

Author's Response to Anonymous Referee #2

The authors are very grateful to all the reviewers and editors for your general and specific comments and instructions on this manuscript. The detailed comments and suggestions are very valuable for the improvement of the quality and clarity of this paper.

Referees' comments:

General comments

This is a good paper quantifying China's anthropogenic atmospheric heavy metal emissions. Results are useful giving China's current concern in controlling heavy metal emissions. Some aspects of this paper, especially the concision and citation support, need to be improved before the publication.

Response: we thank the anonymous reviewer #2 for the support to publish this paper and for your valuable review comments. Addressing these comments will greatly improve the reliability and concision of the manuscript. Detailed below is our point-to-point responses to the queries and comments raised by the reviewer #2 and a list of the specific changes made in the text by the authors themselves.

Specific comments

1. The title: I suggest you change "spatial variation distribution" to "spatial distribution".

Response: Thanks for the comment. The good suggestion has been taken.

Changes to the title of new revised manuscript:

"Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: historical trend, spatial distribution, uncertainties and control policies"

2. The Introduction: I would suggest you shorten the Introduction part. The first 4 paragraphs can be merged into one paragraph describing the importance of heavy metals. Paragraphs 5-7 can be merged together to describe what existing studies have done and what the knowledge gap is. The

rest paragraphs can describe what you have done in this paper.

Response: Thanks for the good comment.

Based on the referee's valuable suggestions, we have shortened and improved the description of "**Introduction Section**" in the new revised manuscript.

Changes to the new revised manuscript text:

"Heavy Metals (HMs) is a general collective term which applies to the group of metals (e.g. Hg, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu, Zn, etc.) and metalloids (e.g. As, Se. etc.) with atomic density greater than 4.5 g cm^{-3} . Although these elements are present in only trace levels in feed coals and raw materials, the huge coal consumption and enormous output of various industrial products have resulted in significant emissions of HMs into the atmosphere. As a result, the mean atmospheric concentration of As, Cd, Ni, and Mn are reported at 51.0 ± 67.0 , 12.9 ± 19.6 , 29.0 ± 39.4 , and $198.8 \pm 364.4 \text{ ng m}^{-3}$ in China, which are much higher than the limit ceilings of 6.6, 5, 25, and 150 ng m^{-3} for WHO guidelines, respectively (Duan and Tan, 2013). Mukherjee et al. (1998) and Song et al. (2003) indicate that various HMs can remain in the atmosphere for 5–8 days and even for 30 days when discharged from elevated stacks associated with fine particles. Therefore, these toxic substances can be transported for long distances before they finally settle down through wet and dry deposition into soil and aqueous systems, causing widespread adverse effects and even trans-boundary environmental pollution disputes. Particularly, the International Agency for Research on Cancer (IARC) has assigned several HMs, like As & its inorganic compounds, Cd & its compounds, Cr (VI) compounds and Ni compounds, to the group of substances that are carcinogenic to humans. Besides, Pb & its compounds, Sb_2O_3 , and Co & its compounds are suspected of being probably carcinogens (IARC, 2014).

Since 1980s, the United States, the United Kingdom, Australia and some other developed countries have begun to compile their national emission inventories of varied hazardous air pollutants (including HMs), such as the US National Emission Inventory (NEI), the UK National Atmospheric Emission Inventory (NAEI), and the Australian National Pollutant Inventory (NPI). Besides, the quantitative assessments of global contamination of air by HMs from anthropogenic sources have been estimated in previous studies (Nriagu, 1979; Nriagu and Pacyna, 1988; Pacyna

and Pacyna, 2001; Streets et al., 2011; Tian et al., 2014b). With the increasing contradiction between economic growth and environmental pollution, some researchers have paid special attention to estimate China's HM emission inventory, especially for Hg, which is regarded as a global pollutant (Fang et al., 2002; Streets et al., 2005; Wu et al., 2006). Streets et al. (2005) and Wu et al. (2006) have developed Hg emission inventory from anthropogenic activities of China for the year 1999 and 1995 to 2003, respectively. The research group led by Tian have established the integrated emission inventories of eight HMs (Hg, As, Se, Pb, Cd, Cr, Ni and Sb) from coal combustion or primary anthropogenic sources on the provincial level during 1980 to 2009 (Cheng et al., 2015; Tian et al., 2010, 2012a–c, 2014a, b). However, comprehensive and detailed studies on anthropogenic atmospheric emissions of 12 typical toxic HMs with highly resolved temporal and spatial distribution information in China are still quite limited. Moreover, we have little knowledge on what the past and accelerated emission levels of HMs are like from anthropogenic sources during the historical period since the founding of the People's Republic of China to the time carrying on the reformation and opening policy (1949 to 1978).

In this study, for the first time, we have evaluated the historical trend and spatial distribution characteristics by source categories and provinces of atmospheric emissions of 12 typical HMs (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) from primary anthropogenic activities during the period of 1949–2012. Especially, we have attempted to determine the temporal variation profiles of emission factors for several significant sources categories (e.g. nonferrous metal smelting, ferrous metal smelting, cement production, MSW incineration, etc.) during the long period of 1949 to 2012, which are brought about by the technological upgrade of industrial process and the progress of application rate for various air pollutant control devices (APCDs)."

3. The Methods: Please give more details about the theory of your S-shaped Curves method. Please give a brief description of your Monte Carlo simulation. What's your assumed distribution pattern? What's your simulation times, 10,000 or 100,000?

Response: Thanks for the comment. The good suggestions have been addressed.

We have added the more details about the theory of S-shaped Curve method in the revised manuscript by combining the similar comments raised by both the Referee #1 and Referee #2.

