**Dear Editors and the two Anonymous referees,**

This is Dr. Hezhong Tian, who comes from the School of Environment at Beijing Normal University of China.

I and the co-authors have revised the manuscript entitled "**Quantitative Assessment of Atmospheric Emissions of Toxic Heavy Metals from Anthropogenic Sources of China: Historical trend, spatial distribution, uncertainties and control policies** (Ms. acp-2015-189)" according to your valuable instruction and the review comments. By now, all the corrections and responses have been incorporated into the new revised manuscript.

The detailed point-point responses and corrections to Referee #1 and #2, as well as the revised manuscript and Supplementary material are listed follows.

If further responses should be made, please don't hesitate to let us know.

We do appreciate your valuable comments and suggestions on our manuscript.

Yours Sincerely

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## Author's Response to Anonymous Referee #1

The authors are very grateful to the reviewers and the 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:*

*The authors developed an anthropogenic emission inventory for toxic heavy metals (HMs) in China for the period 1949-2012. The emission inventory for HMs is essential and important data for assessment of their effects on human health and policymaking for their emission control. The topic certainly is suitable for ACP. The manuscript presents the spatial and temporal variations for HMs emissions in China, the comparison with other inventories, and uncertainty analysis. Compared to previous works, the author's inventory has advantages in the targeted period covering almost 60 years (1949-2012) and in the comprehensive emission covering 12 typical HMs. However, there are some points which should be clarified. In conclusion, the reviewer is recommending the minor revision of the manuscript.*

**Response:** we thank the anonymous reviewer #1 for the support to publish this paper and for your valuable review comments. Addressing the comments will greatly improve the quality and clarity of the manuscript. Detailed bellow is our detailed point-to-point responses to the queries and comments raised by the reviewer #1 and a list of the specific changes made in the text.

*(Major comments)*

*(1) One of the advantages of the author's work is the using of time-varying (dynamic) emission factors. Why do the authors apply the S-shaped curve in dynamic emission factors? The authors should explain the reason. Additionally, the authors should demonstrate how to set the shape parameter, $S_k$.*

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

We have added the reasons to explain why we apply the S-shaped curve to assess the dynamic HM emission factors in the new revised manuscript by combining the similar comments raised by both the Reviewer #1 and Reviewer #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."

Moreover, the interpretation how to set the shape parameter for industrial process is supplied in the new revised manuscript.

Changes to the new revised manuscript text:

"Actually, on the basis of Eq. (5), the specific vales of shape parameter of the curve (s) can be determined when we obtain the definite values of unabated emission factor in pre-1900 and the best emission factor achieved at present for each industrial process in China. In addition, several

values of *s* are cited from Street et al. (2011) if only limited information about emission level for certain processes can be gained."

Related references citation is added 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, Energy 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.

*(2) Another advantage of the manuscript is a long-term historical emission inventory for HMs during 1949-2012. The authors should add the uncertainty analysis for historical emissions in section 3.5. Additionally, it is recommended that the authors make the verification for historical emissions. For example, the trends of the historical emissions are consistent with those of ambient concentrations of HMs?*

**Response:** Thanks for the good comment. We find the suggestion inspiring.

We follow the same methodology used for twelve HM emissions from primary anthropogenic sources of China in 2010 in the text to assess uncertainties in the historical emission estimates during the period of 1949 to 2012. All input parameters and their corresponding probability distributions are incorporated into a Monte Carlo framework with Crystal Ball software and 10000 simulations are performed. Moreover, we have added a new figure–"**Fig. S8. The uncertainty bounds for China's anthropogenic atmospheric emissions of twelve HMs during 1949 to 2012**" in the new revised Supplement.

New added Fig. S8 in Supplement:

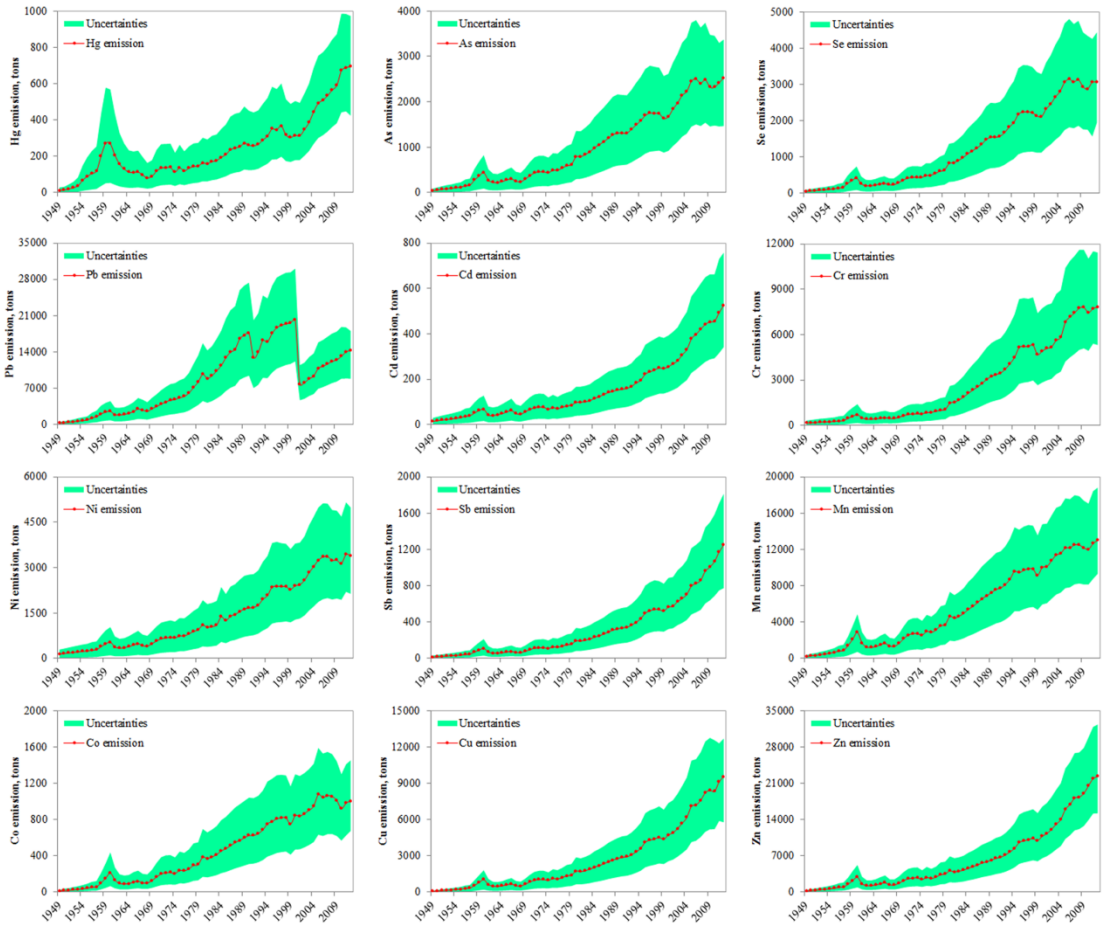


Fig. S8. The uncertainty bounds for China's anthropogenic atmospheric emissions of twelve HMs during 1949 to 2012

Changes to new revised manuscript text:

"The combined uncertainty bounds for the national emissions of twelve HMs during the historical period are shown in Fig. S8. In general, the range of uncertainty has gradually diminished over time. For example, we calculate an uncertainty level of -90.1–125.7% (95% confidence interval) in the estimate of national Hg emissions in 1949, which is higher than those of other eleven HM emissions (between -90.0% and 119.3%). This is mainly attributed to remarkable emissions from several Hg sources that have the largest uncertainty in both activity levels and emission factors, such as gold smelting and mercury mining. Since then, the relative uncertainties have gradually decreased from the beginning to the end of the period. This is primarily because more reliable activity data with smaller coefficient of variation (CV) from related yearbooks and reports become available. The uncertainty range of national Hg emissions is estimated to -40.6–55.8% by 2003,

which is well comparable with estimates of ±44% for China's Hg emissions by Wu et al. (2006). By the end of 2012, the overall uncertainty level has reduced to -39.0–47.0% for the national HM emissions."

It is of significance to verify the historical HM emissions. Undoubtedly, the historical trend of ambient concentration of HM is a valid verification index, which is generally consistent with the historical HM emissions. However, till now, unlike the regulated air pollutants (e.g., $PM_{2.5}$, $PM_{10}$, $SO_2$, $NO_X$, etc.), continuous monitoring system for atmospheric HM concentrations in different cities of China are still not built by the MEP (Ministry of environmental protection of the People's Republic of China), and at the same time, long-term ground-level observations of HM concentrations in the different sampling sites of one city or region are still quite limited. Duan and Tan (2013) summarize the research results about atmospheric HM concentrations in aerosols of 44 major cities in China from published literatures during the last 10 years. Nevertheless, the veritably temporal variations of atmospheric HM concentrations in China are still not characterized due to similar reasons discussed above.

The validation of historical variation of ambient HM concentrations requests an extensive work of ground-level observations and a large number of literature investigations. Both of these two parts should be paid much more attentions. Due to the limited information, we mainly focused on the comparison between the temporal characteristics of atmospheric concentrations of As, Pb, Cr and Cu and the historical emissions of these four HMs in Beijing during 2000 to 2012 in Section 3.1 Simultaneously, new Fig. S6 and Table S21 are added in the revised supplementary material.

We are carrying on the research work about observing and investigating ground-level concentrations of twelve HMs in several cities in China. However, the relevant works are still on-going. We hope this part of work will be presented and discussed in our future submission.

We thank you a lot for your understandings on this point.

Changes to the new revised manuscript text:

"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."

New added Table S21 and Fig. S6 in Supplement:

Table S21 The atmospheric concentrations of As, Pb, Cr and Cu in $PM_{2.5}$ in Beijing during 2000 to 2012

| Year | Atmospheric concentration (ng $m^{-3}$) | | | | Literature cited |
|---|---|---|---|---|---|
| | As | Pb | Cr | Cu | |
| 2000 | 30.0 | 300.0 | 20.0 | 30.0 | (Song et al., 2006) |
| 2001 | | 170.0 | | 50.0 | (Duan et al., 2006) |
| 2002 | 38.3 | 218.3 | 26.7 | 58.3 | (Sun et al., 2004) |
| 2003 | 38.3 | 218.3 | 26.7 | 58.3 | (Sun et al., 2004) |
| 2005 | 16.0 | 189.5 | 50.0 | 53.0 | (Yu et al., 2012; Zhang et al., 2012) |

| | | | | | |
|---|---|---|---|---|---|
| 2006 | 20.2 | 173.3 | 73.6 | 43.1 | (Cui et al., 2008; Yang et al., 2008a, b; Yu et al., 2012) |
| 2007 | 19.0 | 189.7 | 31.7 | 51.3 | (Gao, 2012; Wang et al., 2010; Yu et al., 2012; Zhang et al., 2010) |
| 2008 | 7.6 | 67.5 | 5.8 | 25.8 | (Mu et al., 2010; Yu et al., 2012; Zhang, 2012; Zhang et al., 2010) |
| 2009 | 17.2 | 135.5 | 13.6 | 40.0 | (Tao et al., 2014; Zhao et al., 2013) |
| 2010 | 22.8 | 142.7 | 16.4 | 36.8 | (Tao et al., 2014; Yu et a., 2013) |
| 2011 | 15.6 | | 13.4 | 47.7 | (Wang et al., 2014) |
| 2012 | 23.4 | 158.0 | 24.6 | 54.7 | (Guo, 2014; Yang et al., 2015; Zhang et al., 2014) |

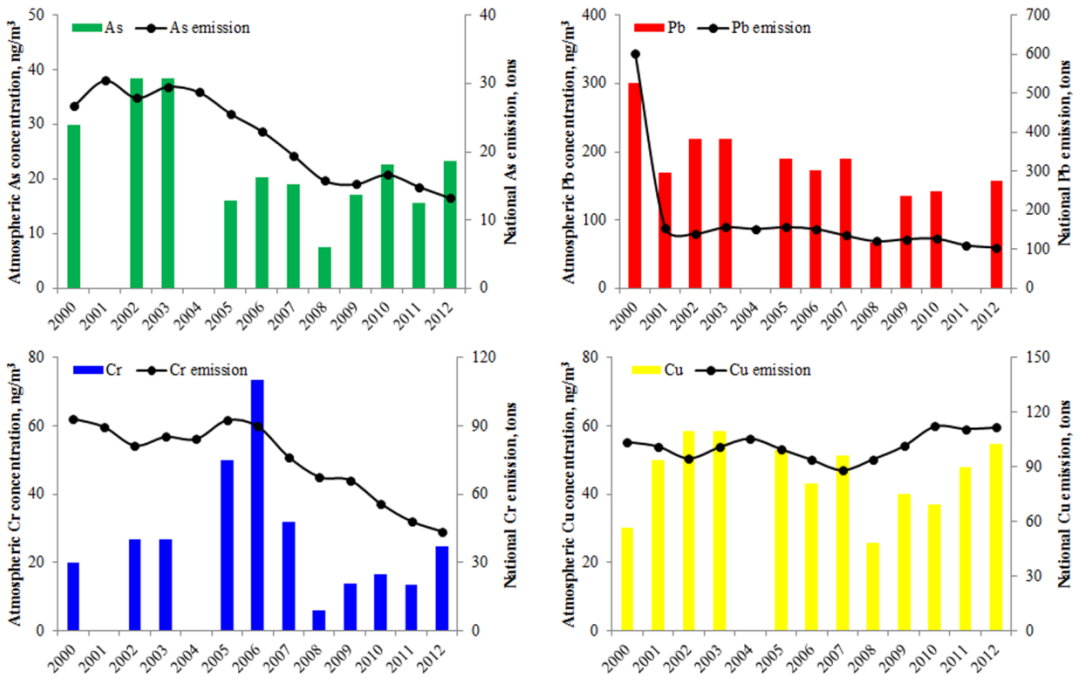


Fig. S6. Comparison between historical HM (As, Cr, Pb, and Cu) emissions and temporal variation of atmospheric concentrations in $PM_{2.5}$ in Beijing during 2000-2012.

## Reference


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Yang, J., Fu, Q., Guo, X. S., Chu, B. L., Yao, Y. W., Teng, Y. G., and Wang, Y. Y.: Concentrations and seasonal variation of ambient $PM_{2.5}$ and associated metals at a typical residential area in Beijing, China, Bull. Environ. Contam. Toxicol., 94, 232–239, doi:210.1007/s00128-00014-01443-y, 2015.

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*(3) In developing country including China, the older statistical data for activity data are considered to have high uncertainty. The author should discuss about the uncertainty and its effects to emission estimation in the uncertainty analysis in section 3.5.*

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

You are right, for less developed statistical systems in the developing country including China, the earlier statistical data for activity level are considered to have high uncertainty. Unfortunately, we have to acknowledge that it is quite difficult to assess the specific uncertainty of activity data from China's earlier official statistics. Akimoto et al. (2006) argues that the energy consumption of China during 1996–2003 is not recommended for use in the study of emission inventories due to the probable underestimate. However, the discrepancies in coal consumption from power sector are considered to be less than ±5%, which do not dominate the emission uncertainties (Wu et al., 2010; Zhao, et al., 2008). In order to approximately quantify the uncertainty of activity data, the whole target period of 1949 to 2012 was divided into three stages with respect to economic development and emission control: before reform and opening (1949–1978), intermediate stage (1979–2005), and the total amount control stage of air pollutants (2006–2012). For activity level of anthropogenic sources obtained from official statistics after 2006, we assume normal distributions with sector-dependent uncertainties, based on Tian et al. (2012a, b) and Zhao et al. (2011) (seen Supplement Table S20). Based on above discussion and consideration, the uncertainty of activity data from official statistics during the early two periods of 1949–1978 and 1979–2005, are assumed to be about 2 and 1.5 times of those in the period of 2006–2012, respectively.

Changes to the new revised manuscript text

"Specially, the earlier statistical data for activity level are considered to have high uncertainty for developing country (including China) with less developed statistical systems. Unfortunately, we

have to acknowledge that it is quite difficult to accurately assess the specific uncertainty of activity data from China's earlier official statistics. Akimoto et al. (2006) argue that the energy consumption of China during 1996–2003 is not recommended for use in the study of emission inventories due to the probable underestimates. However, the discrepancies in coal consumption from power sector are considered to be less than ±5%, which do not dominate the emission uncertainties (Wu et al., 2010; Zhao, et al., 2008). In order to approximately quantify the uncertainty of activity data, we divide the whole period of 1949 to 2012 into three stages with respect to economic development and emission control: before reform and opening (1949–1978), intermediate stage (1979–2005), and the total amount control stage of atmospheric pollutants (2006–2012). For activity level of anthropogenic sources obtained from official statistics after 2006, we assume normal distributions with sector-dependent uncertainties (see Supplement Table S20). On the basis of above discussion and consideration, the uncertainty of activity data from official statistics during the two early periods of 1949–1978 and 1979–2005, are assumed to be about 2 and 1.5 times of those in the period of 2006–2012, respectively."

In addition, the effects of uncertainty discrepancies of activity level during 1949 to 2012 on total emission estimations in the uncertainty analysis are supplemented in section 3.5, combining with the uncertainty analysis for historical emissions.

Changes to the new revised manuscript text

"The combined uncertainty bounds for the national emissions of twelve HMs during the historical period are shown in Fig. S8. In general, the range of uncertainty has gradually diminished over time. For example, we calculate an uncertainty level of -90.1–125.7% (95% confidence interval) in the estimate of national Hg emissions in 1949, which is higher than those of other eleven HM emissions (between -90.0% and 119.3%). This is mainly attributed to remarkable emissions from several Hg sources that have the largest uncertainty in both activity levels and emission factors, such as gold smelting and mercury mining. Since then, the relative uncertainties have gradually decreased from the beginning to the end of the period. This is primarily because more reliable activity data with smaller coefficient of variation (CV) from related yearbooks and reports become available. The uncertainty range of national Hg emissions is estimated to -40.6–55.8% by 2003, which is well comparable with estimates of ±44% for China's Hg emissions by Wu et al. (2006).

By the end of 2012, the overall uncertainty level has reduced to -39.0–47.0% for the national HM emissions."

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*(Minor comments)*

*(1) Eq. (1): In the right hand, Ei, Ej, and Ek are needed? The averaged fraction of HM which is removed from flue gas by the conventional emission control devices can be separated into PM/$SO_2$/NOx emission control devise?*

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

We are sorry for making the reviewer confusing. We made a mistake about spelling between "*E*" and "∑" applied in Eq. (1) on the right side. As a result, the Eq. (1) in the revised manuscript is modified as follow in the new revised manuscript:

$$E(t)=\sum_{i}\sum_{j}\sum_{k}\left[C_{i,j,k}\times A_{i,j,k}\times R_{i,j}\times\left(1-\eta_{PM(i,j)}\right)\left(1-\eta_{SO_2(i,j)}\right)\left(1-\eta_{NO_X(i,j)}\right)\right] \quad (1)$$

In this study, field test data about HM contents in ash samples from different sampling sites (e.g., before and after SCR, before/ after particulate collector such as ESP and FFs, before and after WFGD, etc.) are summarized from available published literature (please see Supplement Table S11 for more details). Based on the field test results, we can estimate the specific removal efficiencies from each air pollution control device (e.g., SCR, ESP/ FF/ cyclone, WFGD, etc.) In addition, not all of coal-fired boilers of China are uniformly equipped with same control devices, but installed with varied configuration of different types of PM/$SO_2$/$NO_X$ emission control devices. Therefore, we adopt the arithmetic mean values of HM removal fractions from each air pollution control device reported in references to calculate the final emissions. The specific values of HM removal fractions from varied APCDs are illustrated in Table 1.

*(2) Lines 14-18, page 12122: It is considered that the emission factors of HMs from biofuel for household use and open burning are different due to different combustion condition.*

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

In this study, biomass is divided into crop straw and firewood. Unfortunately, our knowledge of HM emissions from biomass burning is extremely limited. Few of long-term investigations on biomass burning practices has been undertaken, and emission factors of HMs from crop straw for household use and firewood for open burning have been seldom estimated in the field. Therefore, the HM emission factors from crop straw for open burning and firewood for household use are applied to estimation of HM emissions from biofuel combustion.

Changes to the new revised manuscript text:

"Because of quite limited field test data about HM emission characteristics from crop straw for household use and firewood for open burning, we presume HM emission factors from biofuel for open burning are equal to those for household use. It is acknowledged that this simple assumption may introduce additional uncertainties, and thus relatively large uncertainty ranges for HM emission factors of biofuel combustion are applied in the analysis, which merits deep investigation in the future."

*(3) Figs. 1 and 4: These figures are not clear. They need to be improved.*

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

In order to meet requirements of figures size (should not exceed 5 MB) regulated by *Manuscript Preparation Guidelines for Authors*, we have increased the resolution ratio of the Fig.1 and Fig. 4 from 300 dpi to 600 dpi in the new revised figure files as much as possible.

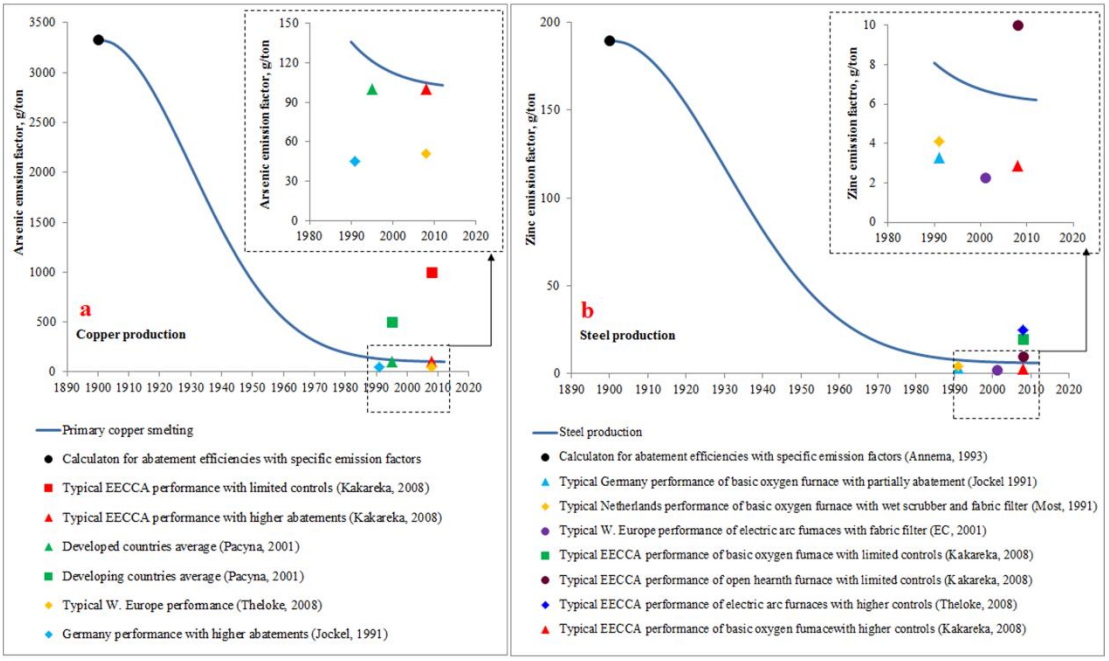


**Figure 1.** Time variation of arsenic emission factors for copper production and zinc emission factors for steel making in China (for instance).

