Replay to interactive comment #1 on "Correlation slopes of GEM/CO, GEM/CO_2, and GEM/CH_4 and estimated mercury emissions in China, South Asia, Indochinese Peninsula, and Central Asia derived from observations in northwest and southwest China"

Reponse to J. Pacyna (Referee):

We thank Prof. J. Pacyna for providing the comments regarding the validity of the correlation slope method. We would like to to elaborate how the method works and its associated limitations.

This is an interesting paper adding to the discussion on amount of mercury emissions, particularly in a gaseous elemental form, emitted from various sources in China. This is the region where emission of mercury is the highest compared to other parts of the world. Therefore, it is of particular importance to assess these emissions in China as accurate and complete as possible. The reviewed paper contributes to this process.

Comments: My major comment relates to the application of correlation slopes of GEM/CO_2, GEM/CO, and GEM/CH_4. I am a bit concerned with the value of such analysis. All four gases are emitted from different sources. The major source of CO_2 and mercury is the combustion of fossil fuels in large power plants, mostly coal-fired power plants. The CO emissions are mostly generated in incomplete combustion processes, basically selected industrial processes with poor industrial installations. Methane has a completely different sources/ processes generating emissions, mainly fermentation processes. How the above mentioned ratios of these gases could serve to explain the amount of these emissions? Or even to be compared with the ratios of the same gases measured in certain receptors in different regions? The authors may wish to provide more explanation on this issue.

Reply: The correlation method was firstly applied by Jaffe et al. (2005) to assess the Hg emissions in Asia using the slope of GEM/CO regression line. Later, Slemr et al. (2006) and Brunke et al., 2012 extended the use of the slopes between GEM and other atmospheric trace gases. The principles and assumptions have been discussed extensively by Jaffe et al. (2005) and the other two studies and the community can directly refer to the original development works. We have expanded the discussion regarding the limitations and uncertainties related to the method in the manuscript (line 527-552 on page 17).

First, it is true that GEM and CO/CO_2/CH_4 may be emitted from different sources with distinct emission characteristics. However, once these different sources are

collocated, the pollutants emitted from different sources will well mixed fast and emission ratios are expected to be reflected by the observed correlation slopes of these long-lived trace gases. Due to the different sources and emission rates, the correlation slopes exhibit both temporal and spatial. To obtain a comprehensive overview on the emission ratios, it is necessary to observe the correlation slopes in different seasons and regions, which was accomplished in this study. Therefore, we are confident that the estimates obtained in this study are representative and reasonably accurate.

One of the major uncertainties, though, is the accuracy of the emission estimates of CO, CO_2, and CH_4 in the two regions. However, many recent advances have been made in this regard. It is therefore perceived that the uncertainties of CO and CO_2 emission estimates are less than 50% (Zhao et al., 2012a;Zhao et al., 2012b;Olivier et al., 2001). Such an uncertainty level is slightly lower than that of anthropogenic GEM (Pacyna et al., 2010;Pirrone et al., 2010). However, the uncertainties of CH_4 emission estimates are expected to be larger, which would results in a greater uncertainty in the estimate of GEM emissions using GEM/CH_4 ratios. Previous studies have suggested that the correlation slopes may give an estimate of total GEM emissions (including both anthropogenic and natural emissions). These estimates based on correlation slopes are consistent with the results from inverse modeling (Pan et al., 2007). This is important because the current understanding on natural emissions of GEM is poor and the knowledge on total GEM emissions is crucial for global Hg modeling.

Comments: Just to even complicate this issue, the two closest gases in the context of common emission sources, such as coal-fired power plants, namely CO_2 and GEM may not be that close in the whole coal energy sector. The point is that GEM emissions from coal-fired power plants are dependent on the type and efficiency of flue gas desulfirization installation (FGDs), while CO_2 emissions are not dependent on this factor. So, even within the coal energy sector one would expect rather large ranges of GEM/CO_2 ratios. How to use this information for the assessment of GEM emissions from this sector in various regions of Asia or the world? Some more discussion on this application shall be added in the paper with explanation of limitations in such application.