Changes to the new revised manuscript text:

“Considering the air pollutant control technologies updating, and outdated enterprises shutdown, the HM emission factors show a gradually declining trend. Generally, the patterns of technologies diffusion through competitive markets are evident, and S-shaped curve is a typical result when plotting the proportion of a useful service or product supplied by each major competing technology (Grübler et al., 1999). At the earliest stage of industrialization, growth rate in removal efficiency of air pollutant is slow as the advanced technology with high investment and operation cost is applied only in specialized niche sectors. Subsequently, along with the progress on technology and awareness of public environmental protection, growth rate accelerates as early commercial investments have resulted in standard-setting and compounding cost reductions, which lead to the increased application of advanced technologies for emission reductions of air pollutants in a wider array of settings. Eventually, growth rate in removal efficiency will gradually approach to nearly zero as the potential market of optimal control technology of HM emissions is saturated. By using of S-shaped curve, both historical and future emissions of carbon aerosol and Hg to the atmosphere from human activities have been evaluated by Bond et al. (2007) and Streets et al. (2004, 2011). Their results show that S-shaped curve fits historical and future trends better than polynomial or linear fits, even though it cannot account for economic shocks because of the form of monotonous smooth transitions. Therefore, S-shaped curves are applied to estimate the dynamic HM emission factors from primary industrial process sources in this study.”

In order to make it more clarity, a brief description of Monte Carlo simulation, including the introduction of probability distribution of input parameters and simulation times, are added in the revised manuscript as a positive response for the reviewer’s comments. Besides, further details about the probability distribution of specific activity level and emission factor for each source are listed in Supplement **Table S20**.

Changes to the new revised manuscript text:

“Most of the input parameters of specific activity levels and emission factors, with corresponding statistical distribution, are specified on the basis of the data fitting, or referred to the related published references (Wu et al., 2010; Zhao et al., 2011; Tian et al., 2012a, b). Besides, for

parameters with limited observation data, probability distributions such as normal distribution and triangular distribution are assumed by the authors for corresponding sources. Further details about the probability distribution for each source discussed in this study are listed in Table S20. Finally, all of the input parameters are placed in a Monte Carlo framework, 10 000 times of simulations are run to estimate the uncertainty ranges of varied HM emissions with a 95% confidence interval.”

Related reference citations are as follows:

- Bond, T. C., Bhardwaj, E., Dong, R., Jogani, R., Jung, S., Roden, C., Streets, D. G., and Trautmann, N. M.: Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850–2000, *Global Biogeochem. Cy.*, 21, 1–16, doi:10.1029/2006GB002840, 2007.
- Grübler, A., Nakićenović, N., and Victor, D. G.: Dynamics of energy technologies and global change, *Energ. Policy*, 27, 247–280, doi:10.1016/S0301-4215(98)00067-6, 1999.
- Streets, D. G., Bond, T. C., Lee, T., and Jang, C.: On the future of carbonaceous aerosol emissions, *J. Geophys. Res.*, 109, 1–19, doi:10.1029/2004JD004902, 2004.
- Streets, D. G., Devane, M. K., Lu, Z., Bond, T. C., Sunderland, E. M., and Jacob, D. J.: All-time releases of mercury to the atmosphere from human activities, *Environ. Sci. Technol.*, 45, 10485–10491, doi:10.1021/es202765m, 2011.
- Tian, H. Z., Cheng, K., Wang, Y., Zhao, D., Lu, L., Jia, W. X., and Hao, J. M.: Temporal and spatial variation characteristics of atmospheric emissions of Cd, Cr, and Pb from coal in China, *Atmos. Environ.*, 50, 157–163, doi:10.1016/j.atmosenv.2011.12.045, 2012a.
- Tian, H. Z., Lu, L., Cheng, K., Hao, J. M., Zhao, D., Wang, Y., Jia, W. X., and Qiu, P. P.: Anthropogenic atmospheric nickel emissions and its distribution characteristics in China, *Sci. Total Environ.*, 417, 148–157, doi:10.1016/j.scitotenv.2011.11.069, 2012b.
- Wu, Y., Streets, D. G., Wang, S. X., and Hao, J. M.: Uncertainties in estimating mercury emissions from coal-fired power plants in China, *Atmos. Chem. Phys.*, 10, 2937–2946, doi:10.5194/acp-10-2937-2010, 2010.
- Zhao, Y., Nielsen, C. P., Lei, Y., McElroy, M. B., and Hao, J.: Quantifying the uncertainties of a bottom-up emission inventory of anthropogenic atmospheric pollutants in China, *Atmos. Chem. Phys.*, 11, 2295–2308, doi:10.5194/acp-11-2295-2011, 2011.

4. Lines 17-18 page 12127: You should give a citation to support your following statement “In term of Pb emissions, the reduced lead content of gasoline was the primary reason for the sharp decrease in total Pb emissions in 1991 and 2001.” You results cannot prove this statement. Similarly, for the sentence “Subsequently, along with the rapid increase of vehicle volume and oil consumption” in this paragraph, give a citation to support your statement. Lines 24-26 page 12127: “Due to the technological process resulting in relatively low emission factors of HMs and economic development bringing about high coal consumption and industrial products output”

This may be true, but giving a citation (or other) support can make your statement easier to believe. Lines 2-4 page 12128: “These were mainly due to the different volatility of these 12 elements during high temperature process resulting in diverse release rates of furnaces and synergistic removal efficiencies of control measures.” Please give a support. There are many other similar situations in this paper. It’s better to give related citations to make your discussion more believable.

Response: Thanks for the comments. The good suggestions have been addressed.

