

Interactive comment on “Extreme haze pollution in Beijing during January 2013: chemical characteristics, formation mechanism and role of fog processing” by K. Huang et al.

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Overall, this manuscript analyzed a winter haze episode in Beijing during January 2013, ranging from the meteorological and synoptic atmospheric conditions in relation to the haze formation, comparison with historical air quality data to highlight this extreme case, to aerosol chemistry from very limited 15 PM_{2.5} samples. Obviously, the new things what this manuscript attempted to tell us are really few, which agrees well with the other two referees' comments. First of all, the detailed meteorological conditions and regional scale atmospheric systems responsible for the January 2013 haze events can be clearly found in Zhang et al. (2014, Science China Earth Sciences 57, 26)

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and Wang et al. (2014a, ACP 14, 3151; 2014b, Science China Earth Sciences 57, 14; and 2014c, Science China Earth Sciences 57, 3). Relevant descriptions and discussion in this manuscript appears to not standing out from the two cited references. Moreover, the regional (covering the whole North China Plain) sources and transport of PM and air pollutants have also been discussed in details using the numerical simulations by Wang et al. (2014a and 2014c), by compiling and comparing the PM_{2.5} data between observation and modeling and between the present haze episode and the past record. Again, section 3.1 of the manuscript cannot give a more comprehensive overview on this haze event than the cited references. Regarding the aerosol chemistry, this manuscript was based on a very limited dataset, and unconvincing and even wrong interpretations can be found, to be specifically described later. In addition to the lacks of originality and novelty, there are many flaws and drawbacks of critical concerns particularly data quantity and quality and contradictory discussion. Other general comments are described specifically as follows.

General comments:

1. The causal relationships among the fog, haze, and the extreme PM_{2.5} pollution episode should be definitely defined, and discuss in logics. Obviously, the manuscript didn't clarify the fundamental issue.
2. In their study, trace elements including a total of 24 elements (Al, Fe, Mn, Mg, Mo, Ti, Sc, Na, Ba, Sr, Sb, Ca, Co, Ni, Cu, Ge, Pb, P, K, Zn, Cd, V, S, and As) were analyzed using ICP-OES (SPECTRO, Germany). To my abundant experience in the usage of ICP-MS and ICP-OES, it is really believed that the ICP-OES cannot achieve the quality data at least for Mo, Sc, Sb, Co, Ge, P, Cd, and As. Even for Mn, Ba, Sr, Ni, Cu, and V, the ICP-OES may also unable to precisely determine some samples with low particle loadings. The authors should clearly describe the QA/QC protocols to guarantee their data quality though they have referred to a study (Zhuang et al., 2001) but published in a local Chinese journal. Accordingly, the authors may best show the error bars in the Figure S2.

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3. In section 3.1, the authors compared the variations of PM₁₀ concentration and AOD in January between 2003 and 2013, showing a similar trend. The authors emphasized a decreasing tendency since 2006 and attributed it to the decrease in SO₂ emission (presumably the fine aerosols), which is really interesting. However, I wonder if this decreasing trend is statistically significant and robust. Then further considering other pollutants such as NO_x, black carbon, and organic carbon emissions in China with a continuously increasing trend (Richter et al., 2005, *Nature* 437, 129; Qin and Xie, 2012, *ACP* 12, 4825; Zhao et al., 2013, *ACP* 13, 9869), it thus appears to be conflicted with the authors' argument. Also it has been projected that SO₂, NO_x, VOC, and NH₃ emission will continuously go up until 2020 (Xing et al., 2011, *ACP* 11, 3119). More importantly, the authors referred to Itahashi et al. (2012) to demonstrate their consistency. Nevertheless, Itahashi et al. (2012) clearly stated that the AOD peaked around 2005 to 2006; in contrast, the manuscript observed a very contrasting result of AOD value between 2005 (low) and 2006 (largest) but PM₁₀ is not the case, which is quite inconsistent with Itahashi et al. (2012). It seems that the authors cannot attribute the observed yearly variation of PM₁₀ concentration simply to AOD variation and then to SO₂ emission.

4. The authors discussed the impact of relative humidity on aerosol chemistry in Section 3.4. They showed the exponential correlations of ionic species with RH in Figure 6, which is really interesting. However, the interpretation that the authors attributed to a hygroscopic growth curve seems unconvincing. Such exponential (might also be linear?) correlation is not only valid for secondary species such as sulfate, nitrate, ammonium, but also for the primary species K and Cl. The increase of K is four time higher during the fog period than the non-fog period, close to that of sulfate. Besides, the higher RH presumably associated with high temperature (temperature shown in Table 1 should be wrong) effect may not favor for ammonium nitrate formation. Accordingly, it may imply the correlations would reveal not only the hygroscopic growth but also (maybe more importantly) simply relate to the emission variability. Therefore the authors may show the temporal variation in NO_x, SO₂ and NH₃ concentrations accom-

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panying with sulfate and nitrate in Figure 6 and look at their partitioning. Additionally, such curves (and thus their regression equations) could be addressed in relation to hygroscopic growth factor which has been postulated as a main factor influencing the discrepancy in AOD/PM_{2.5} ratios between the fog and non-fog days and in turn the aerosol extinction coefficient (see Page 7532), otherwise those curves can tell us not much.

5. The authors draw a conclusion that vehicle emission is an important source of PM_{2.5} during the severe haze episode. Actually, the conclusion sounds making sense. However, their results provided and the relevant discussion in the present study are considerably weak to support their conclusion. The conclusion is drawn chiefly based on two results: SO₂/NO₂ and/or sulfate/nitrate ratio, and trace elements V, Ni, and Pb. The variability in sulfate/nitrate ratio may be not only a function of the relative magnitudes of their precursor emissions, but also a complex factors such as meteorological conditions (as the authors recognized in the manuscript), and preexisting aerosol loading and composition. Moreover, the authors assigned V and Ni to traffic origins, which obviously is wrong. Very few studies attribute the two elements to vehicle emission in polluted urban as their emission rates are very small (Liacos et al., 2012, *Science of the Total Environment* 435–436, 159–166). As for Pb, it is well known that since the phase out of leaded gasoline in China, coal combustion and non-ferrous metal smelting are the main emission sources of anthropogenic Pb in China (Li et al., 2012, *AE* 60, 1-8). Besides, from Pb isotope measurements, a similar conclusion that coal combustion is the most dominant source of airborne Pb (Mukai et al., 2001, *ES&T* 35, 1064; Hu et al., 2014, *EP* 187, 42; Zheng et al., 2004, *AE* 38, 1191) was obtained. Furthermore, when looking at Fig. S2, the daily variation of Pb is relatively similar to those of S and As which have been used as tracers of coal combustion. As for Ni and V, their temporal variations were somewhat like those of Al and Ti. Also, one may roughly calculate the enrichment factors of Ni and V (though the authors didn't report them) from the figure's data, and the EF values of Ni and V should mostly lower than 10, indicating a dominance of mineral dust (may including

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coal fly ash).

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C1600/2014/acpd-14-C1600-2014-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 7517, 2014.

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