**Manuscript No.**: acp-2014-309

**Title**: Exploring the severe winter haze in Beijing

We would like to thank Prof. D. Parrish and the anonymous referee for their valuable and constructive comments/suggestions on our manuscript. We have revised the manuscript accordingly and please find our point-to-point responses below.

**Comments in RC C5319 by D. Parrish:**

*(Note: I am not an expert in PM measurements, so I am unable to critically evaluate the various PM methods that were applied in this study. Hopefully, other reviewers can address the accuracy and reliability of the measurement techniques. The following comments assume that the measurements as well as the modeling can be taken as reasonably accurate and artifact free. The validity of this assumption regarding the measurements may be aided by the very large PM concentrations reported here.)*

*This paper presents an interesting description of the episodes of very high PM concentrations observed in the Beijing area during January 2013. Although there is not a great deal of detailed analysis of the PM character during the episodes or the chemistry responsible for the secondary PM formation, I found this to be a very interesting paper well worthy of publication after the major issues discussed below are addressed. Section 5, which discusses the relative importance of local chemical production vs. regional transport, is particularly important. Indeed, the temporal variability at a single location is not simply due to local production and loss; the effect of transport must be kept fully in mind. Indeed, the clarity and brevity of the paper enhance its usefulness.*

***Major issues:***

***1.*** *The figures in the paper are not clearly described. A clear explanation of the exact quantities plotted must be given. Some specific examples follow.*

***(1)*** *The Figures 2a, 5, 8b and 10 present representative values of various variables for four pollution level classes. The derivation of these representative values must be*

*clearly explained. That is, for pollutant concentrations and other variables are they means? Medians?*

**Response:**

Thanks for pointing these out. We have made the corresponding changes accordingly.

(a) Figure 2a

In Line 155 ~ 156 in the revised manuscript:

"Mean percentile compositions of major components in $PM_{2.5}$ under different pollution levels were shown in Fig. 2a."

Caption of Figure 2:

"Major composition of $PM_{2.5}$ with respect to pollution level. (a) Mean percentile composition and (b) hourly concentration of individual species plotted against $PM_{2.5}$ mass concentration. Values showed in (a) were derived as average of ratios."

(b) Caption of Figure 5:

"Mean diurnal variation of meteorological parameters under various pollution levels."

(c) Figure 8b: We deleted this figure from the revised manuscript. As the reviewer have pointed out in #4-(3), the statistical uncertainties could be much larger for the "clean" data. Thus all discussion based on the diurnal variation has been removed in the revised manuscript.

(d) Caption of Figure 10:

"Variation of $SO_4^{2-}$/EC, $NO_3^-$/EC, $SO_2$, $NO_2$, SOR and NOR with pollution level. "C", "S", "P", "H" refer to "clean", "slightly polluted", "polluted" and "heavily polluted", respectively. Normalized *X* in Column 4 refers to the average concentration of *X* in any pollution level, scaled by its average concentration during clean periods. In the box-whisker plots, the boxes and whiskers indicated the 95th, 75th, 50th (median), 25th and 5th percentiles, respectively."

***(2)*** *And in Figure 8b how are the ratios calculated? Are they arithmetic or geometric (geometric is preferable over arithmetic) means, or median ratios? Or are they ratios of mean or median concentrations? The question regarding the ratios is particularly important, as some of these statistical measures give distorted results.*

**Response:**

We deleted this figure from the revised manuscript. As the reviewer have pointed out in #4-(3), the statistical uncertainties could be much larger for the "clean" data. Thus all discussion based on the diurnal variation has been removed in the revised manuscript.

***(3)*** *How are the results for EC/ PM2.5 in Figure 2a related to the results in Figure 8b4? To my eye, the results in Figure 2a are smaller than the results in Figure 8b4.*

**Response:**

The data in Figure 2a and Figure 8b4 were calculated as follows. Firstly the EC to $PM_{2.5}$ ratios for each hour were calculated, and these ratios were used in the following calculations. This is the same for Figure 2a and Figure 8b4.

The mean values shown in Figure 2a are calculated by averaging all ratios in each pollution level. For the diurnal variation shown in Figure 8b4, each point represents averaged ratios at certain time of day under certain pollution level. A weighted average of Figure 8b4 (weighted by the number of samples at each time) will give the same result as in Figure 2a.

In fact, we have deleted the diurnal plots in Figure 8b from the revised manuscript and made new box plot instead. As the reviewer has pointed out in #4-(3), the statistical uncertainties could be much larger for the "clean" data. Thus all discussion based on the diurnal variation has been removed in the revised manuscript.

***(4)*** *Do Figures 2b, 9a and 9b and 11a and 11b show hourly averages, and do these plots include all times of day?*

**Response:**

Yes, these data are hourly averaged concentrations, and include all times of day in the original version. While in the revised manuscript, only daytime (7:00~18:00) data were selected for Figure 9, to exclude possible inference caused by day-night source variation (such as the heavy-duty diesel truck traffic which is allowed only during nighttime in Beijing), as well as to focus on the impact of air pollution on photochemistry (see more details in #4-(2)).

See changes in caption of Figure 2, 9 and 11:

"Figure 2. Major composition of $PM_{2.5}$ with respect to pollution level. (a) Mean percentile composition and (b) hourly concentration of individual species plotted against $PM_{2.5}$ mass concentration. Values showed in (a) were derived as average of ratios."

"Figure 9. Evaluation of SOC formation. (a) Estimation of SOC with EC-tracer method. Squares indicate data used to calculate primary OC/EC, while open circles indicate other OC/EC data. (b) Change of SOC, OC and SOC/EC with RH**.** Data points shown in a and b referred to hourly concentrations in daytime (7:00~18:00). (c)-(d) Variation of SOC, SOC/OC and SOC/EC (c) in the morning (7:00~12:00) and (d) in the afternoon (13:00~18:00) with pollution level. "C", "S", "P", "H" refer to "clean", "slightly polluted", "polluted" and "heavily polluted", respectively. In the box-whisker plots, the boxes (b, c, d) and whiskers (c, d) indicated the 95th, 75th, 50th (median), 25th and 5th percentiles, respectively. "

"Figure 11. Importance of heterogeneous chemistry in sulfate and nitrate formation. (a-b) Hourly SOR and NOR plotted against RH, colored with temperature. (c-d) EC-scaled precursors ($SO_2$ and $NO_2$) and products ($SO_4^{2-}$ and $NO_3^-$) plotted against RH. EC concentrations at different RH levels were shown for reference."

***2.*** *In Section 4 a more detailed discussion of Figure 3 is required. What quantity is plotted? What are the units? Are these average values for January, or is this for a particular date and time? Very importantly, how do these calculated quantities compare with those measured? My suspicion is that these are PM2.5 calculations for a severe episode, and that the model cannot predict the highest observed concentrations. This shortcoming must be discussed.*

**Responses:**

Figure 3 shows the model simulation results of monthly-averaged $PM_{2.5}$ concentrations ($\mu g/m^3$) under different scenarios. We have included this information in the revised manuscript, Fig. 3 and the text (Line 182~186 in the revised manuscript).

"Figure 3. Revised WRF-CMAQ simulated monthly-averaged $PM_{2.5}$ concentration ($\mu g/m^3$) under different scenarios. (a) Base scenario. Actual Jan. 2013 emission and

Jan. 2013 meteorology data were used. (b) Jan. 2012 meteorology data were used, and (c) Jan. 2012 emissions were used. The different $PM_{2.5}$ concentrations ($\mu g/m^3$) caused by meteorology (d; equivalent to a–b) and emission (e, equivalent to a–c) are also shown."