We have added the related reference citations corresponding to related information to support these descriptions or judgments. **Specially, the number (No.) of page and the line are based on the ACPD manuscript.**

Changes to the new revised manuscript text:

Line 6-8 page 12115: “The release rates of HMs in flue gas from various boiler categories vary substantially due to the different combustion patterns and operating conditions, as well as their genetic physical and chemical characteristics (Reddy et al., 2005).”

Line 1-3 page 12125: “Hence, the HMs (especially for Sb and Cu) associated with particulate matter are mainly emitted from brake wear due to relatively higher average contents of HMs in brake lining, compared to those from tyre wear (EEA, 2013).”

Lines 17-18 page 12127: “In term of Pb emissions, the reduced lead content of gasoline was the primary reason for the sharp decrease in total Pb emissions in 1991 and 2001 (Li et al., 2012).”

Lines 24-26 page 12127: “Due to the technological process resulting in relatively low emission factors of HMs and economic development bringing about high coal consumption and industrial products output (Cheng et al., 2015), ...”

Lines 2-4 page 12128: “These were mainly due to the different volatility of these 12 elements during high temperature process resulting in diverse release rates of furnaces and synergistic removal efficiencies of control measures (Xu et al., 2004).”

Lines 12-14 page 12128: “However, this trend began to change after 2006 due to the implementation of policies of energy-saving and pollution reduction, especially the strengthening of SO₂ emission control for coal-fired power plants (Zhu et al., 2015).”

Lines 23-28 page 12128: “This was mainly due to policies for replacement of small coal-fired plant units with large and high efficiency units and the continuously increasing application rate of advanced APCDs systems (e.g., ESP, FFs, WFGD, SCR, etc.), in order to achieve the emission reduction of PM, SO₂ and NO_x for satisfying the national or local emission reduction goals for the year 2010 (the end year of 11th FYP) (NBS, 2011; Tian et al., 2014a).”

Lines 8-11 page 12130: “As can be seen from Fig. 2, the emission trends of HMs from coal consumption by industrial boilers were consistent with the national total emissions trends between 1949 and 1997, and negative growth appeared in 1998 and 1999 due to the decreased coal consumption resulting by the Asian financial crisis (Hao et al., 2002; Tian et al., 2007, 2012b).”

Lines 26-28 page 12130 and line 1 page 12131: “Because of high temperatures during roasting, sintering and smelting process for the extraction of copper, lead and zinc from ores, part of HMs in nonferrous metal ores will inevitably be vaporized and released into the flue gas, and impose adverse impacts on the human health and regional ecosystems (Wu et al., 2012).”

Lines 24-27 page 12132: “Specifically, because of the emphasis on the backyard furnaces for steel production in the period of Great Leap Forward Movement, a sharp fluctuation of emissions occurred during the period of 1958 to 1963, with the emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Cu and Zn almost doubling (NBS, 2013a).”

Lines 11-13 page 12133: “the liquid fuels consumption is also one of major contributors for atmospheric Ni emissions due to the relatively high content of Ni in fuel oil (Tian et al., 2012b).”

Lines 22-26 page 12133: “Notably, the total Ni emissions from liquid fuels consumption category had increased slightly (less than 2% annually) since 1980 despite of the rapid growth of distillate oils (gasoline, diesel oil, and kerosene), which was mainly because of the lower Ni content in distillate oils and relatively constant supply of fuel oil in China in the past three decades (NBS, 2013a; Wang et al., 2003b; Tian et al., 2012b).”

Lines 8-10 page 12137: “As can be seen from Fig. 4a, the source contributions on the provincial scale in 2010 varied substantially due to the difference of industrial conformations and energy structures (Cheng et al., 2015; NBS, 2013a, b).”

Lines 18-21 page 12138: “With respect to non-metallic mineral manufacturing sector, the discharge of Se from glass production contributed about 92.9% of the total emissions of this source due to the widespread application of selenium powder as decolorizing agent in glass production process and huge output of glass production (Kavlak and Graedel, 2013).”

Lines 8-13 page 12143: “The coal consumption by industrial boilers, coal consumption by other sectors and coal combustion by power plants were identified as the dominant sources in these three provinces due to the booming coke making industry in Shanxi, high coal consumption by coal consumption by industrial boiler and the prosperous electric power generation in Shandong, and the obviously high average concentration of Co in feed coals in Guizhou (NBS, 2013a, b; Wu et al., 2008).”

The associated references are as follows:

- Cheng, K., Wang, Y., Tian, H. Z., Gao, X., Zhang, Y. X., Wu, X. C., Zhu, C. Y., Gao, J. J.: Atmospheric emission characteristics and control policies of five precedent-controlled toxic heavy metals from anthropogenic sources in China, *Environ. Sci. Technol.*, 49, 120–1214, doi:10.1021/es5037332, 2015.
- European Environment Agency (EEA): EMEP/EEA air pollutant emission inventory guidebook 2013, available at: <http://www.eea.europa.eu/publications/emep-eea-guidebook-2013> (last access: 12 November 2013), 2013.
- Hao, J. M., Tian, H. Z., and Lu, Y. Q.: Emission inventories of NO_x from commercial energy consumption in China, 1995–1998, *Environ. Sci. Technol.*, 36, 552–560, doi:10.1021/es015601k, 2002.
- Kavlak, G., and Graedel, T. E.: Global anthropogenic selenium cycles for 1949–2010, *Resour. Conserv. Recycl.*, 73, 17–22, doi:10.1016/j.resconrec.2013.01.013, 2013.
- Li, Q., Cheng, H. G., Zhou, T., Lin, C. Y., and Guo, S.: The estimated atmospheric lead emissions in China, 1990–2009, *Atmos. Environ.*, 60, 1–8, doi:10.1016/j.atmosenv.2012.06.025, 2012.
- National Bureau of Statistics (NBS), P. R. China: Report on “12th Five-Year Plan” of the electric power industry. National Bureau of Statistics of China, Beijing, China, 2011 (in Chinese).
- National Bureau of Statistics (NBS), P. R. China: China Energy Statistical Yearbook, China Statistics Press, Beijing, 2013b.
- National Bureau of Statistics (NBS), P. R. China: China Statistical Yearbook, China Statistics Press, Beijing, 2013a.
- Reddy, M. S., Basha, S., Joshi, H. V., and Jha, B.: Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion, *J. Hazard. Mater.*, 123, 242–249, doi:10.1016/j.jhazmat.2005.04.008, 2005.
- Xu, M. H., Yan, R., Zheng, C. G., Qiao, Y., Han, J., Sheng, C. D.: Status of trace element emission in a coal