Reply: First, we would like to point out that the emission factors of GEM, CO, CO_2, and CH_4 for emissions sources used in the present study were cited from most updated studies (line 371-375 on page 12). These emission factors were calculated on the basis of comprehensive field observations and the control measures can represent the predominant technologies used in industrial emission sources. Therefore they represent the most recently updated emission factors.

We agree that there may be significant variations in the emission factors. However,

the emission factors in different emission sources varied more significantly than the emission factors among common sources and therefore can be used to trace the sources using observed correlation slopes. For example, the emission ratios of GEM/CO and GEM/CO_2 for lead, zinc, mercury, gold productions were two orders of magnitudes higher than that of industrial coal combustion and cement productions. Pollution control devices may change the emission ratios, but the magnitudes of changes are much smaller than the emission ratio differences between different sources.

The correlation slopes method in the present study cannot be used to estimate GEM emissions from a certain emission source. It was used to estimate GEM emissions from different regions, where many sources are located in a given geographic boundary.

References

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Reponse to Anonymous Referee #2:

Firstly, we would like to acknowledge the anonymous reviewer for dictating the time to read our original manuscript and provide valuable suggestions. These suggestions are very helpful and constructive. We have made careful revision in the revised manuscript based on the reviewer's recommendations.

The authors present measurements of GEM concentrations made at three remote sites in China. Using concurrently measured CO, CO_2, and CH_4 mixing ratios they calculate GEM/CO, GEM/CO_2, and GEM/CH_4 concentration ratios for a number of pollution events. The authors compare these ratios with ratios reported by others for China and some other areas. The origin of the individual pollution events are attributed to four major source areas using backward trajectories. The transport from the source area to the measurement sites takes usually only a few days and thus chemical reactions of all measured species can be neglected. The measured GEM/CO, GEM/CO_2, and GEM/CH_4 concentration ratios then represent the emission ratios of the source area. Using the CO, CO_2, and CH_4 emission inventories for the source areas, the authors then calculate the GEM emissions for these areas. The authors find that the GEM emissions for all areas are substantially higher than the anthropogenic emissions from inventories.

The method is scientifically sound, the assumptions on which it is based were discussed by Jaffe el al. (2005) and Brunke et al. (2012) – see references in the paper. The paper is generally well organized and well written and should be published in a final version. However, the authors should address several weaknesses in the final version:

Major comment 1: The discussion is difficult to follow because the measured ratios in ng m^{-3} ppb^{-1} or ng m^{-3} ppm^{-1} are compared with emission ratios in t t^{-1} (in the text though not in the Table 2). Using molar or mass ratios for both the measured and inventory ratios would help. Please use uniform units.

Reply: We agree that using different units in the manuscript made the manuscript somewhat difficult to read. Most of the previous studies used the units of pg m^{-3}/ppb and pg m^{-3}/ppm for correlation slopes of GEM/CO, GEM/CH_4 and GEM/CO_2. To be consistent with these previous studies while maintaining the readability of the paper, we have provided the conversions of pg m^{-3}/ppb and pg m^{-3}/ppm to g/g in the revised manuscript. The added information can be found in section 3.2, Table 1 and Table 2.

Major comment 2: One possible source of mismatch between observed ratios and ratios

from inventories is ignored. The authors state that different circulation patterns (e.g. monsoon) transport the pollution to the measurement sites only during certain seasons. Because the GEM, CO, CO_2, and CH_4 emissions have all their specific seasonal variation (e.g. wetlands as a source of CH_4 peak in summer whereas CO and CO_2 emissions from residential heating peak in winter), their ratios will vary with season. Thus comparing annual emission ratios from inventories with observed emission ratios in a certain seasons can introduce a seasonal mismatch. Such mismatch could perhaps explain the overestimation of GEM emissions from GEM/CH_4 emission ratio and CH_4 annual emission inventory. The proper solution would be to calculate the regional emissions for the seasons for which the emission ratios were observed and using this as a basis for the estimation of GEM emissions instead of annual emissions. This would need a temporally resolved CO, CO_2, CH_4 emission inventories. This approach would of course provide only seasonal GEM emissions. If the temporally resolved CO, CO_2, and CH_4 emissions are not available the authors should at least mention this caveat.

