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

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Atmospheric emission inventory of heavy metals in China

H. Z. Tian et al.

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 established 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 allocated the annual emissions of these heavy metals in 2010 at a high spatial resolution of $0.5^{\circ} \times 0.5^{\circ}$ 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 %, amounting to about 79 570 t 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 were 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.

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 some elements (e.g., Se, Cr, Cu, Zn, etc.) are essential to the daily life activity of living beings, high concentrations of HMs not only impose a long term and irreversible burden on biogeochemical cycling in the ecosystem, but also threaten the health and life of animals and human beings by way of air pollutants inhalation and food intake (Cheng, 2003). Particularly, the International Agency for Research on Cancer (IARC) has assigned several HMs, like As and its inorganic compounds, Cd and its compounds, Cr (VI) compounds and Ni compounds, to the group of substances that are carcinogenic to humans. Besides, Pb and its compounds, Sb_2O_3, and Co and its compounds are suspected of being probably carcinogens (IARC, 2014).

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. Compared with natural sources, the contribution of anthropogenic emissions is regarded to be the primary factor influencing HM pollution and poisoning accidents (Pacyna and Pacyna, 2001; Huang et al., 2013). Therein, thermal power plants, coal-fired industrial boilers, leaded gasoline combustion (especially for Pb emission), brake wear (especially for the emission of Sb, Cu, etc.), non-ferrous metals smelting and steel making are regarded as the major contributors for different HM emissions among various anthropogenic sources (Hjortenkrans et al., 2007; Tian et al., 2010, 2012a–c; Li et al., 2012; Wang et al., 2012; Shao et al., 2013; H. G. Cheng et al., 2014).

With the rapid development of urbanization and industrialization, poisoning accidents associated with various HMs have happened frequently in China, such as arsenic poisoning in Dushan county of Guizhou province, children with excessive blood lead levels in Qingyuan city of Guangdong province and Fengxiang county of Guangxi province, cadmium poisoning in Zhuzhou city of Hunan provinces, etc. (Williams et al., 2009; Chen et al., 2012). According to release data from the Ministry of Environmental Protection of the People's Republic of China (MEP), 12 cases of HM incidents occurred in

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the Chinese mainland in 2009, resulting in 182 blood cadmium level exceedances and 4035 blood lead level exceedances.

Generally, at high temperatures, HMs will be released from the raw materials and/or feed fuels of anthropogenic activities as suspended particulate matter or in a gaseous form. Mukherjee et al. (1998) and Song et al. (2003) indicated 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.

Recently, elevated atmospheric concentrations of various HMs in urban areas have been reported in several studies (Wang and Stuanes, 2003; Lu et al., 2009). For instance, the mean atmospheric concentration of As, Cd, Ni, and Mn are reported at 51.0 ± 67.0, 12.9 ± 19.6, 29.0 ± 39.4, and $198.8 \pm 364.4\,\mathrm{ng\,m^{-3}}$ in China, which are much higher than the limit ceilings of 6.6, 5, 25, and $150\,\mathrm{ng\,m^{-3}}$ for WHO guidelines, respectively (Duan and Tan, 2013). Furthermore, more than 2 % of China's total 135.4 million ha of arable land is declared to be too polluted with HMs and other chemicals to use for growing food (CDN, 2014). Previous studies have indicated that atmospheric deposition is the primary source of most HMs entering agricultural land (Nicholson et al., 2003; Luo et al., 2009).

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).

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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) developed Hg emission inventory from anthropogenic activities of China for the year 1999 and 1995 to 2003, respectively. The research group led by Tian 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).

