Reply to Comments from Referee #1

1. In the section of non-ferrous smelting, I suggest some more discussion about mercury use and emission from golden smelting should be added.

Response:

We have added the discussion on mercury speciation in the gold smelting process based on our recent measurements. Please see the updated Table 2, Lines 272-278 on Page 10 and Lines 389-392 on Page 14 in the revised manuscript:

"The case in the industrial gold smelting process is an exception. Based on the recent on-site measurements, only 85% of the mercury in gold concentrate evaporates into the flue gas with the roasting temperature at 600°C (Yang, 2015). The low mercury release rate in the tested gold smelter is due to the chemical properties of mercury and gold. According to a previous study (Li, 1990), mercury at certain chemical speciation in gold ores only releases when the temperature exceeds 780°C."

"The mercury speciation profile (Hg^0:Hg^{2+}:Hg_p) in the exhausted flue gases in gold smelters with the double-conversion-double-absorption process is estimated to be 32:57:11 (Yang, 2015)."

Dr. Mei Yang has contributed to this part, so we have added her as a co-author.

References:

Li, J.: Distribution features of mercury compounds in gold deposits, Geology and Exploration, 11, 46–51, 1990.

Yang, M.: Research on atmospheric mercury emission inventory and control technology of gold production in China, Postdoctoral work report, Tsinghua University, Beijing, China, 2015.

2. Except for sources associated with combustion or high temperature industrial process, additional discussion and summary for some other Hg emission source are suggested to be added to make the critical review more complete and integrated.

Response:

We have added discussion on waste incineration, biomass burning, cremation and

PVC production to Section 5 (previous Section 6 because iron and steel production has been combined to this section). Please see the updated Section 5 in the revised manuscript:

"In this section, the behavior of mercury in flue gases from other emission sources, including iron and steel production, waste incineration, biomass burning, cremation, and PVC production, are introduced. Although there are still other mercury emission sources not discussed in this study, such as oil combustion, few field measurements are available for mercury speciation and transformation inside these sources."

"5.2 Mercury speciation and transformation in flue gas from waste incineration

Waste incineration is a potential predominant source in the global mercury emission inventory. The major incineration types are municipal solid waste (MSW) incineration, medical waste incineration and industrial/hazardous waste incineration. A significant proportion of mercury (80–96%) in the MSW releases from the incinerator into the flue gas is in the form of Hg^0 at 850–1000°C (Park et al., 2008). Grate furnace combustor (GFC) and circulation fluidized bed combustor (CFBC) are the two most commonly used incinerators. The flue gas from CFBC has a larger proportion of Hg_p than that from GFC. Typical APCDs for incinerators are combinations of semi-dry or dry flue gas deacidification (SD-FGD or D-FGD) for SO_2 and HCl removal and dust controller (e.g., WS+ESP, FF, FF+WS, etc.). SCR is sometimes used as well for NO_x control. Activated carbon injection (ACI) is used for the control of persistent organic pollutants (POPs), which is required for incinerators in China.

The overall mercury removal efficiency of the APCDs for MSW incineration ranges from 60% to over 99% (Zhang et al., 2008; Takahashi et al., 2012). Previous studies in Europe and the USA indicated that the Hg^{2+} proportion in the exhausted flue gas ranges from 75% to 85%(Pacyna and Münch, 1991; Carpi, 1997). A Korean study found the Hg^{2+} proportion in MSW incinerators to be in the range of 78–89%, and that in industrial waste incinerators are even as high as 96.3–98.7% (Park et al., 2008). Kim et al. (2010a) tested two medical waste incinerators with SD-FGD+FF+WS and got the Hg^0 proportion to be 43.9% and 96.8% respectively. A Japanese study showed that an industrial waste incinerator with WS and wet ESP has the Hg^0 proportion of 92.7% (Takahashi et al., 2012). Based on field measurements in eight MSW incinerators in China, Chen et al. (2013) found that average Hg^{2+} proportion in flue gas from the outlet of GFC+SD-FGD+ACI+FF is 96%, while that for CFBC+SD-FGD+ACI+FF is 64%. High chlorine content in the waste results in

high Hg^{2+} proportion in the flue gas. Limestone slurry or powder sprayed in SD-FGD or D-FGD absorbs a large amount of Hg^{2+} and activated carbon adsorbs a large amount of both Hg^0 and Hg^{2+}. Particles from SD-FGD and ACI are captured by the downstream FF. Hg_p is removed by all types of dust controllers. The high Hg^{2+} formation rate due to the oxidative condition in flue gas and the high Hg^{2+} removal rate by APCDs (especially SD-FGD, FF and ACI) cause the significant variation in mercury speciation profiles for incinerators."

