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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Exploring the severe winter haze in Beijing" *by* G. J. Zheng et al.

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Review of "Exploring the severe winter haze in Beijing" by G.J. Zheng et al. MS Number: acp-2014-309

Summary:

(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 con-

centrations 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. 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? 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. How are the results for EC/$PM_{2.5}$ 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. Do Figures 2b, 9a and 9b and 11a and 11b show hourly averages, and do these plots include all times of day?

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 $PM_{2.5}$ calculations for a severe episode, and that the model cannot predict the highest observed concentrations. This shortcoming must be discussed.

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 semi-quantitative 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.

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

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. 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.

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

5) Section 6.2 must also be strengthened. 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.

It is not clearly explained how either NO_3^- or SO_4^{-2} 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 O_3 or photochemically produced oxidants like OH, peroxides, or additional O_3. NOx is generally emitted as NO, which is oxidized to NO_2 by O_3. NO_2 is oxidized to NO_3 (again by O_3) or to HNO_3 by OH before it can be incorporated into the aerosol phase by heterogeneous chemistry. Similarly SO_2 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 O_2 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 $PM_{2.5}$ model simulations show with regard to the influence of heterogeneous chemistry? This modeling should be discussed.

Minor issues:

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

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 $PM_{2.5}$, ..."

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

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 ..."

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.

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".

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

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