Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

Atmospheric Chemistry and Physics
Discussions
Open Access

Updated atmospheric mercury emissions from iron and steel production in China during 2000-2015

Qingru Wu[1,2], Wei Gao[1,2], Shuxiao Wang[1,2*], Jiming Hao[1,2]

[1]School of Environment, and State Key Joint Laboratory of Environment Simulation and Pollution Control, Tsinghua University, Beijing 100084, China

[2]State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

Correspondence to: S. X. Wang (shxwang@tsinghua.edu.cn)

Abstract

Iron and steel production (ISP) is one of the significant atmospheric Hg emission sources in China. Atmospheric mercury (Hg) emissions from ISP during 2000-2015 were estimated by using a technology-based emission factor method. To support the application of this method, databases of Hg concentrations in raw materials, technology development trends, and Hg removal efficiencies of air pollution control devices (APCDs) were constructed through national sampling and literature review. Hg input to ISP increased from 21.6 t in 2000 to 94.5 t in 2015. In the various types of raw materials, coking coal and iron concentrates contributed 41%-55% and 22%-30% of the total Hg input. Atmospheric Hg emissions from ISP increased from 11.5 t in 2000 to 32.7 t in 2015 with the peak of 35.6 t in 2013. During the study period, although sinter/pellet plant and blast furnace were the largest two emission processes, emissions from roasting plant and coke oven accounted for 22%-34% of ISP's emissions, which indicated that attention should also be paid on the emissions from these processes when estimating ISP's emissions. Overall Hg speciation shifted from 50/44/6 (gaseous elemental Hg (Hg^0) / gaseous oxidized Hg (Hg^{II}) / particulate-bound Hg (Hg_p)) in 2000 to 40/59/1 in 2015, which indicated higher proportion of Hg deposition around the emission points. In the coming years, emissions from ISP are expected to decrease due to the projection of decreasing steel productions, increasing energy consumption efficiency, and improvement of APCDs. With the coming of high-yield-period of steel scrap production, the increasing application proportion of short process steel making method will not only reduce Hg emissions, but also increase the emission proportion of Hg^0.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

1 Introduction

China is the largest iron and steel production (ISP) country in the world. Crude steel production has increased from 127 Mt in 2000 to 804 Mt in 2015 (CISIA, 2001-2016). Rapid growth of ISP has led to large emissions of air pollutants including mercury (Hg) (Wang K. et al., 2016). To reduce Hg pollution, it is important to quantify atmospheric Hg emissions from ISP.

According to existing national inventories, atmospheric Hg emissions from ISP increased from 4.9 t in 1999 to 25.5 t in 2010 (AMAP/UNEP, 2008; Streets et al., 2005; Wu et al., 2006; Zhang L. et al., 2015). In these studies, Hg emissions were determined as the product of crude steel production and unique emission factor of 0.04 g/t steel produced. Later long-term emission inventories revised the unique emission factor with dynamic factors by adopting transformed normal distribution function (Tian et al., 2015; Wang K. et al., 2016; Wu et al., 2016). Such method was based on the assumption that the emission factor was gradually improved according to the simulation curve and attempted to simulate the impact of technology improvement and pollution control on emission factor variation. However, the emission factors actually did not link with technology and APCDs directly. Thus, the simulated emission factors may be quite different from actual situation during a certain short-term period (e.g. ten years) when technology and APCDs experienced dramatic change (Wu et al., 2016), especially under the background of tightening requirement of environmental protection in China in the past decades (MEP, 2011; NEA, 2014; SC, 2013). Recent global assessment report applied a technology-based emission factor method for global ISP including China's (AMAP/UNEP, 2013). However, most of the parameters which were used to calculate the emission factors were from developed countries, which may impact the accuracy of emissions from developing countries such as China. In addition, emissions due to the use of steel scrap were not calculated in the report. With the coming of high-yield-period (after 2020) of steel scrap production in China (Guo and Wei, 2010), emissions due to the consumptions of steel scrap cannot be ignored.

The dominant parameters of a technology-based emission factor included Hg removal efficiencies of APCDs and Hg concentrations in raw materials (Wu et al., 2016; Wu et al.,

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

2012; Zhang L. et al., 2015). As to Hg removal efficiencies of APCDs, we hypothesized that the use of data from recent filed experiments on atmospheric Hg emission characteristics in China's ISP will provide a foundation for the technology-based emission factor model (Wu et al., 2016; Wu et al., 2012; Zhang L. et al., 2015). However, current studies cannot support the construction of Hg concentration databases for raw materials. Various raw materials were used in ISP, covering iron concentrates, iron block, alloy materials, steel scrap, coal, and additives (mainly limestone and dolomite). Field experiments in three China's steel smelters indicated that the concentration of iron concentrates was in the range of 23-66 ng/g (Wang F. Y. et al., 2016a; Zhang L. et al., 2015). However, the Hg concentration data from limited samples may lead to large uncertainty of the national inventory. Large studies have reported Hg concentrations in coal (Swaine, 1992; Tian et al., 2010; USGS, 2004; Zhang et al., 2012). But the specific requirement of low-sulfide coal (less than 1.2%) may make the Hg concentration in the consumed coal in ISP different from previous databases (Tao and Wang, 1994), since low-sulfide coal was generally companied by low-Hg (Zhang, 2012). Rarely studies have reported Hg concentrations in steel scrap and dolomite. Therefore, constructing Hg concentration databases of raw materials was the base to apply a technology-based emission factor model for China's ISP.

In this study, a technology-based emission factor model was constructed to estimate atmospheric Hg emissions from China's ISP. To fulfill this aim, raw materials consumed in steel smelters have been sampled and Hg concentrations have been analyzed to construct the Hg concentration databases. Up-to-date Hg removal efficiencies from field experiments and the development trends of production technology and APCDs have been summarized to support the application of emission factor model.

2 Methodology

2.1 Technology-based emission factor model for ISP

Generally speaking, ISP method included long process steel making method and short process steel making method. The long process steel making method included roasting plant, coke oven, sinter/pellet plant, blast furnace, and oxygen steel making (**Fig. 1**). The short

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

Atmospheric Chemistry and Physics Discussions

process steel making method produced crude steel in arc steel making process directly.