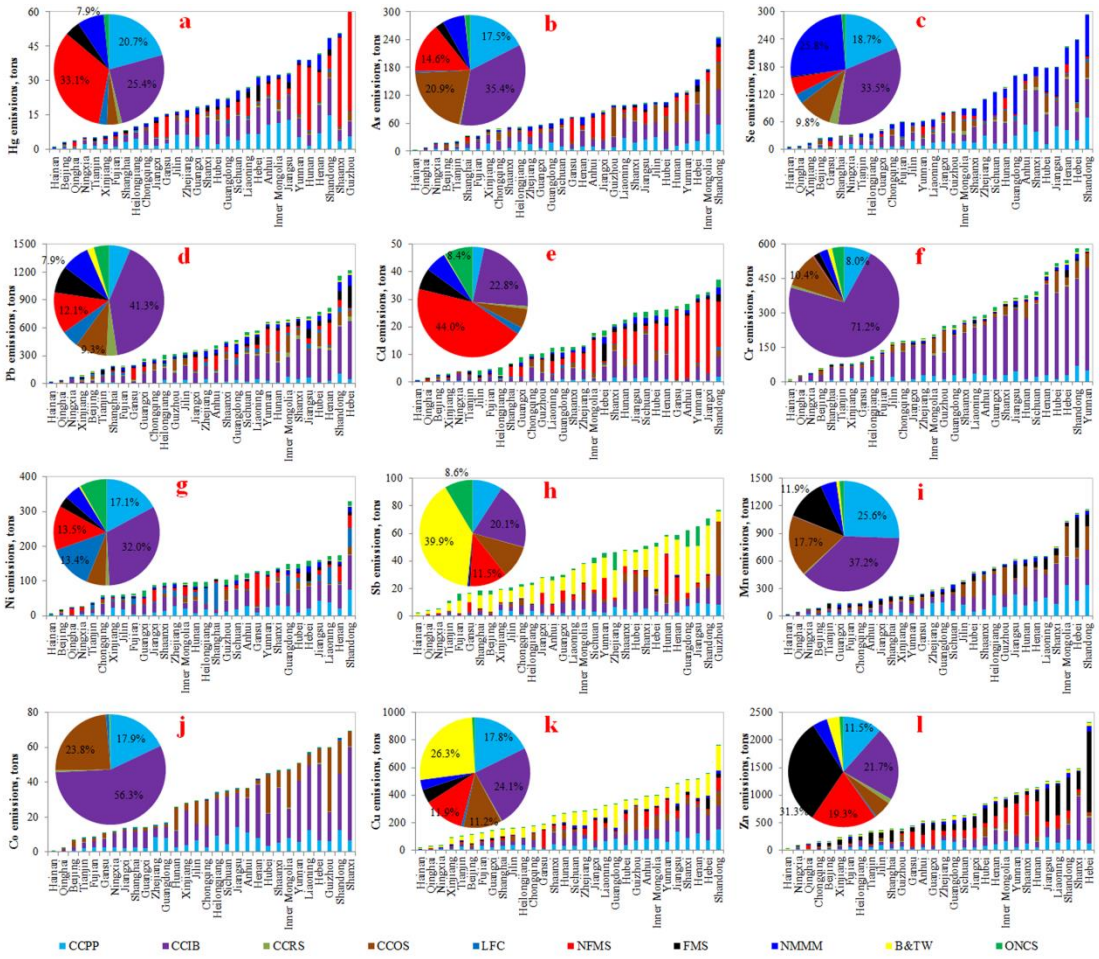


**Figure 4.** Provincial HM emissions from anthropogenic sources and national composition by source categories in 2010.

## 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 bellow 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 ± 364.4 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 $SO_2$ 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, $SO_2$ 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 begin to change after 2006 due to the implementation of policies of energy-saving and pollution reduction, especially the strengthening of $SO_2$ 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 $SO_2$ 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 1060t 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, $SO_2$ 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-l, 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 μg $g^{-1}$, 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 μg $g^{-1}$, 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).

# Quantitative Assessment of Atmospheric Emissions of Toxic Heavy Metals from Anthropogenic Sources in China: Historical trend, Spatial Distribution, Uncertainties and Control Policies

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**Abstract.** Anthropogenic atmospheric emissions of typical toxic heavy metals have received worldwide concerns due to their adverse effects on human health and the ecosystem. By determining the best available representation of time-varying emission factors with S-shape curves, we establish the multiyear comprehensive atmospheric emission inventories of 12 typical toxic heavy metals (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) from primary anthropogenic activities in China for the period of 1949−2012 for the first time. Further, we allocate the annual emissions of these heavy metals in 2010 at a high spatial resolution of 0.5° × 0.5° grid with ArcGIS methodology and surrogate indexes, such as regional population and gross domestic product (GDP). Our results show that the historical emissions of Hg, As, Se, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn during the period of 1949–2012, have been increased by about 22−128 times at an annual average growth rate of 5.1−8.0%, reaching about 526.9−22319.6 tons in 2012. Nonferrous metal smelting, coal combustion of industrial boilers, brake and tyre wear, and ferrous metals smelting represent the dominant sources for Hg/ Cd, As/ Se/ Pb/ Cr/ Ni/ Mn/ Co, Sb/ Cu, and Zn, respectively. In terms of spatial variation, the majority of emissions are concentrated in relatively developed regions, especially for the northern, eastern and southern coastal regions. In addition, because of the flourishing nonferrous metals smelting industry, several southwestern and central-southern provinces play a prominent role in some specific toxic heavy metals emissions, like Hg in Guizhou and As in Yunnan. Finally, integrated countermeasures are proposed to minimize the final toxic heavy metals discharge on accounting of the current and future demand of energy-saving and pollution reduction in China.

**Key words:** heavy metals (HMs), anthropogenic sources, time-varying dynamic emission factor, emission inventory, temporal and spatial distribution characteristics, coal combustion, non-ferrous smelting, China

## 1 Introduction

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 ± 364.4 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).

## 2 Methodologies, data sources and key assumptions

We estimate the atmospheric emissions of the targeted 12 HMs (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) from primary anthropogenic sources by combining the specific annual activities and dynamic emission factors by source category in this study. Table S1 in the separate Supplementary Material file lists out the targeted heavy metal species and the associated emission sources. Generally, we classify all sources into two major categories: coal combustion sources and non-coal combustion sources.

### 2.1 Methodology of HM emissions from coal combustion sources

Currently, coal plays a dominant role in China's energy consumption, making up about 70 percent of its total primary energy consumption (Tian et al., 2007; Tian et al., 2012b). Consequently, tons of hazardous HM pollutants can be released into the atmospheric environment, although the concentration of heavy metals in Chinese

coals is normally parts per million (ppm) levels.

Atmospheric emissions of varied HMs from coal combustion are calculated by combining the provincial average concentration of each heavy metal in feed coals, the detailed coal consumption data, and the specific emission factors, which are further classified into subcategories with respect to different boiler configurations and the application rates and removal efficiencies of various APCDs. The basic formulas can be expressed as follows:

$$E(t)=\sum_{i}\sum_{j}\sum_{k}\left[C_{i,j,k}\times A_{i,j,k}\times R_{i,j}\times\left(1-\eta_{PM(i,j)}\right)\left(1-\eta_{SO_2(i,j)}\right)\left(1-\eta_{NO_X(i,j)}\right)\right] \quad (1)$$

where $E$ is the atmospheric emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn; $C$ is the averaged concentration of each HM in feed coals in one province; $A$ is the amount of annual coal consumption; $R$ is the fraction of each heavy metal released with flue gas from varied coal combustion facilities; $\eta_{PM}$, $\eta_{SO_2}$ and $\eta_{NO_X}$ represent the averaged fraction of one heavy metal which is removed from flue gas by the conventional PM/$SO_2$/$NO_X$ emission control devices, respectively; $i$ represents the province (autonomous region or municipality); $j$ represents the sub-category emission source which is classified by different economic sectors and combustion facilities, as well as the equipped PM, $SO_2$ and $NO_X$ control devices (the detailed source classification can be seen in Supplement Table S2); $k$ represents the type of coal as consumed (raw coal, cleaned coal, briquette, and coke); and $t$ represents the calendar year.

### 2.1.1. Average concentrations of varied HMs in feed coals

Previous studies have demonstrated that concentrations of HMs in Chinese coals vary substantially depending on the type of the feed coals and their origin, as well as the affinity of the element for pure coal and mineral matters (Tang et al., 2002; Ren et al., 2006).

In this study, we have compiled and summarized provincial-level test data of HM content in coal from published literature to date: Hg (879 samples), As (1018 samples), Se (472 samples), Pb (831 samples), Cd (616 samples), Cr (956 samples), Ni (863 samples), Sb (1612 samples), Mn (545 samples), Co (888 samples), Cu (765 samples) and Zn (828 samples), and then we calculate the average concentration of each heavy metal in coal as produced and coal as consumed on a provincial-level by

using bootstrap simulation and coal transmission matrix (Tian et al., 2011a; Tian et al., 2013; Tian et al., 2014a). More details about the algorithms to determine HM concentrations in cleaned coals, briquettes and coke are given in our previous publications (Tian et al., 2010; Tian et al., 2012a). The brief introduction of bootstrap simulation as well as averaged concentration values of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn in feed coals on provincial-level can be seen in Supplement Section S1−S2 and Table S3−S9, respectively.

### 2.1.2. HM emission factors from coal combustion sources

In this study, various coal combustion facilities are separated into five sub-categories: pulverized-coal boilers, stoker fired boilers, fluidized-bed furnaces, coke furnaces, and domestic coal-fired stoves. Therein, pulverized-coal boilers are predominant in coal-fired power plants in most of the provinces in China, representing over 85.0% of the total installed capacities. The remaining share is divided between fluidized-bed furnaces and stoker fired boilers, which are mainly used in relatively small unit-size coal-fired power plants. Different from thermal power plants sector, stoker fired boilers take a large proportion in coal-fired industrial sector and other commercial coal-fired sectors. 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). Therefore, it is necessary to develop a detailed specification of the methods by which the coals are fed and burned in China. In this study, we have compiled the release rates of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn for different combustion boilers from published literatures (see Supplement Table S10). The arithmetic mean values of release rates of these 12 HMs from different combustion boilers reported in literatures are adopted to calculate the final emissions (see Table 1).

Besides, the conventional APCDs used to reduce criteria air pollutant (e.g., PM, $SO_2$, and $NO_X$) from boilers can be effective in reducing the final HM discharge from the stack flue gas. By the end of 2012, the application rate of dust collectors for removing fly ash in thermal power plants of China has been dominated by electrostatic precipitators (ESPs), with a share approximately 94% of totals, followed by about 6 percent of fabric filters (FFs) or FFs plus ESPs. Meanwhile, the wet flue gas desulfurization (WFGD) and selective catalytic reduction (SCR) have been

increasingly utilized in coal-fired power plants to reduce $SO_2$ and $NO_X$ emissions in recent years, and the installed capacity proportion of FGD and SCR have amounted to about 86.2% and 25.7% of the total installed capacity, respectively (MEP, 2014a, b). However, compared with coal-fired power plant boilers, there are still many small and medium scale industrial boilers which are equipped with cyclones and wet dust collectors to reduce fly ash emissions, and fewer FGD and de-$NO_X$ devices have been installed to abate $SO_2$ and $NO_X$ emissions. In this study, we adopt the arithmetic mean values of those reported in available literatures as the average synergistic removal efficiencies by different APCD configurations, as shown in Table 1 and Supplement Table S11.

Residential sector is another important coal consumer in China. The traditional cook stoves and improved cook stoves are major combustion facilities for residential cooking and heating, both of which are normally without any PM and $SO_2$ control devices. There is little information about the real-world test results of HM emissions through residential coal use of China. Hence, we choose to use the averaged emission factors for coal/briquette combustion provided by AP42 (US EPA, 1993), NPI (DEA,1999) and NAEI (UK, 2012), and the assumed emission factors of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn by residential coal use are also listed in Table 1.

## 2.2 Methodology of HM emissions from non-coal combustion sources

HM emissions from non-coal categories are calculated as a product of annual activity data (e.g., fuel consumption, industrial products yields, etc.) and specific emission factors of varied HMs. The basic calculation can be described by the following equation:

$$\mathrm{E}(\mathrm{t}) = \sum_{i}\sum_{j}(A_{i,j} \times EF_j) \quad (2)$$

where $E$ is the atmospheric emissions of each heavy metal; $A$ is the annual production yield of industrial producing processes, volume of municipal solid wastes incineration, or liquid fuel and biofuel consumption, etc.; $EF$ is the assumed average emission factors; and $j$ is the emission source classified by source sub-categories (see Supplement Table S1).

Notably, atmospheric emissions of Pb have significantly dropped in China, as a result of unleaded gasoline introduction since the early 2000s. The proportion of lead

in leaded gasoline emitted to the air is estimated at about 77% (Biggins and Harrison, 1979) or 75% (Hassel et al., 1987), and thus this parameter is assumed at about 76% for the period before 2000 in this study. Consequently, for leaded gasoline used by motor vehicles in China, the total Pb emitted to the atmosphere is calculated according to the following equation:

$$E(t) = \sum_i (0.76 \times C_{Pb} \times A_i) \quad (3)$$

where *E(t)* is the emissions of Pb from motor vehicle gasoline combustion in calendar year *t*; $C_{Pb}$ is the average content of lead in gasoline; $A_i$ is annual gasoline consumption in one province, autonomous region or municipality *i*.

For brake and tyre wear, the atmospheric emissions of several HMs are estimated by the following equation:

$$E(t) = \sum_i \sum_j \sum_k (P_{i,j} \times M_j \times EF_{j,k} \times C_k) \quad (4)$$

where *E(t)* is the atmospheric emissions of As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu or Zn in calendar year *t*; $P_{i,j}$ is the population of vehicles in category *j* (passenger car, bus and coach, light-duty truck, and heavy-duty vehicle) in province, autonomous region or municipality *i*; $M_j$ is the average annual mileage driven by vehicle in category *j*; $EF_{j,k}$ is the emission factor of TSP (total suspended particles) for brake lining or tyre *k* by vehicle category *j*; $C_k$ is the averaged concentration of each heavy metal in brake lining or tyre *k* . Relevant parameters are summarized in the Supplement Table S12−S13.

### 2.2.1. Algorithm for determination of dynamic emission factors

Because remarkable changes in products, devices, processes as well as practices (technology improvement) have imposed positive effects on emission reductions of pollutants with the growth of economy and the increasing awareness of environment protection, the resulting pollutant emission level at any given time is a competition between technology improvement and production growth. Consequently, one of the major challenges in this study is to develop a reasonable representation of the time-varying dynamic emission factors of HMs associated with each primary industrial activity.

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. The basic formulas can be expressed as follows:

$$EF_k(t) = \left(EF_{a_k} - EF_{b_k}\right) e^{\left(-\frac{(t-t_0)^2}{2s_k^2}\right)} + EF_{b_k} \quad (5)$$

where $EF_k(t)$ is the emission factor for process $k$ in calendar year $t$; $EF_{a_k}$ represents the emission level for process $k$ in pre-1900; $EF_{b_k}$ is the best emission factor achieved in China for process $k$ at present; $s_k$ is the shape parameter of the curve for process $k$ (like the SD); and $t_0$ is the time at which the technology transition begins (pre-1900).

Based on the above method, we build the dynamic representation of HM emission factors to reflect the transition from uncontrolled processes in pre-1900 to the relatively high efficiency abatement processes in 2012. Parameters for some of these transitions are discussed throughout the paper, and are summarized in Supplement Table S14. Actually, on the basis of Eq. (5), the specific vales of shape parameter of the curve ($s$) can be determined when we obtain the definite values of unabated emission factor in pre-1900 and the best emission factor achieved at present

for each industrial process in China. In addition, several values of *s* are cited from Street et al. (2011) if only limited information about emission level for certain processes can be gained.

### 2.2.2. Dynamic HM emission factors of nonferrous metals smelting

By 2010, bath smelting (e.g. Ausmelt smelting, Isa smelting, etc.), flash smelting and imperial smelting process (ISP) smelting represent the three most commonly used techniques for copper smelting, representing about 52%, 34% and 10% of Chinese copper production, respectively. For lead smelting, sintering plus blast furnace technique (traditional technique) and bath smelting (e.g. oxygen side-blowing, oxygen bottom-blowing, etc.) plus blast furnace technique (advanced technique) are the two most commonly used techniques in China, accounting for about 48% and 47% of lead production, respectively. With respect to zinc smelting, hydrometallurgy is the predominant technique in China, representing about 77% of the zinc production capacity. The remaining share is divided among vertical retort (VR) pyrometallurgy (~10%), imperial smelting process (ISP) pyrometallurgy (~7%) and other pyrometallurgy (~6%). Especially, VR pyrometallurgy is regarded as an outdated technique which is mandated to be shut down gradually and will be totally eliminated in the near future.

Because of limited information and lack of field experimental tests on HM emissions in these source categories in China, some emission factors for this source category are cited from published literature, with only nationally averaged levels. Streets et al. (2011) indicate that China, Eastern Europe and Former USSR can be regarded as a uniform region with similar levels of technology development, whose emission factor trajectories are identical. Therefore, we presume the emission factors of HMs with higher abatement implementation in Eastern Europe, Caucasus and Central Asia countries are equivalent to those in China at the same calendar year (see Fig. 1a). Based on above assumptions and default abatement efficiencies of HMs in nonferrous metals smelting sectors (EEA, 2013), as well as other specific emission factors of HMs from published literature to date (Nriagu, 1979; Pacyna, 1984; Pacyna and Pacyna, 2001), the unabated emission factors are determined (see Supplement Table S15−S16).

Presently, compared to those for primary smelting of Cu/ Pb/ Zn, there is much less information about emission factors of HMs for secondary metals smelting of Cu/

Pb/ Zn and other nonferrous metals (Al, Ni and Sb) smelting from published literature. Hence, it is much difficult to estimate the all-timing emission factors of HMs from above sectors by using of S-shaped Curves due to lacking of necessary baseline information. We presume the average emission factors for secondary metal (Cu, Pb and Zn) smelting, aluminum smelting, antimony smelting and nickel smelting remain unchanged before the year 1996, at which the *Emission Standard of Pollutants for Industrial Kiln and Furnace* is first issued in China. We also presume the average emission factors of HMs from secondary metals smelting and other nonferrous metals smelting for developing countries used in Pacyna and Pacyna report (2001) and Eastern Europe, Caucasus and Central Asia countries with limited abatement referred in EEA Guidebook (EEA, 2009; S. V. Kakareka, personal communication, 2008), as well as United Kingdom applied in emission factors database of NAEI pre-1990 (UK, 1995) are reasonable for China before the year 1996. Subsequently, atmospheric emission factors of HMs from nonferrous metals industry in China decrease gradually with the implementation of tightened emission limits regulated by the gradually stricter *Emission Standards of Pollutants from Nonferrous Metals Industry* (e.g., GB 9078−1996, GB 25465−2010, GB 25466−2010, GB 25467−2010, etc.).

With respect to gold smelting (large scale) and mercury mining industries, the time-varying Hg emission factors from these two subcategories are determined by referring to studies carried out by Feng (2005), Streets et al. (2005; 2011), Pacyna and Pacyna (2006) and Pirrone et al., (2010). Specific emission factors of HMs from nonferrous metals smelting sectors can be seen in Supplement Table S16.

### 2.2.3. Dynamic HM emission factors of ferrous metal smelting

Currently, the blast furnace is the most primary technique for pig iron production in China. For steel making, there are two main routes: (1) “Ore-BF-BOF-Steelmaking route” based on blast furnace (BF) and basic oxygen furnace (BOF), (2) “scrap-EAF-Steelmaking route” based on electric arc furnace (EAF) using steel scrap or sponge iron as basic raw materials (Zhang and Wang, 2008). In spite of environmental friendly and flexibility to produce variety of value added grades of steel for EAF, the share of electric furnace steel in Chinese output of crude steel only accounts for about 8.9% in 2012 mainly due to the shortness of steel scrap resources in China (CISA, 2013).

Comparing with the national emission standard of air pollutants for iron smelting

industry in China with those in certain European Union countries (e.g. United Kingdom, Germany, Netherlands, Austria, etc.), we choose to use the emission factors of HMs for iron smelting industry obtained from emission factors database of NAEI in 2000 as the national average emission factors for iron smelting of China in 2015. This is mainly because the PM emission limits of existing facilities for iron smelting of China in 2015 (20 mg $m^{-3}$) is approximately comparable to these of European Union countries in the early 2000s (IRIS, 2005; MEP, 2012). With respect to steel smelting, the emission factors of HMs with higher abatement in Eastern Europe, Caucasus and Central Asia countries are chosen as the national average emission factors of this sector in China at the same calendar year (see Fig. 1b). The unabated emission factors of HMs for pig iron and steel production are determined by using of the similar method discussed above for nonferrous metals smelting industry. Please see Supplement Table S16 and Table S17 for more details about specific emission factors.

### 2.2.4. Dynamic HM emission factors of non-metallic mineral manufacturing

Cement, glass and brick manufacturing are the major mineral commodity industries. During the manufacturing process, various HMs vaporing from raw materials and feed fuels associated with fine particulate matters are emitted from the kiln system at high temperatures.

Currently, the new dry rotary kiln process is the dominant technology in cement manufacturing factories of China, representing over 92% of the national total cement output. The emission ceilings of air pollutants for cement, glass or brick manufacturing specified in the present standards of China (e.g., GB 4915−2013, GB 26453−2011, GB 29620−2013, etc.) are less stringent compared with those of developed countries (see Supplement Table S18). By contrasting the emission limits of air pollutants from non-metallic minerals (cement, glass and brick) manufacturing between China and developed countries, we presume the best emission factors of air pollutants achieved in China today are approximately identical to the average emission factors of developed countries in the end of 1990s. With respect to cement production, the unabated emission factors of HMs can be obtained from the Web Factor Information Retrieval System (WebFIRE) (US EPA, 2012). Moreover, the average emission factors for glass and brick manufacturing are assumed to remain unchanged pre-1996. Subsequently, atmospheric emission factors of HMs from these

two sub-source categories decrease gradually with the implementation of gradually tightened emission limits from above mentioned Emission Standards of Pollutants from non-metallic mineral manufacturing industry. Specific emission factors of various HMs from non-metallic mineral manufacturing can be seen in Supplement Table S16.

### 2.2.5. HM emission factors of biomass burning

China is the biggest developing country in the world. The rural population still accounts for nearly 47.4% of total population in 2012 (NBS, 2013a), and it has had a long history of using agricultural residues and firewood to satisfy household energy demand for cooking and heating. Recently, crop residues have become more commonly burned in open fields during the harvest season. Abundant gaseous and particulate pollutants emitted by open biomass burning have caused severe regional air pollution and contributed to worsening of haze events in the central and eastern China (Cheng et al., 2014; Li et al., 2014).

In this paper, the total mass of ten crop straws burned is calculated based on the method discussed in previous studies by Tian et al. (2011b) and Lu et al. (2011), including paddy, wheat, maize, other grains, legumes, tubers, cotton, oil plants, fiber crops and sugar crops. Because of quite limited field test data about HM emission characteristics from crop straw for household use and firewood for open burning, we presume HM emission factors from biofuel for open burning are equal to those for household use. It is acknowledged that this simple assumption may introduce additional uncertainties, and thus relatively large uncertainty ranges for HM emission factors of biofuel combustion are applied in the analysis, which merits deep investigation in the future. The average emission factors of HMs from these ten crop straw and firewood are summarized in Supplement Table S16.

### 2.2.6. HM emission factors of liquid fuels combustion

Besides major conventional pollutants (PM, $SO_2$ and $NO_X$), liquid fuels combustion generates emissions of potentially toxic HMs. Here, the liquid fuels are sorted into crude oil, fuel oil, kerosene, diesel and gasoline.