- combustion process: a review. *Fuel Process. Technol.*, 85, 215-23, doi:10.1016/S0378-3820(03)00174-7, 2004.
- Tian, H. Z., Hao, J. M., Hu, M. Y., and Nie, Y. F.: Recent trends of energy consumption and air pollution in China, *J. Energy Eng.*, 133, 4–12, doi: 10.1061/(ASCE)0733-9402(2007)133:1(4), 2007.
- Tian, H. Z., Lu, L., Cheng, K., Hao, J. M., Zhao, D., Wang, Y., Jia, W. X., and Qiu, P. P.: Anthropogenic atmospheric nickel emissions and its distribution characteristics in China, *Sci. Total Environ.*, 417, 148–157, doi:10.1016/j.scitotenv.2011.11.069, 2012b.
- Wang, Y. F., Huang, K. L., Li, C. T., Mi, H. H., Luo, J. H., and Tsai, P. J.: Emissions of fuel metals content from a diesel vehicle engine, *Atmos. Environ.*, 37, 4637–4643, doi:10.1016/j.atmosenv.2003.07.007, 2003b.
- 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, doi:10.5194/acp-12-11153-2012, 2012.
- Wu, Y. Y., Qin, Y., Yi, T. S., and Xia, X. H.: Enrichment and geochemical origin of some trace elements in high-sulfur coal from Kaili, eastern Guizhou Province, *Geochimica*, 37, 615–622, 2008 (in Chinese with English abstract).
- Zhu, C. Y., Tian, H. Z., Cheng, K., Liu, K. Y., Wang, K., Hua, S. B., Gao, J. J., and Zhou, J. J.: Potentials of whole process control of heavy metals emissions from coal-fired power plants in China, *J. Cleaner Prod.*, doi: 10.1016/j.jclepro.2015.05.008, 2015 (in press).

5. I would suggest you merge sections 3.1 and 3.2 and shorten them to make your paper more concise. Similar suggestion to section 3.3. This section is too long. Several short paragraphs can give enough information.

Response: Thanks for the comment. The good suggestions have been addressed.

Firstly, we have merged Sections 3.1 and 3.2 in the revised manuscript and shortened them to make our paper more concise. Concretely, we have shortened the Section 3.3.1–3.3.4 in the new revised manuscript and put Sections 3.1.5–3.1.6 into the Supplement Section S3. It is necessary to state that we also add the related discussion about the verification for historical emissions of HMs based on the suggestions from Referee #1 in the Section 3.1.

Changes to the new revised manuscript text:

3.1 Temporal trend of HM emissions by source categories

The historical trend of atmospheric emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn by different source categories from 1949 to 2012 are illustrated in Fig. 2. The total emissions of HMs from primary anthropogenic sources since 1949 have shown substantial shifts among varied source categories that reflect technological and economic trends and transition over

this over 60 years long period. Within the year of the establishment of the People's Republic of China in 1949, the total emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn from anthropogenic sources are estimated at about 11.5–312.6 t (see Table 2). The discharges of HMs on a national scale have increased by 3–20 times from 1949 to 1960 due to the increasing demands for energy consumption and industrial production (especially for the period of Great Leap Forward from 1958 to 1960 resulting in remarkably increasing output of industrial products), then decrease tumultuously in 1961 and 1962 by 27.6–55.7% compared to those in 1960 on account of the serious imbalance of economic structure and Great Leap Forward Famine caused by policy mistakes together with natural disaster (Kung and Lin, 2003). In spite of negative growth of heavy metal emissions in individual years such as 1967, 1974 and 1976, the annually averaged growth rates of national emissions of HMs from primary anthropogenic sources are still as high as 0.2–8.4% during the periods from 1963 to 1977.

Subsequently, the policy of openness and reformation is issued by the Chinese central government. With the implementation of this policy from 1978 to 2012, China's GDP has been growing at an average annual growth rate of about 9.8% resulting in tremendous energy consumption and enormous output of industrial products. As can be seen from Fig. 2, historically there have been two periods during which the total emissions of HMs (except Pb) increased rapidly after 1978. The first one is the period of 1978 to 2000, except for one remarkable fluctuation from 1998 to 1999, which reflects a decrease in input of raw materials and output of industrial products mainly owing to the influence of Asian financial crisis (Hao et al., 2002). The second one is the period of the 10th FYP (from 2001 to 2005), a sharp increase of emissions of Hg, As, Se, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn have occurred, with the emissions from about 268.0–11308.6 t in 2001 increase to about 378.9–15987.9 t in 2005, at an annually average growth rate of 4.8–12.0%, respectively (see Table 2).