Reply: This is an important point. Due to the different sources between GEM and CO, CH_4, and CO_2, the correlation slopes for GEM/CO, GEM/CH_4 and GEM/CO_2 vary temporally and spatially. We recognize that the correlation slopes cannot be observed uniformly throughout seasons and across the studied regions. This could be an inherent limitation for the correlation method. We introduced this artifact in many sections in the revised manuscript such as in line 402-407 on page 13 and line 539-552 on page 17. We believe that these revisions improve the discussion of the manuscript.

Major comment 3: The authors have data at disposal from which also CO/CO_2, CH4/CO_2 and CH_4/CO ratios of the events could be calculated and compared for consistency with the official CO, CO_2, and CH_4 inventories. This could provide an insight into the seasonal mismatch mentioned above and perhaps also answer the question about the reliability of CH_4 emissions.

Reply: This is an excellent suggestion. We have added the correlation slopes for CO/CO_2, CH4/CO_2 and CH_4/CO for the studied regions in the revised manuscript (line 342-355 on page 11, Table 1 and Table 2). The addition of the information helps better understand the discrepancy between observed correlation slopes of GEM/CO, GEM/CH_4 and GEM/CO_2 and estimated emission ratios. For example, we found the CO/CO_2 correlation slopes were consistent with anthropogenic emission inventories whereas observed CH4/CO_2 and CH_4/CO were much lower than anthropogenic inventories, indicating anthropogenic inventories on CO and CO_2 may be more accurate than CH_4. This is in a good agreement with the assessment of uncertainties in CH_4, CO, and CO_2 inventories and also help explain why we got higher estimated emissions on the basis of GEM/CH_4 slopes. However, we did not go further to study the seasonal patterns because we have not obtained a sufficient number of correlation slopes in each season and correlation slopes in different season may be related to air masses for different

regions. The temporal aspect of correlation slopes may also introduce uncertainties.

Major comment 4: The ranges of the GEM emissions calculated in this paper for different regions are rather narrow probably because the uncertainties of CO, CO_2, and CH_4 emissions were not considered. It should be mentioned that the inventories of CO_2, CO, and CH_4 in EDGARv3.0 are themselves uncertain by 10%, 50%, and 50%, respectively (Olivier et al., RIVM Bilthoven, RIVM Report #773301 001, NOP Report #410200051, 2001). Including the CO_2, CO and CH_4 emissions uncertainties of the used inventory would make many differences in the discussion insignificant.

Reply: We agree with this comment. The effect of uncertainties of CO, CO_2, and CH_4 emissions was discussed in the revised manuscript in line 527-536 on page 16.

Major comment 5: The calculated GEM emissions should be compared with the latest EDGARv4 gridded mercury inventory (Muntean et al., Sci. Total Environ. 494-495, 337-350, 2014).

Reply: The study by Muntean et al. (2014) is the most updated emission inventories. We have added this study into the manuscript.

I think that the authors in their final version of the paper should also address some minor problems listed below:

Minor points 1: Section 2, "Experimental": The authors investigated pollution events lasting 8-24 hours (page 24994). What criteria were used to find out a "pollution event"?

Reply: These events were defined in line 204 and line 213-217 on page 7.

Minor points 2: Page 24987, line 13: There are 4 regions but only 3 GEM/CO_2 ratios listed here.

Reply: There are some errors in the original manuscript, and we corrected them already (line 28-29 on page 2).