Historically, leaded gasoline combustion by vehicles has been recognized as the most significant contributor for the increase of human blood lead level (Robbins et al., 2010). Leaded gasoline has been forced out of the market place in China since July 1,

2000 due to the adverse health effects on the neurologic and/or hematologic systems (Xu et al., 2012). Compared to the Pb content limits of 0.64 g $L^{-1}$ (GB 484−64, 1949−1990,) and 0.35 g $L^{-1}$ (GB 484−89, 1991−2000) in leaded gasoline, the average lead content in unleaded gasoline is regulated less than 0.005 g $L^{-1}$ (GB 17930−1999, 2001−2012). Consequently, $C_{Pb}$ in equation 3 is chosen to be 0.64 g $L^{-1}$, 0.35 g $L^{-1}$, and 0.005 g $L^{-1}$ for the three corresponding periods, respectively (Qin, 2010). All the other average emission factors of HMs from each type of liquid fuel are summarized in Supplement Table S16.

### 2.2.7. Dynamic HM emission factors of municipal solid waste incineration

For municipal solid waste (MSW) incineration, emission characteristics of HMs significantly depend on the concentration of metals in the feed wastes, the performance of installed APCDs, combustion temperatures, as well as composition of the gas stream (Chang et al., 2000).

Presently, stoke grate and fluidized-bed combustion are the major MSW incineration technologies being used in China. Because of relatively high costs and the heat content requirement for the feed MSW (> 6000−6500 kJ $kg^{-1}$, or supplementary fuel is necessary), stoke grate incinerators are typically used in eastern coastal areas, especially in the economically more developed cities (Nie, 2008), taking a share of over 58% by the end of 2010 (Cheng and Hu, 2010; Tian et al., 2012d). Fluidized-bed incinerators, in contrast, are mainly adopted in the eastern small and mid-sized cities, as well as the large cities in the middle and western parts of China, taking a relatively small proportion, mainly due to the lower treatment capacities (Cheng and Hu, 2010).

To estimate the hazardous air pollutant emission inventory from MSW incineration in China, Tian et al. (2012d) have compiled and summarized the comprehensive average emission factors of hazardous HMs (Hg, As, Pb, Cd, Cr, Ni and Sb) for MSW incineration from published literature. Additionally, the emission ceiling of HMs for the existing incinerators in the newly issued standard (GB 18485−2014) which will be conducted in 2016 is approximately comparable to those in Directive 2000/76/EC (see Supplement Table S18). Here, we presume the best emission factors of HMs in China for MSW at 2016 are almost equivalent to those in developed EU countries at 2000. Based on specific emission factors of HMs for MSW incineration from published literature (Nriagu, 1979; Pacyna, 1984; Nriagu and

Pacyna, 1988) and certain emission factors of HMs with uncontrolled technology from *AP42, Fifth Edition, Volume I, Chapter 2: Solid Waste Disposal* (US EPA, 1996), the unabated emission factors of HMs from this source category are determined. Specific emission factors of various HMs from MSW incineration can be seen in Supplement Table S16.

### 2.2.8. HM emission factors of brake and tyre wear

Brake linings as well as tyres wear of vehicles is known as one of the important emission sources of particulate matter to the surrounding environment, particularly in urban areas (Hjortenkrans et al., 2007). Notably, not all of the worn materials of brake lining and tyre will be emitted into atmosphere as airborne particulate matter (Hulskotte et al., 2006). Here, we adopt the average emission factors of TSP from brake wear and tyre wear for passenger cars (0.0075 g $km^{-1}$ and 0.0107 g $km^{-1}$), light-duty trucks (0.0117 g $km^{-1}$ and 0.0169 g $km^{-1}$) and heavy-duty vehicles (0.0365 g $km^{-1}$ and 0.0412 g $km^{-1}$) obtaining from EEA Guidebook (EEA, 2013) as the average emission factors of airborne particulate matter from brake and tyre wear.

In addition to steel as brake pad support material, the agents present in brake linings usually consist of Sb, Cu, Zn, Ba, Sn and Mo (Bukowiecki et al., 2009). Further, antimony is presented in brake linings as $Sb_2S_3$ that serves as a lubricant and filler to improve friction stability and to reduce vibrations. Then, $Sb_2S_3$ is oxidized to $Sb_2O_3$ (possibly carcinogenic substance) during the braking process, which have been proved to be partially soluble in physiological fluids (Gao et al., 2014; von Uexküll et al., 2005). Because of the excellent characteristic of thermal conductivity, copper or brass are widely used for automotive braking as a major ingredient in friction materials (Österle et al., 2010). Additionally, although zinc is a less specific marker for brake wear than antimony and copper, it has also been reported to be another important constituent of brake wear (Johansson et al., 2009). 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).

Because of limited information and lack of field experimental tests on HM contents in brake linings and tyre in Chinese vehicles, and substantial quantity of vehicles sold in China that are imported from foreign countries or manufactured by the foreign-invested transnational vehicle companies, we presume the composition of

worn materials from brake and tyre wear in term of HMs are consistent with foreign countries (see Supplement Table S13).

## 2.3 Activity data

Coal and liquid fuels consumption data by sectors in provincial-level (e.g., power plant, coal-fired industrial boiler, coal-fired residential sector, coal-fired other sectors, etc.) are collected from *China Energy Statistical Yearbooks*. Industrial production data by provinces (e.g., the output of ferrous/nonferrous metals products, production of cement/glass/brick, amount of municipal wastes incineration, population of vehicle, etc.) are compiled from relevant statistical yearbooks, such as *China Statistical Yearbooks*, *the Yearbook of Nonferrous Metals Industry of China*, *China Steel Yearbook*, etc. The detailed data sources for the main sectors are listed in Supplement Table S19. Furthermore, trends of activity levels by different sectors in China between 2000 and 2012 are summarized in Supplement Fig. S1−S5.

## 2.4 Evaluation of Potential Uncertainties

It is necessary to examine the potential uncertainty in emissions by sources and regions to quantify the reliability and identify improvements space of emission inventory in the future. A detailed uncertainty analysis is conducted by combining uncertainties of both activity levels and emission factors, through adopting Monte Carlo simulation (Zhao et al., 2011; Tian et al., 2014a; Tian et al., 2014b). Streets et al. (2003) indicate that there is no way to judge the accuracy of activity data estimates. Furthermore, uncertainties are still inevitable when representative values are selected for specific emission sources, countries and regions in spite of emission factors adopting from detailed experiments.

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.

## 3 Results and discussion

### 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 begin to change after 2006 due to the implementation of policies of energy-saving and pollution reduction, especially the strengthening of $SO_2$ 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 $SO_2$ 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 1060t 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

698 dominant contributor to the Zn emissions, accounting for about 60.9–62.9% during
699 this period.
700 In order to facilitate understanding of historical HM emissions in China, the
701 details about temporal variation trends of HM emissions from liquid fuels combustion
702 and brake and tyre wear are discussed in the Supplement Section S3.

703 **3.2 Composition of HM Emissions by province and source category in 2010**

704 The total emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn from
705 primary anthropogenic sources by provinces in China for the year 2010 are estimated
706 at about 72955.1 t. As can be seen in Fig. 4, coal combustion sources represent the
707 major contributors of Hg, As, Se, Pb, Cr, Ni, Mn, Co and Cu emissions and are
708 responsible for about 50.6, 74.2, 64.6, 60.1, 90.4, 56.2, 80.9, 98.6 and 53.4% of total
709 emissions, while their contribution to the total Cd, Sb and Zn emissions are relatively
710 lower, at about 32.7, 39.3 and 39.8%, respectively.
711 Among all the coal consuming sub-sectors, coal consumption by industrial
712 boilers ranks as the primary source in national total emission of twelve HMs, with the
713 average proportion about 57.7% of the total emission from coal combustion. This may
714 be attributed to the significant coal consumption of industrial boilers (about 1117.3 Mt
715 in 2010) and relative high share of boilers with inadequate APCDs (Cheng et al., 2015;
716 NBS, 2013b).
717 As the largest coal consumer in China, coal consumption by power plants is
718 identified as the second largest contributor and takes about 14.0% in national total
719 emission of twelve HMs. In order to achieve the emission reduction of PM, $SO_2$ and
720 $NO_X$ for satisfying the national or local emission reduction goals for the year 2010
721 (the end year of 11th FYP) (NBS, 2011; Tian et al., 2014a), a series of control policies
722 have been implemented, including replacement of small coal-fired plant units with
723 large and high efficiency units and the continuously increasing application rate of
724 advanced APCDs systems (e.g., ESP, FFs, WFGD, SCR, etc.). Consequently, the final
725 discharge rates of HM from power plants have decreased obviously even though the
726 volume of coal consumption has grown substantially (see Fig. 2 and Fig. S1).
727 China has been the world's largest producer of pig iron and steel by a rapidly
728 growing margin. By the end of 2012, the output of steel has amounted to 723.9 Mt,
729 accounting for about 46% of worldwide steel production (CISA, 2013). Despite
730 enormous achievement obtained by China's iron and steel industry, China is still

731 featured as a steel producer with low energy efficiency and high pollutants emission
732 level compared with other major steel-producing countries (Guo and Fu, 2010).
733 Because of limited application of FGD and de-$NO_X$ devices and poor control of PM,
734 ferrous metals smelting sector ranks as the third largest contributor, occupying about
735 13.2% of the national total emission of twelve HMs. In terms of Zn emission, the
736 share from this sector is dominant, accounting for about 32.2% of the total.

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

749 It can be concluded that the emissions of HMs from brake wear are well
750 associated with vehicle amount, vehicle mileage as well as the contents of HMs in
751 brake linings and tyre. Currently, numerous of studies have reported that airborne
752 HMs (e.g. Sb, Cu, Zn, etc.) in urban areas are associated with road traffic and more
753 definitely with emissions from brake wear (Gómez et al., 2005; Hjortenkrans et al.,
754 2007). As can be seen from Fig. 4h, k, brake and tyre wear sector takes the largest part
755 of 39.9 and 26.3% in national Sb and Cu emissions, respectively. Therein, brake wear
756 is the absolutely dominant sub-contributor, accounting for over 99.9 and 99.6% for Sb
757 and Cu emissions from this sector in 2010, respectively. This is mainly due to the high
758 contents of Sb and Cu in the brake linings (see Table S13, Hjortenkrans et al., 2007)
759 and the explosive expansion of vehicle population in China (see Fig. S5).
760 Nevertheless, the adverse effects of airborne PM originated from brake wear on
761 human health and ecosystem are still not received sufficient attention from the
762 policymakers as well as the public.

763 Specially, although non-metallic mineral manufacturing sector is not the
764 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-l, 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 μg $g^{-1}$, 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 μg $g^{-1}$, which is two times higher than the national averaged concentration of Cr in coal as consumed in China, see Table S8).

### 3.3 Spatial variation characteristics of HM emissions

The spatial distribution patterns of HM emissions from anthropogenic sources are illustrated in Fig. 5. In this study, 1796 power plants with capacity larger than 6000 kW, 566 copper/lead/zinc smelting plants, 33 large iron and steel plants and 101 MSW incineration plants are identified as large point sources and their emissions are precisely allocated at their latitude/longitude coordinates (the geographical distribution of 2496 point sources in China is shown in Supplement Fig. S7). It should be noted here, the emissions from point sources of nonferrous metals smelting industry and ferrous metals smelting industry contain two parts: emissions originate from fuel combustion and emissions emit from industrial production processes.

Except the emissions from point sources discussed above, the remaining anthropogenic sources in provincial level are all treated as regional area sources. The specific method of geographical location for area sources has been discussed in our previous studies (Tian et al., 2012b; Tian et al., 2012c).

The spatial variation is closely related with the unbalanced economic development and population density in the Chinese mainland, so that these twelve typical HM emissions are distributed very unevenly from one area to another, with the annual As emissions at province level ranging from 0.009 kg $km^{-2}$ in Qinghai to 1.6 kg $km^{-2}$ in Shandong, for instance. One notable characteristic of the spatial distribution of China's HM emissions is that the HM emission intensities are much higher in the central and eastern China than those in the western China, and the coastal regions are zoned as most polluted areas of varied HMs. The emissions of HMs from Hebei, Shandong, Henan, Jiangsu, Shanxi, and Liaoning provinces almost account for about 39.4% of the total emissions of these HMs. These above six provinces are characterized by extensive economy growth mode, large volume of coal consumption and various industrial products output, as well as high population density. Therefore, more energy consumption and higher travel demand need to be fulfilled in these six provinces, compared to those in other provinces and districts, resulting in higher HM emission intensity.

Moreover, several provinces in the southwestern and central-southern regions also play a prominent role in these twelve HM emissions, especially for Guizhou, Sichuan, Yunnan, Hubei and Hunan provinces. In general, Guizhou province starts out with high emissions of HMs from coal consumption by other sectors, mainly owing to both the high HM contents in the feed coals and the large magnitude of coal consumption by this sector. In addition, the nonferrous industries of Hunan and Yunnan provinces are flourishing, especially the copper and zinc smelting industries. Consequently, nonferrous metals smelting sector is demonstrated as one of major source of Cu and Zn emission in these two provinces.

The situations of atmospheric HM concentrations in aerosols of 44 major cities in China during the last 10 years have been reviewed comprehensively by Duan and Tan (2013). Their results indicate that the ambient concentrations of HMs (As, Pb, Cd, Cr, Ni, Mn, Cu and Zn) is high in some cities, including Beijing, Tianjin, Shijiazhuang, Shenyang, Harbin, Jinan, Zhengzhou, Hangzhou, Nanjing, Hefei, Xian, Yinchuan, Urumqi, Wuhan, Changsha, Chongqing, Guangzhou, Shenzhen, Foshan,

Shaoguan, etc. For HM emissions on the civic scale in 2010, these above twenty cities with high HMs concentrations also represent primary cities with HM emissions in China (see Fig. 5). In general, the spatial distribution characteristics of gridded HM emissions from primary anthropogenic sources for the year 2010 in this study are reasonable and representative of the real situation of these HM pollutions.

### 3.4 Uncertainty analysis

Emissions of varied HMs from primary anthropogenic sources with uncertainties in 2010 are summarized in Fig. 6 and Supplement Table S22. As can be seen, the overall uncertainties of the total emissions in our inventories quantified by Mote Carlo simulation are -39.1−50.8%. Among all the coal combustion sectors, uncertainties for thermal power plants emissions are smallest, whereas those for coal-fired residential sectors and coal-fired other sectors are considerable. These are mainly attributed to the relatively poor resolution of coal burning technologies and emission control devices in these two sub-categories. In contrast, relatively higher uncertainties are observed in the non-coal combustion categories, particular for non-metallic mineral manufacturing and brake and tyre wear emissions. These high uncertainties of HM emissions can be mainly attributed to imprecise statistics information, poor source understanding, as well as lacking adequate field test data in China.

Specially, the earlier statistical data for activity level are considered to have high uncertainty for developing country (including China) with less developed statistical systems. Unfortunately, we have to acknowledge that it is quite difficult to accurately assess the specific uncertainty of activity data from China's earlier official statistics. Akimoto et al. (2006) argue that the energy consumption of China during 1996–2003 is not recommended for use in the study of emission inventories due to the probable underestimates. However, the discrepancies in coal consumption from power sector are considered to be less than ±5%, which do not dominate the emission uncertainties (Wu et al., 2010; Zhao, et al., 2008). In order to approximately quantify the uncertainty of activity data, we divide the whole period of 1949 to 2012 into three stages with respect to economic development and emission control: before reform and opening (1949–1978), intermediate stage (1979–2005), and the total amount control stage of atmospheric pollutants (2006–2012). For activity level of anthropogenic sources obtained from official statistics after 2006, we assume normal distributions with sector-dependent uncertainties (see Supplement Table S20). On the basis of

above discussion and consideration, the uncertainty of activity data from official statistics during the two early periods of 1949–1978 and 1979–2005, are assumed to be about 2 and 1.5 times of those in the period of 2006–2012, respectively.

The combined uncertainty bounds for the national emissions of twelve HMs during the historical period are shown in Fig. S8. In general, the range of uncertainty has gradually diminished over time. For example, we calculate an uncertainty level of -90.1–125.7% (95% confidence interval) in the estimate of national Hg emissions in 1949, which is higher than those of other eleven HM emissions (between -90.0% and 119.3%). This is mainly attributed to remarkable emissions from several Hg sources that have the largest uncertainty in both activity levels and emission factors, such as gold smelting and mercury mining. Since then, the relative uncertainties have gradually decreased from the beginning to the end of the period. This is primarily because more reliable activity data with smaller coefficient of variation (CV) from related yearbooks and reports become available. The uncertainty range of national Hg emissions is estimated to -40.6–55.8% by 2003, which is well comparable with estimates of ±44% for China's Hg emissions by Wu et al. (2006). By the end of 2012, the overall uncertainty level has reduced to -39.0–47.0% for the national HM emissions.

Generally speaking, emission inventories are never complete and perfect, and most emissions estimates possess a significant associated uncertainty mainly owing to the lack of representativeness of specific emission factors and the reliability of each-source specific activity data. In this study, we have made great efforts to evaluate the historical trend of these HM emissions by collecting detailed activity levels for various source categories, adopting the best available dynamic emission factors for various anthropogenic sources in China today, and integrating publication literature and reports from developed countries and districts. Nevertheless, considerable uncertainties are still present, and this may lead to under- or over-estimation of HM emissions from some source categories. Consequently, more detailed investigation and long-term field tests for all kinds of coal-fired facilities and industrial production processes are in great demand.

### 3.5 Proposals for future control policies

Presently, control of atmospheric HM emissions still has not received sufficient attention by the government and public in spite of the frequent occurrence of HM

pollution in China (especially for provinces with high point sources of HM emissions). The implementation of more rigorous emission standards on primary anthropogenic sources (thermal power plant, coal-fired boiler, nonferrous metallurgy, pig iron and steel production, etc.) and national ambient air quality standards (NAAQS) are regarded as the important triggers to promote enterprises diminishing HM emissions. Therefore, the MEP should speed up the revision of the system of hazardous air pollutant (including HM) emission standards, and strengthen the amendment of NAAQS. Especially, brake wear has been confirmed to be the main source of HM emissions from traffic, particularly in urban areas. However, there is no related emission standard of air pollutants for brake wear. In the near future, the promulgation of emission standards of brake wear should be expected, which will further strengthen the control of atmospheric HM emissions in China.

In addition, some specific actions are suggested as follows: (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); (2) promote coal washing before combustion (the removal efficiencies of coal preparation for heavy metals can reach as high as approximately 30.0−60.0%, see Supplement table S9); (3) increase the application rate of advanced APCDs configurations in newly built or retrofitted coal-fired boilers; (4) initiate pilot-tests or demonstration projects for specified mercury control (SMC) technologies in some sectors with high Hg emissions and develop comprehensive HM control technologies capable of simultaneously removing multiple heavy metals; (5) strengthen energy conservation and boost electricity and/or heat generation using cleaned energy and renewable energy, such as nuclear, wind and solar energy; (6) suspend small-scale coal-fired boiler and industrial production plants with backward emission control technologies (e.g., cement plants, ferrous smelting plants, nonferrous smelting plants, etc.); (7) eliminate outdated production technology, such as VR pyrometallurgy and ISP pyrometallurgy; (8) improve cyclic utilization rate of nonferrous metals and ferrous metals during the period of 12th FYP; (9) etc.

## 4 Conclusions

We have calculated the historical emissions of 12 typical HMs from primary

manmade activities during the period of 1949−2012, based on the detailed statistical data at provincial level from various statistical yearbooks and adopting comprehensive time-varying dynamic emission factors from relevant researches and literature. Undoubtedly, taking consideration of the economic transition and emission control technology improvement, the dynamic emission factors used in this study will enhance the accuracy and reliability of estimation of HM emissions.

The total national atmospheric emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn from anthropogenic sources have increased by about 22−128 times during the period of 1949-2012, reaching at about 526.9−22319.6 tons in 2012.

In spite of the increasing coal consumption and gross industrial production, the national emissions of certain HMs (e.g., As, Se, Ni, Mn, Co, etc.) have been well restrained with the implementation of energy-saving and pollution reduction policies during 2006 to 2012. Especially, the declining share of HM emissions from industrial process sources (e.g., nonferrous metals smelting, ferrous metals smelting, non-metallic mineral manufacturing, etc.) caused by increasing installation of advanced pollutants control devices, has been partially counteracted by the added industrial production yields. Additionally, both high contents of antimony and copper in brake lining and the rapid growth of civilian vehicle population are thought to be the primary reasons for continuous significant growth rate of Sb and Cu emissions from brake and tyre wear during 2000 to 2012.

The spatial distribution characteristics of HM emissions are closely related with the unbalanced regional economic development and population density in China. One notable characteristic is that the HM emission intensities are much higher in the central and eastern China than those in western China, and the coastal regions are zoned as most polluted areas of HMs. Notably, because of the flourishing of nonferrous metals smelting industry, the southwestern and central-southern provinces also play a prominent role in HM emissions.

The overall uncertainties in our bottom-up inventories are thought to be reasonable and acceptable with the adequate data availability. Nevertheless, to achieve the more reliable estimation of HM emissions in China, much more detailed investigation and long-term field tests for all kinds of coal-fired facilities and industrial process are still in great demand in the future.

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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).