In terms of lead content requirement in gasoline, the past 64 years since the foundation of the PR China (1949 to 2012) can be divided into two phases: the leaded gasoline period (1949 to 1990: gasoline with high lead content (0.64 g L^{-1}); 1991–2000: gasoline with low lead content (0.35 g L^{-1}) and the unleaded gasoline period (2001 to 2012). As a result, the discharge of Pb from primary anthropogenic sources has experienced two fluctuations over the 64 year period. The first

sharp emission decline occurs in 1991, and the total emission has decreased by 26.2% from 17 644.0 t in 1990 to 13 029.6 t in 1991, this is mainly because the average Pb content in leaded gasoline regulated by GB 484–89 is decreased about 45.3% compared to that in GB 484–64. The other sharp decline occurs in 2001, and the total Pb emissions from primary anthropogenic sources are reduced abruptly by about 61.6% in 2001. Subsequently, along with the rapid increase of vehicle volume and oil consumption, a substantial increase is once again experienced from 7747.2 t in 2001 to 14 397.6 t in 2012, at an annual average growth rate of about 5.8%.

Due to the technological progress resulting in relatively low emission factors of HMs and economic development bringing about high coal consumption and industrial products output, the trends of total atmospheric emissions for different HMs in China are diverse during the period of 2006 to 2012 (Cheng et al., 2015). Generally speaking, the national atmospheric emissions of Hg, Pb, Cd, Cr, Sb, Cu and Zn have increased at an annual average growth rate of 1.5–7.2% from 2006 to 2012. In spite of the remarkable growth in coal consumption and gross industrial production, the national As, Se, Ni, Mn and Co emissions are well restrained in this period. These are mainly due to the different volatility of these 12 elements during high temperature process resulting in diverse release rates of furnaces and synergistic removal efficiencies of control measures (Xu et al., 2004).

Due to limited information about historical ground-level concentrations of twelve HMs in different cities in China, the temporal characteristics of atmospheric concentrations of four HMs (As, Pb, Cr and Cu) in Beijing during 2000 to 2012 are used as valid index to verify whether or not the trend of historical HM emissions are reasonable (see Supplement Fig. S6). The data sources and specific values about atmospheric concentrations of As, Pb, Cr and Cu in Beijing during 2000 to 2012 are listed in Supplement Table S21. It should be acknowledged that this verification method applied in this study has certain limitations on account of sample's discrepancies, including sampling time, sampling site and detection method, etc. Therefore, the historical variation trends of HM emissions may be not well consistent with those of ambient concentrations of HMs in some years.

As can be seen from Fig. S6, minimum values of the atmospheric concentrations of As, Pb, Cr and Cu occur in 2008. This is mainly because most of aerosol samples compiled from

published paper are collected at August in this year, the time as host of the Beijing Olympics under which a series of strict measures about energy-saving and pollution reduction are implemented, such as moving or suspending high polluting industries in the Beijing and neighboring municipalities, restricting vehicles on alternate days under an even–odd license plate system, limiting pollutant emission from coal combustion facilities in Beijing and the surrounding provinces, etc. Consequently, the variation trends of atmospheric concentrations of As, Pb, Cr and Cu have some discrepancies with those of historical emissions of above four HMs in Beijing in 2008. However, the historical emission trends of As, Pb, Cr and Cu are consistent well with those of atmospheric concentrations of above four HMs during 2000 to 2012 in general (see Fig. S6), which indicate that the historical trend of HM emissions estimated by this study are reasonable.

Until now, the comprehensive and special studies on various HM (except Hg) emissions in China are quite limited. Therefore, only detailed comparison with Hg emission estimates from other studies are discussed in this study (see Fig. 3). Specifically, limited data of China's Hg emissions can be cited directly from the global Hg inventories estimated by Pacyna and Pacyna (2001), Pacyna et al. (2006, 2010) and Streets et al. (2011). In consequence, here, we mainly focus on comparing our estimations with the results about the specialized China's Hg emission inventories estimated by Streets et al. (2005) and Wu et al. (2006).

Overall, the estimated Hg emissions from fuel combustion (except subcategory of coal consumption by residential sectors) in this work are well consistent with those reported by Streets et al. (2005) and Wu et al. (2006), although the values for the same year calculated are somewhat different. This may be mainly attributed to the difference in the averaged provincial content of Hg in raw coal. In our study, according to a comprehensively investigation of published literature, we determine the national averaged Hg content in China to be 0.18 mg kg^{-1} by using a bootstrap simulation method, a little lower than those used by above two studies (0.19 mg kg^{-1}). Another important factor influencing the result is the difference of removal effectiveness of Hg through traditional APCDs. Nevertheless, the estimated Hg emissions from coal consumption by residential sectors by Streets et al. (2005) and Wu et al. (2006) are higher than our estimation in the same year. This is mainly because the emission factor of Hg from coal consumption by residential sectors is cited from Australia NPI in this paper, which is only approximately half of

that from EPA adopted in the above two studies. In terms of Hg emissions from industrial process, the estimated Hg emissions in this study are generally lower than those in other Hg emission inventories in the same year. This may be because that we have adopted S-shaped Curves to quantify the positive effects on emission reduction of pollutants by technology improvement, so that the emission factors adopted in this study are generally lower than those used in studies of Streets et al. (2005), Wu et al. (2006) and Wu et al. (2012) in the same year. Besides, some anthropogenic sources with high uncertainties are not taken into account in this work due to the lack of detailed activity data for the long period. Certain natural sources (e.g., forest burning, grassland burning, etc.) are also not included in this study. Consequently, our estimated total Hg emissions are lower than those in inventories estimated by Streets et al. (2005) and Wu et al. (2006).