Especially, in February 2011, in order to tackle with the increasing emission and contamination of HMs from anthropogenic activities, a specific *Comprehensive Prevention Plan for HM Pollution* for the 12th Five-Year Plan (FYP) (2011–2015) was ratified by the State Council of Chinese government, in which a rigorous goal of 15 % HM reduction compared with reference emissions in 2007 has been set for the target year 2015. 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 were 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 estimated 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 Supplement file listed out the targeted heavy metal species and the associated emission sources. Generally, we classified 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 % of its total primary energy consumption (Tian et al., 2007, 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 were 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 were further classified into subcategories with respect to different boiler configurations and the application rates and removal efficiencies of various APCDs. The basic formulas could be expressed as follows:

$$E(t) = E_i E_j E_k [C_{i,j,k} \times A_{i,j,k} \times R_{i,j} \times (1 - \eta_{\mathrm{PM}(i,j)})(1 - \eta_{\mathrm{SO_2}(i,j)})(1 - \eta_{\mathrm{NO}_x(i,j)})] \quad (1)$$

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; η_{PM}, $\eta_{\mathrm{SO_2}}$ and η_{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

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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 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 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 calculated 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, 2013, 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, 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 Sects. S1 and S2 and Tables S3–S9, respectively.

2.1.2 HM emission factors from coal combustion sources

In this study, various coal combustion facilities were 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. 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 Table S10). The arithmetic mean values of release rates of these 12 HMs from different combustion boilers reported in literatures were 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 % 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 adopted the arithmetic mean values of those reported in available

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literatures as the average synergistic removal efficiencies by different APCD configurations, as shown in Tables 1 and 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 were 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:

$$E(t) = \sum_i \sum_j (A_{i,j} \times \mathrm{EF}_j) \tag{2}$$

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 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 was estimated at about 77 % (Biggins and Harrison, 1979) or 75 % (Hassel et al., 1987), and thus this parameter was 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 could be calculated

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according to the following equation:

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

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 were estimated by the following equation:

$$E(t) = \sum_i \sum_j \sum_k (P_{i,j} \times M_j \times \mathrm{EF}_{j,k} \times C_k) \tag{4}$$

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; $\mathrm{EF}_{j,k}$ 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 Tables S12 and 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 had 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.

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Here, we used S-shaped Curves (transformed normal distribution function) to determine the yearly variations of emissions factors of HMs over time period:

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

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).

Although S-shaped curves cannot account for economic shocks because of the form of monotonous smooth transitions, they fit historical and future trends better than polynomial or linear fits. Use of such S-shaped Curves to simulate the dynamics of technology change have been previously discussed by Grübler et al. (1999) and Geroski (2000) to represent technology transition and upgrade. Bond et al. (2007) and Streets et al. (2004, 2011) have demonstrated the use of this technique in estimating both historical and future emissions of carbon aerosol and Hg to the atmosphere from human activities. Based on the above method, we built 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 Table S14.

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

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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 (2011) indicated that China, Eastern Europe and Former USSR could be regarded as a uniform region with similar levels of technology development, whose emission factor trajectories are identical. Therefore, we presumed the emission factors of HMs with higher abatement implementation in Eastern Europe, Caucasus and Central Asia countries were 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 were determined (see Tables S15 and 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 presumed the average emission factors for secondary metal (Cu, Pb and Zn) smelting, aluminum smelting, antimony smelting and nickel smelting remained unchanged before the year 1996, at which the *Emission Standard of Pollutants for Industrial Kiln and Furnace* was first issued in China. We also presumed the average emission factors of HMs from secondary metals smelting and other nonferrous metals

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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) were reasonable for China before the year 1996. Subsequently, atmospheric emission factors of HMs from nonferrous metals industry in China would 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 were 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 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 accounted 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 chose 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 was mainly

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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 were 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 were determined by using of the similar method discussed above for nonferrous metals smelting industry. Please see Tables S16 and 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 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 presumed the best emission factors of air pollutants achieved in China today were 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 could be obtained from the Web Factor Information Retrieval System (WebFIRE) (US EPA, 2012). Moreover, the average emission factors for glass and brick manufacturing were assumed to remain unchanged pre-1996. Subsequently, atmospheric emission factors of HMs from these two sub-source categories would decrease gradually with

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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 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, 2013d), and it 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 (Z. Cheng et al., 2014; Li et al., 2014).