1216 **Table 1.** Averaged release rates and removal efficiencies of various HMs from coal-fired facilities and the installed APCDs.

| Category | | Hg | As | Se | Pb | Cd | Cr | Ni | Sb | Mn | Co | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Release rate (%) | Pulverized-coal boiler | 99.4 | 98.5 | 96.2 | 96.3 | 94.9 | 84.5 | 57.1 | 89.4 | 75.7 | 85.4 | 92.7 | 91.6 |
| | Stoker fired boiler | 83.2 | 77.2 | 81 | 40.1 | 42.5 | 26.7 | 10.5 | 53.5 | 16.2 | 25.2 | 25.7 | 16.3 |
| | Fluidized-bed furnace | 98.9 | 75.6 | 98.1 | 77.3 | 91.5 | 81.3 | 68.4 | 74.4 | 51.2 | 62.8 | 60.9 | 61.2 |
| | Coke furnace | 85.0 | 30.0 | 40.0 | 31.5 | 20.0 | 24.0 | 9.8 | 53.5 | 28.2 | 31.7 | 22.0 | 44.0 |
| | Residential stoves (mg $kg^{-1}$) | 0.065 | 0.095 | 0.65 | 3.7 | 0.033 | 0.52 | 0.30 | 0.009 | 0.22 | 0.047 | 0.094 | 0.33 |
| Removal efficiency (%) | ESP | 33.2 | 86.2 | 73.8 | 95.0 | 95.5 | 95.5 | 91.0 | 83.5 | 95.8 | 97.0 | 95.0 | 94.5 |
| | EF | 67.9 | 99.0 | 65.0 | 99.0 | 97.6 | 95.1 | 94.8 | 94.3 | 96.1 | 98.0 | 98.0 | 98.0 |
| | Cyclone | 6.0 | 43.0 | 40.0 | 12.1 | 22.9 | 30.0 | 39.9 | 40.0 | 67.0 | 72.0 | 60.0 | 64.0 |
| | Wet scrubber | 15.2 | 96.3 | 85.0 | 70.1 | 75.0 | 48.1 | 70.9 | 96.3 | 99.0 | 99.8 | 99.0 | 99.0 |
| | WFGD | 57.2 | 80.4 | 74.9 | 78.4 | 80.5 | 86.0 | 80.0 | 82.1 | 58.5 | 56.8 | 40.4 | 58.2 |
| | SCR+ESP+WFGD | 74.8 | 97.3 | 93.4 | 98.9 | 99.1 | 99.4 | 98.2 | 97.0 | 98.3 | 98.7 | 97.0 | 97.7 |

1217 **Table 2.** HM emissions from primary anthropogenic sources in China, 1949−2012 (tons/year).

| Year | Hg | As | Se | Pb | Cd | Cr | Ni | Sb | Mn | Co | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1949 | 12.7 | 45.2 | 53.7 | 312.6 | 15.5 | 158.6 | 147.3 | 16.3 | 212.1 | 11.5 | 74.0 | 226.8 |
| 1978 | 144.1 | 593.6 | 607.6 | 7206.2 | 82.5 | 1021.2 | 891.9 | 151.1 | 3616.5 | 295.3 | 1356.8 | 3396.0 |
| 1980 | 163.1 | 791.3 | 825.8 | 9744.8 | 98.0 | 1481.4 | 1101.5 | 193.9 | 4637.4 | 387.2 | 1745.6 | 4128.4 |
| 1985 | 209.7 | 1055.5 | 1168.7 | 12922.5 | 123.7 | 2353.5 | 1250.0 | 250.6 | 5736.8 | 478.8 | 2194.9 | 4896.5 |
| 1990 | 261.3 | 1311.7 | 1546.4 | 17644.0 | 156.2 | 3374.7 | 1667.5 | 337.3 | 7607.8 | 624.0 | 2880.5 | 6541.9 |
| 1995 | 351.1 | 1699.7 | 2179.8 | 17620.3 | 223.3 | 5155.0 | 2354.2 | 499.4 | 9454.9 | 778.7 | 4131.5 | 9564.5 |
| 2000 | 316.1 | 1673.2 | 2113.0 | 20193.5 | 255.9 | 4928.7 | 2407.0 | 566.1 | 10034.7 | 842.7 | 4733.0 | 10788.6 |
| 2005 | 492.3 | 2454.4 | 3058.1 | 10887.1 | 378.9 | 6828.5 | 3246.4 | 797.9 | 12195.4 | 1075.8 | 7101.1 | 15987.9 |
| 2006 | 509.3 | 2501.2 | 3146.8 | 11250.2 | 398.5 | 7179.0 | 3356.7 | 826.2 | 12181.6 | 1042.8 | 7201.1 | 16895.0 |
| 2007 | 533.8 | 2407.2 | 3067.2 | 11729.0 | 420.8 | 7445.2 | 3369.6 | 822.8 | 12528.9 | 1064.5 | 7600.0 | 18147.6 |
| 2008 | 564.8 | 2489.7 | 3136.1 | 12213.6 | 442.4 | 7755.7 | 3248.3 | 962.9 | 12499.8 | 1056.5 | 8208.7 | 18337.4 |
| 2009 | 589.7 | 2325.8 | 2936.1 | 12519.9 | 453.7 | 7810.2 | 3250.8 | 1006.0 | 12195.4 | 1010.7 | 8428.6 | 19035.8 |
| 2010 | 672.0 | 2322.9 | 2880.5 | 13194.5 | 455.8 | 7465.2 | 3138.6 | 1068.1 | 12015.9 | 919.2 | 8318.8 | 20503.7 |
| 2011 | 688.4 | 2422.8 | 3062.4 | 14032.4 | 493.9 | 7733.0 | 3440.1 | 1172.8 | 12657.3 | 981.2 | 9115.5 | 21876.0 |
| 2012 | 695.1 | 2529.0 | 3061.7 | 14397.6 | 526.9 | 7834.1 | 3395.5 | 1251.7 | 13006.6 | 1004.6 | 9547.6 | 22319.6 |

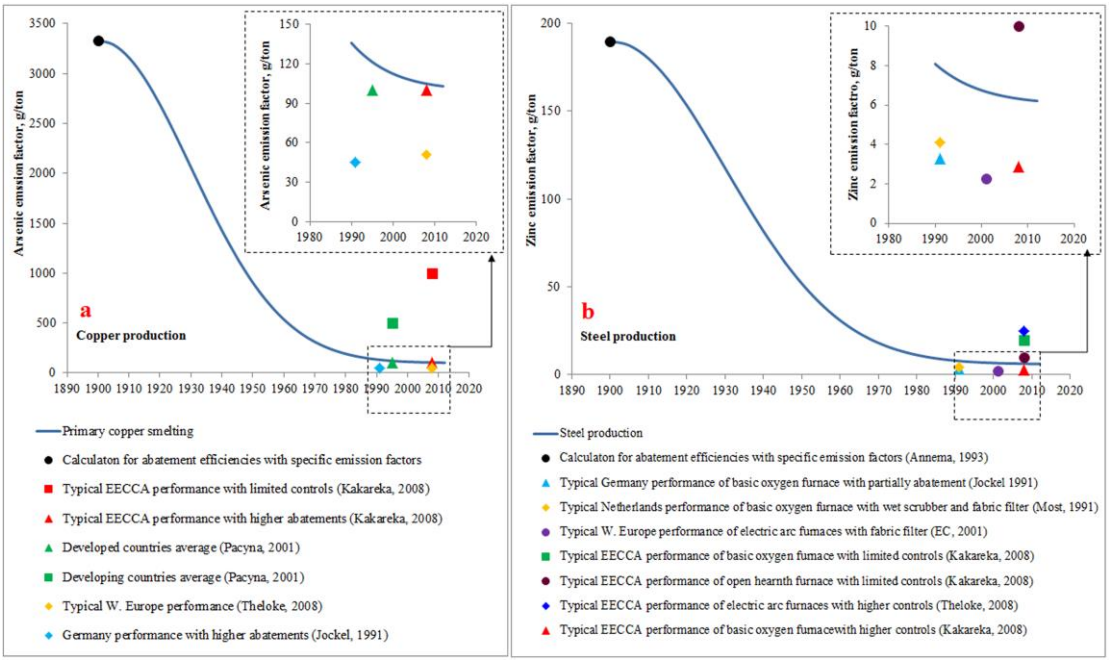


**Figure 1.** Time variation of arsenic emission factors for copper production and zinc emission factors for steel making in China (for instance)

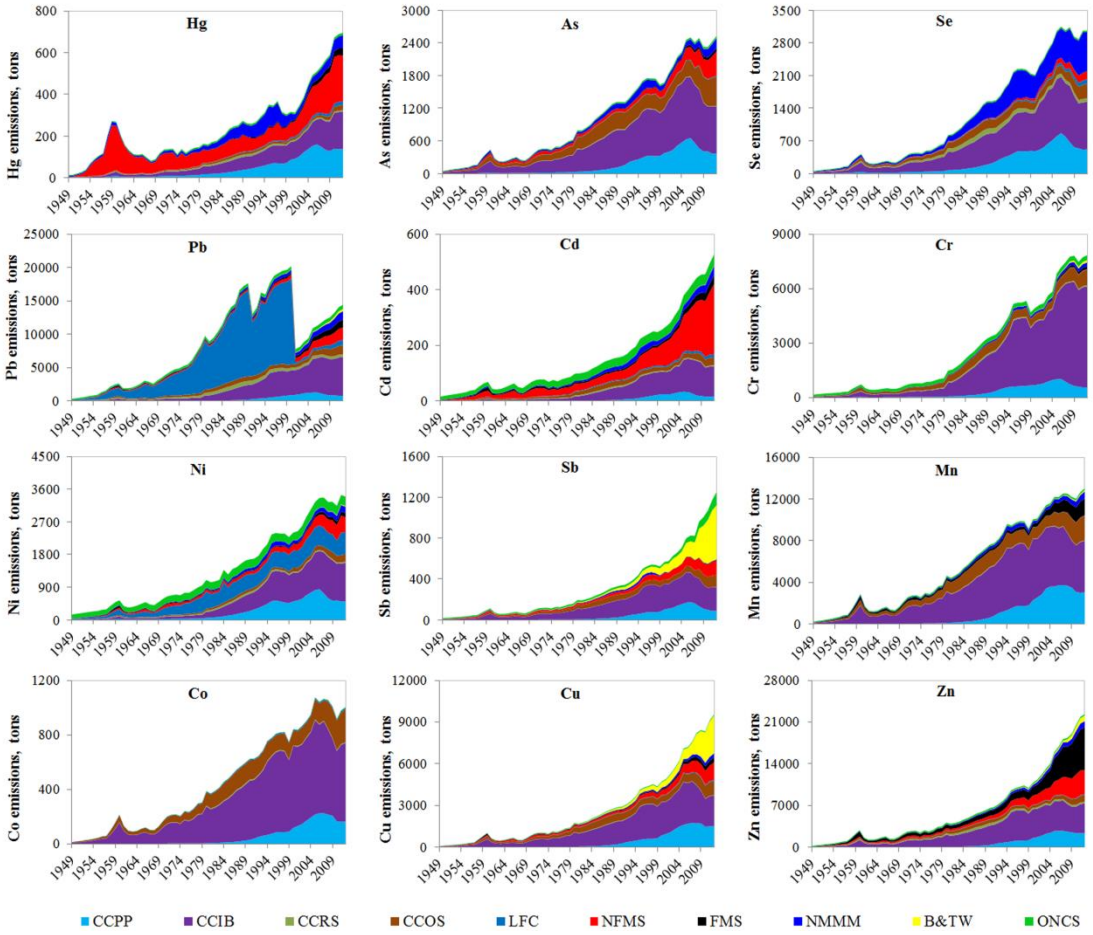


**Figure 2.** Historical trends of atmospheric HMs (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) emissions from primary anthropogenic sources in China, 1949−2012. CCPP, coal consumption by power plants; CCIB, coal consumption by industrial boilers; CCRS, coal consumption by residential sectors; CCOS, coal consumption by other sectors; LFC, liquid fuels combustion; NFMS, nonferrous metals smelting; FMS, ferrous metal smelting; NMMM, non-metallic minerals manufacturing; B&TW, brake and tyre wear; ONCS, other non-coal sources (including BB, biomass burning; MSWI, municipal solid waste incineration

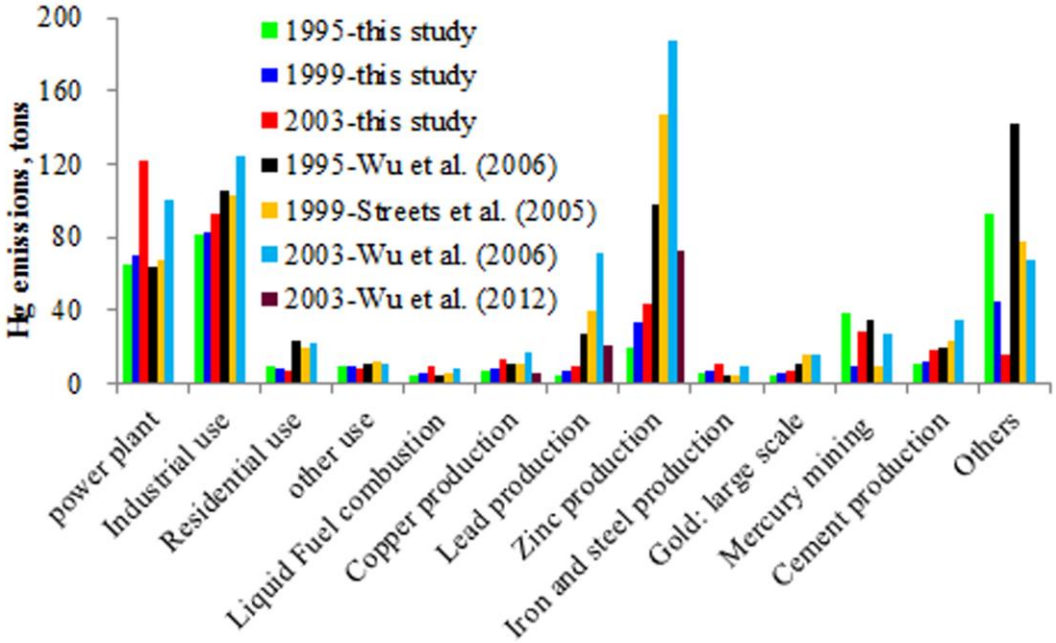


**Figure 3.** Estimate of annual Hg emissions from primary anthropogenic sources among various studies (t $yr^{-1}$).

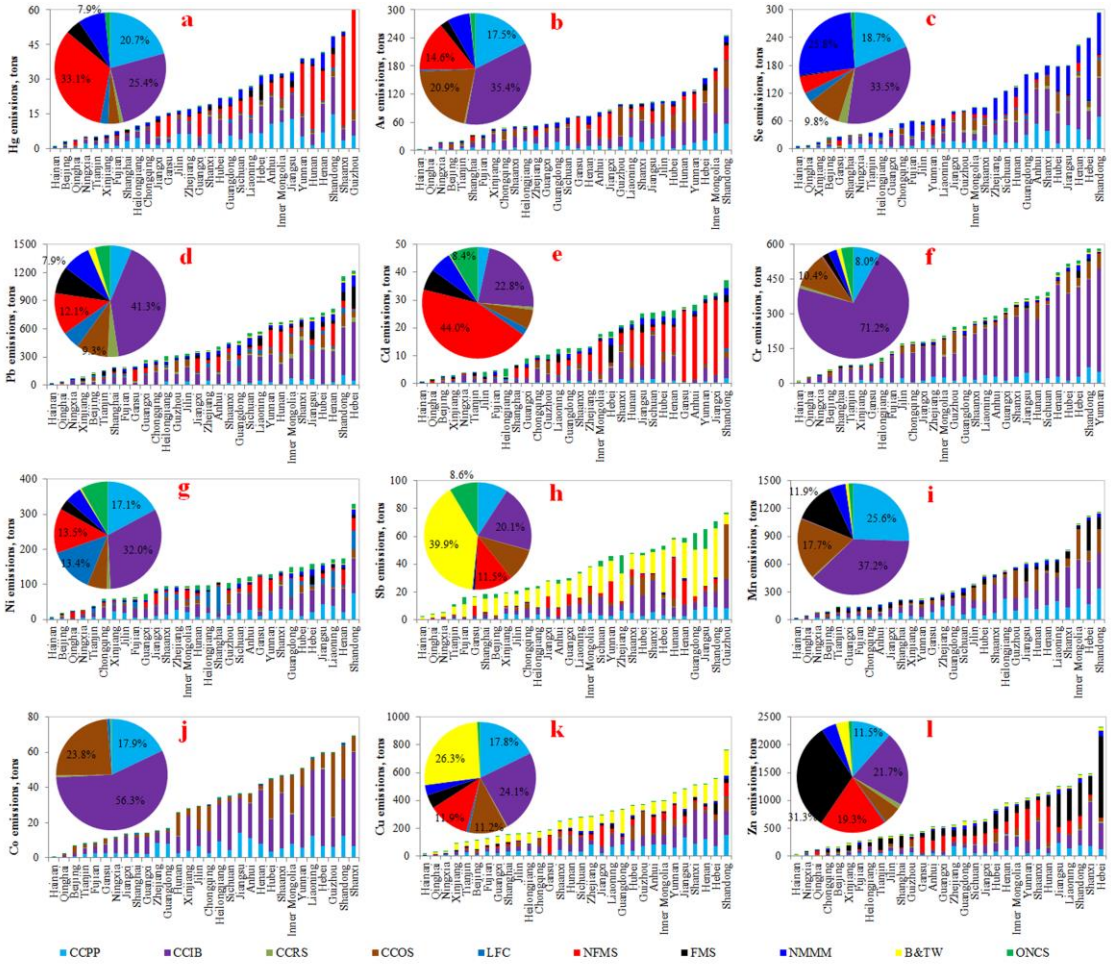


**Figure 4.** Provincial HM emissions from anthropogenic sources and national composition by source categories in 2010.

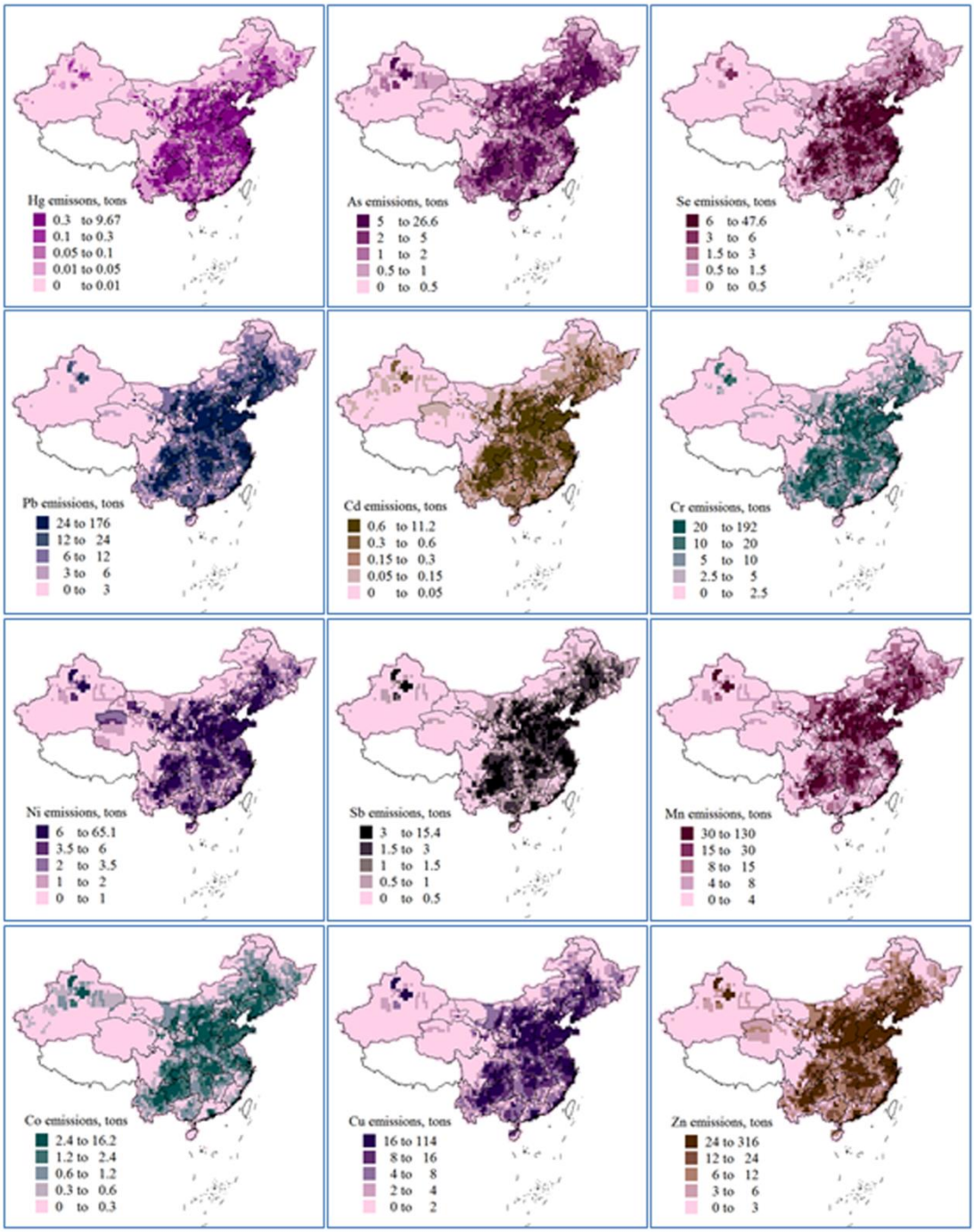


**Figure 5.** Gridded HM emissions from anthropogenic sources for the year 2010 (0.5° × 0.5° resolution; units, kilograms per year per grid cell).

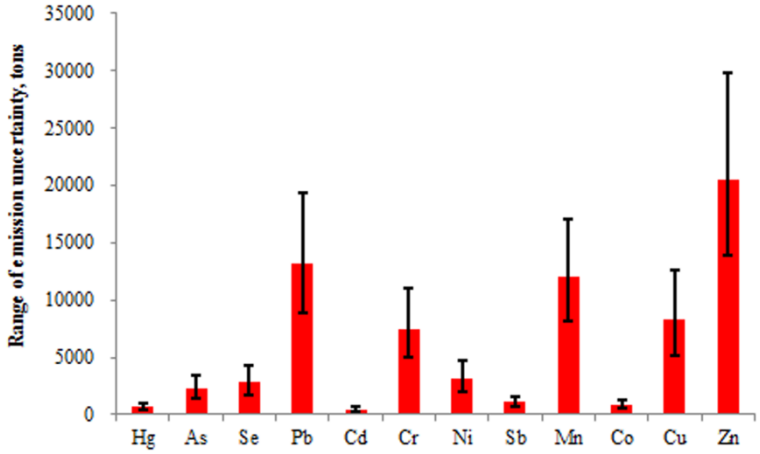


**Figure 6.** Uncertainties in the total emissions of HMs in China in 2010 (Uncertainties in the emissions of HMs by source categories in China in 2010 can be seen Supplement Table S22).

**Supplementary Material**

**Summited to:** Atmospheric Chemistry and Physics (ACP)

**Title:** Quantitative Assessment of Atmospheric Emissions of Toxic Heavy Metals from Anthropogenic Sources of China: Historical trend, spatial variation distribution, uncertainties and control policies

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## Section S1. Mathematical description of bootstrap simulation

Bootstrap is a numerical technique originally developed for the purpose of estimating confidence intervals for statistics. This method can provide solutions of confidence intervals in situations where exact analytical solutions may be unavailable and in which approximate analytical solutions are inadequate. Confidence intervals for a statistic are inferred from its sampling distribution. For example, the 2.5th and 97.5th percentiles of sampling distribution enclose a 95% confidence interval. The brief mathematical description of bootstrap simulation is as follows:

A random sample $X=(x_1, x_2, ..., x_n)$ of size $n$ is observed from a completely unspecified probability distribution F. The sampling distribution $R(X, F)$ is the function of $X$ and $F$. Assume $\theta=\theta(F)$ is a parameter of $F$, $F_n$ is the empirical distribution function of $X$, $\hat{\theta} = \hat{\theta}(F_n)$ is the estimator of $\theta$, and the estimation error can be expressed as:

$$\mathrm{R}(X, F) = \hat{\theta}(F_n) - \theta(F) \triangleq T_n \qquad (1)$$

The basic steps of computing the distribution R (X, F) by bootstrap simulation are summarized as follows:

(1) The value of observed samples $X=(x_1, x_2, ..., x_n)$ are finite overall samples (called original samples), $x_i \sim F(x)$, $i=1, 2, ..., n$. The empirical distribution function of original samples is shown as:

$$F_n = \begin{cases} 0 & x < x_{(1)} \\ k/n & x_{(k)} \le x < x_{(k+1)} \\ 1 & x \ge x_{(n)} \end{cases} \qquad (2)$$

where, $x_{(1)} \le x_{(2)} \le ... \le x_{(n)}$ is the statistics of $x_1, x_2, \ldots, x_n$ sorted in ascending order.

(2) Monte Carlo simulation is used to randomly simulate N groups of samples $x^*_{(j)} = (x^*_1, x^*_2, ..., x^*_n)$, $j=1, 2, ..., N$ (a very large number) from $F_n$, and these regeneration samples called bootstrap samples. The generation method of empirical distribution function by Monte Carlo simulation can be expressed as: (a) generate a random integer $\eta$ with independence and uniformity between *0* and $M$ $(M>>n)$ by computer; (b) let $i=\eta$ % $n$, and $i$ is the remainder of $n$ divide $\eta$; (c) find the sample $x_i$ as the regeneration sample $x^*$ in observed samples, and $x^*$ is the needed random sample.