3.1.1. HM emissions from coal combustion by power plants

The power plant sector represents the largest consumer of coal in China. The thermal power generation has increased from 3.6 TWh in 1949 to 3925.5 TWh in 2012 (NBS, 2013a). Meanwhile, coal burned by power plants has increased from 5.2 to 1785.3 Mt (NBS, 2013b), with an annual growth rate of 9.9% and a percentage share of the total coal consumption increasing from 22.7 to 50.6%. For the period of 1949 to 2005, the emissions of HMs from coal combustion by power plants have increased in rough proportion to coal consumption. However, this trend began to change after 2006 due to the implementation of policies of energy-saving and pollution reduction, especially the strengthening of SO₂ emission control for coal-fired power plants (Zhu et al., 2015).

Presently, the combination of pulverized-coal boilers plus ESPs plus WFGD is the most common APCDs configuration in coal-fired power plants of China. By the end of 2012, the installed capacities of FGD in power plants have increased by nearly 14 times compared with those in 2005, reaching about 706.4 GWe, accounting for approximately 86.2% of the installed capacity of total thermal power plants (MEP, 2014a). Of all of the units with FGD installation, approximately 89.7% adopt limestone gypsum WFGD process. The discharges of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn from coal combustion by power plants in 2012 are estimated at about 15.2–3038.9 t (see Fig. 2), which have decreased by 1.7–11.8% annually since 2006. Moreover, the distinction of integrated co-benefit removal efficiencies of these elements for the

typical APCD configurations is the primary reason for the obvious variations of the declining rates among varied HMs, as illustrated in Table 1 and Fig. 2.

3.1.2. HM emissions from coal consumption by industrial boilers

In general, coal combusted by industrial boilers is used to provide hot water and heating for industrial production processes. With the development of China's economy (GDP increased from CNY 46.6 billion in 1949 to CNY 51 894.2 billion in 2012), coal consumption by industrial boilers has increased at a relatively lower growth rate than the power sector, from 11.5 Mt in 1949 to 1205.6 Mt in 2012 (NBS, 2013b). According to the statistical data from China Machinery Industry Yearbook, the combination of stoker fired boiler plus wet scrubber and cyclone is the most common configuration in coal-fired industrial sectors of China, especially for the small and medium scale boilers (CMIF, 2013).

As can be seen from Fig. 2, the emission trends of HMs from coal consumption by industrial boilers are consistent with the national total emissions trends between 1949 and 1997, and negative growths appear in 1998 and 1999 due to the decreased coal consumption resulting by the Asian financial crisis (Hao et al., 2002; Tian et al., 2007, 2012b). Subsequently, the emissions of different toxic HMs from coal consumption by industrial boilers have appeared distinct variation tendencies mainly due to the different removal efficiencies of HMs through typical APCDs. Generally, Hg and Pb emissions from coal consumption by industrial boilers have increased almost monotonically from 85.1 and 3717.8 t in 2000 to 179.0 and 5770.0 t in 2012, with an annual growth rate of about 6.4 and 3.7%, respectively. However, the discharges of Mn from coal consumption by industrial boilers have decreased to about 1.2 times from 5866.0 to 4951.8 t during this period (2000–2012). Moreover, the discharges of other nine HMs (As, Se, Cd, Cr, Ni, Sb, Co, Cu and Zn) from coal consumption by industrial boilers present a trend of first increase and then decrease as a whole with the implementation of policies of saving-energy and pollution reduction in coal-fired industrial boilers sector, especially the growing application of high-efficiency dust collectors and various types of combined dust and SO₂ removal devices.

3.1.3 HM emissions from metal smelting and other primary sources

Historically, a sharp fluctuation of Hg discharges from nonferrous metals smelting sector has

occurred in the period of Great Leap Forward to Great Leap Forward Famine (increase from 92.6 t in 1957 to 221.7 t in 1959, then decrease rapidly to 104.0 t in 1963), this is mainly due to the rapid increase or decline of mercury mining outputs in this period (increase from 1060 t in 1957 to 2684 t in 1959, then decrease rapidly to 1345 t in 1963). Subsequently, a sharp increase of emissions of Hg has occurred, with the emission from about 60.6 t in 1998 increases to about 218.6 t in 2012, at an annually averaged growth rate of 9.6%. Simultaneously, the primary contributor of Hg emissions from nonferrous metals smelting sector has changed to the subsector of primary-Zn smelting, which occupies about 36.9–52.7% during 1998 to 2012. Unlike Hg emission, the emissions of As, Se, Pb, Cd, Ni, Sb, Cu and Zn from nonferrous metals smelting sector have increased by approximately 7–15 times to 442.3, 1856.4, 251.8, 412.7, 140.6, 1240.9 and 4025.6 t in 2012, respectively. This is mainly because the reduced shares of HM emissions from nonferrous metals smelting sector, caused by increasing advanced pollutants control devices installation, have been partly counteracted by the rapid growth of nonferrous metals production.

A steady increase of HM emissions from the pig iron and steel industry accompanying by certain undulations has occurred from 1949 to 1999 (see Fig. 2). Specifically, because of the emphasis on the backyard furnaces for steel production in the period of Great Leap Forward Movement, a sharp fluctuation of emissions has occurred during the period of 1958 to 1963, with the emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Cu and Zn almost doubling (NBS, 2013b). Although emission factors have leveled off between 2000 and 2012, the output of pig iron and steel has rapidly increased from 131.0 and 128.5 Mt in 2000 to 663.5 and 723.9 Mt in 2012 and, as a result, the emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Cu and Zn from this sector has quadrupled or quintupled in the past twelve years. Especially, the share of Zn emissions from ferrous metals smelting sector to the national emissions has increased from 13.1 to 32.2%. Therein, the steel making industry represents the dominant contributor to the Zn emissions, accounting for about 60.9–62.9% during this period.

