

Response to Anonymous Referee #1

We thank the reviewer for the constructive suggestions/comments. Below we provide a point-by-point response to individual comments (comments in italics, responses in plain font; page numbers refer to the ACPD version; figures used in the response are labeled as Fig. R1, Fig. R2,...).

Comments and suggestions:

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

Responses and Revisions:

Differential Optical Absorption Spectroscopy (DOAS) is used to retrieve NO₂ and O₄ differential slant column densities (DSCDs) from the measured scattered sunlight spectra (Platt, 1994). In this study, each MAX-DOAS scanning cycle consists of eight elevation viewing angles (2°, 3°, 6°, 8°, 10°, 20°, 30° and 90°) and lasts about 15 min. The spectra are analyzed using the QDOAS spectral-fitting software suite developed at BIRA-IASB (<http://uv-vis.aeronomie.be/software/QDOAS/>). Detail information about the spectral fitting for NO₂ and O₄ is listed in Table S2 (in the revised supplement). As pointed out by the reviewer, MAX-DOAS vertical column densities could not fully represent the NO₂ surface concentration. So we used the HEIPRO (Heidelberg Profile, developed by IUP Heidelberg) retrieval algorithm to retrieve NO₂ vertical profiles for each MAX-DOAS scanning cycle. The purpose of calculating NO₂ profiles is to know the NO₂ vertical distribution. More details about NO₂ profile retrieval are described in the revised supplement. The NO₂ vertical profile

was shown in Fig. R1, indicating that the NO₂ is not homogeneously distributed vertically. We agree with the reviewer that converting NO₂ DSCD_S to mixing ratios by assuming that the trace gases were homogeneous within the 500 m height of the boundary is not suitable. We took the suggestion from the reviewer and updated the NO₂ results in the revision. The retrieval altitude grid is 80 layers of 50m thickness between 0.02 and 3.97 km. Thus, in the revised manuscript we have revised our method by using the surface NO₂ concentration (0.02 km) which from the NO₂ vertical profile (Fig. R1) to analyze. Due to the large computational requirement, we were not able to complete the calculation of the NO₂ vertical profile for the whole year. However, in Figure R1 we showed the result of one such NO₂ vertical profile (20th November, 2013), and the DFS and the errors of the retrieval are to determine whether the retrieved method is reasonable or not. As shown in Figure R2, the results suggest that the retrieved NO₂ vertical profile is reliable according to the experience of other research (Wang et al., 2014).