Thus, atmospheric Hg emissions from ISP by province can be calculated as follows.

$$\begin{aligned} E_i(t) &= E_{i,l}(t) + E_{i,s}(t) \\ &= E_{i,l,r}(t) + E_{i,l,c}(t) + E_{i,l,p}(t) + E_{i,l,b}(t) + E_{i,l,o}(t) \\ &+ E_{i,s,a}(t) \end{aligned} \quad \text{(E1)}$$

where, E was atmospheric Hg emissions from ISP, t; i was province; t referred to studied year; l and s referred to long and short process steel making method; r, c, p, b, o, a referred to roasting plant, coke oven, sinter/pellet plant, blast furnace, oxygen steel making, and arc steel making.

For each process x, the technology-based emission factor and speciated Hg emissions can be calculated as follows.

$$EF_{i,x,k}(t) = \sum_j C_{i,x,j} \times M_{i,x,j}(t) \times S_i(t)^{-1} \times \gamma_x \times \sum_m \theta_m(t) \times \delta_{k.m} \times (1-\eta_m) \times 1000^{-1} \quad \text{(E2)}$$

$$E_{i,x,k}(t) = EF_{i,x,k}(t) \times S_i(t) \quad \text{(E3)}$$

where, EF was emission factor, g/t; x was studied process; k was speciated Hg; j was the type of consumed raw material; C was Hg concentration in the consumed raw material, ng/g (see section 2.2.1); M was the consumption of raw material, Mt (see section 2.2.2); S was the production of crude steel, Mt (see section 2.2.2). γ was Hg release rate, which meant the percentage of Hg released to flue gas from raw material, %. Hg release rate were collected from filed experiment studies (**Table S1**). That was 98% for roasting plant, 80% for coke oven, 85% for sinter/pellet plant, 98% for blast furnace, 80% for oxygen steel making furnace, and 95% for arc steel making furnace. m referred to the type of APCD combination (see section 2.2.3); δ was the proportion of different Hg speciation (see section 2.2.3), %; θ was the application rate of different APCD combinations (see section 2.2.3), %; η was Hg removal efficiency (see section 2.2.3), %.

2.2 Parameters for model

2.2.1 Hg concentrations in raw materials

For the long process steel making method, the dominant raw materials included iron concentrates, iron block, coal, limestone, dolomite, alloy, and steel scrap (**Fig. 1**). In the roasting plant, limestone and dolomite were roasted together or separately to make quick lime and caustic dolomite. In the coke oven, washed coal was used to produce coke. In the sinter/pellet plant, iron-containing materials (mainly iron concentrates), quick lime, caustic dolomite, and produced coke were mixed to produce sintered/pellet block, which were used as raw materials with coal and produced coke in the blast furnace. The produced pig iron from blast furnace and additional scraps were used to produce steel in the oxygen steel making processes. For the short process steel making method, arc steel making process was applied to produce steel by mainly using scraps as raw materials. In each process, Hg input due to the use of intermediated products (e.g., quick lime, caustic dolomite, and coke) was calculated by using mass balance method (Wu et al., 2012).

National sampling and Hg concentration analysis were conducted to construct the Hg concentration databases for the consumed raw materials. The sampling, preparation and analysis methods were described in detail in our previous studies (Wu et al., 2012; Zhang et al., 2012). Lumex 915M + pyro attachment (with a detection limit of 0.5 ng/g) was applied to analyze Hg concentration by using U.S. EPA Method 7473 (US EPA, 1998). Number of samples and Hg concentrations in dominant raw materials by province were shown in **Table 1**. National Hg concentrations (median value) in the consumed iron ore were 20 (0.6-387) ng/g, which were lower than the median value of 30 (0.6-600) ng/g used in the global assessment report (AMAP/UNEP, 2013). Overall Hg concentrations in the consumed coking coal (82 ng/g) and pulverized coal injection (PCI) coal (73 ng/g) were lower than the 170 (8-2248) ng/g (Zhang, 2012) used in China's coal combustion sectors but higher than the 55 (50-60) ng/g of global assessment report. Hg concentrations in the limestone were 18 (0.9-2753) ng/g. Although the median value was lower than value of 30 (20-50) ng/g applied in the global assessment report, the variation range was much wider according to our analysis. Hg concentrations (median value) in the dolomite and iron block were 9 ng/g and 19 ng/g. In oxygen and arc steel making processes, the main iron-containing materials were steel scrap, alloy scrap, and pig iron. Hg concentrations (median value) in steel scrap and alloy scrap were 48 and 2 ng/g while the concentrations in pig iron were less than detection limit. For province with samples no less than 15, the distribution characteristics of Hg concentrations of the samples were generated by using the batch fit function of Crystalball software. Otherwise, Hg concentrations were assumed to fit normal distribution.

2.2.2 Provincial consumptions of raw materials

Provincial consumptions of raw materials in 2015 were shown in **Table S2**. National limestone consumptions were converted from quick lime consumptions (Ma, 2011) by using the factor of 1.95 t limestone to produce 1 t quick lime (CISIA, 2001-2016) (**Table S3**). National dolomite consumptions were derived from China steel statistics report (Ma, 1995) according to the production trends of crude steel. The limestone and dolomite can be consumed in the roasting and sinter/pellet plant. In the sinter/pellet plants, additives (including limestone and dolomite) consumptions were approximately 153.9 kg/t sinter produced or 10.5 kg/t pellet produced (CISIA, 2001-2016). We assumed that 88% of the additives were limestone and 12% were dolomite according to filed experiments (Wang F. Y. et al., 2016). The rest of limestone and dolomite were consumed in the roasting plants. Provincial consumptions of limestone and dolomite were distributed according to the proportions of provincial pig iron productions in national production (Table S2). Provincial pig iron productions were collected directly from yearbooks (CISIA, 2001-2016).

Provincial coking coal consumptions were converted from provincial coke consumptions (CISIA, 2001-2016). Generally, there were two main types of coke production methods, including machining coke production method and indigenous coke production method. Coal consumptions were 1.35 t to produce 1 t of machining coke or 1.65 t to produce 1 t of indigenous coke (UNEP, 2013; Wang, 1991). The produced cokes were used as raw materials in both sinter/pellet plant and blast furnace. Provincial coke consumptions in blast furnace were converted according coke ratio of 363-388 kg coke per t pig iron produced (CISIA, 2001-2016). The rest of cokes were assumed to be consumed in sinter/pellet plant.