(3) Calculate the statistics of bootstrap samples:

$$R^*(X^*, F_n) = \hat{\theta}(F_n^*) - \hat{\theta}(F_n) \to R_n \qquad (3)$$

where, $F_n^*$ is the empirical distribution function of bootstrap samples. As small samples can't derive $\theta(F)$, $\hat{\theta}(F_n)$ is used to approximate it.

(4) Use the distribution of $R_n$ (under given situation) to simulate the distribution of $T_n$, say:

$\theta(F) \approx \hat{\theta} - R_n$, which can receive *N* numbers of *θ(F)*. Then, the distribution and eigenvalue of unknown parameter *θ* can be obtained.

## Section S2. Removal efficiencies of 12 HMs through coal cleaning and coke process

Some studies have reported that coal cleaning is an effective and feasible way to reduce atmospheric emissions of heavy metals before coal burning (Luttrell et al., 2000; Wang et al., 2006). By the year of 2012, only about 20.9% of total raw coal production is washed before burning, and is primarily used for coke making in iron and steel industry (NBS, 2013a). In view of the operation characteristics and the application situation of coal cleaning processes in China, we assume the average removal efficiency of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn to be 50.0%, 54.0%, 30.0%, 36.3%, 32.2%, 58.0%, 58.5%, 35.7%, 68.2%, 39.3%, 31.8% and 48.6% (Quick and Irons, 2002; Bai, 2003; Wang et al., 2003a; Yao et al., 2012), respectively.

Due to excessive temperature range (400 °-1000 °) in coke process (Zajusz-Zubek and Konieczyński, 2003), high emission will be found, especially for volatile substance. According to analyze the data of heavy metals discharge in coke process as described in other studies (Helble et al., 1996; Guo et al., 2002; Guo et al, 2003; Yi et al., 2007; Konieczyński et al., 2012), we presume that 10.0% of Hg, 70.0% of As, 60.0% of Se, 68.5% of Pb, 80.0% of Cd, 76.0% of Cr, 90.3% of Ni, 30.0% of Sb, 92.4% of Mn, 92.9% of Co, 80.0% of Cu and 73.9% of Zn remains after the coking process.

## 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.

**Table**

Table S1 Summary of heavy metal species and the associated emission sources categories

| Sector | | Category | Hg | As | Se | Pb | Cd | Cr | Ni | Sb | Mn | Co | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Coal combustion | Power plant | Raw coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Cleaned coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Briquette | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Coke | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | Industrial sector | Raw coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Cleaned coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Briquette | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Coke | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | Residential sector | Raw coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Cleaned coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Briquette | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Coke | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | Other sector | Raw coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Cleaned coal | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Briquette | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Coke | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| Non-coal combustion | Biomass burning | Straw | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Wood | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | Liquid fuel combustion | Crude oil | ● | ● | ● | ● | ● | ● | ● | | ● | ● | ● | ● |
| | | Gasoline | ● | ● | ● | ● | ● | ● | ● | | ● | ● | ● | ● |
| | | Diesel for stationary sources | ● | ● | ● | ● | ● | ● | ● | | ● | ● | ● | ● |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Diesel for transportation | ● | ● | ● | ● | ● | ● | ● | | ● | ● | ● | ● |
| | | Fuel oil | ● | ● | ● | ● | ● | ● | ● | | ● | ● | ● | ● |
| | | Kerosene for stationary sources | ● | ● | ● | ● | ● | ● | ● | | ● | ● | ● | ● |
| | | Kerosene for transportation | | | ● | ● | ● | ● | ● | | ● | ● | ● | ● |
| | | Primary copper | ● | ● | ● | ● | ● | ● | ● | ● | ● | | ● | ● |
| | | Secondary copper | ● | ● | ● | ● | ● | ● | ● | ● | | | ● | ● |
| | | Primary lead | ● | ● | ● | ● | ● | ● | ● | ● | | | ● | ● |
| | | Secondary lead | ● | ● | | ● | ● | ● | | | | | ● | ● |
| | | Primary zinc | ● | ● | ● | ● | ● | ● | ● | ● | | | ● | ● |
| | Nonferrous smelting | Secondary zinc | ● | ● | | ● | ● | ● | | | | | | ● |
| | | Primary aluminum | | | | | ● | ● | ● | | | | | ● |
| | | Secondary aluminum | ● | ● | | ● | ● | ● | ● | | ● | | ● | ● |
| | | Nickel | | | | | | | ● | | | | | |
| | | Antimony | | | | | | | | ● | | | | |
| | | Gold (large scale) | ● | | | | | | | | | | | |
| | | Mercury mining | ● | | | | | | | | | | | |
| | Non-metallic minerals manufacturing | Cement | ● | ● | ● | ● | ● | ● | ● | | ● | | ● | ● |
| | | Glass | ● | ● | ● | ● | ● | ● | ● | | | | ● | ● |
| | | Brick | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | | |
| | Ferrous smelting | Pig iron | ● | ● | ● | ● | ● | ● | ● | ● | ● | | ● | ● |
| | | Steel | ● | ● | ● | ● | ● | ● | ● | ● | ● | | ● | ● |
| | Municipal solid waste (MSW) incineration | Municipal solid waste | ● | ● | ● | ● | ● | ● | ● | ● | ● | | ● | ● |
| | Brake and Tyre wear (B&TW) | Brake pad | | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |
| | | Tyre | | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● | ● |

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Table S2 The emission source classification by coal combustion sector

| Economic sector | Fuel type | Boiler type | PM control device | $SO_2$ control device | $NO_X$ control device |
|---|---|---|---|---|---|
| Coal-fired power plant | raw coal | pulverized-coal boiler | ESP | WFGD | SCR |
| | raw coal | pulverized-coal boiler | ESP | WFGD | |
| | raw coal | pulverized-coal boiler | ESP | | |
| | raw coal | pulverized-coal boiler | FF | WFGD | SCR |
| | raw coal | pulverized-coal boiler | FF | WFGD | |
| | raw coal | pulverized-coal boiler | FF | | |
| | raw coal | pulverized-coal boiler | wet scrubber | WFGD | |
| | raw coal | pulverized-coal boiler | wet scrubber | | |
| | raw coal | pulverized-coal boiler | cyclone | WFGD | |
| | raw coal | pulverized-coal boiler | cyclone | | |
| | raw coal | fluidized-bed furnace | ESP | WFGD | SCR |
| | raw coal | fluidized-bed furnace | ESP | WFGD | |
| | raw coal | fluidized-bed furnace | ESP | | |
| | raw coal | fluidized-bed furnace | FF | WFGD | SCR |
| | raw coal | fluidized-bed furnace | FF | WFGD | |
| | raw coal | fluidized-bed furnace | FF | | |
| | raw coal | fluidized-bed furnace | wet scrubber | WFGD | |
| | raw coal | fluidized-bed furnace | wet scrubber | | |
| | raw coal | fluidized-bed furnace | cyclone | | |
| | raw coal | stoker fired boiler | ESP | WFGD | |
| | raw coal | stoker fired boiler | ESP | | |
| | raw coal | stoker fired boiler | FF | | |
| | raw coal | stoker fired boiler | wet scrubber | | |

| | | | | | |
|---|---|---|---|---|---|
| raw coal | stoker fired boiler | cyclone | | |
| cleaned coal | pulverized-coal boiler | ESP | WFGD | SCR |
| cleaned coal | pulverized-coal boiler | ESP | WFGD | |
| cleaned coal | pulverized-coal boiler | ESP | | |
| cleaned coal | pulverized-coal boiler | FF | WFGD | SCR |
| cleaned coal | pulverized-coal boiler | FF | WFGD | |
| cleaned coal | pulverized-coal boiler | FF | | |
| cleaned coal | pulverized-coal boiler | wet scrubber | WFGD | |
| cleaned coal | pulverized-coal boiler | wet scrubber | | |
| cleaned coal | pulverized-coal boiler | cyclone | WFGD | |
| cleaned coal | pulverized-coal boiler | cyclone | | |
| cleaned coal | fluidized-bed furnace | ESP | WFGD | SCR |
| cleaned coal | fluidized-bed furnace | ESP | WFGD | |
| cleaned coal | fluidized-bed furnace | ESP | | |
| cleaned coal | fluidized-bed furnace | FF | WFGD | SCR |
| cleaned coal | fluidized-bed furnace | FF | WFGD | |
| cleaned coal | fluidized-bed furnace | FF | | |
| cleaned coal | fluidized-bed furnace | wet scrubber | | |
| cleaned coal | fluidized-bed furnace | cyclone | | |
| cleaned coal | stoker fired boiler | ESP | WFGD | |
| cleaned coal | stoker fired boiler | ESP | | |
| cleaned coal | stoker fired boiler | wet scrubber | | |
| cleaned coal | stoker fired boiler | cyclone | | |
| briquette | pulverized-coal boiler | ESP | WFGD | |
| coke | pulverized-coal boiler | ESP | WFGD | |

| | | | |
|---|---|---|---|
| Coal-fired industrial boiler | raw coal | stoker fired boiler | ESP |
| | raw coal | stoker fired boiler | FF |
| | raw coal | stoker fired boiler | wet scrubber |
| | raw coal | stoker fired boiler | cyclone |
| | raw coal | stoker fired boiler | |
| | raw coal | fluidized-bed furnace | wet scrubber |
| | raw coal | coke furnace | FF |
| | raw coal | coke furnace | wet scrubber |
| | raw coal | coke furnace | |
| | cleaned coal | stoker fired boiler | ESP |
| | cleaned coal | stoker fired boiler | FF |
| | cleaned coal | stoker fired boiler | wet scrubber |
| | cleaned coal | stoker fired boiler | cyclone |
| | cleaned coal | stoker fired boiler | |
| | cleaned coal | fluidized-bed furnace | wet scrubber |
| | cleaned coal | coke furnace | FF |
| | cleaned coal | coke furnace | wet scrubber |
| | cleaned coal | coke furnace | |
| | briquette | stoker fired boiler | wet scrubber |
| | briquette | stoker fired boiler | cyclone |
| | briquette | stoker fired boiler | |
| | coke | stoker fired boiler | wet scrubber |
| | coke | stoker fired boiler | cyclone |
| | coke | stoker fired boiler | |
| Coal-fired residential | raw coal | stove | |

| | | | |
|---|---|---|---|
| sector | cleaned coal | stove | |
| | briquette | stove | |
| | coke | stove | |
| Coal-fired other sectors | raw coal | stoker fired boiler | wet scrubber |
| | raw coal | stoker fired boiler | cyclone |
| | raw coal | stoker fired boiler | |
| | cleaned coal | stoker fired boiler | |
| | briquette | stoker fired boiler | |
| | coke | stoker fired boiler | |

168 Table S3 Statistical parameters of bootstrap mean contents of Hg, As, Se, Pb, Cd, Cr, Ni and Sb in
169 produced coal by provinces (Tian et al., 2013)

| Provinces | Hg | As | Se | Pb | Cd | Cr | Ni | Sb |
|---|---|---|---|---|---|---|---|---|
| Anhui | 0.43 | 2.89 | 7.54 | 13.24 | 0.11 | 31.25 | 19.57 | 0.25 |
| Beijing | | | | | | | | |
| Chongqing | 0.31 | 5.66 | 3.69 | 30.44 | 1.22 | 28.44 | 20.9 | 1.71 |
| Fujian | 0.07 | 9.93 | 1.22 | 25.53 | 0.31 | 30.48 | 16.42 | 0.38 |
| Gansu | 0.27 | 4.14 | 0.51 | 8.35 | 0.08 | 23.7 | 19.3 | 0.7 |
| Guangdong | 0.07 | 8.3 | 0.6 | 24.4 | 0.25 | 74 | 24.9 | |
| Guangxi | 0.33 | 16.94 | 5.03 | 29.94 | 0.41 | 116.41 | 22.48 | 5.55 |
| Guizhou | 0.39 | 6.68 | 3.82 | 23.81 | 0.79 | 28.47 | 22.87 | 6.01 |
| Hainan | | | | | | | | |
| Hebei | 0.15 | 4.88 | 2.31 | 29.3 | 0.23 | 32.52 | 14.61 | 0.41 |
| Heilongjiang | 0.12 | 3.42 | 0.9 | 22.15 | 0.13 | 15.48 | 10.49 | 0.79 |
| Henan | 0.2 | 2.2 | 4.86 | 16.78 | 0.54 | 24.94 | 11.84 | 0.37 |
| Hubei | 0.2 | 5.3 | 8.76 | 47.39 | 0.36 | 40.52 | 18.61 | 1.17 |
| Hunan | 0.12 | 10.59 | 3.72 | 26.29 | 0.64 | 37.03 | 13.25 | 1.54 |
| Inner Mongolia | 0.22 | 5.77 | 1.1 | 26.67 | 0.1 | 13.02 | 6.35 | 0.7 |
| Jiangsu | 0.69 | 2.74 | 6.11 | 20.98 | 0.06 | 19.82 | 15.48 | 0.55 |
| Jiangxi | 0.16 | 7.41 | 8.39 | 19.33 | 0.56 | 39.75 | 22.66 | 1.83 |
| Jilin | 0.4 | 11.57 | 4.06 | 29 | 0.15 | 23.09 | 15.34 | 1.02 |
| Liaoning | 0.17 | 5.51 | 0.85 | 19.68 | 0.16 | 26.24 | 24.13 | 0.81 |
| Ningxia | 0.22 | 3.65 | 4.27 | 14.05 | 1.1 | 10.63 | 10.95 | 0.27 |
| Qinghai | 0.25 | 2.68 | 0.3 | 10.72 | 0.03 | 30.82 | 12.2 | 0.91 |
| Shaanxi | 0.21 | 3.87 | 3.43 | 35.17 | 0.75 | 32.73 | 18.86 | 2.95 |
| Shandong | 0.18 | 5.23 | 3.66 | 16.64 | 0.39 | 20.62 | 23.77 | 0.47 |
| Shanghai | | | | | | | | |
| Shanxi | 0.17 | 3.84 | 3.85 | 26.23 | 0.75 | 21.57 | 15.41 | 1.13 |
| Sichuan | 0.29 | 5.38 | 3.31 | 28.29 | 1.95 | 33 | 19.28 | 1.7 |
| Tianjin | | | | | | | | |
| Xinjiang | 0.06 | 2.97 | 0.24 | 2.68 | 0.12 | 7.83 | 8.26 | 0.67 |
| Yunnan | 0.36 | 8.82 | 1.48 | 42.54 | 0.8 | 73.62 | 24.32 | 0.97 |
| Zhejiang | 0.65 | 12.04 | 12.02 | 17.25 | 0.47 | 24.2 | 9.95 | 0.73 |

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171 Table S4 Mn Content of Raw Coal as Mined in China, by Province

| Provinces[a] | Number of samples | Minimum (μg/g) | Maximum (μg/g) | Arithmetic mean (μg/g) | Literature cited |
|---|---|---|---|---|---|
| Anhui | 47 | 0.80 | 76.30 | 27.69 | (Tang et al., 2002; Wu, 2006; Li et al., 2011) |
| Beijing[b] | / | / | / | 45.80 | / |
| Chongqing | 20 | 5.23 | 291.00 | 66.65 | (Zhao et al., 2002; Zhuang et al., 2003) |

| | | | | | |
|---|---|---|---|---|---|
| Fujian | 7 | 30.00 | 459.00 | 134.28 | (Yan and Lu, 1995) |
| Gansu | 13 | 31.00 | 1820.00 | 671.32 | (Ren et al., 2006) |
| Guangxi | 15 | 4.00 | 128.70 | 52.49 | (Yan and Lu, 1995; Tang et al., 2002) |
| Guizhou | 101 | 7.00 | 937.00 | 152.62 | (Zhuang et al., 2000; Tang et al., 2002; Wu et al., 2008) |
| Hebei | 5 | 20.00 | 111.00 | 45.80 | (Zhao et al., 2002) |
| Heilongjiang | 1 | 219.80 | 219.80 | 219.80 | (Tang et al., 2002; Ren et al., 2006) |
| Henan | 10 | 22.53 | 367.46 | 101.39 | (Yan and Lu, 1995; Guo et al., 2005) |
| Hubei | 9 | 4.00 | 100.00 | 49.53 | (Yan and Lu, 1995) |
| Hunan | 7 | 4.00 | 690.00 | 266.01 | (Wang and Mo, 1999; Tang et al., 2002) |
| Inner Mongolia | 10 | 12.70 | 510.00 | 149.43 | (Tang et al., 2002; Guo et al., 2005; Li et al., 2008) |
| Jiangsu | 3 | 3.90 | 188.00 | 95.95 | (Tang et al., 2002; Xiu and Wen, 2004; Ren et al., 2006) |
| Jiangxi | 21 | 8.00 | 224.00 | 79.59 | (Tang et al., 2002) |
| Jilin | 10 | 3.30 | 270.90 | 84.39 | (Ma et al., 2000; Tang et al., 2002; Ren et al., 2006) |
| Liaoning | 6 | 7.00 | 200.34 | 120.56 | (Tang et al., 2002; Guo et al., 2005; Ren et al., 2006) |
| Ningxia | 16 | 7.75 | 209.50 | 48.49 | (Zhao et al., 2002) |
| Qinghai | 4 | 22.08 | 212.00 | 82.54 | (Ren et al., 2006) |
| Shaanxi | 31 | 6.39 | 3950.00 | 398.87 | (Dou et al., 1998; Yang et al., 2008a; Yang et al., 2008b) |
| Shandong | 19 | 9.00 | 239.50 | 87.06 | (Yan and Lu, 1995; Tang et al., 2002; Guo et al., 2005) |
| Shanxi | 64 | 0.20 | 1624.00 | 80.90 | (Tang et al., 2002; Guo et al., 2005) |
| Sichuan | 14 | 7.20 | 412.00 | 121.37 | (Tang et al., 2002; Zhuang et al., 2003) |
| Xinjiang | 99 | 2.00 | 501.00 | 52.18 | (Cui et al., 2004; Zhou et al., 2010) |
| Yunnan | 9 | 31.00 | 125.30 | 51.41 | (Tang et al., 2002; Guo et al., 2005; Dai et al., 2009) |
| Zhejiang | 3 | 28.00 | 41.24 | 32.71 | (Li et al., 1993; Tang et al., 2002) |

[a] Hong Kong, Macao, Taiwan are not included in this table, Guangdong, Hainan, Shanghai, Tianjin and Tibet do not produce raw coal.

[b] Beijing lack of corresponding date, in this study, we choose the Mn content of Hebei instead.

Table S5 Co Content of Raw Coal as Mined in China, by Province

| Provinces[c] | Number of samples | Minimum (μg/g) | Maximum (μg/g) | Arithmetic mean (μg/g) | Literature cited |
|---|---|---|---|---|---|
| Anhui | 97 | 1.32 | 65.70 | 12.12 | (Tang et al., 2002; Wu, 2006; Chen et al., 2009) |
| Beijing[d] | / | / | / | 8.91 | / |
| Chongqing | 38 | 1.38 | 90.30 | 13.38 | (Zhao et al., 2002; Bai et al., 2007) |

| | | | | | |
|---|---|---|---|---|---|
| Fujian | 4 | 1.24 | 15.50 | 7.55 | (Yan and Lu, 1995; Wang et al., 1997; Xu et al., 2001) |
| Gansu | 3 | 1.54 | 15.90 | 7.05 | (Ren et al., 2006) |
| Guangxi | 35 | 2.24 | 19.90 | 7.05 | (Yan and Lu, 1995; Wang et al., 1997; Xu et al., 2001; Zeng et al., 2005) |
| Guizhou | 148 | 0.40 | 119.00 | 11.91 | (Zhuang et al., 1999; Zhuang et al., 2000; Tang et al., 2002; Yang, 2006; Wu et al., 2008) |
| Henan | 9 | 3.25 | 12.77 | 5.93 | (Yan and Lu, 1995; Xu et al., 2001; Tang et al., 2002) |
| Hubei | 13 | 3.00 | 45.00 | 8.91 | (Yan and Lu, 1995; Xu et al., 2001) |
| Hebei | 38 | 1.00 | 24.40 | 6.80 | (Wang et al., 1997; Zhuang et al., 1999; Tang et al., 2002; Dai et al., 2003; Tang et al., 2005; Tang et al., 2009) |
| Heilongjiang | 7 | 5.60 | 25.50 | 12.42 | (Tang et al., 2002; Ren et al., 2006) |
| Hunan | 12 | 0.80 | 18.50 | 6.15 | (Wang and Mo, 1999; Tang et al., 2002) |
| Inner Mongolia | 99 | 0.20 | 28.20 | 4.08 | (Wang et al., 1997; Tang et al., 2002; Dai et al., 2003; Li et al., 2008) |
| Jilin | 13 | 4.98 | 38.50 | 10.91 | (Ma et al., 2000; Ren et al., 2006) |
| Jiangsu | 3 | 1.30 | 20.10 | 11.20 | (Tang et al., 2002; Xiu and Wen, 2004) |
| Jiangxi | 20 | 1.00 | 13.00 | 5.48 | (Xu et al., 2001; Tang et al., 2002) |
| Liaoning | 24 | 3.60 | 53.66 | 13.59 | (Kong et al., 2001; Tang et al., 2002; Ren et al., 2004) |
| Ningxia | 18 | 0.88 | 22.60 | 7.29 | (Zhao et al., 2002; Bai, 2003) |
| Qinghai | 4 | 2.19 | 4.03 | 2.85 | (Zhao et al., 2002; Bai, 2003) |
| Sichuan | 21 | 0.80 | 47.60 | 9.39 | (Tang et al., 2002; Zhuang et al., 2003) |
| Shandong | 73 | 0.34 | 46.30 | 5.89 | (Yan and Lu, 1995; Huang et al., 2000; Xu et al., 2001; Tang et al., 2002) |
| Shaanxi | 34 | 0.94 | 32.90 | 8.65 | (Dou et al., 1998; Tang et al., 2002; Yang et al., 2008a; Yang et al., 2008b) |
| Shanxi | 69 | 0.40 | 28.30 | 4.82 | (Wang et al., 1997; Zhuang et al., 1999; Tang et al., 2002; Dai et al., 2003) |
| Xinjiang | 62 | 0.45 | 25.80 | 6.63 | (Tang et al., 2002; Zhou et al., 2010) |
| Yunnan | 40 | 1.79 | 37.86 | 11.84 | (Tang et al., 2002; Dai et al., 2009; Hu et al., 2009) |
| Zhejiang | 3 | 2.65 | 7.39 | 4.64 | (Li et al., 1993; Tang et al., 2002) |

177 [c] Hong Kong, Macao, Taiwan are not included in this table, Guangdong, Hainan, Shanghai, Tianjin
178 and Tibet do not produce raw coal.
179 [d] Beijing lack of corresponding date, in this study, we choose the Co content of Hebei instead.
180

181 Table S6 Cu Content of Raw Coal as Mined in China, by Province

| Province[e] | Number of | Minimum (μg/g) | Maximum (μg/g) | Arithmetic mean | Literature cited |
|---|---|---|---|---|---|

| | samples | | | (μg/g) | |
|---|---|---|---|---|---|
| Anhui | 85 | 5.03 | 140.00 | 36.21 | (Tang et al., 2002; Wu, 2006; Chen et al., 2009) |
| Beijing[f] | / | / | / | 27.37 | / |
| Chongqing | 28 | 14.50 | 156.00 | 42.57 | (Zhuang et al., 2003; Bai et al., 2007; Zhu and Li, 2009) |
| Fujian | 4 | 21.60 | 59.00 | 38.48 | (Yan and Lu, 1995; Xu et al., 2001) |
| Gansu | 1 | 7.25 | 7.25 | 7.25 | (Bai, 2003; Ren et al., 2006) |
| Guangxi | 45 | 3.00 | 69.00 | 25.79 | (Yan and Lu, 1995; Xu et al., 2001; Zeng et al., 2005) |
| Guizhou | 131 | 0.90 | 370.00 | 55.04 | (Zhuang et al., 2000; Yang, 2006; Wu et al., 2008; Cheng et al., 2013) |
| Henan | 8 | 23.30 | 60.37 | 40.86 | (Yan and Lu, 1995; Xu et al., 2001; Tang et al., 2002) |
| Hubei | 9 | 19.00 | 81.00 | 33.89 | (Yan and Lu, 1995; Xu et al., 2001) |
| Hebei | 31 | 6.90 | 78.40 | 27.37 | (Zhuang et al., 1999; Tang et al., 2002; Dai et al., 2003; Tang et al., 2005; Tang et al., 2009) |
| Heilongjiang | 12 | 4.10 | 69.00 | 15.62 | (Tang et al., 2002; Ren et al., 2006) |
| Hunan | 5 | 4.28 | 51.50 | 25.79 | (Wang and Mo, 1999; Tang et al., 2002) |
| Inner Mongolia | 93 | 1.60 | 92.20 | 18.63 | (Tang et al., 2002; Dai et al., 2003; Li et al., 2008) |
| Jilin | 10 | 5.00 | 98.70 | 28.17 | (Ma et al., 2000; Tang et al., 2002) |
| Jiangsu | 2 | 21.60 | 76.30 | 48.95 | (Tang et al., 2002; Xiu and Wen, 2004) |
| Jiangxi | 20 | 7.00 | 60.70 | 21.13 | (Xu et al., 2001; Bai, 2003) |
| Liaoning | 19 | 7.90 | 85.00 | 30.38 | (Kong et al., 2001; Ren et al., 2004) |
| Ningxia | 4 | 1.49 | 8.07 | 4.52 | (Zhao et al., 2002; Bai, 2003) |
| Qinghai[g] | / | / | / | 15.71 | / |
| Sichuan | 12 | 11.20 | 65.90 | 33.52 | (Tang et al., 2002; Bai, 2003; Zhuang et al., 2003) |
| Shandong | 37 | 2.64 | 238.00 | 34.78 | (Yan and Lu, 1995; Liu et al., 2001; Xu et al., 2001; Tang et al., 2002) |
| Shaanxi | 31 | 5.60 | 164.00 | 31.93 | (Dou et al., 1998; Tang et al., 2002; Yang et al., 2008a; Yang et al., 2008b) |
| Shanxi | 57 | 0.00 | 264.00 | 27.89 | (Zhuang et al., 1999; Tang et al., 2002; Dai et al., 2003) |
| Xinjiang | 96 | 0.80 | 36.00 | 6.58 | (Zhao et al., 2002; Bai, 2003; Zhou et al., 2010) |
| Yunnan | 24 | 0.00 | 169.00 | 59.38 | (Tang et al., 2002; Dai et al., 2009; Hu et al., 2009) |
| Zhejiang | 1 | 93.28 | 93.28 | 93.28 | (Zhao et al., 2002; Bai, 2003) |

[e] Hong Kong, Macao, Taiwan are not included in this table, Guangdong, Hainan, Shanghai, Tianjin and Tibet do not produce raw coal.