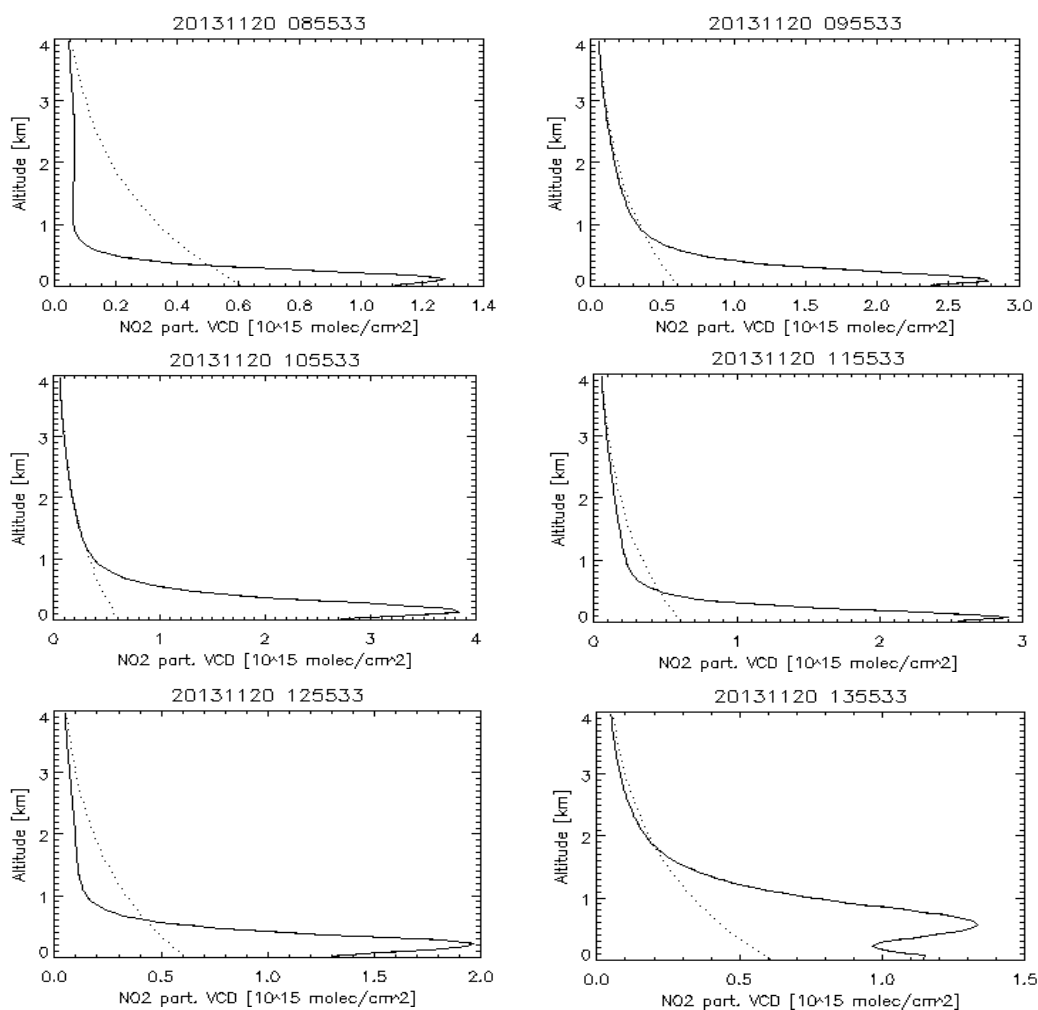


Figure R1. Example NO₂ vertical profiles at six different times (shown on top of each graph as YYYYMMDD hhmmss) from MAX-DOAS measurements in Hefei (20 November, 2013).

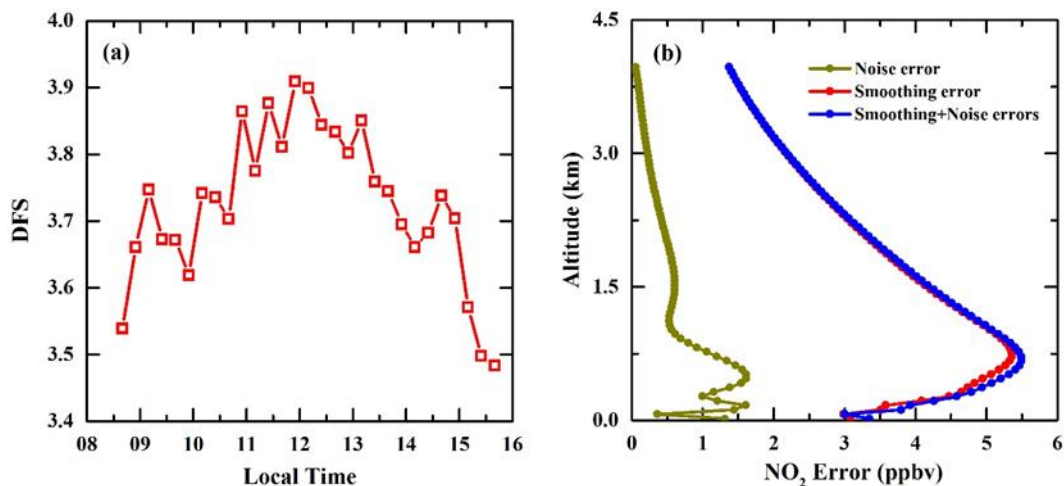


Figure R2. (a) DFS diurnal cycles corresponding to the NO₂ profile retrievals; (b) Errors of NO₂ vertical profile retrieval from MAX-DOAS measurements at Hefei (20 November, 2013 at 10:25LT).

Comments and suggestions:

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. Dttto about the Figure 6: two seasonal data sets should be presented, one for hazy days and one for non-hazy ones.

Responses and Revisions:

We have updated and merged PSCF results for potential source areas analysis of GEM in the revised manuscript. Two seasonal data sets are now include, one for haze days and the one for non-haze days. Since the number of haze days accounts only for 5.6% of the total days in spring and summer, we did not provide haze and non-haze PSCF results for spring and summer seasons. As autumn and winter are the prevalent

seasons for haze pollution, one PSCF result for haze days and another for non-haze days are shown for autumn and winter, respectively. We have combined Figure 5 and Figure 6 into a new figure (Figure 4) in the revised manuscript. The updated PSCF results showed that higher GEM concentration was mainly influenced by local emission sources during haze days. For non-haze days, the most important mercury sources to the monitoring site were not only the local emission sources, but also those from the neighboring region of Shandong, Henan and Jiangxi provinces. In summary, the increase of GEM concentration during haze days was mainly caused by local emission.

Comments and suggestions:

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 be 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 fire counts 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.