National iron concentrate consumptions were converted from sinter/pellet productions. Approximately 0.91-0.92 t and 0.96-0.97 t of iron concentrates were needed to produce 1 t sinter and 1 t pellet, respectively (CISIA, 2001-2016). National sinter and pellet productions were obtained directly from yearbooks (CISIA, 2001-2016) and provincial data were converted according to provincial pig iron productions.

National PCI coal consumptions in blast furnace were collected from national energy statistical yearbook (NESA, 2001-2016) and the provincial data were converted according to provincial pig iron productions. The iron block consumption in blast furnace were converted from pig iron production by using the factor of 156 kg iron block per t pig iron produced (CISIA, 2001-2016).

The steel scrap was consumed in both oxygen and arc steel making process. Consumptions of steel scrap in oxygen and arc steel making process were approximately 59.4 and 361.9 kg/t crude steel produced. Alloy consumptions to produce per t crude steel were 16-17 kg in oxygen steel making process and 140-156 kg in arc oxygen making process. Oxygen and arc steel productions were collected directly from yearbooks (CISIA, 2001-2016). Based on these ratios, provincial steel scrap and alloy consumptions were converted from provincial crude steel productions.

2.2.3 Application rate, Hg removal efficiency, and Hg speciation

In the roasting plant, blast furnace, and steel making process, dust collectors such as venturi, cyclone (CYC), wet scrubber (WS), electrostatic precipitator (ESP), and fabric filter (FF) were used for flue gas dedusting. In coke oven process, the coal was firstly washed before consumed and the flue gas was cleaned with dust collectors or with additional washing scrubbers. For flue gas from sinter/pellet plant, they were generally cleaned with dust collectors. Additional flue gas desulfurization towers (FGD) were gradually applied after 2010. The application rates of different APCD combinations by process during 2005-2010 were collected from previous studies (Wang et al., 2014; Zhao et al., 2013). The data of 2000-2004 and 2011-2015 were mainly derived from yearbooks (CISIA, 2001-2016; NBS, 2001-2016) (Table S4). Hg removal efficiencies and speciation profiles of APCDs (**Table S4**) were collected from filed experiments and literature on emission studies (Gao, 2016; Wang F. Y. et al., 2016; Zhang L. et al., 2015). The distribution characteristics of Hg removal efficiencies were assumed to fit normal distribution characteristics.

2.3 Uncertainty analysis

Monte Carlo simulation was introduced to estimate the uncertainty of emissions. Detailed description of the simulation processes has been reported in our previous studies (Hui et al., 2016; Wu et al., 2016; Zhang L. et al., 2015). In this study, the (P50-P10)/P50 and (P90-P50)/P50 values were still regarded as lower and upper limits of uncertainties with 80% confidence degree, where P10, P50, and P90 meant that the probabilities of actual results lower than corresponding values were 10%, 50%, and 90%, respectively.

3 Results and Discussion

3.1 Hg input trends

Hg input to ISP increased from 21.6 t in 2000 to 94.5 t in 2015 (**Fig. 2**). The peak of Hg input was in 2014 when the crude steel production reached the highest value (**Table S1**). During 2000-2014, the average annual growth rate (AAGR) of Hg input was 11% while Hg input reduced by 3% from 2014 to 2015. In the various types of raw materials, coking coal and iron concentrates contributed the largest amount of Hg input, accounting for 35%-46% and 25%-32% of the total, respectively. Hg input due to the use of coking coal increased from 9.9 t in 2000 to 33.5 t in 2015. Hg input with iron concentrates increased at AAGR of 12% from 2000 and reached 29.2 t in 2015. The PCI coal brought approximately 6%-9% of Hg to ISP. Hg in the additives (including limestone and dolomite) contributed 12%-18% of total Hg input. Hg in the iron block was in the range of 0.6-3.6 t. Hg input due to the use of steel scrap and alloy was 4.1 t in 2015, accounting for 4% of national total. However, steel scrap and alloy contributed 7% of total crude steel production in 2015 (CISIA, 2016).

3.2 Hg emission trends

3.2.1 Hg emission trends by process

Atmospheric Hg emissions from ISP increased from 11.5 t in 2000 to 32.7 t in 2015 (**Fig. 3**). The peak of emissions was in 2013 when the emissions reached 35.6 t. In 2015, emissions from long process steel making method and short process steel making were 32.2 t and 0.5 t, accounting for 98.3% and 1.7% of national total, respectively. Thus, emissions from long process steel making were still the dominant source of Hg emissions from China's ISP.

Among the processes, emissions from sinter/pellet plant accounted for 42%-49% of annual total. Its emissions increased from 4.8 t in 2000 at the AAGR of 10.1% and reached 15.9 t in 2015. Blast furnace was also significant Hg emission process. Its emissions increased from 1.9 t in 2000 to 7.9 t in 2015 at AAGR of 10.0%. AAGR for roasting plant and coke oven was 8.3% and 1.2%. In 2015, both emissions from roasting plant and coke oven were 3.5 t, respectively.

The slower AAGR of Hg emissions (7.2%) than that of crude steel production (13%) reflected the impact on Hg emission reduction due to energy saving and environmental protection in ISP. On one hand, Hg input to produce unitary crude steel decreased from 0.17 to 0.12 g/t, which mainly benefited from the improvement of coke production efficiency and energy utilization efficiency of sinter/pellet plant and blast furnace. Since 2004, indigenous coke production method with high coal consumption has been gradually replaced with machine coke production method. The coke ratio in sinter/pellet plant has been reduced from approximately 388 kg/t pig iron produced in 2000 to 363 kg/t in 2015 (CISIA, 2001-2016). On the other hand, the improvement of APCDs increased the overall Hg removal efficiency from 54% in 2000 to 72% in 2015. APCDs for coke oven have shown the largest Hg removal efficiencies (64%-87%) while the improvement of APCDs in sinter/pellet plant contributed most to the rapid Hg reduction speed during 2000-2015. The replacement of CYC and WS with ESP and FF in sinter/pellet plant improved Hg removal efficiency from 21% in 2000 to 44% in 2010. The application of FGD in addition to dust collectors was the main driver of Hg reduction in sinter/pellet process during 2011-2015. Hg removal efficiency in sinter/pellet plant was 53% in 2015.