The original WRF-CMAQ model cannot reproduce the highest observed concentrations. Therefore, a revised model was developed which included additional heterogeneous reactions (Wang et al., 2012). The simulations based on the revised model agree well observation during the heavily polluted periods, not only for the magnitude and temporal variation of $PM_{2.5}$ (with normalized mean biases (NMB) being 0.4 %), but also for the chemical composition (Figure R1). We have revised the manuscript by including a brief summary of the model performance:

"Since the original WRF-CMAQ model cannot reproduce the observed concentrations under heavily polluted conditions (B. Zheng et al. 2014), a revised WRF-CMAQ system with enhanced heterogeneous reactions (Wang et al., 2012) was adopted to improve the model performance. The revised model could effectively capture the measured concentrations of total $PM_{2.5}$ (with normalized mean biases (NMB) being 0.4 %) and its different chemical compositions for both clean and heavily polluted haze days (B. Zheng et al., 2014). Details of the model configuration, modifications, and validation are described in B. Zheng et al. (2014)."

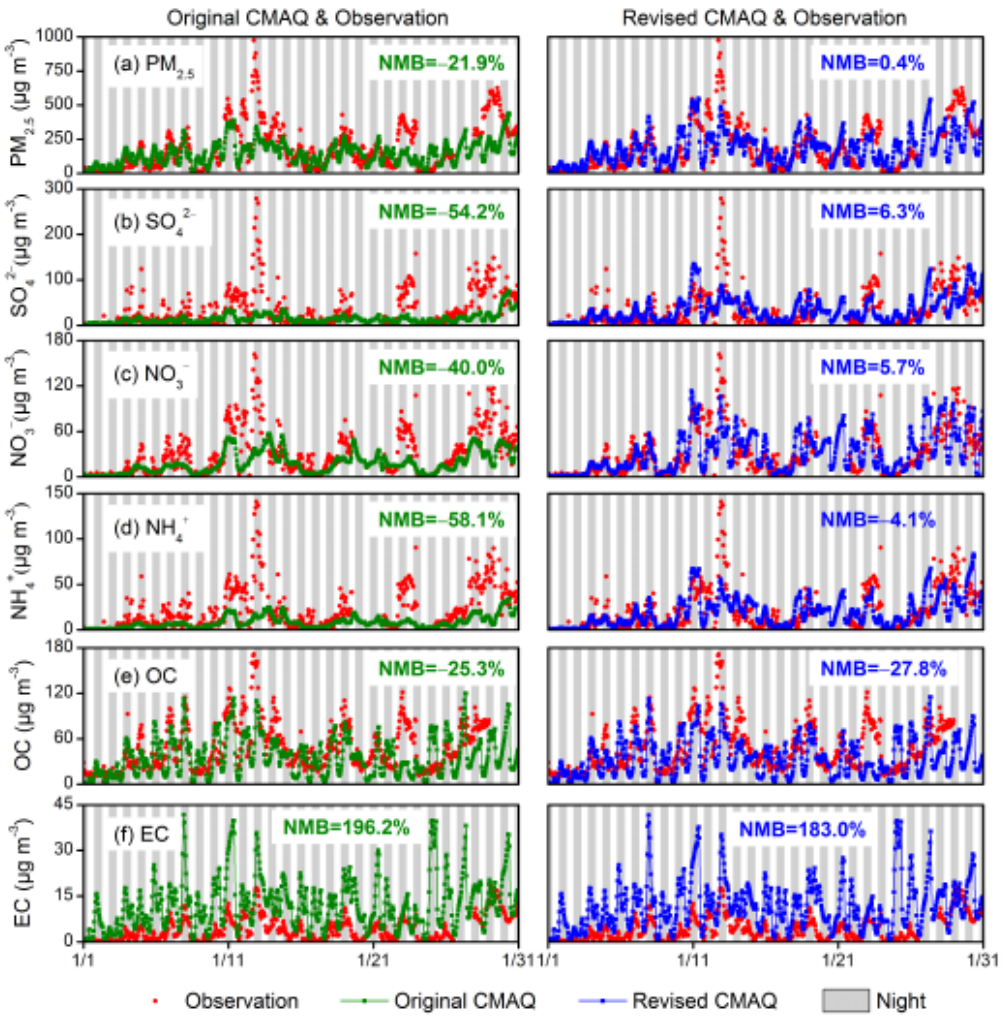


Figure R1. Observed and simulated hourly aerosol compositions from the original and revised CMAQ at the THU site: (a) $PM_{2.5}$; (b) $SO_4^{2-}$; (c) $NO_3^-$; (d) $NH_4^+$; (e) OC; (f) EC. NMB referred to normalized mean biases. (***Source: Fig. 3 in B. Zheng et al., 2014)***.

***3.*** *In the abstract the authors state "... we analyzed the hourly observation data of $PM_{2.5}$ and its major chemical composition, with support of model simulations." However, I do not find any $PM_{2.5}$ model simulations in Section 6 of the paper. This is a major shortcoming that must be corrected. As it stands, Section 6 is weak (see following comments). I think that at least 0-dimensional box modeling, of at a least a semiquantitative nature is required to support the discussion of the evolution of gas-phase to particle-phase species. Otherwise the discussion of PM evolution in that section should be removed. As it stands, it has significant inconsistencies and cannot be correct on even a semi-quantitative level.*

**Responses:**

Yes, we agree with the reviewer. Accordingly, we included the discussions about the related WRF-CMAQ model simulation results, which could support our deductions based on observation, in the revised manuscript. Please find detailed information about the corresponding changes in our response to comments #4 and #5.

***4.*** *Section 6.1 requires improvement; the arguments must be strengthened or removed.*

***(1)*** *Figures 8b5 and 8b6 show clear differences in the ratios in the afternoon between the "clean" and the 3 classes of polluted air. However, there is little difference in either ratio between the 3 classes of polluted air. The authors have already quite correctly shown that there are large differences in the regional transport patterns between the "clean" and "polluted" periods. If the authors really think that the weakened local photochemistry plays the dominant role in the ratio differences, then a robust analysis is required to show that the differences in the ratios are due to differences in the local photochemical processing, rather than to differences in the clean and polluted air masses transported into Beijing. Such an analysis has not yet been included in the paper.*

**Responses:**

This is a good point. We didn't make it clear in the original manuscript. The ratios observed at our measurement site are not only subject to the influence of local photochemistry but are also controlled by the regional photochemistry, i.e., the photochemical processing during the transport of air masses. Therefore, the observed ratios partly reflect the regional process of **high aerosol→strong radiative reduction→weakened photochemistry.** The weakened photochemistry at a regional scale is also confirmed by both observations and model simulations. During all heavy pollution episodes in Jan. 2013, extremely low ozone concentration (less than 10 ppb) without clear diurnal variation was observed, for all the three large cities (i.e., Beijing, Tianjin and Shijiazhuang) in the Jing-Jin-Ji Area (Wang et al., 2014) (See Figure R2). Similar phenomenon was observed in other heavy pollution episodes in winter Beijing (Zhao et al., 2013). In accordance with the observational data, model simulations also show a reduction in the atmospheric oxidation capacity (represented by the concentrations of ozone and OH here) at the regional scale (Figure R3, Figure 8 in the revised manuscript). Average daytime oxidants concentrations were significantly

lower during polluted periods than clean periods. For most areas in the NCP, $O_3$ and OH dropped from 12~44 ppbV and 0.004 ~ 0.020 pptV to less than 12 ppbV and 0.004 pptV from clean to heavily polluted periods, respectively.