Responses and Revisions:

Upon further examination of our data, we agree with the reviewer that our original interpretation of the low GEM/CO was not fully supported. Therefore, we have removed Figure S2 (in the ACPD supplement) and revised thoroughly section 4.1 regarding the GEM/CO ratio. The definition of mercury pollution events are not same as haze days in this paper. These mercury pollution episodes were defined as a period with hourly average GEM concentration higher than seasonal average GEM concentration and the duration of elevated hourly GEM concentration lasted for over 10 hours (Kim et al., 2009). We discussed the correlation coefficients and slopes between GEM concentration and CO concentration during pollution events (Table 3 in the revised manuscript). In previous research, the Hg/CO slope and correlation between GEM and CO concentrations has been used to identify long-range transport episodes or local episodes: significant positive correlation for long-range transport episodes and poor correlation for local episodes (Kim et al., 2009). According to the correlations between GEM concentration and CO concentration, the mercury pollution episodes in autumn and winter mainly belong to local episodes. Incomplete combustion like residential coal and biomass burning combustion could lead to a lower Hg/CO ratio. We agree with the reviewer's point. In summary, the low GEM/CO ratio may be characteristic for the local emissions of Hefei.

As for water-soluble potassium (K^+) in 24-hr PM_{10} samples, the correlation between K^+ and Air Quality Index maybe not reliable. So we did the correlation between K^+ and GEM during the 24-hr PM_{10} sampling period (Fig. R3). Although the concentration of water-soluble potassium (K^+) in PM_{10} shows a good correlation ($R^2=0.67$) with GEM, due to the small number of compared samples ($n=6$), so it has great accidental and uncertainty. In addition, most pollutant concentration increased during this heavy pollution episodes (Nov-Dec, 2013). Good correlation might occur between K^+ and other pollutant, so it cannot fully prove that GEM come from the emission of biomass burning through good correlation between K^+ and GEM. Thus, we agree with the reviewer's comment and shortening this section. We have removed the discussion about K^+ and biomass burning altogether in the revised manuscript and supplement.

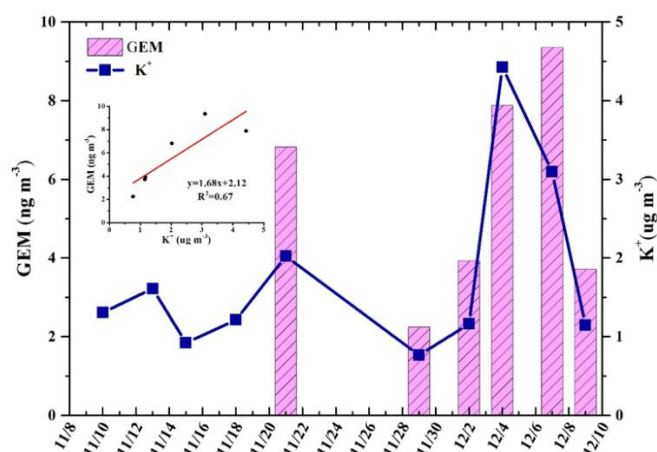


Figure R3. Correlation between water-soluble potassium (K⁺) and GEM during heavy pollution periods (from 10 Nov to 9 Dec, 2013). Notes: water-soluble potassium (K⁺) concentrations were analyzed from 24-hr PM₁₀ (particulate matter less than 10 μm in diameter) samples, GEM concentrations were the average value during the 24-hr PM₁₀ sampling period.

Comments and suggestions:

Section 4.2: Highest PBM and PM_{2.5} 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 PM_{2.5} correlation.

Responses and Revisions:

We agree with the reviewer’s suggestion. Unfortunately, we did not obtain the precipitation data during our monitoring period, so we were not able to directly examine the influence of precipitation on PBM. This is something we will investigate in our future studies.

Although on average the PBM concentrations in March differ hardly from other months (April-June), they fluctuated much greatly in March when compared to other months. We have re-examined the wind rose diagrams for March and April (see Fig.

R4). The prevailing wind direction in March indeed varied much greatly than in April. Thus, the larger fluctuation of PBM in March might be related to the frequency of change in wind direction. We have thus removed our original interpretation that “higher temperatures in the warmer months do not favor mercury adsorption”, and replaced it with reference to changes in wind direction.