3.2.2 Hg emission trends by province

Provincial Hg emissions in 2000, 2005, 2010, and 2015 were shown in **Table 2**. In 2000, Shanxi, Shanghai, Henan, Hebei, and Shandong were the top five largest emitters with emissions larger than 1 t. Emissions from these five provinces contributed to 58% of national Hg emissions. Following these five provinces were Liaoning, Beijing, Gansu, Jiangsu, and Jiangxi. Summation of the emissions from all the above ten provinces were 9.0 t, accounting for 78% of national emissions in 2000. At the provincial level, we noted significant differences of Hg emission trends during the past 16 years. The AAGR of provincial Hg emissions varied from -40% to 26%. Negative AAGR existed in Beijing and Shanghai provinces, the two most economically developed regions in China. Hg abatement in these two regions was mainly caused by the reduction of crude steel production, which was transferred to nearby provinces such as Hebei, Zhejiang, Jiangsu, and Shandong. Thus, Hg emissions in these nearby provinces all presented high AAGR of more than 10%. In 2015, the largest five Hg emission provinces were changed to Hebei, Shandong, Henan, Jiangsu, and Shanxi provinces. Emissions from these provinces reached 21.5 t, accounting for 68% of national emissions. Liaoning, Jiangxi, Inner Mongolia, Gansu, and Shanghai were also in the list of the top ten largest emitters.

3.2.3 Hg emission trends by species

Overall Hg speciation profile of ISP experienced great change during the study period, from 50/44/6 (gaseous elemental Hg (Hg^0)/gaseous oxidized Hg (Hg^{II})/particulate-bound Hg (Hg_p)) in 2000 to 40/59/1 in 2015 (**Fig. 4**). The proportion of Hg^{II} increased 15%, whereas both Hg^0 and Hg_p proportion showed decreasing trend. Such shift indicated higher deposition proportion of Hg around the emission points since Hg^{II} has larger deposition velocity and higher water-solubility. For the long process steel making, Hg speciation profile shifted from 49/44/7 in 2000 to 39/60/1. The speciation shift in roasting plants was mainly impacted by the replacement of WS and CYC with FF, which increased the emitted Hg^{II} proportion from 38% to 75%. The replacement of indigenous coke production method with machine coke production method mainly contributed to Hg^{II} proportion increase from 42% to 52% at first. However, the gradual installation of WS in addition to cooler for air pollution control of machine coke production method further washed Hg^{II} and reduced Hg^{II} proportion to 49% in 2015. Hg^{II} proportion in the exhaust gas of sinter/pellet plant has increased by 20%. The increase of Hg^{II} proportion in sinter/pellet plant was mainly impacted by the substitute of WS with ESP, FF, ESP+WFGD, or ESP+DFGD+FF which generally emitted gas with higher Hg^{II} proportion (**Table S4**). Increase of Hg^{II} emission proportion in blast furnace was due to higher Hg^{II} emission proportion after FF than venturi. In the oxygen steel making process, Hg speciation profile almost unchanged. For the short process steel making, Hg^0 was the dominant speciation during the whole study period and the proportion of Hg^0 increased from 66% in 2000 to 79% in 2015.

3.3 Uncertainty analysis

In 2015, overall uncertainty of atmospheric Hg emissions from ISP was in the range of (-29%, 77%) (**Fig. 5)**. Previous studies in ISP indicated the emission uncertainties of this source were (-80%.100%) in the study of Zhang et al. (2015) and (-100%, 100%) in the study of Streets et al. (2005) and Wu et al. (2006). The improvement of emission estimation of this study was contributed by better knowledge on the Hg concentrations of raw materials and Hg removal efficiencies of APCDs. In all ISP processes, the largest uncertainties existed in emissions from roasting plant (-59%, 130%) and sinter/pellet process (-45%, 126%). These mainly due to larger distribution range of Hg concentrations in limestone and iron ore as well as Hg removal efficiencies of APCDs. The uncertainties of Hg emissions from other processes were much lower, (-49%, 48%) for coke oven, (-23%, 46%) for blast furnace, (-41%, 27%) for oxygen steel making, and (-60%, 54%) for arc steel making.

3.4 Comparison and implications

Due to the complicated ISP processes and limitations of data availability, the process combinations included in different emission inventories was divided in to four types (**Fig. 6**) (AMAP/UNEP, 2008, 2013; Wang K. et al., 2016; Wu et al., 2016; Wu et al., 2006; Zhang L. et al., 2015). The first type included sinter plant and blast furnace, which were the basic assumption in the emission inventories of Wu et al. (2003), Zhang L. et al. (2015), and AMAP/UNEP (2005). In these studies, unique emission factor of 0.0400 g/t was applied (**Table S5**) and their emissions were similar in the same inventory year. Our emissions for this process combination were almost the same as above estimations around 2005. However, the gap grew with time when FGD was gradually applied in sinter/pellet plant. Therefore, emission factor for this type of combination was reduced from 0.0527 g/t in 2000 to 0.0296 g/t in 2015 (**Table S5**). The second type also consisted of steel making in addition to the first type. Our estimation was much higher than the study of Wang K. et al. (2016) because the emission factors applied in Wang K.'s study were mainly derived from European technical

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

Atmospheric Chemistry and Physics Discussions

report (EMEP/CORINAIR, 2001; EMEP/EEA, 2013). However, the technology applied in Europe may be better than China's situation. For example, the emission factor of 0.00019 g/t applied for blast furnace with FF was used as best emission factor in Wang K.'s study (2016). However, the combination of WS and venturi scrubber was the dominant APCD type in China's blast furnace (Zhao et al., 2013), Hg removal efficiency of which was lower than that of FF. The third type of process combination also included coke oven as part of ISP in addition to the second type. Lower Hg emissions estimated by AMAP/UNEP (2013) were due to their lower Hg concentration in coal. In addition, although different processes were considered in the report, unique APCDs profile was applied in different process where the application of ESP+FGD reached 55%. However, FGD were mainly installed in sinter/pellet plant but rarely applied in other processes. The forth type also considered the emissions from roasting process where emissions accounted for 9%-11% of total emissions.

The comparison of emissions from different types of process combination in this study indicated the significance of our new inventory. The proportion of emissions from these two processes accounted for 22%-34% of ISP's emissions during the whole study period, which indicated the importance of including emissions from roasting plant and coke oven in the ISP emission inventories. In addition, given the impact of APCDs on the emission estimation, inventories in ISP should also apply distrinct APCDs profiles for different processes so as to reduce the uncertainty of inventories. In the inter-annual emission inventories, the technology-based estimation method by linking emissions with technology and APCDs directly has shown its advantage in the discussion of emission trends and quantification of Hg removal due to air pollutants control measures.