This discussion was now added into the revised manuscript (See Figure 8 and Paragraph 2 in Section 6.1):

"As the haze pollution spread over most of the NCP, we will also expect a weakening of photochemistry on the regional scale, which is confirmed by both observations and model simulations. Extremely low ozone concentration (less than 10 ppb) in the absence of diurnal variation was observed during heavy pollution episodes for all of the three major cities in Jing-Jin-Ji Area (i.e., Beijing, Tianjin and Shijiazhuang) in Jan. 2013 (Y. Wang et al., 2014). Similar phenomenon was observed before in another heavy pollution episode in winter Beijing (Zhao et al., 2013). In accordance with the observed low ozone concentration, model simulations also showed a regional-scale reduction in the concentrations of ozone and OH (Fig. 8). Average daytime concentrations of oxidants were significantly lower during polluted periods than clean periods. For most areas in the NCP, $O_3$ and OH dropped from 12~44 ppbV and 0.004 ~ 0.020 pptV to less than 12 ppbV and 0.004 pptV, respectively as the air quality changed from clean to heavily polluted conditions. This regional drop in oxidant concentrations demonstrates the impact of air pollution on the photochemistry."

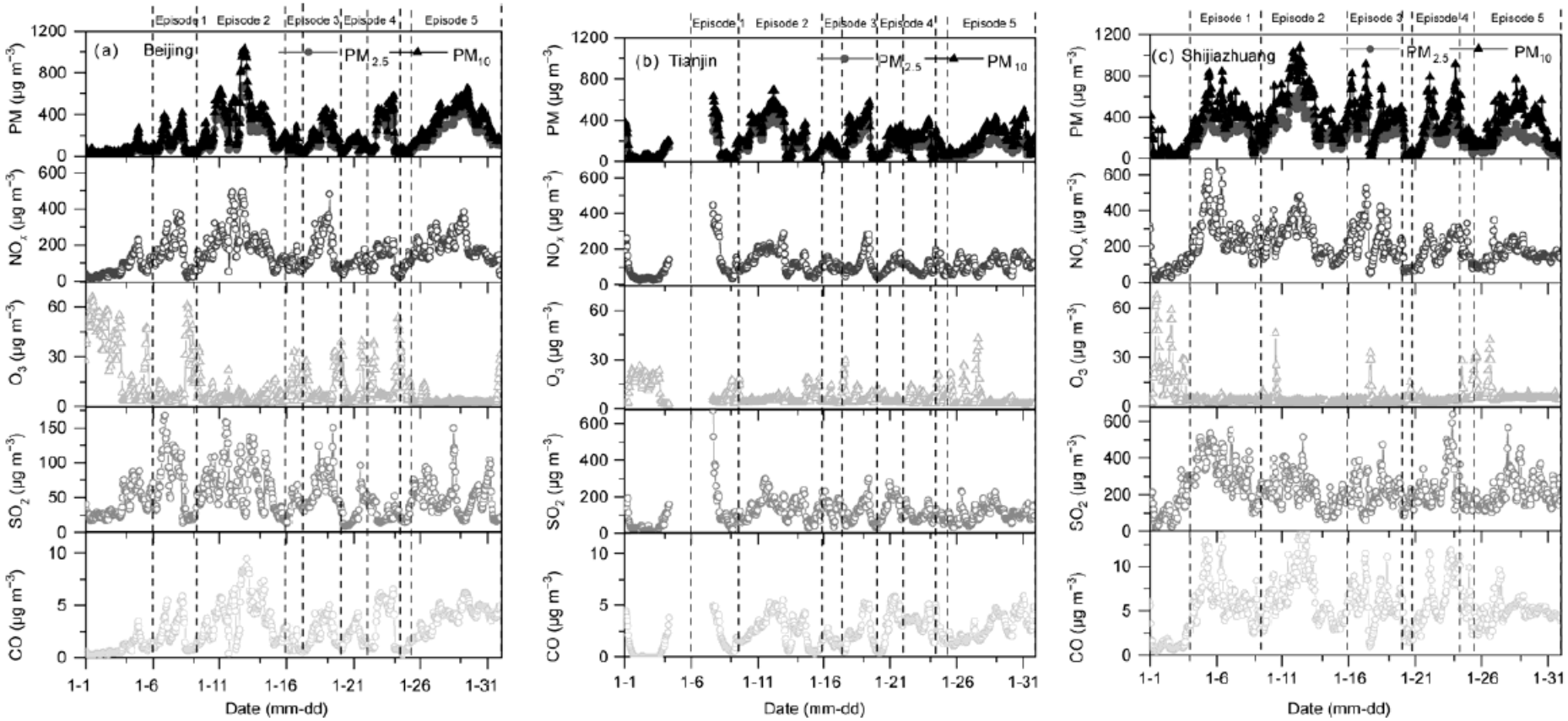


Figure R2. Variation of particle matter and gaseous pollutants in three megacities (Beijing, Tianjin and Shijiazhuang) in January 2013. The five haze episodes are marked between the dote lines. (***Source: Fig. 1 in Wang et al., 2014)***.

