accumulation mode was still ~80% despite the increases in Aitken mode. Thus the changes in the cross section should be rather limited. I'm not convinced that the spike of "mass threshold" was due to increases of Aitken mode aerosols. Moreover, in terms of size distribution, I think that the cases of high coarse mode fraction also worth to be investigated further.

Reply:

Thank you very much for this comment.

This is an important advice and we think further analysis is necessary to make the problem clear. We calculated the contribution ratios of Aitken mode, accumulation mode, and coarse mode particles to the total extinction and added this information into Fig. 14 for investigating the detail impact mechanism. The related statement is added in line 348-368. As shown by the analysis, the particles of accumulation mode provided the most part of the extinction effect. A small variation of the extinction contribution ratio of accumulation mode could obviously change the mass threshold of haze occurrence. However, it seems that the spike of mass threshold appeared on July 29 was caused by the influence of the extinction contribution ratio of Aitken mode particles. Even though the mass concentration ratio of coarse particle could reach 10%-20%, their extinction was quite weak. Thus, the coarse particle may not play an important role unless its mass concentration is far higher than that of accumulation mode, such as the case of strong dust event. For the detail analysis, please check the contents in line 363-368.

Reference:

Lei, Y., Zhang, Q., He, K. B. and Streets, D. G.: Primary anthropogenic aerosol emission trends for China, 1990–2005, Atmos. Chem. Phys., 11, 931-954, 2011.

Zhang, Q., Streets, D. G., He, K., Wang, Y., Richter, A., Burrows, J. P., Uno, I., Jang, C., Chen, D., Yao, Z., and Lei Y.: NO_x emission trends for China, 1995–2004: The view from the ground, J. Geophys. Res., 112, D22306, doi:10.1029/2007JD008684, 2007.

Zhang, R., Jing, J., Tao, J. Hsu, S.-C., Wang, G., Cao, J. Lee, C. S., Zhu, L., Chen, Z., Zhao, Y., and Shen, Z.: Chemical characterization and source apportionment of $PM_{2.5}$ in Beijing: seasonal perspective, Atmos. Chem. Phys., 13, 7053-7074, 2013.