Based on the comprehensive consideration of dominant parameters (e.g., steel production, air pollution control measures) in the technology-based method and the emission trends from China's ISP during 2000-2015, we expected a decreasing trend of Hg emissions in the coming years. On one aspect, emissions of pollutants are required to be reduced by 15% for ISP before 2020 in China (MIIT, 2016). To fulfill this goal, corresponding emission standards have been issued (Wu, 2013), which will accelerate the applications of improved APCDs. During 2010-2015, the increase of SO_2 emission limits from 1500 mg/m^3 to 200 mg/m^3 promoted the large-scale application of desulfurization devices in the sinter/pellet plant of ISP. After 2015, ISP will move forward to NO_x control by using related technologies such as selective catalytic reduction (SC, 2013), the synergic Hg removal efficiencies of which have been proved in other industries (Wang et al., 2010). On the other aspect, excess steel production capacity combined with decreasing steel consumption currently will lead to the reduction of steel production, as what we have seen during 2014-2015 (CISIA, 2016; MIIT, 2016). The crude steel production trends will thereby substantially reduce Hg input to ISP. Besides, energy consumptions are required to be reduced by more than 10% during the 2016-2020 (MIIT, 2016). The improvement of energy efficiency in the main processes will also be one dominant measure to reduce energy consumption (Li et al., 2015), which will reduce fuel consumption and further lead to the reduction of Hg input. In addition, with the coming of high-yield-period of steel scrap production (Guo and Wei, 2010), the application proportion of short process steel making method is expected to increase according to the experiences in developed countries (e.g., Europe), which will indirectly reduce the requirement of steel production from long process steel making method. The replacement of steel production method will also be one driver of Hg emission reduction considering lower Hg emission factors of short process. In addition, since Hg^0 is the dominant Hg speciation from arc steel making process, the emission proportion of Hg^0 is expected to increase.

4 Conclusion

In this study, updated atmospheric Hg emissions from ISP during 2000-2015 were estimated by using technology-based emission factor method with up-to-date parameters. The input of Hg as impurity of raw materials for ISP increased from 21.6 t in 2000 to 94.5 t in 2015. In the various types of raw materials, coking coal and iron concentrates contributed to the largest amount of Hg input, 35%-46% and 25%-31% of national total, respectively. Atmospheric Hg emissions from ISP increased from 11.5 t in 2000 to the peak of 35.6 t in 2013, and then reduced to 32.7 t in 2015. Overall Hg speciation shift from 50/44/6 ($Hg^0/Hg^{II}/Hg_P$) in 2000 to 40/59/1 in 2015. In the coming years, emissions from ISP are expected to decrease due to the projection of Hg input reduction and improvement of APCDs.

In 2015, emissions from long process steel making method and short process steel making were 32.2 t and 0.5 t, accounting for 98.3% and 1.7% of national total, respectively. Sinter/pellet plant and blast furnace were the largest two emission processes, emissions from which accounted for 49% and 24% of national emissions. However, emissions from roasting and coke oven should cause attention because their emissions accounted for 22% of national emissions. The largest five Hg emission provinces were Hebei, Shandong, Henan, Jiangsu, and Shanxi provinces. Emissions from these provinces reached 21.5 t, accounting for 68% of national emissions.

With better understanding of Hg flow in ISP, the uncertainty of atmospheric Hg emissions from ISP estimated by using technology-based emission factor model has largely reduced. However, with the continuously change of APCD combinations, extensive and dedicated field experiments are still required to generate suitable database of Hg removal efficiencies for the improved APCDs in the future.

Acknowledgment. This study was supported by the Major State Basic Research Development Program of China (973 Program) (2013CB430001), Natural Science Foundation of China (21607090), and China Postdoctoral Science Foundation (2016T90103, 2016M601053)

References

Arctic Monitoring and Assessment Programme and United Nations Environment Programme (AMAP/UNEP): Technical background report to the global atmospheric mercury assessment, AMAP/UNEP, Geneva, Switzerland, 2008.

Arctic Monitoring and Assessment Programme and United Nations Environment Programme (AMAP/UNEP): Technical background report for the global mercury assessment, AMAP/UNEP, Geneva, Switzerland, 2013.

China Iron and Steel Industry Association (CISIA): China Steel yearbook, CISIA, Beijing, China, 2001-2016.

China Iron and Steel Industry Association (CISIA): China Steel yearbook, CISIA, Beijing, China, 2016.

European Monitoring and Evaluation Programme/Core Inventory of Air Emissions Project (EMEP/CORINAIR): Emission inventory guidebook, EMEP/CORINAIR, Copenhagen, Denmark, 2001.

European Monitoring and Evaluation Programme/European Economic Area (EMEP/EEA): Air pollutant emission inventory guidebook 2013, EMEP/EEA, Copenhagen, Danmark, 2013.

Gao, W.: Study on Atmospheric Mercury Emission Characteristics for Iron and Steel Producing Process in China, Tsinghua University, School of Environment, Beijing, China, 2016.

Guo, T., and Wei, L.: Development direction of the recycling industry of secondary zinc resources, China Nonferrous Metall., 4, 2010.

Hui, M. L., Wu, Q. R., Wang, S. X., Liang, S., Zhang, L., Wang, F. Y., Lenzen, M., Wang, Y. F., Xu, L. X., Lin, Z. T., Yang, H., Lin, Y., Larssen, T., Xu, M., and Hao, J. M.: Mercury Flows in China and Global Drivers, Environ. Sci. Technol., 51, 222-231, 2016.

Li, X. C., Gao, X., and Jiang, X. D.: Analysis on potential of energy conservation of Chinese steel industry in the 13th five-year period, The tenth annual conference of China steel and the sixth annual academic conference of Baogang, Shanghai, Beijing, 2015-10-21, 2015.

Ma, H. L.: China steel statistics, Development and Planning Division of Ministry of Metallurgical, Beijing, China, 1995.

Ma, J.: Review and projection of technology development of lime used in China's steel industry, China steel, 6, 17-20, 2011.

Ministry of Environmental Protection (MEP): "Twelfth Five-year" plan for the comprehensive prevention and control of heavy metal pollution, MEP, Beijing, China, 2011.