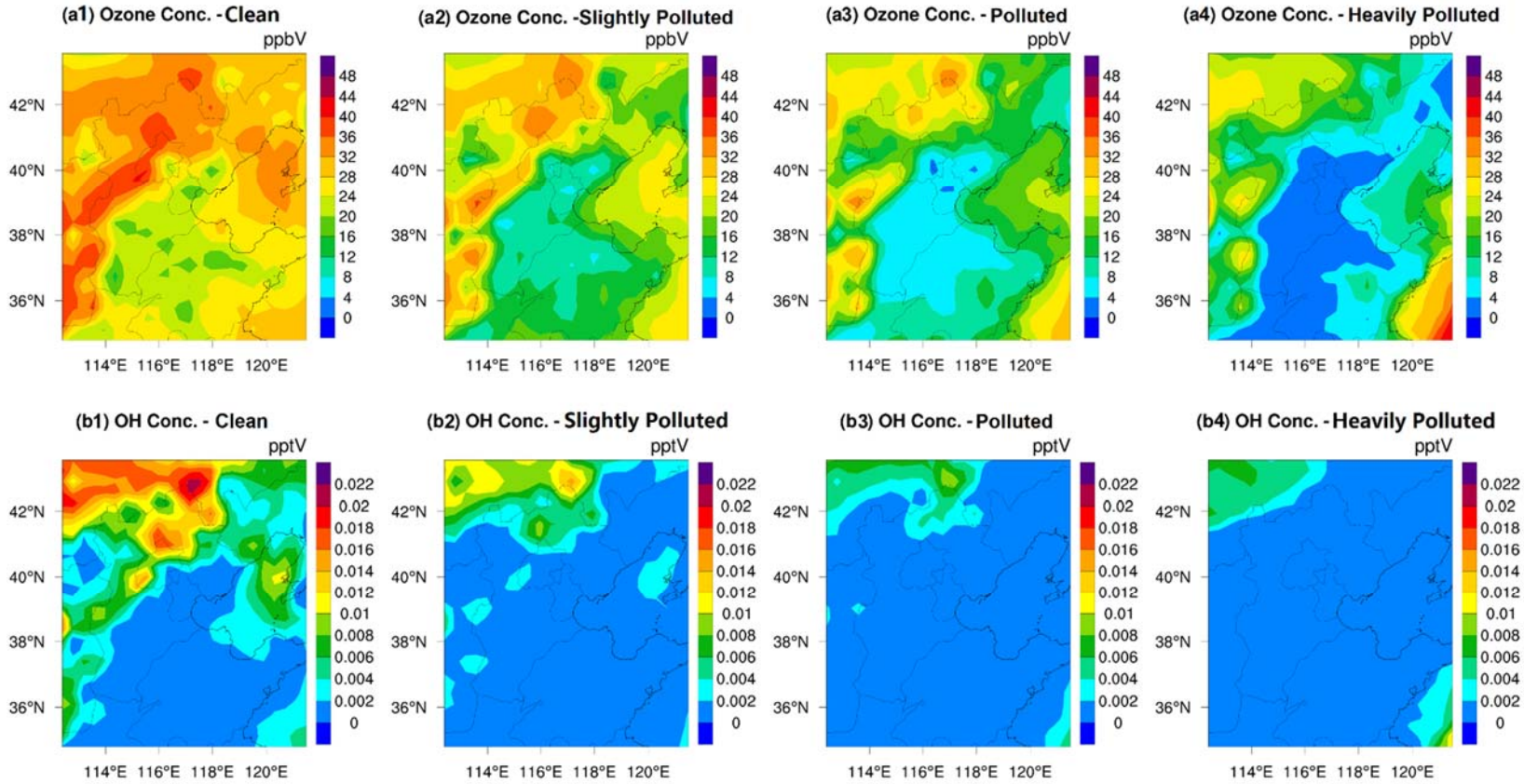


Figure R3. (***Added as Fig. 8 in the revised manuscript)*** Revised WRF-CMAQ simulated regional distribution of daytime (7:00 ~ 18:00) concentration of (a) $O_3$ (ppbV) and (b) OH (pptV) at different pollution level.

***(2)*** *The SOC discussion beginning on 17919 is weak. The attempt to derive the (OC/EC)pri is not convincing, since the difference in the slope of OC vs. EC is small and may be due to other causes. If I understand correctly, heavy-duty diesel truck traffic in Beijing is limited to nighttime. It may be that lower OC/EC ratios are caused by the heavier truck traffic at night. A robust error analysis is required to definitively show that the derived (OC/EC)pri ratio is statistically significantly different from the average OC/EC ratio. This error analysis must be propagated through to give statistical uncertainties for the derived SOC. It may well be that it is not possible to derive statistically significant SOC concentrations from this data set.*

**Responses:**

Thanks to the reviewer to point this out. We agree that the estimation method (Lim and Turpin, 2002) requires caveats. Therefore we performed the same analysis only based on daytime (7:00~18:00) data. As shown in Fig. R4, the analysis of daytime data leads to a (OC/EC)pri of 4.99, which is of no significant difference with that of 4.81 (previous estimation), suggesting a minor effect of nighttime truck traffic. We also performed a one-tail T-test to test the significance of different OC/EC ratios. The analysis showed that the derived (OC/EC)pri ratio is significantly different from the rest ratios at the confidence level of 99% ($p=3.53*10^{-13}$). The variation in (OC/EC)pri (4.99 vs 4.81), however, will not significantly change the derived SOC concentrations and relevant conclusions.

In the revised manuscript, we used only daytime (7:00~18:00) OC and EC data to estimate SOC (Figure R4, Figure 9 in the revised manuscript) and adjusted the relevant text:

"The basic assumptions and underlying principles of this method are discussed in Lim and Turpin (2002) and Lin et al. (2009). Only daytime (7:00~18:00) carbonaceous aerosol data were used here to exclude possible interference from day-night source variations (such as the heavy-duty diesel truck traffic which is allowed only during nighttime in Beijing). In our study, data pairs with the lowest 10% percentile of ambient OC/EC ratios were used to estimate the primary OC/EC ratio (Fig. 9a). York regression (York et al., 2004) was used to estimate the intercept N and the slope, i.e., values of (OC/EC) pri, according to Saylor et al. (2006)."

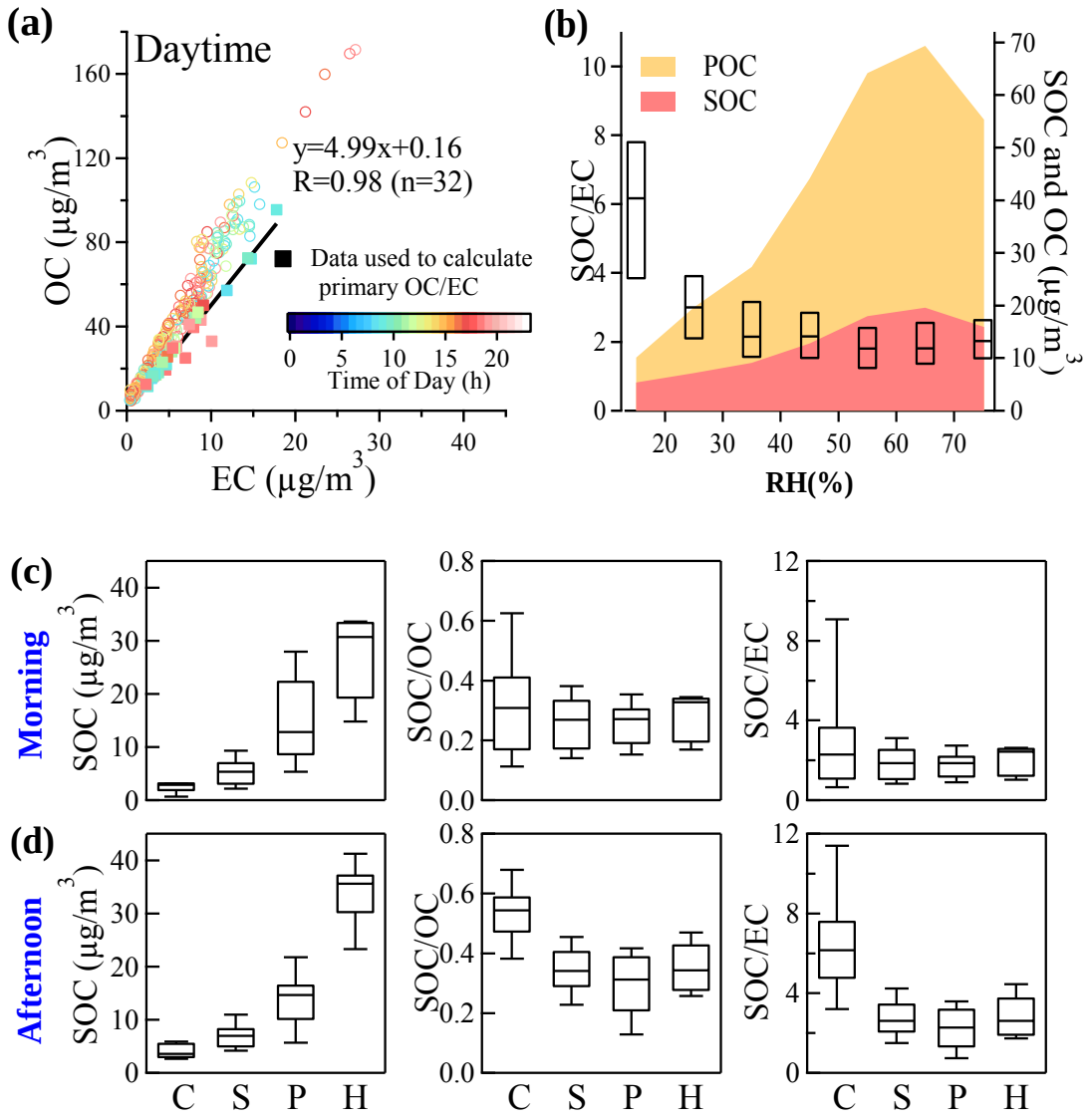


Figure R4 (***Added as Fig. 9 in the revised manuscript)*** Evaluation of SOC formation. (a) Estimation of SOC with EC-tracer method. Squares indicate data used to calculate primary OC/EC, while open circles indicate other OC/EC data. (b) Change of SOC, OC and SOC/EC with RH**.** Data points shown in a and b referred to hourly concentrations in daytime (7:00~18:00). (c)-(d) Variation of SOC, SOC/OC and SOC/EC (c) in the morning (7:00~12:00) and (d) in the afternoon (13:00~18:00) with pollution level. "C", "S", "P", "H" refer to "clean", "slightly polluted", "polluted" and "heavily polluted", respectively. In the box-whisker plots, the boxes (b, c, d) and whiskers (c, d) indicated the 95th, 75th, 50th (median), 25th and 5th percentiles, respectively.