[f,g] Beijing and Qinghai lack of corresponding date, in this study, we choose the Cu content of

185 Hebei and the average Cu content of surrounding province (Gansu, Sichuan and Xinjiang) instead,
186 respectively.
187

188 Table S7 Zn Content of Raw Coal as Mined in China, by Province

| Provinces[h] | Number of samples | Minimum (μg/g) | Maximum (μg/g) | Arithmetic mean (μg/g) | Literature cited |
|---|---|---|---|---|---|
| Anhui | 100 | 1.00 | 112.00 | 26.17 | (Tang et al., 2002; Wu, 2006; Chen et al., 2009; Li et al., 2011) |
| Beijing[i] | / | / | / | 49.54 | / |
| Chongqing | 26 | 1.00 | 39.00 | 23.41 | (Zhao et al., 2002; Zhuang et al., 2003) |
| Fujian | 4 | 90.00 | 299.00 | 174.75 | (Yan and Lu, 1995; Wang et al., 1997) |
| Gansu | 2 | 6.40 | 54.30 | 30.35 | (Ren et al., 2006) |
| Guangxi | 38 | 1.41 | 212.00 | 56.88 | (Yan and Lu, 1995; Wang et al., 1997; Zeng et al., 2005) |
| Guizhou | 157 | 0.79 | 561.00 | 56.97 | (Zhuang et al., 1999; Zhuang et al., 2000; Yang, 2006; Li et al., 2011; Wei et al., 2012; Cheng et al., 2013) |
| Henan | 8 | 10.41 | 60.00 | 31.93 | (Yan and Lu, 1995) |
| Hubei | 11 | 5.00 | 384.00 | 63.46 | (Yan and Lu, 1995) |
| Hebei | 40 | 5.13 | 131.00 | 49.54 | (Zhuang et al., 1999; Tang et al., 2002; Dai et al., 2003; Tang et al., 2005; Tang et al., 2009) |
| Heilongjiang | 2 | 21.40 | 33.00 | 27.20 | (Ren et al., 2006) |
| Hunan | 4 | 19.80 | 158.00 | 60.35 | (Zhao et al., 2002) |
| Inner Mongolia | 97 | 23.90 | 257.00 | 43.18 | (Wang et al., 1997; Dai et al., 2003; Li et al., 2008) |
| Jilin | 14 | 5.40 | 360.00 | 79.71 | (Ma et al., 2000; Tang et al., 2002) |
| Jiangsu | 2 | 17.20 | 18.94 | 18.07 | (Tang et al., 2002; Xiu and Wen, 2004) |
| Jiangxi | 17 | 3.40 | 173.00 | 92.12 | (Zhao et al., 2002) |
| Liaoning | 20 | 22.00 | 310.00 | 70.71 | (Kong et al., 2001; Tang et al., 2002; Ren et al., 2004) |
| Ningxia | 9 | 7.30 | 73.96 | 21.60 | (Song et al., 2011) |
| Qinghai[j] | / | / | / | 30.89 | / |
| Sichuan | 13 | 22.30 | 99.50 | 45.65 | (Zhao et al., 2002; Zhuang et al., 2003) |
| Shandong | 62 | 2.67 | 68.70 | 16.38 | (Yan and Lu, 1995; Huang et al., 2000; Liu et al., 2001; Tang et al., 2002) |
| Shaanxi | 33 | 8.75 | 1511.00 | 114.64 | (Dou et al., 1998; Yang et al., 2008a; Yang et al., 2008b) |
| Shanxi | 62 | 0.56 | 864.85 | 65.05 | (Wang et al., 1997; Zhuang et al., 1999; Tang et al., 2002; Dai et al., 2003) |
| Xinjiang | 65 | 4.00 | 112.00 | 16.55 | (Tang et al., 2002; Zhou et al., 2010) |
| Yunnan | 40 | 0.00 | 204.00 | 59.11 | (Dai et al., 2009; Hu et al., 2009) |

| | | | | | |
|---|---|---|---|---|---|
| Zhejiang | 1 | 14.81 | 14.81 | 14.81 | (Zhao et al., 2002) |

[h] Hong Kong, Macao, Taiwan are not included in this table, Guangdong, Hainan, Shanghai, Tianjin and Tibet do not produce raw coal.

[i,j] Beijing and Qinghai lack of corresponding date, in this study, we choose the Zn content of Hebei and the average Zn content of surrounding province (Gansu, Sichuan and Xinjiang) instead, respectively.

194 Table S8 Averaged concentrations of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn in coals as consumed by province (unit: μg/g).

| Provinces | Hg | As | Se | Pb | Cd | Cr | Ni | Sb | Mn | Co | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Anhui | 0.40 | 2.94 | 7.19 | 13.82 | 0.16 | 30.37 | 19.16 | 0.28 | 34.85 | 11.37 | 36.36 | 27.00 |
| Beijing | 0.17 | 4.02 | 3.59 | 26.74 | 0.66 | 23.39 | 15.27 | 1.01 | 75.49 | 5.16 | 27.82 | 63.24 |
| Chongqing | 0.32 | 5.74 | 3.70 | 29.91 | 1.19 | 28.44 | 21.06 | 2.05 | 73.65 | 13.29 | 43.67 | 26.11 |
| Fujian | 0.12 | 4.48 | 2.32 | 15.23 | 0.29 | 18.53 | 12.93 | 0.37 | 86.32 | 6.55 | 29.83 | 68.99 |
| Gansu | 0.23 | 3.74 | 0.43 | 7.48 | 0.08 | 21.31 | 16.30 | 0.72 | 166.54 | 6.50 | 8.05 | 27.64 |
| Guangdong | 0.14 | 4.04 | 2.78 | 19.20 | 0.53 | 18.67 | 12.29 | 1.41 | 99.33 | 6.09 | 27.99 | 59.28 |
| Guangxi | 0.14 | 6.31 | 1.75 | 14.04 | 0.22 | 44.78 | 9.73 | 1.86 | 52.55 | 6.78 | 23.12 | 38.71 |
| Guizhou | 0.39 | 6.69 | 3.81 | 23.86 | 0.79 | 28.60 | 22.87 | 6.00 | 153.52 | 11.88 | 55.20 | 57.30 |
| Hainan | 0.09 | 2.07 | 2.08 | 14.16 | 0.40 | 11.64 | 8.32 | 0.61 | 68.33 | 5.23 | 21.91 | 46.98 |
| Hebei | 0.19 | 5.17 | 1.94 | 27.45 | 0.25 | 20.71 | 10.50 | 0.68 | 104.34 | 5.08 | 22.95 | 49.06 |
| Heilongjiang | 0.16 | 4.39 | 0.97 | 23.76 | 0.12 | 14.97 | 9.46 | 0.76 | 187.49 | 9.30 | 17.24 | 35.33 |
| Henan | 0.19 | 2.64 | 4.58 | 19.47 | 0.59 | 24.61 | 12.87 | 0.61 | 96.01 | 5.77 | 37.72 | 41.57 |
| Hubei | 0.21 | 3.85 | 4.22 | 33.40 | 0.70 | 31.65 | 17.70 | 2.26 | 98.98 | 8.00 | 32.77 | 92.46 |
| Hunan | 0.14 | 8.10 | 3.80 | 25.46 | 0.66 | 31.66 | 13.72 | 1.34 | 200.45 | 5.75 | 27.19 | 59.80 |
| Inner Mongolia | 0.21 | 5.57 | 1.13 | 25.54 | 0.11 | 12.97 | 6.63 | 0.69 | 142.62 | 4.18 | 18.60 | 42.68 |
| Jiangsu | 0.25 | 4.13 | 3.47 | 26.28 | 0.44 | 24.72 | 15.73 | 1.50 | 103.15 | 7.38 | 30.50 | 64.74 |
| Jiangxi | 0.18 | 5.25 | 6.19 | 22.91 | 0.61 | 33.52 | 19.09 | 1.71 | 88.56 | 6.28 | 27.96 | 81.93 |
| Jilin | 0.28 | 7.77 | 2.38 | 26.86 | 0.15 | 18.10 | 11.33 | 0.86 | 128.46 | 8.23 | 22.62 | 57.68 |
| Liaoning | 0.18 | 5.42 | 1.18 | 21.94 | 0.16 | 20.25 | 16.05 | 0.77 | 130.45 | 9.77 | 24.51 | 56.64 |
| Ningxia | 0.21 | 3.67 | 4.22 | 15.44 | 1.06 | 11.88 | 11.46 | 0.37 | 51.87 | 7.00 | 7.19 | 26.70 |
| Qinghai | 0.24 | 2.89 | 1.16 | 11.44 | 0.26 | 26.46 | 11.93 | 0.77 | 75.08 | 3.81 | 13.29 | 28.88 |
| Shaanxi | 0.21 | 3.85 | 3.51 | 33.16 | 0.78 | 30.63 | 18.11 | 2.70 | 102.92 | 8.48 | 29.21 | 104.21 |
| Shandong | 0.19 | 5.05 | 2.76 | 22.77 | 0.37 | 18.26 | 15.05 | 0.71 | 108.20 | 4.97 | 27.19 | 38.62 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Shanghai | 0.28 | 4.92 | 2.73 | 24.01 | 0.20 | 17.07 | 10.94 | 0.68 | 118.85 | 5.76 | 25.58 | 39.93 |
| Shanxi | 0.16 | 3.76 | 3.64 | 24.81 | 0.70 | 20.74 | 14.96 | 1.08 | 79.91 | 4.88 | 27.06 | 63.26 |
| Sichuan | 0.29 | 5.45 | 3.27 | 29.64 | 1.74 | 34.39 | 19.63 | 1.76 | 110.71 | 9.90 | 35.28 | 49.16 |
| Tianjin | 0.17 | 3.98 | 3.65 | 26.52 | 0.69 | 22.39 | 15.14 | 1.05 | 76.65 | 5.09 | 27.84 | 63.76 |
| Xinjiang | 0.06 | 3.00 | 0.25 | 2.93 | 0.12 | 7.88 | 8.24 | 0.67 | 53.35 | 6.62 | 6.71 | 16.83 |
| Yunnan | 0.36 | 8.73 | 1.58 | 41.73 | 0.80 | 71.66 | 24.26 | 1.19 | 55.82 | 11.90 | 59.63 | 59.34 |
| Zhejiang | 0.20 | 4.05 | 3.41 | 27.76 | 0.60 | 24.73 | 15.81 | 1.63 | 95.01 | 6.55 | 28.43 | 74.94 |

Table S9 Removal efficiencies of 12 HMs through coal cleaning and coke process

| Categories | Hg | As | Se | Pb | Cd | Cr |
|---|---|---|---|---|---|---|
| Coal cleaning | 50.0% | 54.0% | 30.0% | 36.3% | 32.2% | 58.0% |
| Coking process | 90% | 30% | 40% | 31.5% | 20% | 24% |
| Category | Ni | Sb | Mn | Co | Cu | Zn |
| Coal cleaning | 58.5% | 35.7% | 68.2% | 39.3% | 31.8% | 48.6% |
| Coking process | 9.7% | 70% | 7.6% | 7.1% | 20% | 26.1% |

Table S10 Release rates of Mn, Co, Cu and Zn from coal-fired facilities.

| Categories | Release Rates (%)[k] | | | | Literature cited |
|---|---|---|---|---|---|
| | Mn | Co | Cu | Zn | |
| Pulverized-coal boiler | 91.70 | | | 94.70 | (Jin et al., 2003) |
| | 67.00 | 88.00 | | | (Nodelman et al., 2000) |
| | 57.00 | 90.00 | | | |
| | 58.00 | 62.00 | | | (Llorens et al., 2001) |
| | 94.40 | 92.86 | 92.31 | | (Benson et al., 1995) |
| | 86.00 | 94.00 | 93.00 | 96.00 | (Xu et al., 2004) |
| | | | | 84.00 | (Álvarez-Ayuso et al., 2006) |
| Stoker fired boiler | 16.24 | 42.44 | 25.69 | 33.34 | (Wang et al., 1996) |
| | 6.30 | 11.40 | | | (Zhang et al., 2003) |
| | 26.00 | 21.88 | | | (Song et al., 2006a) |
| | | | | 15.00 | |
| | | | | 5.00 | (He et al., 2005) |
| | | | | 12.00 | |
| Fluidized-bed furnace | 47.70 | 57.50 | 50.20 | 51.40 | |
| | 50.20 | 55.30 | 43.40 | 49.70 | (Reddy et al., 2005) |
| | 42.70 | 56.20 | 45.75 | 44.80 | |
| | 64.29 | 66.70 | 83.30 | | (Benson et al., 1995) |
| | | 76.45 | 78.90 | 82.01 | (Klika et al., 2001) |
| | | 82.29 | 87.26 | 77.94 | |
| | | 47.00 | 30.00 | | (Bartoňová and Klika, 2009) |
| | | 61.00 | 68.00 | | |
| Coke furnace | 28.00 | | | | (Zajusz-Zubek and Konieczyński, 2003) |
| | 23.00 | 22.00 | 11.00 | | |
| | 38.00 | 36.00 | 22.00 | | (Chen et al., 2008) |
| | 40.00 | 37.00 | 33.00 | | |
| | 12.00 | | | | (Guo et al., 2004) |
| | | | | 58.00 | (Helble et al., 1996) |
| | | | | 30.00 | (Wei et al., 2012) |

[k] the release rate of Hg, As, Se, Pb, Cd, Cr, Ni and Sb from different combustion boilers can be referred in our previously studies (Tian et al., 2010; Tian et al., 2011; Tian et al., 2012a; Tian et al., 2012b).

Table S11. Removal efficiencies of Mn, Co, Cu and Zn by different control devices

| Categories | Release Rates (%)[1] | | | | Literature cited |
|---|---|---|---|---|---|
| | Mn | Co | Cu | Zn | |
| ESPs | 93.00 | 97.00 | 97.00 | | (Benson et al., 1995) |
| | 95.00 | | | | |
| | 97.90 | 97.20 | | 92.90 | (Ondov et al., 1979) |
| | 99.90 | 99.80 | | | |
| | 99.10 | 99.80 | | | (Nyberg et al., 2009) |
| | 97.20 | 99.40 | | | |
| | | 97.70 | | | |
| | 98.50 | 98.20 | | | (Helble, 2000) |
| | 86.00 | 94.00 | 93.00 | 96.00 | (Xu et al., 2004) |
| | | 90.02 | | | (Han et al., 2002) |
| FFs | 87.00 | 93.00 | 97.75 | 97.50 | (Nodelman et al., 2000) |
| | 98.00 | 99.00 | | | |
| | 99.70 | 99.90 | | | (Nyberg et al., 2009) |
| | 99.80 | 99.90 | | | |
| Cyclone | 67.00 | 72.00 | 60.00 | 64.00 | (Gogebakan and Selçık, 2009) |
| Wet scrubber | 98.97 | 99.82 | 98.97 | 99.03 | (Ondov et al., 1979) |
| WFGD | 65.79 | 76.19 | 55.56 | 29.09 | (Córdoba et al., 2012a) |
| | 37.50 | 66.67 | 86.49 | 52.50 | |
| | 72.08 | 78.95 | 24.56 | 71.38 | (Córdoba et al., 2012b) |
| | | 68.93 | 35.26 | 80.00 | |
| | | 32.30 | 27.27 | | (Tang et al., 2013) |
| | | 41.95 | 22.17 | | |
| | | 32.88 | 31.29 | | |

[1] the removal efficiencies of Hg, As, Se, Pb, Cd, Cr, Ni and Sb by different control device can be referred in our previously studies (Tian et al., 2010;Tian et al., 2012a;Tian et al., 2012b;Tian et al., 2011).

Table S12 TSP emission factors for vehicle brake and tyre wear

| Vehicle categories | TSP emission factor (g/km) | Uncertainty range(g/km) |
|---|---|---|
| **TSP emission factors for vehicle tyre wear** | | |
| Two-wheel vehicles | 0.0046 | 0.0042–0.0053 |
| Passenger cars | 0.0107 | 0.0067–0.0162 |
| Light-duty trucks | 0.0169 | 0.0088–0.0217 |
| Heavy-duty vehicles | 0.0412 | 0.0227–0.0898 |
| **TSP emission factors for vehicle brake wear** | | |
| Two-wheel vehicles | 0.0037 | 0.0022 –0.0050 |
| Passenger cars | 0.0075 | 0.0044 –0.0100 |
| Light-duty trucks | 0.0117 | 0.0088 –0.0145 |
| Heavy-duty vehicles | 0.0365 | 0.0235 –0.0420 |

209 Table S13 Composition of tyre and brake wear in term of heavy metals, ppm

| Element | tyre | | | brake | | |
|---|---|---|---|---|---|---|
| | mean | min | max | mean | min | max |
| As | 3.8 | 1.6 | 6 | 67.5 | 10 | 130 |
| Se | 20 | / | / | 20 | / | / |
| Pb | 176 | 6.3 | 670 | 6072 | 120 | 20000 |
| Cd | 4.7 | 1.4 | 9 | 22.4 | 1.5 | 57 |
| Cr | 23.8 | 2 | 61 | 2311 | 115 | 8050 |
| Ni | 29.9 | 2.4 | 63 | 327 | 80 | 600 |
| Sb | 2 | / | / | 10000 | / | / |
| Mn | 51 | 2 | 100 | 2460 | 1700 | 3220 |
| Co | 12.8 | 0.9 | 24.8 | 6.4 | / | / |
| Cu | 174 | 1.8 | 490 | 51112 | 370 | 142000 |
| Zn | 7434 | 430 | 13494 | 8676 | 270 | 21800 |

Table S14 Parameter values used in the transformed normal distribution function computation of the variation of heavy metals emission factors over time

| Elements | Parameters | Hg | As | Se | Pb | Cd | Cr | Ni | Sb | Mn | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Copper | $ef_a$ | 27.50 | 3333.33 | 300.00 | 4000.00 | 1250.00 | 25.00 | 5000.00 | 336.67 | 100.00 | 8333.33 | 6000.00 |
| | $ef_b$ | 8.50 | 100.00 | 15.00 | 200.00 | 50.00 | 1.00 | 50.00 | 10.10 | 4.50 | 250.00 | 300.00 |
| | s | 40 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Lead | $ef_a$ | 43.60 | 400.00 | 330.00 | 8000.00 | 500.00 | 57.50 | 166.67 | 506.67 | / | 83.33 | 680.00 |
| | $ef_b$ | 6.00 | 1.00 | 16.50 | 200.00 | 5.00 | 2.30 | 5.00 | 15.20 | / | 5.00 | 20.00 |
| | s | 40 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | / | 30 | 30 |
| Zinc | $ef_a$ | 75.00 | 600.00 | 66.67 | 2900.00 | 500.00 | 39.00 | 68.00 | 200.00 | / | 420.00 | 16000.00 |
| | $ef_b$ | 17.00 | 5.00 | 10.00 | 50.00 | 5.00 | 1.17 | 1.36 | 6.00 | / | 25.00 | 500.00 |
| | s | 40 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Gold (large scale) | $ef_a$ | 520 | / | / | / | / | / | / | / | / | / | / |
| | $ef_b$ | 25 | / | / | / | / | / | / | / | / | / | / |
| | s | 36 | / | / | / | / | / | / | / | / | / | / |
| Mercury mining | $ef_a$ | 182 | / | / | / | / | / | / | / | / | / | / |
| | $ef_b$ | 45 | / | / | / | / | / | / | / | / | / | / |
| | s | 36 | / | / | / | / | / | / | / | / | / | / |
| Iron | $ef_a$ | 0.06 | 3.50 | 0.26 | 3.50 | 1.60 | 2.67 | 12.00 | 0.40 | 0.83 | 20.00 | 57.14 |
| | $ef_b$ | 0.04 | 0.08 | 0.01 | 0.07 | 0.02 | 0.08 | 0.12 | 0.00 | 0.08 | 0.40 | 4.00 |
| | s | 40 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Steel | $ef_a$ | 0.05 | 0.56 | 0.12 | 74.32 | 2.47 | 4.11 | 3.15 | 0.20 | 129.27 | 5.79 | 190.00 |
| | $ef_b$ | 0.01 | 0.01 | 0.00 | 1.49 | 0.02 | 0.12 | 0.03 | 0.00 | 2.02 | 0.12 | 6.05 |
| | s | 40 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cement | $ef_a$ | 0.10 | 13.94 | 2.54 | 54.43 | 2.28 | 11.79 | 8.12 | / | 55.34 | 24.20 | 57.20 |
| | $ef_b$ | 0.02 | 0.07 | 0.01 | 0.38 | 0.01 | 0.05 | 0.04 | / | 0.28 | 0.12 | 0.29 |
| | s | 35 | 25 | 25 | 25 | 25 | 25 | 25 | / | 25 | 25 | 25 |
| MSW | $ef_a$ | 2.80 | 2.14 | 0.50 | 107.00 | 5.45 | 4.49 | 3.93 | 6.00 | 9.00 | 14.00 | 60.00 |
| | $ef_b$ | 0.06 | 0.05 | 0.01 | 0.12 | 0.01 | 0.04 | 0.09 | 3.00 | 0.21 | 0.13 | 0.11 |
| | s | 32 | 28 | 28 | 28 | 28 | 28 | 28 | 28 | 28 | 28 | 28 |