Ministry of industry and information Technology (MIIT): Adjustment and upgrading plan of iron and steel industry (2016-2020), MIIT, Beijing, China, 2016.

National Statistical Bureau of China (NBS): China Environmental Statistics Yearbook, NBS, Beijing, China, 2001-2016.

National Energy Administration (NEA): Action plan of coal clean utilization, NEA, Beijing, China, 2014.

National energy statistical agency of China (NESA): China Energy Statistical Yearbook, NESA, Beijing, China, 2001-2016.

State Council of the People's Republic of China (SC): Action plan of national air pollution prevention and control, SC, Beijing, China, 2013.

Streets, D. G., Hao, J. M., Wu, Y., Jiang, J. K., Chan, M., Tian, H. Z., and Feng, X. B.: Anthropogenic mercury emissions in China, Atmos. Environ., 39, 7789-7806, 2005.

Swaine, D. J.: Environmental Aspects of Trace-Elements in Coal, Environ. Geochem. Health, 14, 2-2, 1992.

Tao, S. R., and Wang, Y. J.: Imapct on the economic benefits of metallurgy industry from coke coal quality, Coal Proce. Compre. Utiliz., 4, 1994.

Tian, H. Z., Wang, Y., Xue, Z. G., Cheng, K., Qu, Y. P., Chai, F. H., and Hao, J. M.: Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980-2007, Atmos. Chem. Phys., 10, 11905-11919, 2010.

Tian, H. Z., Zhu, C. Y., Gao, J. J., Cheng, K., Hao, J. M., Wang, K., Hua, S. B., Wang, Y., and Zhou, J. R.: Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: historical trend, spatial distribution, uncertainties, and control policies, Atmos. Chem. Phys., 15, 10127-10147, 2015.

United Nations Envieonment Programme (UNEP): Toolkit for identification and quantification of mercury releases. Guideline for Inventory Level 2, Version 1.3. , 2013.

United States Environmental Portection Agency (US EPA): Method 7473: Hg in solids and solutions by thermal decomposition amalgamation and atomic absorption spectrophotometry, US EPA, Washinton D. C., United States, 1998.

United States Geological Survey (USGS): Mercury content in coal mines in China, Reston, Virginia, United States, 2004.

Wang, F. Y., Wang, S. X., Zhang, L., Yang, H., Gao, W., Wu, Q. R., and Hao, J. M.: Mercury mass flow in iron and steel production process and its implications for mercury emission control, J. Environ. Sci., 43, 293-301, 2016.

Wang, K., Tian, H. Z., Hua, S. B., Zhu, C. Y., Gao, J. J., Xue, Y. F., Hao, J. M., Wang, Y., and Zhou, J. R.: A comprehensive emission inventory of multiple air pollutants from iron and steel industry in China: Temporal trends and spatial variation characteristics, Sci. Total Environ., 559, 7-14, 2016.

Wang, S. X., Zhang, L., Li, G. H., Wu, Y., Hao, J. M., Pirrone, N., Sprovieri, F., and Ancora, M. P.: Mercury emission and speciation of coal-fired power plants in China, Atmos. Chem. Phys., 10, 1183-1192, 2010.

Wang, S. X., Zhao, B., Cai, S. Y., Klimont, Z., Nielsen, C. P., Morikawa, T., Woo, J. H., Kim, Y., Fu, X., Xu, J. Y., Hao, J. M., and He, K. B.: Emission trends and mitigation options for air pollutants in East Asia, Atmos. Chem. Phys., 14, 6571-6603, 2014.

Wang, Y. F.: Analysis on the harm of indigenous coking, Coal Eco. Res., 1, 1991.

Wu, Q., Wang, S., Li, G., Liang, S., Lin, C.-J., Wang, Y., Cai, S., Liu, K., and Hao, J.: Temporal Trend and Spatial Distribution of Speciated Atmospheric Mercury Emissions in China During 1978–2014, Environ. Sci. Technol., 50, 13428-13435, 2016.

Wu, Q. R., Wang, S. X., Zhang, L., Song, J. X., Yang, H., and Meng, Y.: Update of mercury emissions from China's primary zinc, lead and copper smelters, 2000-2010, Atmos. Chem. Phys., 12, 11153-11163, 2012.

Wu, S. H.: Interpretation about “Emission Standards of Iron and Steel Industrial Pollutants”, Indus. Safety Environ. Pro., 29, 2, 2013.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

Wu, Y., Wang, S. X., Streets, D. G., Hao, J. M., Chan, M., and Jiang, J. K.: Trends in anthropogenic mercury emissions in China from 1995 to 2003, Environ. Sci. Technol., 40, 5312-5318, 2006.

Zhang, L.: Emission characteristics and synergistic control strategies of atmospheric mercury from coal combustion in China, Ph.D. Dissertation, Tsinghua University, School of Environment, Beijing, China, 2012.

Zhang, L., Wang, S. X., Meng, Y., and Hao, J. M.: Influence of mercury and chlorine content of coal on mercury emissions from coal-fired power plants in China, Environ. Sci. Technol., 46, 6385-6392, 2012.

Zhang, L., Wang, S. X., Wang, L., Wu, Y., Duan, L., Wu, Q. R., Wang, F. Y., Yang, M., Yang, H., Hao, J. M., and Liu, X.: Updated emission inventories for speciated atmospheric mercury from anthropogenic sources in China, Environ. Sci. Technol., 49, 3185-3194, 2015.

Zhang, Y. H., Zhang, C., Wang, D. Y., Luo, C., Yang, X., and Xu, F.: Characteristic of mercury emissions and mass balance of the typical iron and steel industry, Environ. Sci., 36, 8, 2015.

Zhao, B., Wang, S. X., Liu, H., Xu, J. Y., Fu, K., Klimont, Z., Hao, J. M., He, K. B., Cofala, J., and Amann, M.: NOx emissions in China: historical trends and future perspectives, Atmos. Chem. Phys., 13, 9869-9897, 2013.