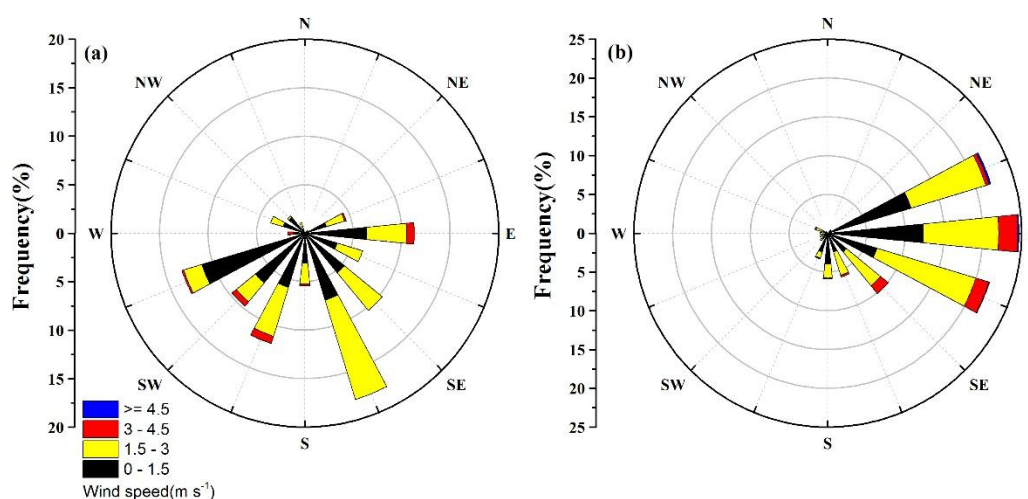


Figure R4. The wind rose diagrams for (a) March and (b) April.

Comments and suggestions:

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 peroxy nitrates. 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 evidential basis.

Responses and Revisions:

We agree with the reviewer that resolving transport and reaction processes of RGM is not straightforward; the fact that we did not measure specific photochemical tracers such as peroxy nitrates did not help. Two processes can affect the RGM concentrations in the boundary layer air. The first is due to transport of RGM from the free troposphere (FT). Diurnal variations of GEM, RGM, O₃ and CO concentrations during non-haze and haze days are shown in Fig. R5 (Figure 7 in the revised manuscript). For both non-haze and haze days, RGM concentrations remained at a relatively constant level during night, and then increased suddenly prior to the sunrise. We agree with the reviewer that such enhancement of RGM in early morning might can be due, at least in part, to its transport from the free troposphere as the height of BL increases. In summary, the observed RGM diurnal variation can be interpreted as a transport phenomenon due to air exchange between BL and FT.

In addition, in situ photochemical oxidation of GEM could also increase the concentration of RGM during daytime. To determine the relative importance of FT transport and in situ photochemical oxidation, we examined the relationship between RGM and the changes in the height of the atmospheric boundary layer and the odd oxygen (O_X = O₃ + NO₂) concentrations. Although we did not measure peroxy nitrates in this study, we believe the concentration of odd oxygen (O_X = O₃ + NO₂ which is produced from the reaction between O₃ and NO) can be used as a tracer of the extent of photochemical processing in the urban atmosphere. Since NO₂ concentrations from MAX-DOAS were only available during daytime, we could only use O_X to be a

indicator for daytime GEM oxidation. As per our manuscript, we selected 20th November 2013 as a case study to probe the importance of photochemical processes. Both RGM and O_x reached higher concentrations from 12:00 to 16:00, along with the lowest value of GEM. The height of atmospheric boundary layer changed very little over this period (12:00-16:00, see Fig. R6). This simple comparison suggests that the transport of FT RGM might be limited and that at least some of the RGM were formed from in situ oxidation of GEM. We further investigated the potential mechanism of the GEM oxidation to GOM.

