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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Speciated Atmospheric Mercury during Haze and Non-haze Days in an Inland City in China" *by* Qianqian Hong et al.

Anonymous Referee #1

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The paper presents one year long continuous measurements of mercury species at an urban site, together with measurements of CO, O3, PM2.5 and K+ in daily PM10. NO2 was also derived from DOAS measurements using sun light. The data set is valuable.

The authors interpret the measurements in terms of sources and the diurnal variations of mercury species in terms of chemistry. The discussion of emissions and source areas is questionable. The interpretation of the diurnal variations in terms of chemistry is highly speculative and unconvincing. Taking into account the value of the data, I still recommend a final publication if the authors are able to respond to the comments below and reinterpret the data accordingly:

1. NO2 measurement: MAX-DOAS measures slant column densities which were converted to vertical column densities as described in line 157 to 162. The authors de-

scribe how they convert a vertical column density to local NO2 concentrations in the Supplement. They assume homogeneous concentrations within a 500 m thick boundary layer (BL) irrespective of daytime. Constant height of a boundary layer (BL) over a daytime is not realistic and will deliver a false diurnal variation of NO2 concentrations. Neither is a constant height of BL of 500 m applicable to different seasons.

2. Section 4.1: The discussion of the PSCF results is difficult to follow. Figure 5 shows potential source areas of GEM during the haze events in December 2013 and January 2014 but the equivalent figures for non-haze days in December 2013 and January 2014 are shown only in supplementary information. It is their difference which can provide the information about the reason for higher GEM during the hazy days. Dtto about the Figure 6: two seasonal data sets should be presented, one for hazy days and one for non-hazy ones.

3. The discussion of GEM vs CO correlations is deeply flawed. The low GEM/CO slopes are interpreted as if biomass burning were the major source for both GEM and CO in Hefei. To start with GEM/CO slopes represent their emission ratios if a) the background concentrations do not change, b) the emissions remain constant, and c) there is only dilution, no chemistry, on the way from the source to receptor during an event. Using monthly or other "non-event" data would violate at least the condition a) and b). In addition, whatever the sources of GEM might be, in a city of 7 million people and some 1 million of vehicles most of the CO at the site within the city will almost certainly come from local tailpipes rather than from distant isolated fire counts shown in Figure S4. The authors present Figure S3 as additional evidence in favour of biomass burning being the major source. The figure shows correlation between K+ and an Air Quality Index, whose definition is not given in the paper. To be halfway credible, K+ has to correlated with CO. Even if K+ correlated with CO, it still will not prove the biomass burning origin of the mercury. For that the density of the firecounts has to be consistent with results of the PSCF analysis which it evidently is not. In addition remote biomass burning would not yield highest GEM, RGM, and PBM concentration

at the lowest wind speeds – see section 4.2. In summary, the low GEM/CO ratio is characteristic for the emissions of Hefei.

4. Section 4.2: Highest PBM and PM2.5 concentrations in January are most likely due to shallower boundary layer in January than in other months. That is probably meant by "poor diffusion conditions in cold months". The average PBM concentrations in March differ hardly from other months except for January but their spread is larger. I think that the precipitation and the frequency of change of air masses should be also taken into account as driving forces for the PBM vs PM2.5 correlation.

5. Section 4.3: The interpretation of the diurnal variations here is almost certainly wrong. The authors interpret GEM and PBM diurnal variation in terms of changing height of boundary layer and declare that the opposite RGM diurnal variation must be of chemical origin. This must not be and probably is not true. RGM correlates with O3 which is probably not formed in situ but admixed from the free troposphere (FT) as the height of BL increases during the morning. Higher RGM concentrations in FT than in BL have been reported by many researchers. Consequently, the RGM correlation with O3 and its anticorrelation with CO can be viewed as solely a transport phenomenon unrelated to any chemical process. The distinction between a transport and chemical processes is a general problem in the interpretation of diurnal variations. It can only be resolved by careful modeling using measured diurnal variation of the BL height and known concentrations in BL and FT or by using specific tracers for photochemical processes such as peroxynitrates. In this particular case, diurnal variations of GEM, PBM, CO, NOx, etc. emissions due to morning and evening rush hours, working times, etc. additionally complicate the interpretation of the diurnal variations. As mentioned before the diurnal variation of NO2 is also flawed by the assumption of constant height of boundary layer. In summary, the observed diurnal variation can be interpreted solely as a transport phenomenon due to air exchange between BL and FT. As long as the authors cannot rule out the transport hypothesis their chemical interpretation of the diurnal variation and discussion of NO2 kinetics are wishful thinking without any evi-

dential basis.

Editorial comments:

Line 66-67: PBM is not highly surface reactive. "Affinity" might be better than "reactivity".

Line 72: The most recent quoted reference is Pacyna et al. (2006). In 2016 and recent discussions about emissions this seems to be quite obsolete. Dtto line 82. Please quote more recent publications.

Line 322: The sentence is flawed both in content as in grammar. If taken at face value, the text insinuates emissions from power plants being "non-normal" although they represent the largest GEM emissions in most inventories.

Reference at line 584 is incomplete.

Figure 8: Bottom plot: which symbol is PBM and which one PM2.5? The caption of the Figure 8 seems to be inconsistent with the time scale of the bottom plot. The time scale of the bottom plot has not equidistant intervals.

Figure 9: The scales of the y-axes should be same for the haze and non-haze days to facilitate a comparison. E.g. CO mixing ratios are much higher on hazy days.

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