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Interactive comment 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" *by* X. W. Fu et al.

Anonymous Referee #2

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The authors present measurements of GEM concentrations made at three remote sites in China. Using concurrently measured CO, CO2, and CH4 mixing ratios they calculate GEM/CO, GEM/CO2, and GEM/CH4 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/CO2, and GEM/CH4 concentration ratios then represent the emission ratios of the source area. Using the CO, CO2, and CH4 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 organised and well written and should be published in a final version. However, the authors should address several weaknesses in the final version:

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.

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, CO2, and CH4 emissions have all their specific seasonal variation (e.g. wetlands as a source of CH4 peak in summer whereas CO and CO2 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/CH4 emission ratio and CH4 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, CO2, CH4 emission inventories. This approach would of course provide only seasonal GEM emissions. If the temporally resolved CO, CO2, and CH4 emissions are not available the authors should at least mention this caveat.

3. The authors have data at disposal from which also CO/CO2, CH4/CO2 and CH4/CO ratios of the events could be calculated and compared for consistency with the official CO, CO2, and CH4 inventories. This could provide an insight into the seasonal mismatch mentioned above and perhaps also answer the question about the reliability of CH4 emissions.

4. The ranges of the GEM emissions calculated in this paper for different regions are rather narrow probably because the uncertainties of CO, CO2, and CH4 emissions were not considered. It should be mentioned that the inventories of CO2, CO, and CH4 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 CO2, CO and CH4 emissions uncertainties of the used inventory would make many differences in the discussion insignificant.

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).

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

Section 2, “Experimental”: The authors investigated pollution events lasting 8 – 24 hours (page 24994). What criteria were used to find out a “pollution event”?

Page 24987, line 13: There are 4 regions but only 3 GEM/CO2 ratios listed here.

Page 24987, line 27: Even different but collocated sources of GEM and CH4 will provide a GEM/CH4 emission ratio for a certain area. If chemical reactions during the transport can be neglected the measured GEM/CH4 emission ratio should correspond to the respective ratio of GEM and CH4 emissions from the area inventories. “Fewer

common emission sources” thus should not be a problem but perhaps the different seasonal variations of GEM and CH4 emissions. The overestimation of CH4 emissions seems thus to be the primary cause for the overestimated GEM emissions.

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.

Page 24993, line 1: “ensure” instead on “insure”

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 R2 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).

Section 3.2: The authors may refer also to Hg/CO, Hg/CO2, and Hg/CH4 emission ratios published in a recent paper by Slemr et al. (Atmosphere 5, 342, 2014).

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.

Section 3.4: A map showing the four areas (China, South Asia, Indochinese Peninsula, Central Asia) of pollution origin for which the CO, CO2, and CH4 emissions from the inventories were calculated is necessary. Were the seasonally resolved CO, CO2, and

CH4 emissions used or only annual emissions? CO/CO2, CH4/CO2, and CH4/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?

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).

Figure 7: What is “warm season”?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 24985, 2014.