In this paper, the total mass of ten crop straws burned was 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. The average emission factors of HMs from these ten crop straw and firewood were summarized in 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 were 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 1 July 2000 due to the adverse health effects on the neurologic and/or hematologic

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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 was regulated less than 0.005 $g L^{-1}$ (GB 17930–1999, 2001–2012). Consequently, C_{Pb} in Eq. (3) was chosen to be 0.64, 0.35, 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 were summarized in 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 depends 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 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) 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 Table S18). Here,

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we presumed the best emission factors of HMs in China for MSW at 2016 were 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 were determined. Specific emission factors of various HMs from MSW incineration can be seen in 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 adopted the average emission factors of TSP from brake wear and tyre wear for passenger cars (0.0075 and 0.0107 $g\,km^{-1}$), light-duty trucks (0.0117 and 0.0169 $g\,km^{-1}$) and heavy-duty vehicles (0.0365 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

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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.

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 presumed the composition of worn materials from brake and tyre wear in term of HMs were consistent with foreign countries (see 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.) were 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.) were 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 Table S19. Furthermore, trends of activity levels by different sectors in China between 2000 and 2012 are summarized in Figs. 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 was conducted by combining uncertainties of both activity levels and emission factors, through adopting Monte Carlo simulation (Zhao et al., 2011; Tian et al., 2014a, b). 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, were 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). Further details can be found in Table S20. 10 000 times of Monte Carlo simulations were run to estimate the range 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 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 were 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 decreased 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,

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1974 and 1976, the annually averaged growth rates of national emissions of HMs from primary anthropogenic sources were still as high as 0.2–8.4 % during the periods from 1963 to 1977.

Subsequently, the policy of openness and reformation was issued by the Chinese central government. With the implementation of this policy from 1978 to 2012, China's GDP had 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 was 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 was 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 268.0–11 308.6 t in 2001 increased to about 378.9–15 987.9 t in 2005, at an annually average growth rate of 4.8–12.0 %, respectively (see Table 2).

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. Since leaded gasoline has been phased out in 2000, the total Pb emissions from primary anthropogenic sources were reduced abruptly by about 62 % in 2001. Subsequently, along with the rapid increase of vehicle volume and oil consumption, a substantial increase was 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 process 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 were diverse during the period of 2006 to 2012. Generally speaking, the national atmospheric emissions of Hg, Pb, Cd, Cr, Sb, Cu and Zn increased at an annual average growth rate of 1.5–7.2 % from 2006 to 2012. In spite of the remarkable growth in coal

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consumption and gross industrial production, the national As, Se, Ni, Mn and Co emissions were well restrained in this period. 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.

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, 2013d). Meanwhile, coal burned by power plants has increased from 5.2 to 1785.3 Mt (NBS, 2013b), with an annual growth rate of 9.9 % and a percentage share of the total coal consumption increasing from 22.7 to 50.6 %. For the period of 1949 to 2005, the emissions of HMs from coal combustion by power plants have increased in rough proportion to coal consumption. However, this trend began to change after 2006 due to the implementation of policies of energy-saving and pollution reduction, especially the strengthening of SO_2 emission control for coal-fired power plants.

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 % used 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 were estimated at about 15.2–3038.9 t (see Fig. 2), which had decreased by 1.7–11.8 % annually since 2006, respectively. 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). Moreover, the distinction of integrated co-

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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.

Compared with United States (13 380 kWh capita^{-1}), Japan (8340 kWh capita^{-1}) and EU (6250 kWh capita^{-1}), the average electricity consumption per capita (ECPC) of China (3153 kWh capita^{-1}) is modest despite the tremendous coal consumption by coal-fired power plants (IEA, 2010). Due to the unique energy resource structure of China (rich coal, deficient oil, and lean gas) and relatively lower price of coal, it is anticipated that coal combustion will continue to be a major component of energy production in the next 50 years in response to the increasing electricity demand for industrial manufacturing sectors, as well as service and residential sectors. Therefore, in order to further abate HM emissions from coal-fired power plants in China, specified HM control technologies (e.g., activated carbon injection, bromide injection into the furnace, etc.) and integrated management strategies proposed on accounting of the current emission status and future pollution reduction demand of coal-fired power plants are in great need.

3.1.2 HM emissions from coal consumption by industrial boilers

The total atmospheric emissions of HMs from coal combustion will be affected by many parameters. Among them, the amount of combusted coal, the contents of HMs in feed coals and the removal efficiencies of HMs through different APCD configurations are the three key factors.