***(3)****The last paragraph of Section 6.1 on pg. 17920 is not convincing. Given the statistical uncertainties, which are certainly much larger for the "clean" data, I suspect that the diurnal cycles discussed with regard to Fig. 8b6 are statistically insignificant, and that there is simply no diurnal cycle in this ratio in any of the pollution realms.*

**Responses:**

We agree that there is no significant difference. The discussion based on the diurnal variation has been removed in the revised manuscript.

Instead, we have added new figure to replace it (Figure R4, Figure 9 in the revised manuscript). In Figure R4, daytime OC and EC data was classified into two groups: morning (7:00~12:00) and afternoon (13:00~18:00). In each group, distributions of SOC, SOC/OC and SOC/EC with pollution level were examnined. Relative discussion was added into the revised manuscript as follows:

"In our study, data pairs with the lowest 10% percentile of ambient OC/EC ratios were used to estimate the primary OC/EC ratio (Fig. 9a). York regression (York et al., 2004) was used to estimate the intercept N and the slope, i.e., values of (OC/EC) pri, according to Saylor et al. (2006). Our analysis shows that SOC constituted ~28% of total OC, consistent with earlier studies in the winter of 2009-2012 (~30%, Cheng et al., 2011; Sun et al., 2013b).

High concentration of aerosol particles can reduce solar radiation and atmospheric photochemistry. Since SOC is a product of photochemical reactions, we would expect a reduced SOC production rate under heavily polluted conditions. This is confirmed by the measured SOC concentrations shown in Fig. 9. Here again the EC-scaled SOC was used to account for the different boundary layer effect (dilution/mixing) on the aerosol concentrations. Both SOC/EC and the accumulated SOC/EC (afternoon – morning values) decrease when it changed from clean to heavily polluted periods. The accumulated SOC/EC is used to better represent the production during the daytime."

***(4)****What do the $PM_{2.5}$ model simulations show with regard to the influence of reduced photochemistry? This modeling should be discussed.*

**Responses:**

In our model configurations, the photolysis rate is calculated online using simulated aerosols and ozone concentrations (B. Zheng et al., 2014). As a result, with the enhanced $PM_{2.5}$ concentration, the photolysis rate will be reduced, and so will the concentrations of photochemical oxidants (Fig. R3) and secondary aerosol particles. During the haze events, this effect can be counteracted by the enhanced heterogeneous reactions and it is difficult to unravel them from the measurement data.

In order to demonstrate the influence of reduced photochemistry, we adopted the original WRF-CMAQ model setup and excluded the enhanced heterogeneous reactions. In this case, only gas phase oxidations are counted for the formation of sulfate and organics (Table R2) (aqueous-phase reactions in the original WRF-CMAQ only happen in clouds and don't apply for the aerosol phase) and their simulated concentrations will directly reflect the influence of reduced photochemistry. As shown in Table R1, the simulated $PM_{2.5}$/EC ratios decreased from 16.05 to 11.72 when the pollution level changed from the "clean" to the "heavily polluted" case, reflecting the reduced gas-phase photochemical production. Note that $PM_{2.5}$ concentration is normalized by EC to counteract the influence of reduced boundary layer. Otherwise, the reduced boundary layer itself could lead to a tremendous increase in the pollutant concentration under heavily polluted conditions, and thus cover the real effect of reduced photochemistry. The simulated individual components of $PM_{2.5}$ also reflected the influence of photochemistry. As shown in Table R1, although primary organic matter (POM) to EC ratios kept nearly constant during all pollution levels, the normalized secondary species all showed a decreasing trend, reflecting the reduced photochemical production. SOA/EC, $SO_4^{2-}$/EC, and $NO_3^-$/EC ratios decreased by 53.3%, 51.9% and 28.6%, respectively from clean to heavily polluted periods. For the formation of $NO_3^-$, two heterogeneous reactions have been included in the original WRF-CMAQ model and therefore the $NO_3^-$/EC shows relatively less reduction than SOA/EC and $SO_4^{2-}$/EC.

This part of discussion was included into the revised manuscript:

"Reduction in photochemistry-related $PM_{2.5}$ production is further supported by model simulation results. In our model configurations, the photolysis rate is calculated online using simulated aerosols and ozone concentrations (B. Zheng et al., 2014). As a result, with the enhanced $PM_{2.5}$ concentration, the photolysis rate will be reduced, and so will the concentrations of photochemical oxidants (Fig. 8) and secondary aerosol particles.

During the haze events, this effect can be counteracted by the enhanced heterogeneous reactions and it is difficult to unravel them from the measurement data.

In order to demonstrate the influence of reduced photochemistry, we adopted the original WRF-CMAQ model setup and excluded the enhanced heterogeneous reactions. In this case, only gas phase oxidations are counted for the formation of sulfate and organics (aqueous-phase reactions in the original WRF-CMAQ only happen in clouds and don't apply for the aerosol phase) (B. Zheng et al., 2014) and their simulated concentrations will directly reflect the influence of reduced photochemistry. As shown in Table S1, the simulated $PM_{2.5}$/EC ratios decreased from 16.05 to 11.72 when the pollution level changed from the "clean" to the "heavily polluted" case, reflecting the reduced gas-phase photochemical production. Note that $PM_{2.5}$ concentration is normalized by EC to counteract the influence of reduced boundary layer. Otherwise, the reduced boundary layer itself could lead to a tremendous increase in the pollutant concentration under heavily polluted conditions, and thus cover the real effect of reduced photochemistry. The simulated individual components of $PM_{2.5}$ also reflected the influence of photochemistry. As shown in Table S1, although primary organic matter (POM) to EC ratios kept nearly constant during all pollution levels, the normalized secondary species all showed a decreasing trend, reflecting the reduced photochemical production. SOA/EC, $SO_4^{2-}$/EC, and $NO_3^-$/EC ratios decreased by 53.3%, 51.9% and 28.6%, respectively from clean to heavily polluted periods. For the formation of $NO_3^-$, two heterogeneous reactions have been included in the original WRF-CMAQ model and therefore the $NO_3^-$/EC shows relatively less reduction than SOA/EC and $SO_4^{2-}$/EC."