Tables

Table 1. Hg concentration in the raw materials

Province[1]	Iron ore				Limestone				Dolomite				Coking coal				PCI coal			
	AM[2]	MV[2]	SV[2]	NS[2]	AM	MV	SV	NS	AM	MV	SV	NS	AM	MV	SV	NS	AM	MV	SV	NS
	ng/g	ng/g	ng/g		ng/g	ng/g	ng/g		ng/g	ng/g	ng/g		ng/g	ng/g	ng/g		ng/g	ng/g	ng/g	
Tianjin	41	44	8	3	9	9	3	1	5	5	2	4					75	66	31	5
Hebei	37	24	40	79	374	117	631	27	7	8	5	5	78	66	39	71	79	85	70	38
Shanxi	30	24	28	25	9	7	8	6					77	71	27	22	114	106	19	3
Shanghai	44	44	50	4	20	20	5	1	39	39	2	2	125	152	71	5	12	12	0	2
Jiangsu					103	68	113	18												
Zhejiang					52	37	35	22												
Anhui	21	20	12	14	11	11	4	12	32	32	2	3	88	58	53	8	98	22	104	7
Fujian	19	14	11	15	11	11	5	4	9	8	5	4	105	100	51	13	255	239	51	7
Jiangxi	57	46	88	18					10	9	4	3	120	93	59	4	185	198	66	7
Shandong	125	128	73	20					24	24	1	2	72	69	21	12				
Henan	32	24	29	18	692	759	629	13												
Hubei					16	14	8	6					92	83	54	39	131	116	91	21
Hunan	33	19	34	77	102	87	62	4	3	3	1	2								
Guangdong					48	44	26	15												
Guangxi					8	8	2	4					210	188	112	27	96	98	30	6
Chongqing													85	79	48	20	65	65	12	4
Sichuan	37	2	44	7	10	9	4	12												
Guizhou					11	10	11	42												
Yunnan	10	10	7	6	17	20	7	6					51	52	7	8	58	56	6	3

Gansu	107	107	3	3	3	3	1	1					166	174	21	5	60	60	5	2
Xinjiang	6	5	4	17									82	82	46	22	31	24	19	15
National	38	20	48	306	153	18	402	204	14	9	12	25	99	82	68	256	99	73	83	120

Note: 1. Provinces without data were not listed in this table;

2. AM: Average mean; MV: Median value; SV: Standard value; NM: Number of samples.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

Atmospheric Chemistry and Physics Discussions
Open Access

Table 2. Provincial Hg emissions during 2000-2015

Province	Atmospheric Hg emissions (t)				
	2000	2005	2010	2015	AAGR
Beijing	0.4	0.3	0.1	0.0	-40%
Tianjin	0.3	0.5	0.9	0.7	7%
Hebei	1.2	4.0	6.7	7.1	13%
Shanxi	1.6	2.2	2.1	1.8	1%
Inner Mongolia	0.3	0.5	0.7	0.8	7%
Liaoning	0.8	1.2	1.7	1.6	4%
Jilin	0.1	0.2	0.3	0.3	6%
Heilongjiang	0.1	0.2	0.3	0.2	6%
Shanghai	1.5	1.2	1.0	0.7	-5%
Jiangsu	0.3	1.1	1.9	2.5	15%
Zhejiang	0.1	0.1	0.4	0.4	11%
Anhui	0.3	0.4	0.6	0.6	6%
Fujian	0.1	0.2	0.2	0.3	11%
Jiangxi	0.3	0.7	1.1	1.0	8%
Shandong	1.1	4.0	6.0	6.1	12%
Henan	1.3	2.2	3.5	4.0	8%
Hubei	0.3	0.4	0.5	0.4	2%
Hunan	0.2	0.5	0.7	0.6	7%
Guangdong	0.1	0.3	0.3	0.4	8%
Guangxi	0.1	0.2	0.4	0.5	13%
Hainan	0.0	0.0	0.0	0.0	26%
Chongqing	0.1	0.1	0.2	0.1	2%
Sichuan	0.2	0.4	0.4	0.4	4%
Guizhou	0.1	0.2	0.2	0.2	4%
Yunnan	0.1	0.3	0.4	0.3	7%
Tibet	0.0	0.0	0.0	0.0	/
Shaanxi	0.1	0.2	0.4	0.7	16%
Gansu	0.4	0.5	0.6	0.7	4%
Qinghai	0.0	0.0	0.1	0.0	5%
Ningxia	0.0	0.0	0.1	0.1	19%
Xinjiang	0.1	0.1	0.3	0.3	13%
Total	11.5	22.2	31.9	32.7	7%