In order to facilitate understanding of historical HM emissions in China, the details about temporal variation trends of HM emissions from liquid fuels combustion and brake and tyre wear are discussed in the Supplement Section S3.

Changes to the Supplement:

Section S3. Temporal variation trends of HM emissions from other primary anthropogenic sources

1 HM emissions from liquid fuels combustion

Although liquid fuels only take up about 8.9% of the total primary energy production and account for nearly 18.8% of total energy consumption in 2012, the liquid fuels consumption is also one of major contributors for atmospheric Ni emissions due to the relatively high content of Ni in fuel oil (Tian et al., 2012b). Furthermore, with the rapid growth of vehicle/plane populations and transport turnover (including passenger and cargo turnover), the consumptions of gasoline, diesel oil and kerosene of China have reached 116.0, 184.1 and 22.0 Mt in 2012, respectively. Because of the large usage of leaded gasoline in China before 2001, none can afford to neglect the accumulated emissions of Pb from gasoline consumption by vehicles during 1949 to 2012, although the leaded gasoline has been forbidden to produce and use since 2001.

In this study, we estimate that the discharge of Ni from liquid fuels combustion have increased from 12.8 t in 1949 to 604.5 t in 2012. Therein, fuel oil combustion contributes over 82.1% of the total liquid fuels consumption category in 2012. Notably, the total Ni emission from liquid fuels consumption category has increased slightly (less than 2% annually) since 1980 despite of the rapid growth of distillate oils (gasoline, diesel oil, and kerosene), which is mainly because of the lower Ni content in distillate oils and relatively constant supply of fuel oil in China in the past three decades (NBS, 2013b; Wang et al., 2003b; Tian et al., 2012b).

In term of Pb emission from gasoline combustion category, the reduced lead content of gasoline is the primary reason for the sharp decrease in total Pb emissions in 1991 and 2001 (Li et al., 2012), as with national total Pb emission. For the first sharp emission decline, the total emission has decreased by 36.8% from 12 832.2 t in 1990 to 8107.5 t in 1991. For the other sharp decline, the total emission has decreased by 98.1% from 12 866.7 t in 2000 to 248.3 t in 2001. However, the Pb emissions from this category have continued to increase in the following years due to the gradually increase of gasoline consumption with the rapid growth of urban vehicle populations (please see Fig. S5).

2 HM emissions from brake and tyre wear

During the period of 1949 to 2012, the amount of civilian vehicles has increased from 0.1 million units to 109.3 million units. Furthermore, the passenger turnover of highways and freight turnover of highways have increased continuously to 1846.8 billion passenger-kilometer and 5953.5 billion ton-kilometer, respectively (NBS, 2013b). As a result, the total Pb, Cr, Sb, Mn, Cu and Zn emissions from brake and tyre wear have increased remarkably to 333.5, 124.0, 530.1, 133.8, 2720.1 and 954.7 t in 2012, respectively. Especially during 2000 to 2012, the annual growth rate of these HM emissions from brake and tyre wear is up to about 17.5%, which is closely related to the rapid growth of civilian vehicle population (see Fig. S5). For other HMs (As, Se, Cd, Ni and Co), the extraordinarily low emissions from brake and tyre wear category are estimated due to trace level of these elements in brake linings.

Moreover, on the basis of the valuable suggestions from the referee #2, we have shortened the section 3.3 to make the paper more concise and better understanding.

Changes to the new revised manuscript text:

“The total emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn from primary anthropogenic sources by provinces in China for the year 2010 are estimated at about 72955.1 t. As can be seen in Fig. 4, coal combustion sources represent the major contributors of Hg, As, Se, Pb, Cr, Ni, Mn, Co and Cu emissions and are responsible for about 50.6, 74.2, 64.6, 60.1, 90.4, 56.2, 80.9, 98.6 and 53.4% of total emissions, while their contribution to the total Cd, Sb and Zn emissions are relatively lower, at about 32.7, 39.3 and 39.8%, respectively.

Among all the coal consuming sub-sectors, coal consumption by industrial boilers ranks as the primary source in national total emission of twelve HMs, with the average proportion about 57.7% of the total emission from coal combustion. This may be attributed to the significant coal consumption of industrial boilers (about 1117.3 Mt in 2010) and relative high share of boilers with inadequate APCDs (Cheng et al., 2015; NBS, 2013b).

As the largest coal consumer in China, coal consumption by power plants is identified as the second largest contributor and takes about 14.0% in national total emission of twelve HMs. In order to achieve the emission reduction of PM, SO₂ and NO_x for satisfying the national or local emission reduction goals for the year 2010 (the end year of 11th FYP) (NBS, 2011; Tian et al.,

2014a), a series of control policies have been implemented, including replacement of small coal-fired plant units with large and high efficiency units and the continuously increasing application rate of advanced APCDs systems (e.g., ESP, FFs, WFGD, SCR, etc.). Consequently, the final discharge rates of HM from power plants have decreased obviously even though the volume of coal consumption has grown substantially (see Fig. 2 and Fig. S1).

China has been the world's largest producer of pig iron and steel by a rapidly growing margin. By the end of 2012, the output of steel has amounted to 723.9 Mt, accounting for about 46% of worldwide steel production (CISA, 2013). Despite enormous achievement obtained by China's iron and steel industry, China is still featured as a steel producer with low energy efficiency and high pollutants emission level compared with other major steel-producing countries (Guo and Fu, 2010). Because of limited application of FGD and de-NO_x devices and poor control of PM, ferrous metals smelting sector ranks as the third largest contributor, occupying about 13.2% of the national total emission of twelve HMs. In terms of Zn emission, the share from this sector is dominant, accounting for about 32.2% of the total.