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

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coal-fired industrial sectors of China, especially for the small and medium scale boilers (CMIF, 2013).

During the period of 2001 to 2012, the final discharge rates of soot into the atmosphere per ton of coal combustion by industrial boilers have been reduced significantly from 16.7 to 5.0 $g\,t^{-1}$ owing to the increasing application rate of high removal efficiency APCDs (NBS, 2013a). Meanwhile, toxic HMs associated with fine particulate could be partly removed synergistically by the conventional APCD configurations.

As can be seen from Fig. 2, the emission trends of HMs from coal consumption by industrial boilers were consistent with the total national 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. Subsequently, the emissions of different toxic HMs from coal consumption by industrial boilers 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 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 presented 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 nonferrous metals smelting

Certain HMs (e.g., Hg, As, and Cd) are important associated elements in nonferrous metals (copper, lead and zinc) ores. 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

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flue gas, and impose adverse impacts on the human health and regional ecosystems. Based on previous studies, nonferrous metals smelting industry accounted for the considerable fraction of certain HMs (e.g., Hg, As, Pb, Cd, Ni, Sb, Cu, Zn, etc.) emitted from anthropogenic activities (Pacyna and Pacyna, 2001; Wu et al., 2012), which is in well accordance with this study.

Generally, because of extremely high Hg emission factors from mercury mining subsector, the emission trends of Hg from nonferrous metals smelting sector were highly correlated with the outputs of mercury mining during 1949 to 1997, which indicated that the subsector of mercury mining represented the major contributor to the Hg emission from nonferrous metals smelting sector before 1997, accounting for about 39.0–98.7 %. Historically, a sharp fluctuation of Hg discharges from nonferrous metals smelting sector occurred in the period of Great Leap Forward to Great Leap Forward Famine (increased from 92.6 in 1957 to 221.7 t in 1959, then decreased rapidly to 104.0 t in 1963), this was mainly due to the rapid increase or decline of mercury mining outputs in this period (increased from 1060 in 1957 to 2684 t in 1959, then decreased rapidly to 1345 t in 1963). Subsequently, a sharp increase of emissions of Hg has occurred, with the emissions from about 60.6 t in 1998 increased 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 changed to the subsector of primary-Zn smelting, which occupied about 36.9–52.7 % during 1998 to 2012.

Unlike Hg emission, the total discharges of As, Se, Pb, Cd, Ni, Sb, Cu and Zn from nonferrous metals smelting sector increased gradually since 1949 (see Fig. 2). Driven by strong economic growth in China over the past thirty years since the openness and reformation, the demand for nonferrous metals products has increased significantly. According to the statistical data from *The Yearbook of Nonferrous Metals Industry of China*, the total output of six nonferrous metals (Al, Cu, Pb, Zn, Ni and Sb) increased by about 44 times from 0.93 in 1978 to 40.8 Mt in 2012 (CNMIA, 2013). Because of the increasing application rate of advanced smelting technologies plus conventional APCD configurations in nonferrous smelting plants to meet more stringent emissions limits

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of pollutants for environmental protection (e.g., GB 9078–1996, GB 25466–2010, GB 30770–2014, etc.), the final discharge rates of HMs per ton of nonferrous metals production have been reduced gradually. However, 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. Consequently, the emissions of As, Se, Pb, Cd, Ni, Sb, Cu and Zn from nonferrous metals smelting sector had 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.

3.1.4 HM emissions from ferrous metal smelting

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). Depite enormous achievement obtained by China's iron and steel industry, China is still a steel producer with low energy efficiency and high pollutants emission level compared with other major steel-producing countries (Guo and Fu, 2010).

The peak output of open-hearth steel with 14.5 Mt occurred in 1993. Thereafter, Open-Hearth Steel making technology fell into disuse in China, and the proportion of open-hearth steel in Chinese output of crude steel had turned out to be negligible after 2003 (NBS, 2013c). The output of basic furnace steel and electric furnace steel increased from 1000 and 32 000 t in 1949 to 652.0 and 64.5 Mt in 2012, accounting for about 90.1 and 8.9 % of total steel output, respectively.