Table R1 Original CMAQ simulated domain-average concentration of pollutant to EC ratios during daytime (7:00~18:00) at different pollution levels

| **Pollution Level** | **$PM_{2.5}$/EC** | **POM/EC** | **$SO_4^{2-}$/EC** | **$NO_3^-$/EC** |
|---|---|---|---|---|
| *Clean* | 16.05 | 3.03 | 3.50 | 3.17 |
| *Slightly Polluted* | 14.69 | 3.09 | 2.83 | 3.00 |
| *Polluted* | 12.97 | 3.22 | 2.19 | 2.53 |
| *Heavily Polluted* | 11.72 | 3.27 | 1.69 | 2.26 |

***5.*** *Section 6.2 must also be strengthened.*

*(1) A figure similar to Figure 8b5 for sulfate/EC and nitrate/EC may be useful to show a) the diurnal cycle of these ratios and b) the dependence of these ratios over the 3 polluted air mass classes. The single sentence on pg. 17920 -"Significant increase of $SO_4^{2-}$/EC and $NO_3^-$/EC ratios were found from clean periods (3.03 and 3.33, respectively) to heavily polluted periods (6.35 and 5.89, respectively), suggesting enhanced chemical productions." - is not an adequate description.*

**Responses:**

According to reviewer's suggestion, we have included $SO_4^{2-}$/EC and $NO_3^-$/EC into modified Figure 10 (as Figure R5 here) and modified relevant text (see paragraph 1 and 2 in Section 6.2):

"Unlike OM, relative contributions of sulfate and nitrate to $PM_{2.5}$ were increasing during the haze events (Fig. 2). Again, we used their ratios to EC to account for the boundary layer effect. An increasing trend of $SO_4^{2-}$/EC and $NO_3^-$/EC ratios was found (Column 1 in Fig. 10) from clean periods (3.03 and 3.33, respectively) to heavily polluted periods (6.35 and 5.89, respectively), suggesting enhanced chemical productions. The SOR and NOR (molar ratio of sulfate or nitrate to sum of sulfate and $SO_2$ or nitrate and $NO_2$) have been used as indicators of secondary transformation (Sun et al., 2006). The fact that SOR and NOR increased much more rapidly than $SO_2$

and $NO_2$ as pollutions became more severe (Column 4 in Fig. 10), is another evidence of elevated secondary formations of sulfate and nitrate during severe haze events.

Both gas-phase and heterogeneous reactions could contribute to the formation of sulfate and nitrate from $SO_2$ and $NO_2$, and thus elevating the SOR and NOR. Sulfate is formed through oxidation of $SO_2$ by gas-phase reactions with OH (Stockwell and Calvert, 1983; Blitz et al., 2003) and stabilized Criegee intermediate (which is formed by $O_3$ and alkenes) (Mauldin et al., 2012), and by heterogeneous reactions with dissolved $H_2O_2$ or with $O_2$ under the catalysis of transition metal (Seinfeld and Pandis, 2006). Nitrate formation is dominated by the gas-phase reaction of $NO_2$ with OH during daylight, and the heterogeneous reactions of nitrate radical ($NO_3$) during nighttime (Seinfeld and Pandis, 2006). Since gas phase production of secondary aerosols is expected to decrease under heavily polluted periods (Section 6.1), the increase of $SO_4^{2-}$/EC and $NO_3^-$/EC ratios is a clear evidence for the dominant contribution from other pathways, most probably from the heterogeneous reactions."

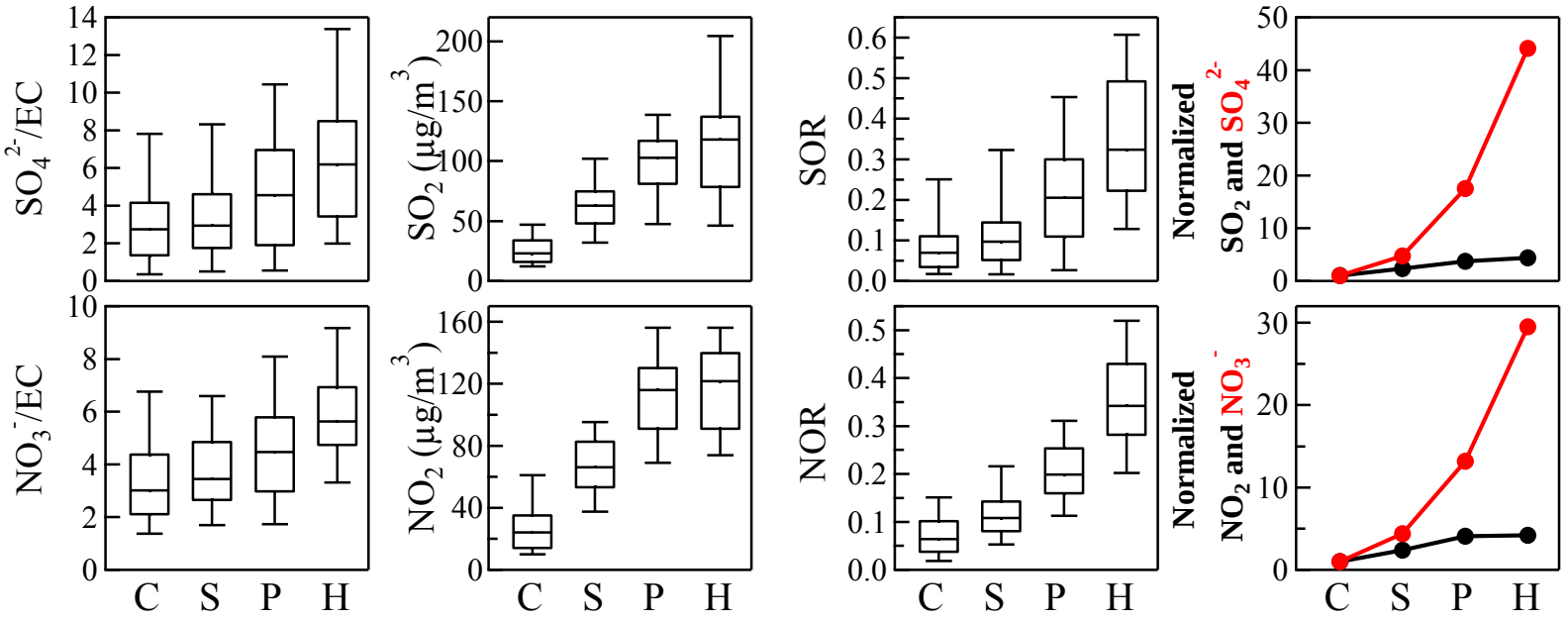


Figure R5 . (***Fig. 10 in the revised manuscript)*** Variation of $SO_4^{2-}$/EC, $NO_3^-$/EC, $SO_2$, $NO_2$, SOR and NOR with pollution level. "C", "S", "P", "H" refer to "clean", "slightly polluted", "polluted" and "heavily polluted", respectively. Normalized X in Column 3 refers to the average concentration of X in any pollution level, scaled by its average concentration during clean periods. In the box-whisker plots, the boxes and whiskers indicated the 95th, 75th, 50th (median), 25th and 5th percentiles, respectively.

*(2) It is not clearly explained how either $SO_4^{2-}$ or $NO_3^-$ can reach such high concentrations as those observed in the sampled air masses, or indeed in any air mass. Simply citing "Enhanced heterogeneous chemistry" is not an adequate explanation. The problem that I see is that heterogeneous chemistry still requires oxidation by an oxidizing agent. Generally this oxidizing agent is background ambient O3 or photochemically produced oxidants like OH, peroxides, or additional O3. NOx is generally emitted as NO, which is oxidized to NO2 by O3. NO2 is oxidized to NO3 (again by O3) or to HNO3 by OH before it can be incorporated into the aerosol phase by heterogeneous chemistry. Similarly SO2 is directly emitted, and it must be oxidized to $SO_4^{2-}$, either in the gas or aerosol phase; in either case, a photochemical oxidant is required (unless the reaction with O2 catalyzed by transition metals is actually important). I suggest that the authors discuss the concentrations of oxidants required to produce the observed levels of $SO_4^{2-}$ and $NO_3^-$ and attempt to explain where such high concentrations can possibly be produced.*

*What do the PM2.5 model simulations show with regard to the influence of heterogeneous chemistry? This modeling should be discussed.*

**Responses:**

We thank the reviewer for this suggestion. We have reanalyzed our data and the results show that the concentrations of oxidants were indeed significantly reduced (see response 4-2). Our explanation for this puzzle is that despite of reduced oxidant concentration, the aerosol volume/surface increases so much that it is enough to compensate its influence, and moreover, leads to a net increase in the formation of secondary aerosols. Detailed discussions are given as follows.

