Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-450-RC1, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions" *by* H. Li et al.

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Received and published: 6 June 2019

In past publications, the authors have reported on the effects of emission controls on China's air quality. This paper focuses on how those emission changes affect aerosol chemical composition. The authors present a comprehensive analysis involving measurements and models to assess the role of just emissions, apart from transport and meteorological differences. The results are interesting and the topic appropriate for this journal, however some details were missing and in many cases the analysis or description of processes was not of sufficient technical detail, such as the thermodynamic analysis. Also, strong conclusions are made with limited analysis to support them. For example, a major finding seems to be that these changes in emissions altered the aerosol formation mechanisms. It is stated in the Abstract and Conclusions

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that lower SO2 suppressed rapid sulfate formation through heterogeneous reactions. But it is not clear that this is really shown or tested in a quantitative way, instead it seems to be mostly speculation, based mainly on this hypotheses being consistent with the observations. Line 324 simply states: the results here imply that... Could not a chemical transport model, or maybe a simpler 0-D or 1D box model be run to further test this hypothesis? Overall, my recommendation is that the authors check closely if their reported findings are truly supported in the manuscript by quantitative analyses, and if only based on a consistency with expectations, that this clearly be stated. More detailed comments are provided below.

Specific Comments:

Line 59-60; I would think atmospheric chemical reactions (secondary aerosol) and deposition would also be a major contributor to PM2.5 composition.

Line 136 to 137, in giving the ambient data vs model comparison, state the integration time, ie 24 hr average data?

ISORROPIA calculations: In this paper the model is run without considering non-volatile cations. Maybe a few words should be added why this is ok, ie, it may be argued that for PM1 this is reasonable. As another example, the nitrate considered in the paper is all semivolatile nitrate (ie, NH4NO3), but it is possible that nonvolatile nitrate also exists in the ambient PM2.5 (eg, Ca(NO3)2). Thus if Ca2+ was considered in the thermodynamic calculations, it could affect predicted pH and NO3- concentrations. Most of this Ca2+ would likely be in the 1 to 2.5 um range, and since the comparison between PM1 and PM2.5 mass is reasonable, the authors could argue that it is not a large contribution. Also, I suggest the authors specifically note what RH range was used in the thermodynamic calculations, many of the assumptions, such as no separate organic/inorganic phases, etc, may be less likely at lower RH. (say <40 to 50%). Line 231-232 notes that the observed RH was about 33 to 34% in the winter of 2017. This a very low RH to comfortably run ISORROPIA under the metastable assumption without some test on the reliability of the results.

In the experimental section, there was no discussion of measurement of HNO3 or NH3 (gas species), yet ISORROPIA was run such that these data are needed, ie, run in forward mode. More information is needed in the paper on how the model was run without these critical gas phase species.

Line 175 or in Table 1 title state this is observational data (not model).

Line 258, what does Until 2017 mean? These changes were completed by 2017?

Line 311, does not tell the complete story. There are publications, see below, that show the predictions of Cheng et al. 2016 and Wang et al, 2016 are likely not correct due to their incorrect calculation of fine particle pH and that this proposed heterogeneous chemistry is highly sensitive to pH. This counter argument should also be noted here in this paper for completeness.

Liu, M., Y. Song, T. Zhoh, Z. Xu, C. Yan, M. Zheng, Z. Wu, M. Hu, Y. Wu, and T. Zhu (2017), Fine Particle pH during Severe Haze Episodes in Northern China, Geophys. Res. Lett., 10.1002/2017GL073210.

Guo, H., R. J. Weber, and A. Nenes (2017), High levels of ammonia do not raise fine particle pH sufficiently to yield nitrogen oxide-dominated sulfate production, Sci. Reports, 7(12109), DOI:10.1038/s41598-41017-11704-41590.

Song, S., M. Gao, W. Xu, J. Shao, G. Shi, S. Wang, Y. Wang, Y. Sun, and M. B. McElroy (2018), Fine particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models, Atm. Chem. Phys., 18, 7423-7438.

Line 318-319, define SOR and NOR (ie, what does the acronym stand for?)

Lines 339 to 344. Although this discussion tends to follow the Seinfeld and Pandis discussion of sulfate/nitrate/ammonium interactions, it is largely based on weak intuitive arguments and not a rigorous thermodynamic discussion. It is suggested that these types of statements be avoided. Below are possible other ways to discuss the interplay between sulfate, nitrate and ammonium and gas species, nitric acid and ammonia:

Change: Particulate nitrate in PM2.5 is mainly formed through the neutralization of HNO3 with NH3 to something like: Semivolatile PM2.5 particulate nitrate is formed through the partitioning of HNO3 to the particle phase, which is more favored at higher aerosol pH. pH is affected by gas phase NH3 concentrations, where higher NH3 generally leads to higher pH and so possibly more particulate nitrate.

Change: Nitrate formation was also affected by the competition for available NH3 between sulfate and nitrate. In the atmosphere, NH3 prefers to react first with H2SO4 to form ammonium sulfate due its stability. To: Because sulfate is nonvolatile, when it is a significant fraction of the aerosol mass it has a dominant influence on aerosol pH, making the aerosol acidic (low pH). In contrast ammonium and nitrate are semivolatile and so their particle-phase concentrations depend on the meteorological conditions (T, RH) their corresponding gas phase concentrations, (NH3 and HNO3 respectively) and aerosol pH. For example, at high sulfate and moderate NH3 concentrations the aerosol can be too acidic for partitioning of HNO3, but at higher NH3, or if sulfate concentrations drop sufficiently (or RH increases), particle pH will increase and can reach a point at which HNO3 partitioning can occur and nitrate aerosol formed. Lower T also favors partitioning to the particle phase through Henry's law constants.

As for the last line, when RH>60% maybe an additional explanation for the trend in Fig 8d is that as RH increases liquid water levels increase resulting in higher pH, which allows more nitrate to partition to the aerosol through a feedback loop, as is discussed later in the paper. That is, the increase in NOR may be due to more than just heterogeneous nitrate production.

Line 366-369, In Fig S9a provide a reference for the calculation of epsilon(NO3-). This pH of 3 at which the sensitivity of epsilon(NO3-) changes, as found in this work, was discussed in detail by Guo et al., ACP 2018, which should be cited.

Finally, there are a number of studies reporting pH in Beijing over different periods. Some of these did analysis to test the thermodynamic model predictions, which was not done here. A summary of these papers and comparison to pH reported in this paper is warranted to support this analysis.

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