Regarding nonferrous metals smelting emissions, the primary smelting processes resulting in HM emissions are far more than those emitted from the secondary smelting processes. Nonferrous metals smelting, as the fourth largest contributor, accounting for about 11.0% of total emission, represents the primary contributor to the discharges of Hg and Cd. Therein, primary-Cu smelting contributes the largest part of most elements, including 89.5% for As, 37.3% for Pb, 74.8% for Cd, 38.7% for Ni and 76.6% for Cu; primary-Pb smelting is the major source of Sb and Pb; primary-Zn smelting accounts for the largest proportion of Hg and Zn emissions among the nonferrous metals smelting category. Besides, with respect to Hg emission from nonferrous metals smelting sector, mercury smelting industry is the other dominant sub-category source, with a share of about 33.0% of nonferrous metals smelting emission in 2010.

It can be concluded that the emissions of HMs from brake wear are well associated with vehicle amount, vehicle mileage as well as the contents of HMs in brake linings and tyre. Currently, numerous of studies have reported that airborne HMs (e.g. Sb, Cu, Zn, etc.) in urban areas are associated with road traffic and more definitely with emissions from brake wear (Gómez et al., 2005; Hjortenkrans et al., 2007). As can be seen from Fig. 4h, k, brake and tyre wear sector

takes the largest part of 39.9 and 26.3% in national Sb and Cu emissions, respectively. Therein, brake wear is the absolutely dominant sub-contributor, accounting for over 99.9 and 99.6% for Sb and Cu emissions from this sector in 2010, respectively. This is mainly due to the high contents of Sb and Cu in the brake linings (see Table S13, Hjortenkrans et al., 2007) and the explosive expansion of vehicle population in China (see Fig. S5). Nevertheless, the adverse effects of airborne PM originated from brake wear on human health and ecosystem are still not received sufficient attention from the policymakers as well as the public.

Specially, although non-metallic mineral manufacturing sector is not the dominant source for most of HMs, the discharge of Se from this sector explains the largest contributor of the total. Among this category, glass production sector discharges about 92.9% of the total Se emissions due to the widespread application of selenium powder as decolorizing agent in glass production process and huge output of glass production (Kavlak and Graedel, 2013).

As can be seen from Fig. 4a-1, the source contributions on the provincial scale in 2010 vary substantially due to the difference of industrial conformations and energy structures (Cheng et al., 2015; NBS, 2013a, b). Among the provinces with high HM emissions, Shandong ranks as the largest province with As, Se, Cd, Ni, Mn and Cu emissions; accounting for about 8.1–10.6% of the national emissions; Hebei contributes the largest part of about 9.3 and 11.3% in national Pb and Zn emissions; Guizhou represents the primary province with Hg and Sb emissions; the key provinces with Cr and Co emissions are found in Yunnan and Shanxi, respectively. These can be mainly attributed to the follow reasons (NBS, 2013a, b; Wu et al., 2008): (1) the enormous coal consumption of industrial boiler, prosperous electric power generation, explosive increase of vehicle population and huge output of industrial products in Shandong, (2) the flourishing pig iron and steel production in Hebei, (3) the dominant outputs of mercury and obviously high average concentration of Sb in feed coals in Guizhou (about $6.0 \mu\text{g g}^{-1}$, which is approximately four times higher than the national averaged concentration of Sb in coal as consumed in China, see Table S8), (4) the booming coke making industry in Shanxi, (5) the relatively higher concentration of Cr in feed coals in Yunnan (about $71.7 \mu\text{g g}^{-1}$, which is two times higher than the national averaged concentration of Cr in coal as consumed in China, see Table S8)."

6. Section 3.6 control policies: *I do not agree with this suggestion “stop mining and burning of coal with high HM concentrations (or stop utilizing high-sulfur coal in China due to the high affinity between HMs and pyrite in coal)”. China is facing energy shortage problem. Stopping some coal mining is not a good idea considering China’s energy supply and energy security.*

Response: Thanks for the comment. The good suggestions have been addressed.

You are right, huge energy shortage in developed regions, unbalanced energy distribution and backward economic development mode relying on local coal mining and burning in certain provinces, are the main obstacles which restrict the government to ban mining and burning such coals with high concentrations of sulfur and heavy metals. Because of relatively low coal production and high contents of HMs in coal as produced, this measure can be carried out by certain provinces where coal with high sulfur and HMs contents are mainly produced by small mines, such as Zhejiang and Guangxi (Zhu et al., 2015). In order to eliminate the ambiguity and make it more clarity, we have revised the related suggestion to make it more clarity.

Changes to the new revised manuscript text:

“(1) lower or stop mining and burning of coal with high HM concentrations in certain provinces where the coals are mainly mined from by small coal mines such as Zhejiang and Guangxi (or lower or stop utilizing high-sulfur coal in corresponding provinces due to the high affinity between HMs and pyrite in coal) (Yuan et al., 2013; Zhu et al., 2015).”

Reference

- Yuan, X. L., Mi, M., Mu, R. M., and Zuo, J.: Strategic route map of sulphur dioxide reduction in China, *Energy Policy*, 60, 844–851, doi:10.1016/j.enpol.2013.05.072, 2013.
- Zhu, C. Y., Tian, H. Z., Cheng, K., Liu, K. Y., Wang, K., Hua, S. B., Gao, J. J., and Zhou, J. R.: Potentials of whole process control of heavy metals emissions from coal-fired power plants in China, *J. Cleaner Prod.*, doi: 10.1016/j.jclepro.2015.05.008, 2015 (in Press).