Table S15 Abatement efficiencies for nonferrous metals smelting (Pacyna et al., 2002)

| Elements | Efficiency, % | 95% confidence interval | |
|---|---|---|---|
| | | lower, % | upper, % |
| Hg | 0 | 0 | 67 |
| As | 97 | 91 | 99 |
| Se | 85 | 55 | 95 |
| Pb | 95 | 85 | 98 |
| Cd | 99 | 96 | 100 |
| Cr | 90 | 70 | 97 |
| Ni | 97 | 90 | 99 |
| Cu | 94 | 81 | 98 |
| Zn | 80 | 40 | 93 |

Table S16 Heavy metals emission factors for non-coal combustion sources: temporal, and process variations

| Categories | | Durable year | Hg | As | Se | Pb | Cd | Cr | Literature cited |
|---|---|---|---|---|---|---|---|---|---|
| Liquid fuel combustion (g $t^{-1}$ fuel | Crude oil | 1949-2012 | 0.01 | 0.17 | 0.09 | 0.19 | 0.05 | 0.11 | (de Souza et al., 2006; UK, 2013) |
| | Fuel oil for stationary | 1949-2012 | 0.01 | 0.17 | 0.09 | 0.19 | 0.05 | 0.11 | (de Souza et al., 2006; UK, 2013) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| combustion) | sources | | | | | | | | |
| | Kerosene for stationary sources | 1949-2012 | 0.0019 | 0.02 | 0.0115 | 0.000009 | 0.0000504 | 0.0000504 | (US EPA, 1996a) |
| | Diesel oil for stationary sources | 1949-2012 | 0.0019 | 0.02 | 0.0115 | 0.000009 | 0.0000504 | 0.0000504 | (US EPA, 1996c) |
| | Gasoline | 1949-2012 | 0.06 | 0.02 | 0.3 | / | 0.01 | 0.01 | (UK, 2013) |
| | Diesel oil for transportation | 1949-2012 | 0.06 | 0.02 | 0.3 | 0.0325 | 0.04 | 0.04 | (Wang et al., 2003b; UK, 2013) |
| | Kerosene for transportation | 1949-2012 | / | / | 0.14 | 0.06 | 0.01 | 0.01 | (UK, 2013) |
| | Primary Al | 1949-1996 | / | / | / | / | 0.197 | / | (UK, 2000, 2013) |
| | | 2012 | / | / | / | / | 0.1 | / | |
| | Secondary Al | 1949-1996 | 0.032 | 0.319 | / | 3.734 | 0.175 | 0.841 | |
| | | 2012 | 0.0161 | 0.162 | / | 1.896 | 0.0887 | 0.427 | |
| Nonferrous metal smelting (g $t^{-1}$ nonferrous metal production) | Primary Cu | Pre-1900 | 27.5 | 3333 | 300 | 4000 | 1250 | 25 | (Habashi, 1978; Nriagu, 1979; Pacyna, 1984; Nriagu and Pacyna, 1988; Skeaff and Dubreuil, 1997; EC, 2001b; Pacyna and Pacyna, 2001; Pacyna et al., 2002; Theloke et al., 2008; Streets et al., 2011; EEA, 2009, 2013) |
| | | 2012 | 8.5 | 100 | 15 | 200 | 50 | 1 | |
| | Secondary Cu | 1949-1996 | 1 | 2 | 5 | 90 | 3 | 1 | |
| | | 2012 | 0.4 | 0.8 | 2 | 36 | 1.2 | 0.4 | |
| | Primary Pb | Pre-1900 | 43.6 | 400 | 330 | 8000 | 500 | 57.5 | |
| | | 2012 | 6 | 1 | 16.5 | 200 | 5 | 2.3 | |
| | Secondary Pb | 1949-1996 | 1 | 0.5 | / | 100 | 2.5 | 1.773 | |
| | | 2012 | 0.4 | 0.2 | / | 40 | 1 | 0.709 | |
| | Primary Zn | Pre-1900 | 75 | 600 | 67 | 2900 | 500 | 39.0 | |
| | | 2012 | 17 | 5 | 10 | 50 | 5 | 1.170 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Secondary Zn | 1949-1996 | 0.013 | 0.945 | / | 10.439 | 5.515 | 1.799 | |
| | | 2012 | 0.0065 | 0.48 | / | 5.3 | 2.8 | 0.913 | |
| | Ni smelting | 1949-1996 | / | / | / | / | / | / | / |
| | | 2012 | / | / | / | / | / | / | |
| | Sb smelting | 1949-1996 | / | / | / | / | / | / | / |
| | | 2012 | / | / | / | / | / | / | |
| | Gold (large scale) | Pre-1900 | 520 | / | / | / | / | / | (Hylander and Meili, 2005; Pacyna, 2006; Pacyna, 2010; Pirrone, 2010; Streets, 2011) |
| | | 2012 | 25 | / | / | / | / | / | |
| | Mercury mining | Pre-1900 | 182 | / | / | / | / | / | |
| | | 2012 | 45 | / | / | / | / | / | |
| Ferrous metals smelting (g $t^{-1}$ ferrous metal production) | Pig iron | Pre-1900 | 0.06 | 3.5 | 0.26 | 3.5 | 1.6 | 2.7 | (Nriagu, 1979; Pacyna, 1984; Nriagu and Pacyna, 1988; Kakareka et al., 1998; UK, 2000; EC, 2001a; Theloke et al., 2008; EEA, 2009; Pirrone et al., 2010; Streets et al., 2011; UK, 2013) |
| | | 2015 | 0.04 | 0.08 | 0.013 | 0.0699 | 0.016 | 0.08 | |
| | Steel produced | Pre-1900 | 0.05 | 0.5584 | 0.12 | 74.3 | 2.5 | 4.1 | |
| | | 2012 | 0.008 | 0.011168 | 0.003 | 1.5 | 0.025 | 0.123 | |
| The output of Non-metallic minerals manufacturing in China, 2000-2012 (g $t^{-1}$ material production) | Glass | 1949-1996 | 0.124 | 0.248 | 49.556 | 24.8 | 0.372 | 6.194 | (EEA, 2000; EC, 2001c) |
| | | 2012 | 0.050 | 0.101 | 20.153 | 10.1 | 0.151 | 2.519 | |
| | Cement | Pre-1900 | 0.1 | 13.94 | 2.54 | 54.4 | 2.28 | 11.8 | (Nriagu and Pacyna, 1988; Passant et al., 2002; NPI, 2008; Streets et al., 2011; US EPA, 2012) |
| | | 2012 | 0.0202 | 0.0697 | 0.0127 | 0.38 | 0.0114 | 0.0511 | |
| | Brick | 1949-1996 | 0.044 | 0.059 | 0.104 | 0.068 | 0.007 | 0.023 | (US EPA, 1996b; NPI, 1998) |
| | | 2012 | 0.015 | 0.020 | 0.036 | 0.023 | 0.002 | 0.008 | |
| Municipal solid waste | MSWI | Pre-1900 | 2.8 | 2.14 | 0.5 | 107 | 5.45 | 4.49 | (Nriagu, 1979; Pacyna, 1984; Nriagu and Pacyna, 1988; US |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| incineration (g $t^{-1}$waste) | | 2016 | 0.060 | 0.053 | 0.0117 | 0.118 | 0.012 | 0.037 | EPA, 1996a; UK, 2000) |
| Biomass burning (g $t^{-1}$ residue) | Crop straw | 1949-2012 | 0.008 | 0.058 | 0.036 | 0.865 | 0.049 | 0.22 | (US EPA, 1996; Li et al., 2007; EEA, 2013; UK, 2013) |
| | Firewood | 1949-2012 | 0.03 | 0.03 | 0.09 | 0.91 | 0.08 | 0.9 | |
| Category | | Durable year | Ni | Sb | Mn | Co | Cu | Zn | Literature cited |
| Liquid fuel combustion (g $t^{-1}$ fuel combustion) | Crude oil | 1949-2012 | 10.6 | / | 0.223 | 0.151 | 0.460 | 1.035 | (de Souza et al., 2006; UK, 2013) |
| | Fuel oil for stationary sources | 1949-2012 | 10.6 | / | 0.223 | 0.151 | 0.460 | 1.035 | (de Souza et al., 2006; UK, 2013) |
| | Kerosene for stationary sources | 1949-2012 | 0.06 | / | 0.0504 | 0.101 | 0.030 | 0.489 | (US EPA, 1996a) |
| | Diesel oil for stationary sources | 1949-2012 | 0.06 | / | 0.0504 | 0.101 | 0.030 | 0.489 | (US EPA, 1996c) |
| | Gasoline | 1949-2012 | 0.04 | / | 0.004 | 0.002 | 0.02 | 0.0275 | (UK, 2013) |
| | Diesel oil for transportation | 1949-2012 | 0.04 | / | 0.040 | 0.0151 | 0.221 | 0.234 | (Wang et al., 2003b; UK, 2013) |
| | Kerosene for transportation | 1949-2012 | 0.03 | / | 0.004 | 0.002 | 0.034 | 0.01 | (UK, 2013) |
| Nonferrous metal smelting (g $t^{-1}$ nonferrous metal | Primary Al | 1949-1996 | 19.7 | / | / | / | / | 19.7 | (UK, 2000; 2013) |
| | | 2012 | 10 | / | / | / | / | 10 | |
| | Secondary Al | 1949-1996 | 0.802 | / | 1.16 | / | 3.2 | 15.2 | |
| | | 2010 | 0.407 | / | 0.588 | / | 1.621 | 7.734 | |
| | Primary Cu | Pre-1900 | 5000 | 337 | 100 | / | 8333 | 6000 | (Nriagu, 1979; Pacyna, 1984; |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| production) | | 2012 | 50 | 10.1 | 4.5 | / | 250 | 300 | Nriagu and Pacyna, 1988; Skeaff and Dubreuil, 1997; EC, 2001a; Pacyna and Pacyna, 2001; Pacyna et al., 2002; Theloke et al., 2008; EEA, 2009, 2013) |
| | Secondary Cu | 1949-1996 | 1 | 3 | / | / | 100 | 200 | |
| | | 2012 | 0.4 | 1.2 | / | / | 40 | 80 | |
| | Primary Pb | Pre-1900 | 167 | 507 | / | / | 83 | 680 | |
| | | 2012 | 5 | 15.2 | / | / | 5 | 20 | |
| | Secondary Pb | 1949-1996 | / | / | / | / | 1 | 20 | |
| | | 2012 | / | / | / | / | 0.4 | 8 | |
| | Primary Zn | Pre-1900 | 68 | 200 | / | / | 420 | 16000 | |
| | | 2012 | 1.36 | 6 | / | / | 25 | 500 | |
| | Secondary Zn | 1949-1996 | 0 | 0 | / | / | / | 270 | |
| | | 2012 | 0 | 0 | / | / | / | 137.1 | |
| | Ni smelting | 1949-1996 | 900 | / | / | / | / | / | (Nriagu, 1979; Tian et al., 2012b) |
| | | 2012 | 360 | / | / | / | / | / | |
| | Sb smelting | 1949-1996 | / | 173 | / | / | / | / | (Tian et al., 2012c) |
| | | 2012 | / | 70 | / | / | / | / | |
| Ferrous metals smelting (g $t^{-1}$ ferrous metal production) | Pig iron | Pre-1900 | 12 | 0.4 | 0.830 | / | 20 | 57.143 | (Nriagu, 1979; Pacyna, 1984; Nriagu and Pacyna, 1988; Kakareka et al., 1998; UK, 2000; EC, 2001a; Theloke et al., 2008; EEA, 2009; Pirrone et al., 2010; UK, 2013) |
| | | 2015 | 0.12 | 0.004 | 0.082 | / | 0.4 | 4 | |
| | Steel produced | Pre-1900 | 3.2 | 0.2 | 129 | / | 5.790 | 190 | |
| | | 2012 | 0.032 | 0.004 | 2.016 | / | 0.116 | 6.0 | |
| Non-metallic minerals manufacturing (g $t^{-1}$ material production) | Glass | 1949-1996 | 5.0 | / | / | / | 1.239 | 24.8 | (EEA, 2000; EC, 2001c) |
| | | 2012 | 2.015 | / | / | / | 0.504 | 10.1 | |
| | Cement | Pre-1900 | 8.1 | / | 55.3 | / | 24.2 | 57.2 | (Nriagu and Pacyna, 1988; Passant et al., 2002; NPI, 2008; US EPA, 2012) |
| | | 2012 | 0.0406 | / | 0.277 | / | 0.121 | 0.286 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Brick | 1949-1996 | 0.033 | 0.012 | 0.132 | 0.001 | / | / | (US EPA, 1996c; NPI, 1998) |
| | | 2012 | 0.011 | 0.004 | 0.045 | 0.0003 | / | / | |
| Municipal solid waste incineration (g $t^{-1}$waste) | MSWI | Pre-1900 | 3.93 | 6 | 9 | / | 14 | 60 | (Nriagu, 1979; Pacyna, 1984; Nriagu and Pacyna, 1988; US EPA, 1996b; UK, 2000) |
| | | 2016 | 0.086 | 3 | 0.208 | / | 0.127 | 0.109 | |
| Biomass burning (g $t^{-1}$ residue) | Crop straw | 1949-2012 | 0.177 | 0.019 | 0.0955 | 0.0045 | 0.1 | 0.028 | (US EPA, 1996a; Li et al., 2007; EEA, 2013; UK, 2013) |
| | Firewood | 1949-2012 | 0.98 | 0.0728 | 0.652 | 0.0045 | 0.1 | 1.25 | |

Table S17 Abatement efficiencies for iron and steel production (Kakareka et al., 1998)

| Elements | Efficiency, % | 95% confidence interval | |
|---|---|---|---|
| | | lower, % | upper, % |
| Pb | 96 | 93 | 98 |
| Cd | 96 | 91 | 98 |
| Ni | 94 | 88 | 97 |
| Zn | 95 | 90 | 98 |

Table S18 The emission limits of air pollutants of relative industrial process in China and developed regions, $mg/m^3$

| Pollutants | GB 25467-2010 | GB 25466-2010 | GB 30770-2014 | GB 25465-2010 | GB 28663-2012 | GB 28664-2012 | GB 4915-2013 | GB 29620-2013 | GB 26453-2011 | GB 18485-2014 | EU 2000/76/EC | EU 2001/80/EC |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| PM | 80 | 80 | 30 | 20-100 | 50 | 50-100 | 30 | 100 | 50 | 20 | 10~30 | 50~100 |
| $SO_2$ | 400 | 400 | 400 | 400 | 100 | / | 200 | 400 | 400 | 80 | 50 | 200~850 |
| $NO_X$ | / | / | 200 | / | 300 | / | 400 | / | 700 | 250 | 200 | 200~400 |
| As & compounds | 0.4 | / | 0.5 | / | / | / | | / | / | / | / | / |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pb & compounds | 0.7 | / | 0.5 | / | / | / | | / | / | / | / | / |
| Hg & compounds | 0.012 | 0.05 | 0.01 | / | / | / | 0.05 | / | / | 0.05 | 0.05 | / |
| Cd & compounds | / | / | 0.05 | / | / | / | | / | / | | 0.05 | / |
| (Cd+Tl) & their compounds | / | / | / | / | / | / | / | / | / | 0.1 | 0.05~0.1 | / |
| (Sb+As+Pb+Cr+Co+Cu+Mn +Ni) & their compounds | / | / | / | / | / | / | / | / | / | 1.0 | 0.5~1.0 | / |

219 Table S19 Data source of activity data for the main heavy metals emitting sectors in China

| Emission sectors | Data Sources |
|---|---|
| Coal consumption by power plants | China Electric Power Yearbook |
| | China Editorial Power Industry Statistics |
| Coal consumption by industrial boilers | China Mechanical Industry Yearbook |
| | China Coal Industry Yearbook |
| | China Energy Statistical Yearbook |
| Coal consumption by residential sectors | China Energy Statistical Yearbook |
| Coal consumption by other sectors | China Energy Statistical Yearbook |
| Biomass burning | China Statistical Yearbook |
| Liquid fuels combustion | China Energy Statistical Yearbook |
| Nonferrous metals smelting | The Yearbook of Nonferrous Metals Industry of China |
| Non-metallic minerals manufacturing | China Cement Almanac |
| Ferrous metal smelting | China Steel Yearbook |
| Municipal solid waste incineration | China Energy Statistical Yearbook |
| Brake and tyre wear | China Automotive Industry Yearbook |
| | China's Auto Market Almanac |

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221 Table S20 Selected parameters showing method and assumption for uncertainty analysis

| Categories | Parameter description | Distribution | Sources or methods |
|---|---|---|---|
| **Coal combustion sources** | | | |
| Coal | power plant | Normal (CV: 5%) | (Zhao et al., 2008) |
| consumption | Industrial sectors | Normal (CV: 5%) | (Tian et al., 2012a) |
| | Residential sectors | Normal (CV: 14%) | (Tian et al., 2012a) |
| | Other sectors | Normal (CV: 16%) | (Tian et al., 2012a) |
| Release rate | Pulverized-coal boiler | Triangular | Data fitting |
| | Stoker fired boiler | Triangular | Data fitting |
| | Fluidized-bed furnace | Triangular | Data fitting |
| | Coke furnace | Triangular | Data fitting |
| Removal | ESPs | Normal (CV: 5%) | Subject judgment |
| efficiency | EFs | uniform | Data fitting |
| | Wet scrubber | Triangular | Subject judgment |
| | Cyclone | Normal (CV: 20%) | Subject judgment |
| | Wet-FGD | Triangular | Subject judgment |
| | Coal washing | Uniform | Data fitting |
| **Non-coal combustion sources** | | | |
| Biomass burning | Biofuel consumption | Normal (CV: 20%) | (Zhao et al., 2011) |
| | Emission factors | Triangular | (Zhao et al., 2011) |
| | Ratio of biomass burning | Normal (province dependent) | (Zhao et al., 2011) |
| | straw-to-crop ratio | Uniform (product dependent) | (Zhao et al., 2011) |
| Liquid fuel | Liquid fuel consumption | Normal (CV: 5%) | (Zhao et al., 2011) |

| | | | |
|---|---|---|---|
| combustion | Emission factors | Normal (CV: 25%) | Subject judgment |
| Nonferrous metal smelting | Nonferrous metal production | Normal (CV: 5%) | (Zhao et al., 2011) |
| | Emission factors | Triangular | Data fitting |
| Non-metallic minerals manufacturing | Output of Cement/ glass / brick | Normal (CV: 20%) | Subject judgment |
| | emission factors (cement, glass) | Normal (CV: 25%) | Subject judgment |
| | emission factors (brick) | Normal (CV: 30%) | Subject judgment |
| Ferrous metal smelting | Pig iron and steel yield | Normal (CV: 15%) | (Zhao et al., 2011) |
| | Emission factors | Triangular | Subject judgment |
| Municipal solid waste incineration | MSW consumption | Normal (CV: 20%) | Subject judgment |
| | Emission factors | Normal (CV: 20%) | Subject judgment |
| Brake and tyre wear | Vehicle number | Normal (CV: 5%) | (Zhao et al., 2011) |
| | Average vehicle mileage | Normal (CV: 5%) | (Zhao et al., 2011) |
| | TSP emission factors | Uniform | Data fitting |
| | Heavy metal content | Triangular | Data fitting |

Table S21 The atmospheric concentrations of As, Pb, Cr and Cu in $PM_{2.5}$ in Beijing during 2000 to 2012

| Year | Atmospheric concentration (ng $m^{-3}$) | | | | Literature cited |
|---|---|---|---|---|---|
| | As | Pb | Cr | Cu | |
| 2000 | 30.0 | 300.0 | 20.0 | 30.0 | (Song et al., 2006b) |
| 2001 | | 170.0 | | 50.0 | (Duan et al., 2006) |
| 2002 | 38.3 | 218.3 | 26.7 | 58.3 | (Sun et al., 2004) |
| 2003 | 38.3 | 218.3 | 26.7 | 58.3 | (Sun et al., 2004) |
| 2005 | 16.0 | 189.5 | 50.0 | 53.0 | (Yu et al., 2012; Zhang et al., 2012) |
| 2006 | 20.2 | 173.3 | 73.6 | 43.1 | (Cui et al., 2008; Yang et al., 2008c, d; Yu et al., 2012) |
| 2007 | 19.0 | 189.7 | 31.7 | 51.3 | (Gao, 2012; Wang et al., 2010; Yu et al., 2012; Zhang et al., 2010) |
| 2008 | 7.6 | 67.5 | 5.8 | 25.8 | (Mu et al., 2010; Yu et al., 2012; Zhang, 2012; Zhang et al., 2010) |
| 2009 | 17.2 | 135.5 | 13.6 | 40.0 | (Tao et al., 2014; Zhao et al., 2013) |
| 2010 | 22.8 | 142.7 | 16.4 | 36.8 | (Tao et al., 2014; Yu et a., 2013) |
| 2011 | 15.6 | | 13.4 | 47.7 | (Wang et al., 2014) |
| 2012 | 23.4 | 158.0 | 24.6 | 54.7 | (Guo, 2014; Yang et al., 2015; Zhang et al., 2014) |