Figures

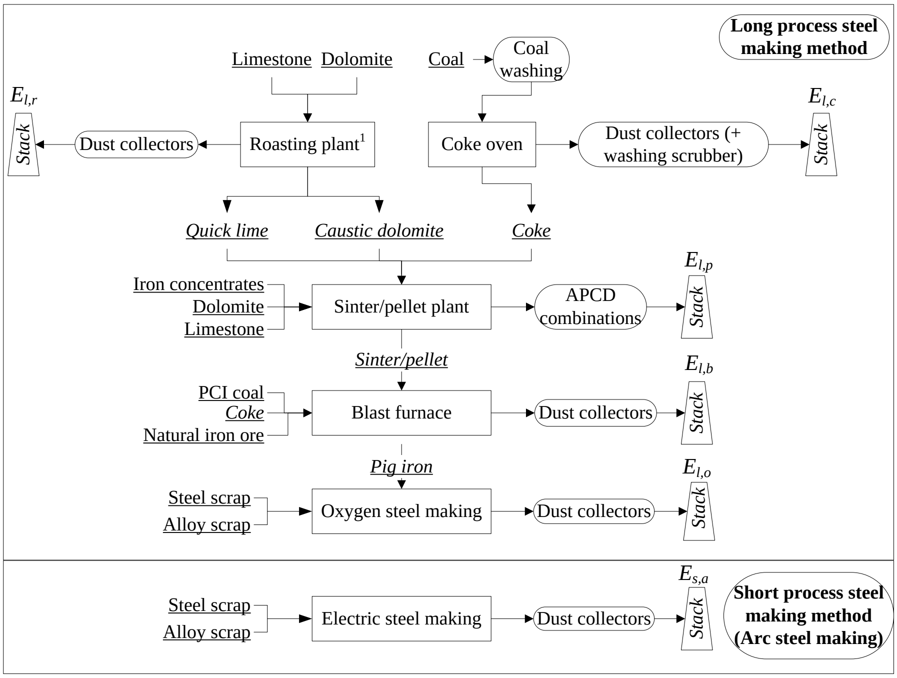
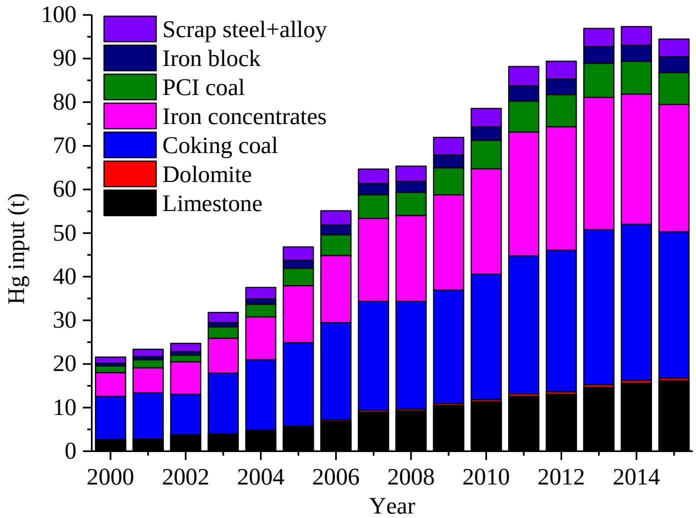
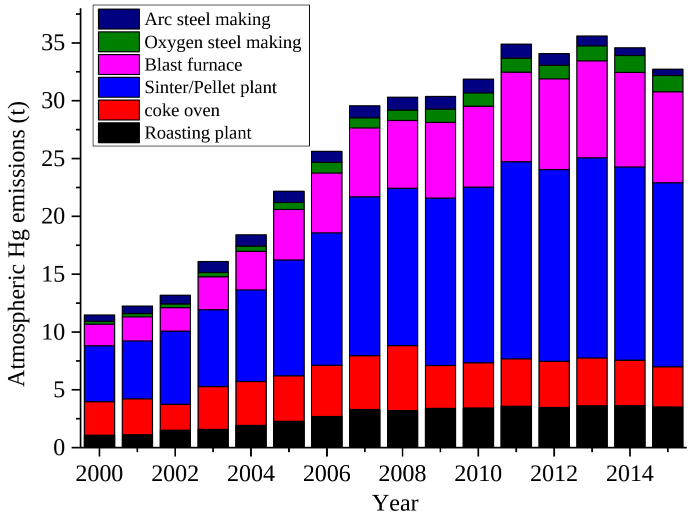


Fig. 1. Flow chart of ISP processes (1. Some plants roasted limestone and dolomite separately.)



500

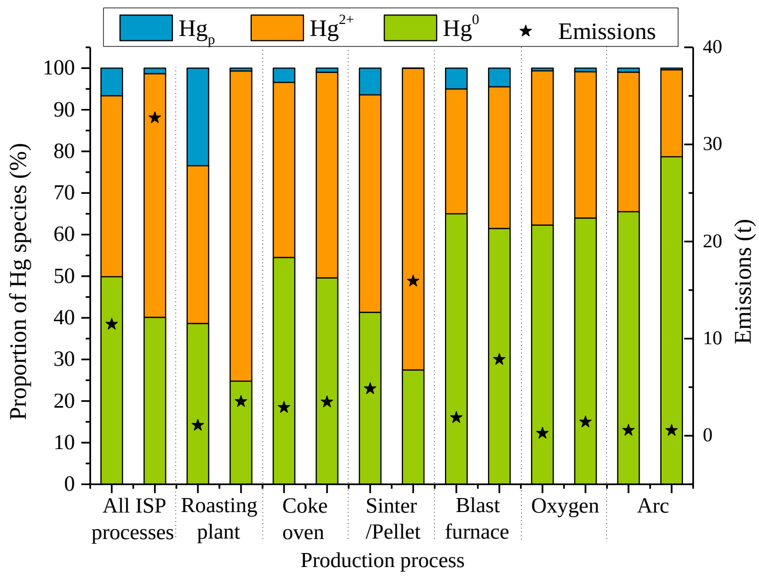
501 **Fig. 2**. Hg input trends by material



502

503 **Fig. 3**. Hg emission trends by process

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

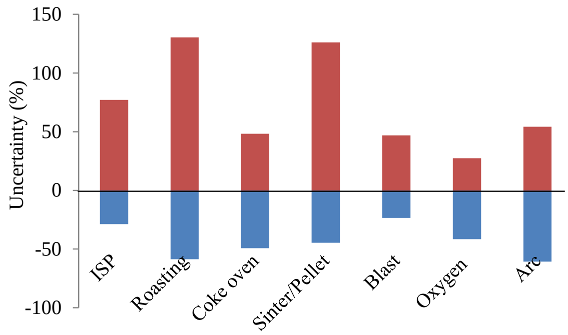


504

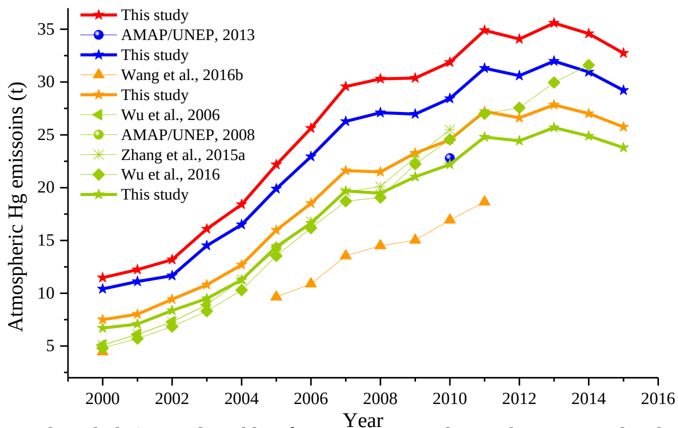
505 **Fig. 4**. Proportion of different Hg species (For each process, the left and right column
506 represents the data in 2000 and 2015, respectively)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-87, 2017
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 27 March 2017

Atmospheric Chemistry and Physics
Open Access
Discussions



507
508 **Fig. 5**. Unertainty analysis



Red symbol: Sinter plant+blast furnace+roasting plant+coke oven+steel making
Blue symbol: Sinter plant+blast furnace+coke oven+steel making
Orange symbol: Sinter plant+blast furnace+steel making
Green symbol: Sinter plant+blast furnace

Fig. 6. Atmospheric Hg emissions of ISP in different studies