"5.3 Mercury speciation and transformation in flue gas from biomass burning

Biomass burning mainly includes biomass fuel burning and open biomass burning. Biomass fuel can be divided into fuel woods, crop residues and biomass pellets. Usually, there is no APCD for biomass burning. Huang et al. (2011) tested four different types of wood fuels and found the Hg^0 proportion to be 95–99% and the rest is basically Hg^{2+}. Wei (2012) found that Hg^0 in flue gas from biomass burning is 70–90% of total mercury while that of Hg^{2+} ranges from 5% to 9%. Hg_p proportion differs a lot between different biomass fuel types: 12%, 25% and 1% for fuel wood, crop residues and biomass pellets, respectively. Hu et al. (2012) differentiated the emission factors for biomass burning and cooking/space heating in rural areas to be 0.035 and 0.515 g Hg/t biomass burned, respectively. W. Zhang et al. (2013) tested 25 types of fuel wood, 8 types of crop residues and 2 types of biomass pellets, and found that the mercury emission rate during biomass burning is 78–99% while the remainder stays in the residue. The mercury speciation profile (ratio of Hg^0, Hg^{2+} and Hg_p to total Hg) for fuel wood was 76%, 6% and 18%, and that for crop residue was similar (73%, 4% and 23%). However, the speciation profile for biomass pellets is quite different. Due to the more complete combustion, Hg^0 accounts for as high as 97% in the flue gas from of biomass pellets combustion. W. Zhang et al. (2013) calculated mercury emission from biomass burning in China and gave the shares of Hg^0, Hg^{2+} and Hg_p at 74%, 5% and 21%, respectively. Open biomass burning generally involves forest wildfires, grassland/savanna wildfires, and agriculture residue burning. Friedli et al. (2003) investigated the mercury speciation from burning of temperate North American forests through both laboratory and airborne measurements. Their research showed that the dominant species is Hg^0, accounting for 87–99% of the total mercury, and the rest is mainly Hg_p."

"5.4 Mercury speciation and transformation in flue gas from cremation

Researches on mercury speciation and transformation in flue gas from cremation

are very limited. Takaoka et al. (2010) conducted field measurements in seven crematories in Japan, two of them without any APCDs, one with ESP and four with FF for particle control. Advanced APCDs such as catalytic reactor and activated carbon filter are installed in three of the tested crematories. In the exhausted flue gases, Hg^0 is averagely the dominant mercury species but with significant variation (25–99%). Extremely large uncertainties exist in this sector due to the large diversity of mercury content in human body and whether the dental amalgam is applied."

"5.5 Mercury speciation and transformation in flue gas from PVC production

Aside from combustion and some high-temperature industrial processes, there are some other processes with intentional mercury use that also have mercury emissions. The production of polyvinyl chloride (PVC) with the calcium carbide process utilizes a catalyst containing large amounts of mercury. Ren et al. (2014) conducted on-site measurements in a PVC production line and found that 71.5% of the total mercury was lost from the catalyst, most of which was recovered by the mercury remover, accounting for 46% of the total mercury. The total mercury emitted to the atmosphere only accounted for less than 1% of the total mercury in the catalyst. The speciation tests indicated that most of the mercury escaped from the catalyst was Hg^0, as no Hg^{2+} was detected virtually."

Added references:

Friedli, H. R., Radke, L. F., Lu, J. Y., Banic, C. M., Leaitch, W. R., and MacPherson, J. I.: Mercury emissions from burning of biomass from temperate North American forests:laboratory and airborne measurements, Atmos. Environ., 37, 253–267, 2003.

Huang, J. Y., Hopke, P. K., Choi, H.-D., Laing, J. R., Cui, H. L., Zananski, T. J., Chandrasekaran, S. R., Rattigan, O. V., and Holsen, T. M.: Mercury (Hg) emissions from domestic biomass combustion for space heating, Chemosphere, 84, 1694–1699, 2011.

Ren, W., Duan, L., Zhu, Z. W., Du, W., An, Z. Y., Xu, L. J., Zhang, C., Zhuo, Y. Q., and Chen, C. H.: Mercury transformation and distribution across a polyvinyl chloride (PVC) production line in China, Environ. Sci. Technol., 48(4), 2321–2327, 2014.

Takaoka, M., Oshita, K., Takeda, N., and Morisawa, S.: Mercury emission from crematories in Japan, Atmos. Chem. Phys., 10, 3665–3671, 2010.