"Take the formation of sulfate for example. The production rate of sulfate (S(VI)) through heterogeneous reactions can be estimated by

$$dC_{S(VI)}/dt \approx k[\text{S(IV) (aq)}]*[\text{oxidants (aq)}]*V_{\text{aerosol}} \quad (1)$$

in which $C_{S(VI)}$ is the sulfate concentration, $k$ is the effective rate coefficient, [S(IV)(aq)] is the S(IV) concentration in the aqueous phase of aerosols, [oxidants (aq)] is the concentration of oxidants in the aqueous phase of aerosols, and $V_{\text{aerosol}}$ is the volume concentration of humidified aerosol at ambient RH.

Equation (1) shows that the oxidants and $V_{\text{aerosol}}$ are both essential for the heterogeneous reactions. From the clean to the heavily polluted case, $O_3$ is reduced by 80%, dropping from > 50μg/m³ to < 10 μg/m³ (Fig. R2). Based on our model

simulation results, $H_2O_2$ concentration also dropped significantly from ~78 ppbV to ~11 ppbV. Thus we assume an upper limit of 90% reduction in [oxidants (aq)]. $V_{aerosol}$ depends on the dry aerosol concentrations $V_{dry}$ and its hygroscopic growth factor (GF) of particle size, which is a function of RH. Assuming a constant aerosol dry density, then $V_{dry}$ is proportional to the mass concentration. From clean to heavily polluted case, average $PM_{2.5}$ mass concentration increased by 25 time, changing from 18 μg/m$^3$ to 450 μg/m$^3$ while average RH increased from dry (~20%) to ~70%. Thus we have:

$$\frac{\left[\text{oxidants (aq)}\right]_{HP}}{\left[\text{oxidants (aq)}\right]_{Clean}} * \frac{(V_{aerosol})_{HP}}{(V_{aerosol})_{Clean}} = \frac{\left[\text{oxidants (aq)}\right]_{HP}}{\left[\text{oxidants (aq)}\right]_{Clean}} * \frac{(V_{dry})_{HP}}{(V_{dry})_{Clean}} * (GF_{HP/Clean})^3 \approx 0.1 * 25 * (1.1)^3 = 3.33 \quad \textbf{(2)}$$

where HP and Clean indicated heavily polluted and clean periods, respectively. A GF of 1.1 was taken from previous measurements in Beijing (Meier et al., 2009).

Equation (2) shows that the increase of aerosol volume concentrations could sufficiently compensate the effect of oxidant reduction, resulting in a net increase of sulfate production.

Similarly, for $NO_3^-$, the influence of oxidant reduction could also be compensated by the increase of aerosol volume concentrations. There might be other oxidants associated with heterogeneous reactions, such as $O_2$ (especially under the catalysis of mineral metals) and other oxidants existed in aerosol phase such as Organic Peroxides (Seinfeld et al., 2006).

Our model simulation results (B. Zheng et al., 2014) also supported the importance of heterogeneous chemistry in sulfate and nitrate productions (Figure R1). With the addition of the heterogeneous reactions (See Table R2), the revised CMAQ showed much better performance in the polluted periods (B. Zheng et al., 2014), which demonstrated the importance of heterogeneous reaction in the production of secondary aerosols."

We added this discussion (quoted text above) into Section 6.2 in the revised manuscript.

Table R2 Main heterogeneous reactions contributing to sulfate and nitrate production in original CMAQ and heterogeneous reactions newly added in revised CMAQ. (***Source: Table 1 in B. Zheng et al., 2014)***.

| Type | Reaction #. | Reaction | Contributions to $PM_{2.5}$ |
|---|---|---|---|
| original CMAQ | | | |
| Gas-phase chemistry (All species in gas phase) | R1 | $SO_2 + OH + H_2O + O_2 \rightarrow H_2SO_4 + HO_2$ | Sulfate |
| | R2 | $NO_2 + OH \rightarrow HNO_3$ | Nitrate |
| | R3 | $N_2O_5 + H_2O \rightarrow 2HNO_3$ | Nitrate |
| | R4 | $NO_3 + HO_2 \rightarrow HNO_3 + O_2$ | Nitrate |
| | R5 | $NTR^a + OH \rightarrow HNO_3$ | Nitrate |
| | R6 | $NO_3 + VOCs^b \rightarrow HNO_3$ | Nitrate |
| Aqueous-phase kinetic chemistry (All species in aqueous phase) | R7 | $HSO_3^- + H_2O_2 \rightarrow SO_4^{2-} + H^+ + H_2O$ | Sulfate |
| | R8 | $HSO_3^- + MHP^c \rightarrow SO_4^{2-} + H^+$ | Sulfate |
| | R9 | $HSO_3^- + PAA^d \rightarrow SO_4^{2-} + H^+$ | Sulfate |
| | R10 | $SO_2 + O_3 + H_2O \rightarrow SO_4^{2-} + 2H^+ + O_2$ | Sulfate |
| | R11 | $HSO_3^- + O_3 \rightarrow SO_4^{2-} + H^+ + O_2$ | Sulfate |
| | R12 | $SO_3^{2-} + O_3 \rightarrow SO_4^{2-} + O_2$ | Sulfate |
| | R13 | $SO_2 + H_2O + 0.5O_2 + Fe(III)/Mn(II) \rightarrow SO_4^{2-} + 2H^+$ | Sulfate |
| Heterogeneous chemistry | R14 | $N_2O_5\,(g) + H_2O\,(aq) \rightarrow 2HNO_3(aq)$ | Nitrate |
| | R15 | $2NO_2\,(g) + H_2O\,(aq) \rightarrow HONO\,(aq) + HNO_3(aq)$ | Nitrate |
| revised CMAQ | | | |
| Newly added Heterogeneous chemistry | R16 | $H_2O_2\,(g) + Aerosol \rightarrow Products$ | Affect R7 |
| | R17 | $HNO_3\,(g) + Aerosol \rightarrow 0.5NO_3^- + 0.5\,NO_x\,(g)$ | Renoxification |
| | R18 | $HO_2\,(g) + Fe(II) \rightarrow Fe(III) + H_2O_2$ | Affect R4 and R7 |
| | R19 | $N_2O_5\,(g) + Aerosol \rightarrow 2\,NO_3^-$ | Nitrate |
| | R20 | $NO_2\,(g) + Aerosol \rightarrow NO_3^-$ | Nitrate |
| | R21 | $NO_3\,(g) + Aerosol \rightarrow NO_3^-$ | Nitrate |
| | R22 | $O_3\,(g) + Aerosol \rightarrow Products$ | Affect R10–R12 |
| | R23 | $OH\,(g) + Aerosol \rightarrow Products$ | Affect R1–R2, R5 |
| | R24 | $SO_2\,(g) + Aerosol \rightarrow SO_4^{2-}$ | Sulfate |

[a]: NTR: organic nitrate.
[b]: VOCs include: formaldehyde, acetaldehyde, propionaldehyde and higher aldehydes, cresol and higher molecular weight phenols, nitro cresol, aromatic ring open products, and isoprene oxidation products.
[c]: MHP: methylhydroperoxide.
[d]: PAA: peroxyacetic acid.