Minor points 3: Page 24987, line 27: Even different but collocated sources of GEM and CH4 will provide a GEM/CH_4 emission ratio for a certain area. If chemical reactions during the transport can be neglected the measured GEM/CH_4 emission ratio should correspond to the respective ratio of GEM and CH_4 emissions from the area inventories. "Fewer common emission sources" thus should not be a problem but perhaps the different seasonal variations of GEM and CH_4 emissions. The overestimation of CH_4 emissions seems thus to be the primary cause for the overestimated GEM emissions.

Reply: This comment helped us better understand the correlation method. We deleted our previous discussions and talked the effect of overestimation of CH_4 emissions on the discrepancy (line 458-468 on page 14).

Minor points 4: Page 24992: What are the standard conditions for mercury concentrations given in the paper? 1013 hPa and 273.16 K or something else? Please state explicitely.

Reply: We added the information in line 160-161on page 6.

Minor points 5: Page 24993, line 1: "ensure" instead on "insure"

Reply: This word was changed.

Minor points 6: Page 24994, correlation analysis: It is not clear to me whether the correlations were made using the normal least-square fit or a bivariate correlation such as described by Cantrell (Atmos. Chem. Phys. 8, 5477, 2008). Both methods provide the same R or R^2 but different slopes, i.e. emission ratios. The problem with the least square fit is that the slope of e.g. GEM/CO is not equal to 1/slope CO/GEM which is physically incorrect. The normal least square fit assumes measurement uncertainty only in y whereas bivariate correlation needs uncertainties both in x and y. Bivariate correlation would be the correct method. If the authors used the normal least-square fit they should recalculate the slopes using the program provided with the paper by Cantrell (2008).

Reply: We thank the reviewer for point this out and would like to clarify it. The correlations were calculated based on SPSS using orthogonal least-square correlation. We also checked the slope and 1/slope for the observations. We found the difference in general fell in the range of 10% (may be due to the fact of significant correlations between GEM and CO, CH_4, and CO_2). Therefore, we did not change the method in the

revised manuscript.

Minor points 7: Section 3.2: The authors may refer also to Hg/CO, Hg/CO_2, and Hg/CH_4 emission ratios published in a recent paper by Slemr et al. (Atmosphere 5, 342, 2014).

Reply: The papers by Slemr et al., (2009 and 2014) have been used in the revised manuscript.

Minor points 8: Section 3.3: Artisanal gold mining is not mentioned in this section. According to the new EDGARv4 gridded mercury inventories (Muntean et al., Sci. Total Environ. 494-495, 337-350, 2014) this should be a very important source, especially for estimating the GEM emissions for South Asia, Indochinese Peninsula, Central Asia, and possibly even for China. This could be another explanation for the difference between the GEM emissions from emission ratios and GEM inventory emissions.

Reply: The contributions of artisanal gold mining is added in the revised manuscript in line 383-387 on page 12.

Minor points 9: Section 3.4: A map showing the four areas (China, South Asia, Indochinese Peninsula, Central Asia) of pollution origin for which the CO, CO_2, and CH_4 emissions from the inventories were calculated is necessary. Were the seasonally resolved CO, CO_2, and CH_4 emissions used or only annual emissions? CO/CO_2, CH4/CO_2, and CH_4/CO emission ratios can be calculated from the correlations of available data. Are they consistent with the inventory ratios? If not what might be the reason and what does it mean for the calculated GEM emissions?

Reply: Figure 1 and Table 2 show the annual emissions of GEM, CO, CH_4, and CO_2. The CO/CO_2, CH_4/CO_2, and CH_4/CO emission ratios were calculated in Table 2 and compared with observed CO/CO_2, CH4/CO_2, and CH_4/CO correlation slopes (line 342-355 on page 11). These discussions helped explain the uncertainties of CO, CH_4, and CO_2 emissions in the studies regions.

Minor points 10: Table 3: The estimated GEM emissions should also be compared with the emissions from the latest EDGARv4 gridded mercury emission inventory (Muntean et al., 2014).

Reply: The most updated inventory by Muntean et al. (2014) was added in Table 3.

Minor points 11: Figure 7: What is “warm season”?

Reply: We defined the “warm season” and “cold season” in the revised manuscript.