226 Table S22 Uncertainties in the sectoral emissions of heavy metals in China in 2010

| Categories | Hg | As | Se | Pb |
|---|---|---|---|---|
| Coal-fired power plant | 139.4 (-21.5%, 25.7%) | 406.4 (-22.6%, 25.2%) | 538.6 (-25.5%, 22.5%) | 833.0 (-25.6%, 25.9%) |
| Coal-fired industrial boiler | 171.0 (-44.6%, 60.7%) | 821.3 (-49.4%, 53.4%) | 965.1 (-49.3%, 56.6%) | 5449.5 (-57.5%, 58.7%) |
| Coal-fired residential sector | 7.4 (-57.4%, 55.7%) | 10.9 (-54.2%, 64.7%) | 74.3 (-57.3%, 65.7%) | 417.2 (-53.2%, 65.3%) |
| Coal-fired other sector | 22.4 (-66.1%, 71.4%) | 485.2 (-70.2%, 78.6%) | 282.9 (-69.4%, 71.9%) | 1224.1 (-57.0%, 80.9%) |
| Biomass burning | 9.1 (-47.5%, 48.4%) | 34.0 (-48.3%, 66.6%) | 33.3 (-50.2%, 42.3%) | 585.6 (-57.8%, 56.4%) |
| Liquid fuel combustion | 15.9 (-62.9%, 63.6%) | 11.8 (-48.2%, 41.3%) | 83.5 (-56.0%, 51.3%) | 678.4 (-89.3%, 68.2%) |
| Nonferrous metal smelting | 222.5 (-45.2%, 54.8%) | 338.9 (-57.1%, 67.6%) | 146.7 (-39.5%, 37.4%) | 1602.9 (39.6%, 37.8%) |
| Ferrous metal smelting | 29.9 (-52.0%, 52.1%) | 57.8 (-55.1%, 61.7%) | 9.9 (-47.2%, 58.4%) | 1047.3 (-53.5%, 72.3%) |
| Non-metallic minerals manufacturing | 52.9 (-81.6%, 98.5%) | 152.4 (-90.2%, 107.5%) | 744.0 (-95.1%, 103.2%) | 1085.0 (-82.3%, 98.7%) |
| Municipal solid waste incineration | 1.6 (-69.4%, 67.9%) | 1.2 (-65.3%, 75.1%) | 0.3 (-55.6%, 64.9%) | 3.8 (-65.3%, 69.2%) |
| Brake and tyre wear | / | 3.1 (-80.9%, 97.3%) | 1.9 (-81.0%, 159.6%) | 267.7 (-89.0%, 157.6%) |
| Total emission | 672.1 (-34.2%, 46.7%) | 2322.9 (-36.4%, 48.8%) | 2880.5 (-39.1%, 50.6%) | 13194.5 (-32.7%, 46.9%) |
| Categories | Cd | Cr | Ni | Sb |
| Coal-fired power plant | 15.5 (-19.0%, 27.0%) | 598.3 (-27.2%, 26.4%) | 537.8 (-19.1%, 23.7%) | 97.9 (-29.4%, 23.9%) |
| Coal-fired industrial boiler | 104.0 (-50.1%, 55.8%) | 5317.6 (-61.9%, 53.8%) | 1005.8 (-46.8%, 52.3%) | 214.8 (-51.6%, 63.6%) |
| Coal-fired residential sector | 3.7 (-58.6%, 60.4%) | 58.9 (-56.6%, 67.1%) | 33.7 (-58.2%, 68.8%) | 1.0 (-58.9%, 77.9%) |
| Coal-fired other sector | 25.7 (-62.5%, 66.5%) | 773.7 (-57.5%, 73.0%) | 185.7 (-69.8%, 80.0%) | 105.9 (-61.1%, 78.7%) |
| Biomass burning | 38.0 (-41.5%, 52.5%) | 263.1 (-45.3%, 59.6%) | 255.4 (-46.5%, 54.6%) | 21.9 (-60.7%, 65.1%) |
| Liquid fuel combustion | 9.6 (-61.0%, 57.9%) | 11.9 (-47.7%, 50.3%) | 422.1 (-58.2%, 67.9%) | / |
| Nonferrous metal smelting | 200.6 (-54.5%, 56.7%) | 19.7 (-35.9%, 37.3%) | 422.5 (-39.9%, 38.9%) | 122.6 (-38.1%, 33.6%) |
| Ferrous metal smelting | 28.3 (-48.7%, 56.7%) | 131.3 (-40.7%, 47.5%) | 102.7 (-55.0%, 45.8%) | 5.4 (-49.0%, 53.0%) |
| Non-metallic minerals | 28.8 (-80.6%, 90.0%) | 190.2 (-85.3%, 93.6%) | 155.4 (-90.4%, 86.9%) | 3.4 (-96.9%, 106.2%) |

| | | | | |
|---|---|---|---|---|
| manufacturing | | | | |
| Municipal solid waste incineration | 0.3 (-66.5%, 76.2%) | 0.9 (-58.8%, 68.3%) | 2.0 (-59.3%, 76.0%) | 69.5 (-75.7%, 71.0%) |
| Brake and tyre wear | 1.2 (-77.1%, 120.7%) | 99.6 (-97.0%, 171.5%) | 15.5 (-70.9%, 85.4%) | 425.7 (-91.1%, 170.0%) |
| Total emission | 455.8 (-35.7%, 49.3%) | 7465.2 (-33.8%, 47.8%) | 3138.6 (-38.2%, 49.4%) | 1068.1 (-35.6%, 48.3%) |

| Categories | Mn | Co | Cu | Zn |
|---|---|---|---|---|
| Coal-fired power plant | 3072.1 (-23.5, 29.1%) | 164.9 (-33.5%, 25.2%) | 1477.5 (-21.6%, 28.7%) | 2367.1 (-23.0%, 31.5%) |
| Coal-fired industrial boiler | 4472.2 (-43.6%, 45.1%) | 517.4 (-39.8%, 43.5%) | 2004.4 (-55.0%, 56.9%) | 4449.7 (-51.6%, 49.0%) |
| Coal-fired residential sector | 43.4 (-57.8%, 56.7%) | 5.3 (-62.6%, 58.4%) | 24.0 (-61.3%, 57.0%) | 284.6 (-59.7%, 57.0%) |
| Coal-fired other sector | 2130.7 (-60.6%, 74.7%) | 218.8 (-59.7%, 63.2%) | 933.0 (-65.2%, 73.4%) | 1058.8 (-65.6%, 65.2%) |
| Biomass burning | 158.8 (-52.3%, 53.4%) | 3.0 (-45.7%, 56.3%) | 66.8 (-45.7%, 46.3%) | 227.4 (-54.5%, 63.6%) |
| Liquid fuel combustion | 15.6 (-51.4%, 53.8%) | 8.6 (-46.7%, 55.1%) | 56.4 (-60.9%, 52.2%) | 81.5 (-62.6%, 44.4%) |
| Nonferrous metal smelting | 15.8 (-59.8%, 56.5%) | / | 990.1 (-66.8%, 53.5%) | 3960.2 (-56.3%, 41.6%) |
| Ferrous metal smelting | 1431.4 (-56.9, 68.2%) | / | 331.2 (-43.7%, 48.5%) | 6421.2 (-56.4%, 43.9%) |
| Non-metallic minerals manufacturing | 563.5 (-89.9%, 85.7%) | 0.3 (-93.3%, 94.1%) | 247.6 (-88.7%, 103.3%) | 889.8 (-86.4%, 94.2%) |
| Municipal solid waste incineration | 4.9 (-87.9%, 60.9%) | / | 3.1 (-61.4%, 66.5%) | 3.1 (-79.2%, 61.9%) |
| Brake and tyre wear | 107.4 (-45.1%, 61.8%) | 0.9 (-79.7%, 159.8%) | 2184.8 (-93.4%, 139.4%) | 760.2 (-84.3%, 113.9%) |
| Total emission | 12015.9 (-32.2%, 42.0%) | 919.2 (-38.1%, 41.4%) | 8318.8 (-37.5%, 50.8%) | 20503.7 (-32.2%, 45.5%) |

**Figures**

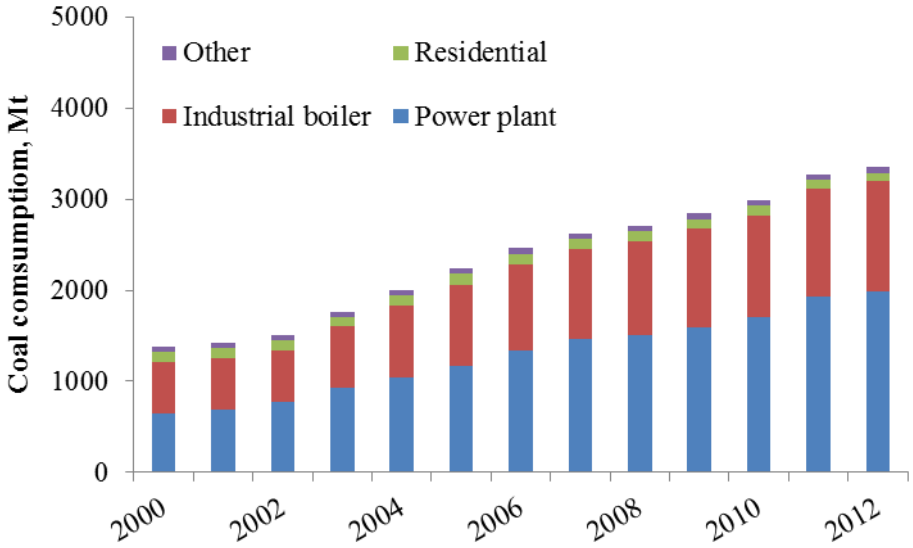



Fig. S1. Coal consumption by different sectors in China, 2000-2012

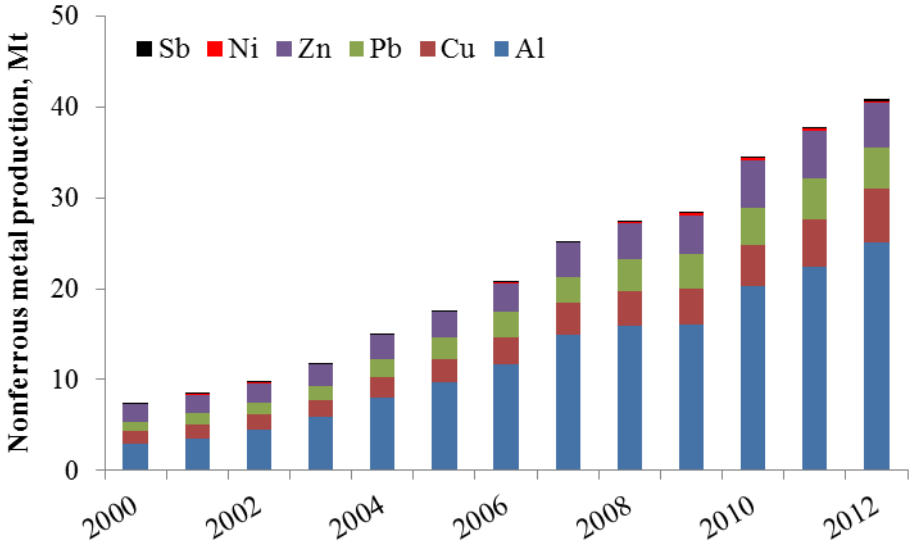
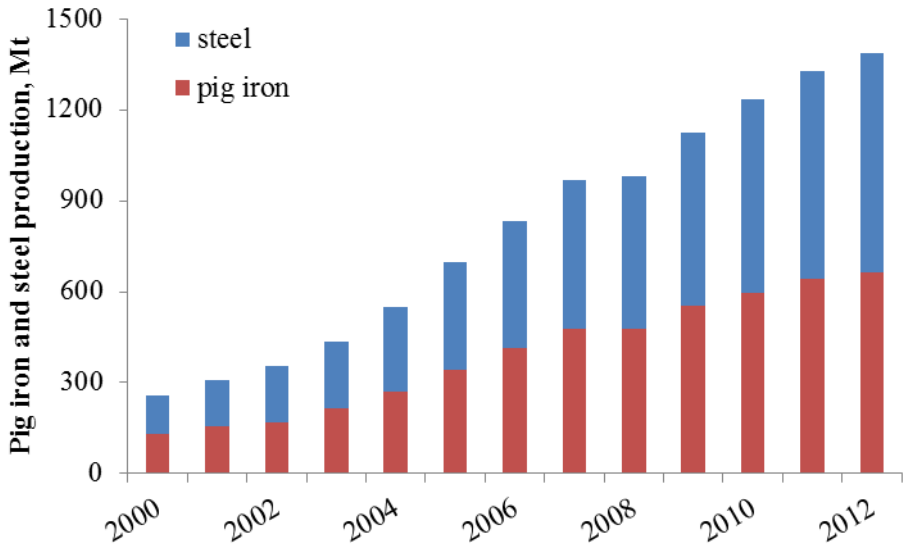



Fig. S2. The output of nonferrous metals in China, 2000-2012

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235 Fig. S3. The output of pig iron and steel products in China, 2000-2012

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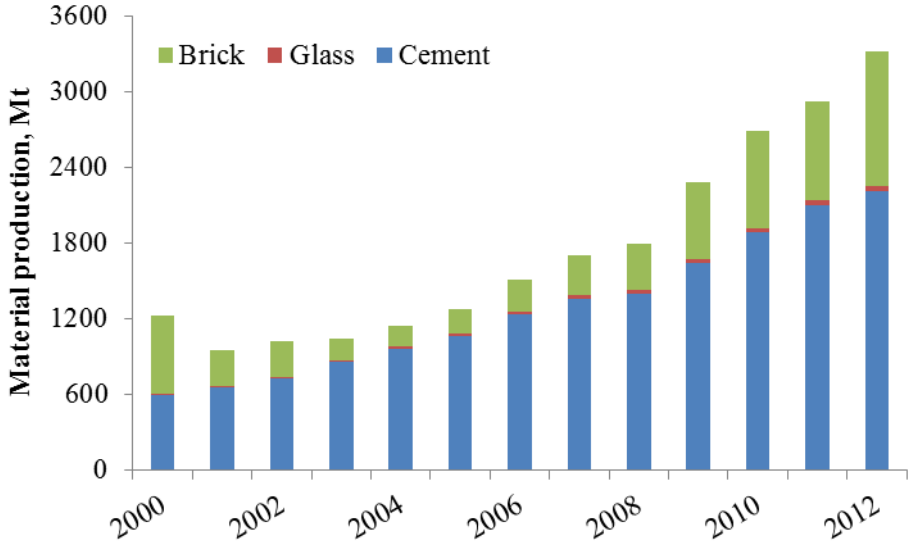


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238 Fig. S4. The output of non-metallic minerals manufacturing in China, 2000-2012

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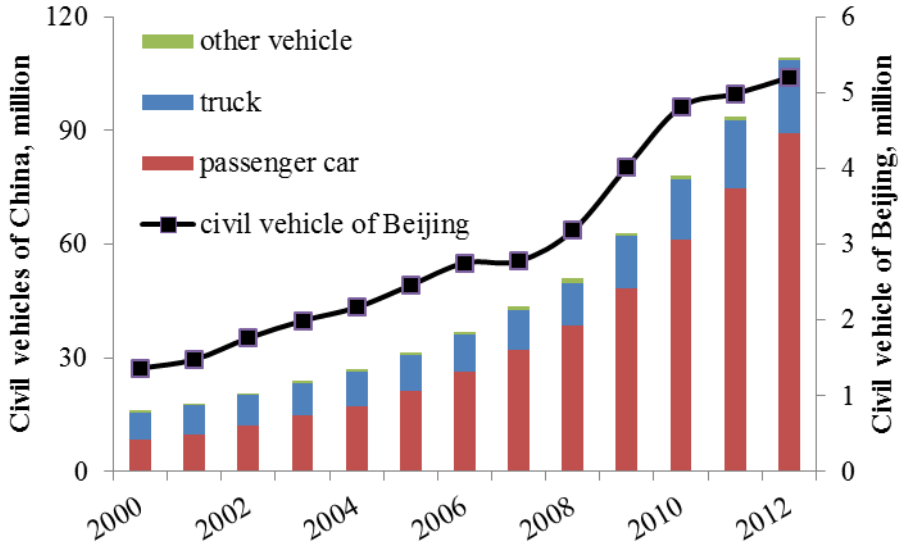



Fig. S5. The number of civil vehicles in China and Beijing, 2000-2012

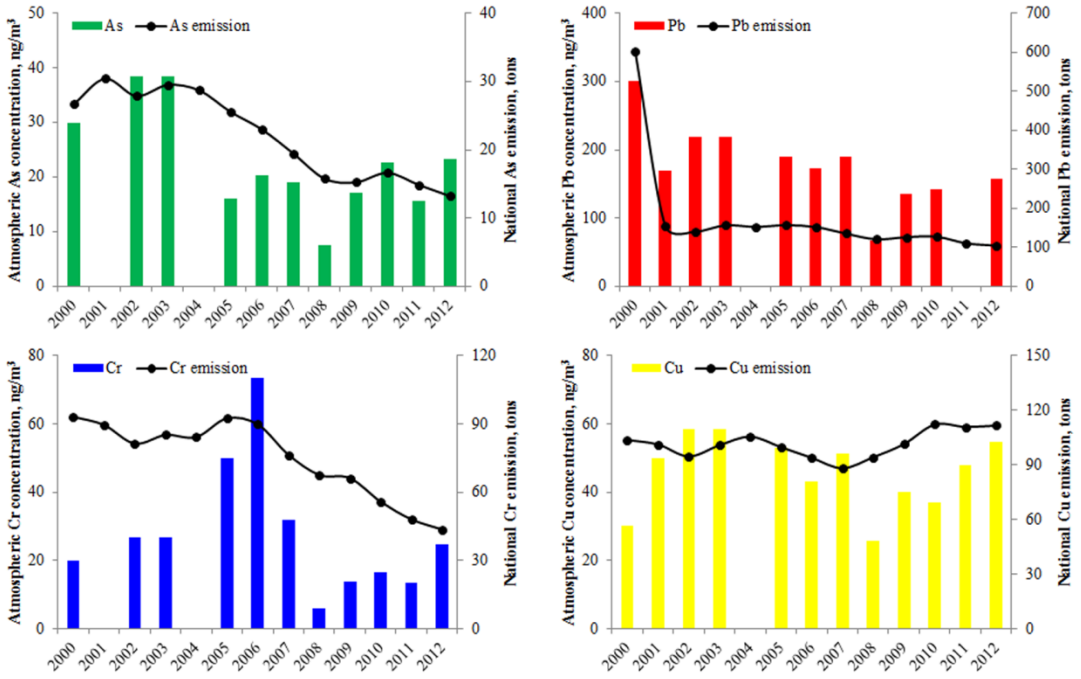
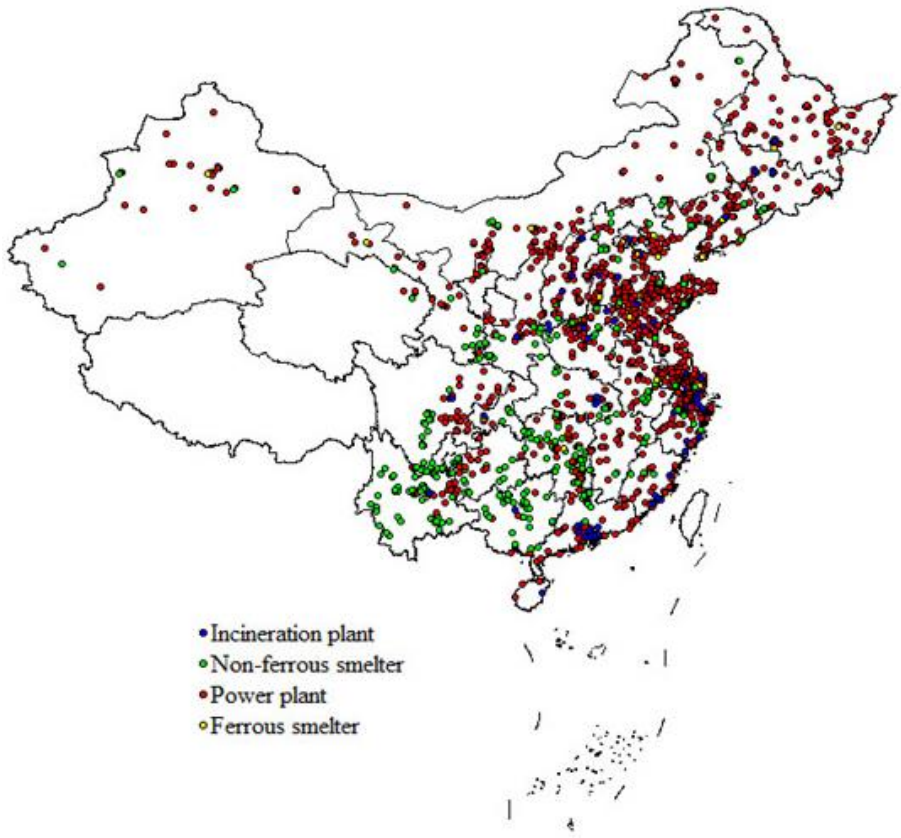



Fig. S6. Comparison between historical HM (As, Cr, Pb, and Cu) emissions and temporal variation of atmospheric concentrations in $PM_{2.5}$ in Beijing during 2000-2012

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248 Fig. S7 The distribution of point sources in China

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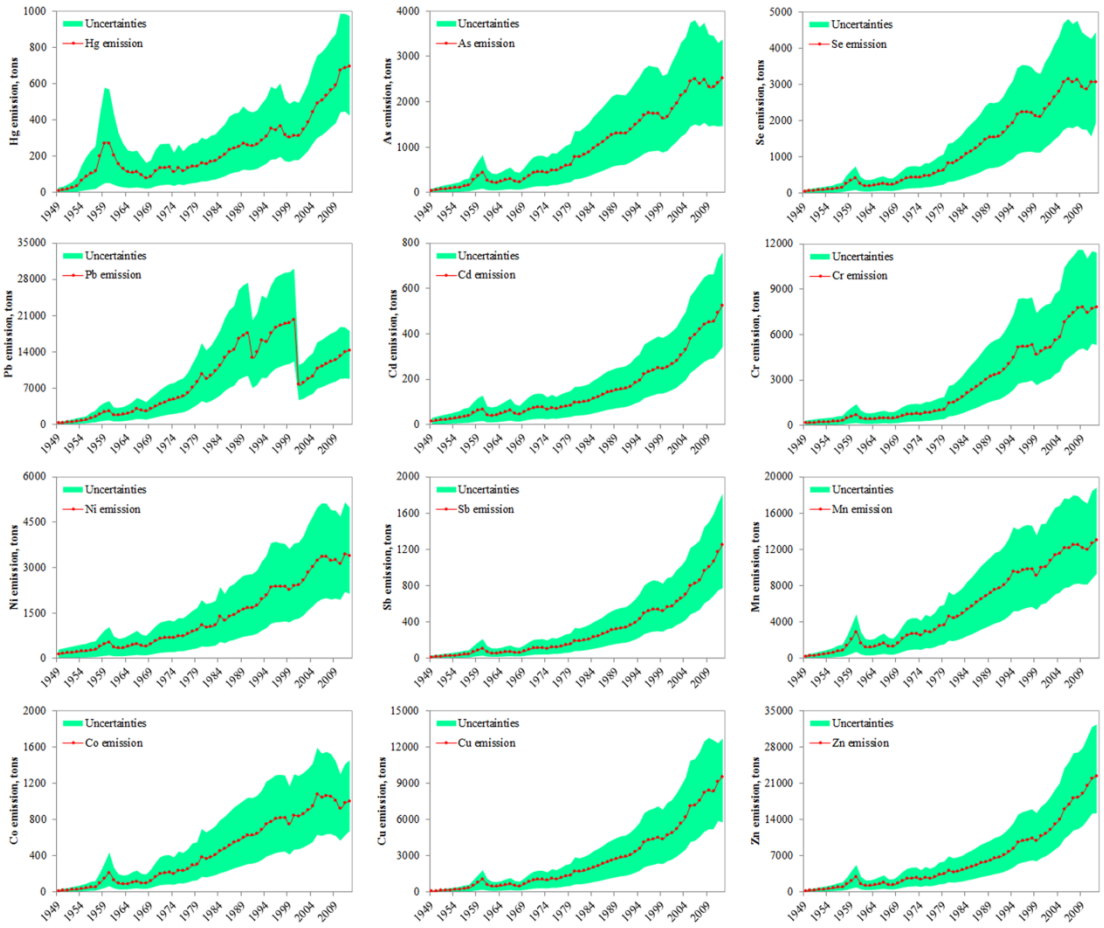


Fig. S8. The uncertainty bounds for China's anthropogenic atmospheric emissions of twelve HMs during 1949 to 2012

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