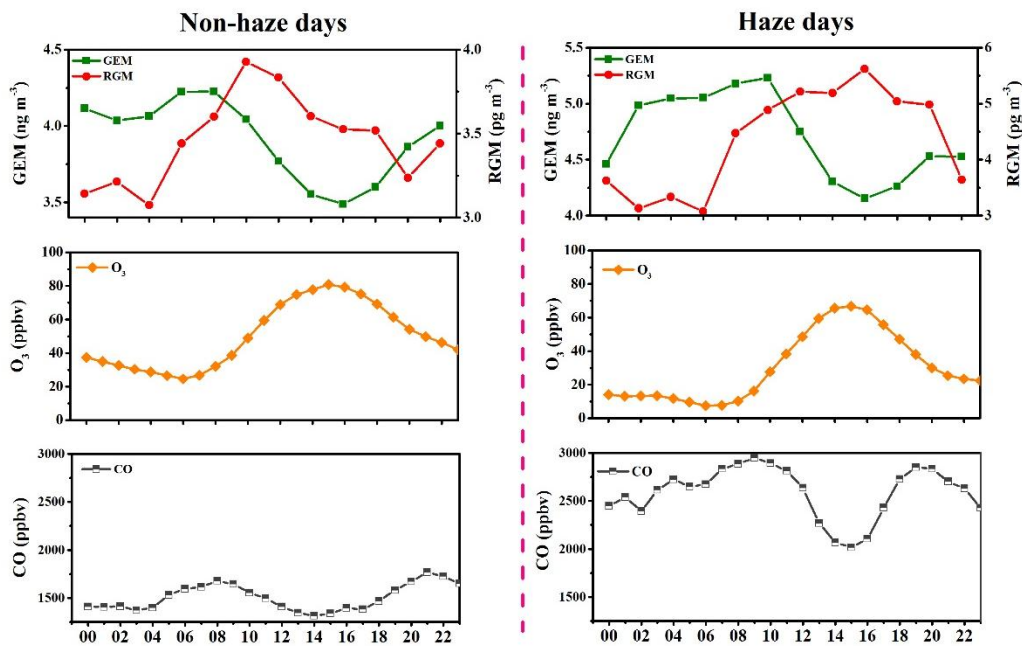


Figure R5. Diurnal variations of GEM, RGM, O_3 , and CO concentrations during non-haze and haze days.

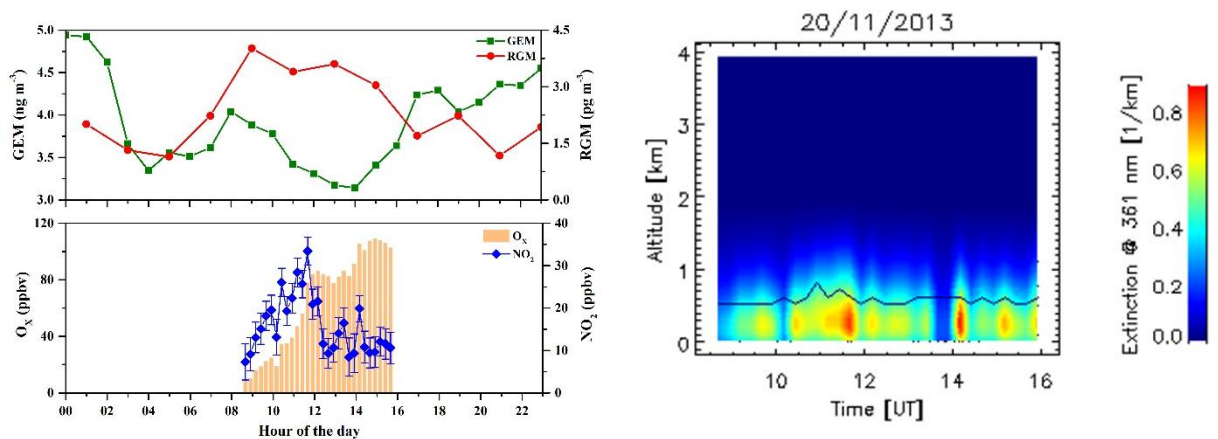


Figure R6. A case study of diurnal variations of GEM, RGM, O_x, and NO₂ at Hefei (20th November, 2013, left panel). The right panel shows the retrieved aerosol extinction profile on the same day; the black line represents the height of the atmospheric boundary layer.

Comments and suggestions:

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

Responses and Revisions:

Corrected.

Comments and suggestions:

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.

Responses and Revisions:

We have updated the section by quoting two recent publications ((Pacyna et al., 2010) and (Zhang et al., 2015)).

Comments and suggestions:

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.

Responses and Revisions:

The sentence in Line 322 has been modified according to the revision in the revised manuscript (second paragraph of section 4.1). We modified this sentence as follows: “GEM and CO often share similar anthropogenic emission sources, such as industrial coal combustion, domestic coal combustion, iron and steel production and cement production (Wu et al., 2006; Wang et al., 2005). However, they also have their own sources. For instance, power plants and nonferrous metal smelters emit mercury but

hardly any CO, while most of CO originates from vehicles which are not a major emitter for mercury.”

We also corrected the reference at line 584 (Hu et al., 2014).

Comments and suggestions:

Figure 8: Bottom plot: which symbol is PBM and which one PM_{2.5}? 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.

Responses and Revisions:

We have rearranged the figures, added the symbols of PBM and PM_{2.5} and updated the caption. The time scale of the bottom plot has corrected and had equidistant intervals.

Comments and suggestions:

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.

Responses and Revisions:

We have redrawn the figures so that the scales of the y-axes are same for the haze and non-haze days.

References

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