***Minor comments:***

**1)** *p. 17909, line 9 - Importantly "The contribution of organic matter ..." should be "The relative contribution of organic matter ..."*

**Responses:** The expression has been corrected as suggested.

**2)** *p. 17909, line 14 - Similarly "..., the strong increase in sulfate and nitrate contributions to $PM_{2.5}$, ..." should be "..., the strong increase in sulfate and nitrate relative contributions to PM2:5, ..."*

**Responses:** The expression has been corrected as suggested.

**3)** *p. 17920, line 15 - Similarly "..., contributions of sulfate and nitrate to $PM_{2.5}$, ..." should be "..., relative contributions of sulfate and nitrate to $PM_{2.5}$, ..."*

**Responses:** The expression has been corrected as suggested.

**4)** *p. 17911, line 1 - Change "In this study, we tried to address the following questions for the winter haze episodes ..." to "In this study, we address the following questions for the winter haze episodes ..."*

**Responses:** The expression has been corrected as suggested.

**5)** *I assume that the color-coding in Fig. 8 is the same as in Fig. 5, but the figure caption should state this explicitly.*

**Responses:** Fig. 8 has been removed in the revised manuscript.

**6)** *p. 17918, line 17 - I suggest that the term "radiative forcing" be replaced by different wording. "Radiative forcing" generally refers to climate change issues. I suggest "radiative reduction".*

**Responses:** The expression has been corrected as suggested.

**7)** *The meaning of the bars and whiskers in Figure 10 must be defined.*

**Responses:** Definition of the boxes and whiskers was added into the caption of Figure 10 as suggested.

**Comments in RC C5497 by Anonymous Referee #2:**

*The paper by Zheng et al. focuses the haze episodes occurred during the winter of 2012–2013. The author utilized hourly chemical composition data of PM2.5, model simulations, and meteorological data to characterize the processes involved in the development of these events. Their manuscript contained the following major points: 1. They determined on the basis of modeling that the severe winter haze was shown to result from stable synoptic meteorological conditions over a large part of northeastern China and not from a change in emissions. 2. The build-up of secondary species was the major driving force behind these polluted periods. 3. The contribution of organic matter decreased with increasing pollution level while sulfate and nitrate contributions increased. 4. There is a weakening of the photochemical activity due to the dimming effect of high loading of aerosol particles. 5. Regional transport of pollutants played an important role during these severe pollution events. The paper was generally well written, and I recommend that this paper can be considered for publication after the following issues are adequately addressed.*

***Major issues:***

*1. My main concern with this paper is that it would benefit if the paper can be more quantitative as a whole. There are many places when they author stated a conclusion, but did not back it up sufficiently with a number. For example in the model discussion, the paper stated that the change of emissions added "+- 10 ug m-3" (Ln 9). It would be helpful if the readers were presented with the initial average PM concentrations and the differing resultant concentrations. Another example in section 6.1, the only*

*direct value presented was 2.77 MJm$^{-2}$, and there were no other values to allow the reader to understand how low this value is compared to the rest of the observational period.*

**Response:**

We have revised the manuscript as suggested. For example, we have modified Paragraph 3 in Section 4 into:

"As expected, the influence of emission difference was negligible (Fig. 3a and 3c). For the whole simulation domain of the North China Plain (NCP), both simulation with Jan. 2012 meteorology (Scenario ***c***) and Jan. 2013 meteorology (Scenario ***a***) resulted in similar $PM_{2.5}$ concentration ranges (~50 to ~500 μg/m³) and spatial distributions. Difference of $PM_{2.5}$ concentration at any site was within ± 10 μg/m$^3$ (Fig. 3e). Simulation results of Scenario ***a*** and ***c*** were not only similar in average concentration levels, but also in temporal variations. For example, in Beijing, simulated hourly $PM_{2.5}$ concentration results under this two scenarios presented not only similar concentration (being 279.1 ± 170.2 μg/m³ and 278.8 ± 168.9μg/m³, respectively) but also excellent correlation with $R^2$ reaching 0.97."

And also relative statement in Section 6.1 into:

"Take Beijing for example, during haze episodes, the amount of solar radiation reaching the ground was significantly lower (e.g., down to 2.77 MJ/m$^2$/day, 13 Jan.) than clean days (averaging 9.36 ± 0.60 MJ/m$^2$/day for all the six clean days), rendering high photochemical activity impossible."

*2. How well did the model reproduce the observations? It would be nice if one could see a figure displaying the accuracy of the plot for a reader to have confidence in the conclusion.*

**Response:**

The original WRF-CMAQ model cannot reproduce the highest observed concentrations. Therefore, a revised model was developed which included additional heterogeneous reactions (Wang et al., 2012). The simulations based on the revised model agree well with the heavily polluted periods, not only for the magnitude and temporal variation of $PM_{2.5}$ (with normalized mean biases (NMB) being 0.4 %), but

also for the chemical composition (Figure R1). We have revised the manuscript by including a brief summary of the model performance:

"Since the original WRF-CMAQ model cannot reproduce the observed concentrations under heavily polluted conditions (B. Zheng et al. 2014), a revised WRF-CMAQ system with enhanced heterogeneous reactions (Wang et al., 2012) was adopted to improve the model performance. The revised model could effectively capture the measured concentrations of total $PM_{2.5}$ (with normalized mean biases (NMB) being 0.4 %) and its different chemical compositions for both clean and heavily polluted haze days (B. Zheng et al., 2014). Details of the model configuration, modifications, and validation are described in B. Zheng et al. (2014)."

*3. The use of quotation marks was awkwardly used throughout the paper. I think the paper would read better if they were removed.*

**Response:**

Most quotation marks were now removed as suggested, except those indicating the quotation of the original text from other documents.

*4. Pg 17919 ln 1-10: I did not follow the thought process in which the authors used the OC/EC ratio to determine the SOA production or how it connected with the boundary layer. The rational and assumption need to be better explained.*

**Response:**

Thanks for pointing this out. The ratio to EC is used for two purposes: (1) one is to estimate the SOA production following the methods of Lim and Turpin (2002) and Lin et al. (2009); and (2) the other purpose is to account for the influence of different dilution/mixing conditions in the boundary layer. For the latter, the basic assumption is that EC comes only from primary emissions, thus, under certain emission rates, the change of EC concentration should be merely subject to atmospheric physical processes, such as the dilution/mixing effect, etc. We have included a paragraph to clarify this issue (See Paragraph 2 in Section 6):

"To evaluate the role of chemical productions, we analyzed the EC-scaled concentrations for individual compounds. The purpose of using EC-scaled

concentration is to eliminate the influence of different dilution/mixing conditions on the variation of observed pollutant concentrations. The observed variations of pollutant concentrations are not only controlled by the chemical reactions but also subject to the influence of boundary layer developments. For the same emission rate and chemical production rate, different mixing condition will result in different pollutant levels. It is thus highly uncertain to conclude a stronger/weaker chemical production based on purely the concentrations data without considering the boundary layer effect. Since EC is an aerosol species coming from only primary emission and quite inertial to chemical reactions, its variations well reflect the influence of atmospheric physical processes (dilution/mixing effect). The ratio of other species to EC will to a large extent eliminate the variations due to mixing/dilution and better represent the contribution from chemical reactions."

***Minor comments:***

*Pg 17917 ln 4: The use of "embrace" in this way personifies the weather system, which is not typically used in scientific writing.*

**Response:**

The expression has been changed from "to embrace it" into "to be scavenged" as suggested.

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