As can be seen from Fig. 2, a steady increase of HM emissions from the pig iron and steel industry accompanying by certain undulations occurred from 1949 to 1999. 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 emisions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Cu and Zn almost doubling. Following that period, HM emissions from the pig iron and steel production show a significantly continuous decrease over the period 1960–

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1963. Although emission factors have levelled 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 had 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 represented the major contributor to the Zn emissons, accouting for about 60.9–62.9 % during this period.

3.1.5 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. 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 it has been forbidden to produce and use leaded gasoline since 2001.

In this study, we estimated that the discharge of Ni from liquid fuels combustion had increased from 12.8 in 1949 to 604.5 t in 2012. Therein, fuel oil combustion had contributed over 82.1 % of the total liquid fuels consumption category in 2012. 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.

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

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gasoline period (1949 to 1999: gasoline with high lead content; 1991–2000: gasoline with low lead content) and the unleaded gasoline period (2001 to 2012). As a result, the discharge of Pb from gasoline combustion category had experienced two fluctuations over the 64 year period. The first sharp emission decline occurred in 1991, and the total emissions decreased by 36.8 % from 12 832.2 t in 1990 to 8107.5 t in 1991, this was mainly because the average Pb content in leaded gasoline regulated by GB 484–89 was decreased about 45.3 % compared to that in GB 484–64. The other sharp decline occurred in 2001, and the total emissions decreased by 98.1 % from 12 866.7 t in 2000 to 248.3 t in 2001. However, the Pb emissions from this category 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).

3.1.6 HM emissions from brake and tyre wear

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).

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. 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, 2013d). 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 was up to about 17.5 %, which was 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 were estimated due to trace level of these elements in brake linings.

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But regrettably, the adverse effects of airborne PM originated from brake wear on human health and ecosystem still did not arouse sufficient attention from central government of China as well as the public.

3.2 Comparison of China's HM emissions with other inventories

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 would be discussed in this study (see Fig. 3). Specifically, limited data of China's Hg emissions could 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 focused 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 were 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 could 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 determined 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 was 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) were higher than our estimation in the same year. This was mainly because the emission factor of Hg from coal consumption by residential sectors was cited from Australia NPI in this paper, which was 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 were generally lower than those in other Hg emission inventories in the same

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year. This might be because that we had 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 were generally lower than those used in studies of Streets et al. (2005), Wu et al. (2006) and Wang et al. (2012) in the same year.

Besides, some anthropogenic sources with high uncertainties were not taken into account in this work due to the lack of detailed activity data. Moreover, certain natural sources (e.g., forest burning, grassland burning, etc.) were also not included in this study. Consequently, our estimated total Hg emissions were lower than those in inventories estimated by Streets et al. (2005) and Wu et al. (2006).

3.3 Composition of HM Emissions by province and source category in 2010

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 were estimated at about 72 955.2 t. As can be seen in Fig. 4, coal combustion sources represented the major contributors of Hg, As, Se, Pb, Cr, Ni, Mn, Co and Cu emissions and were 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.

3.3.1 Mercury (Hg)

In terms of source category contribution, emissions from nonferrous metals smelting sector, coal consumption by industrial boilers and coal combustion by power plants represented the top three major sources, with a share of 33.1, 25.4 and 20.7 %, of total emissions, respectively. Regarding nonferrous metals smelting emissions, primary-Zn smelting industry and mercury smelting industry were the two dominant sub-category sources, which occupied about 41.4 and 33.0 % of nonferrous metals smelting emissions in 2010, respectively.

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For provincial emissions and source contributions on the provincial level in 2010, the top five provinces with largest Hg emissions were identified as Guizhou (64.5 t), Shaanxi (50.6 t), Shandong (48.8 t), Henan (41.8 t) and Hunan (39.2 t). However, Wu et al. (2006) indicated that Henan, Guizhou, Guangdong, Hunan, Liaoning were the highest Hg emitting provinces in 2003. This was mainly because of enormously provincial variations of output of industrial products and coal combustion between 2003 and 2010 (e.g., the outputs of Pb in Henan contributed 33 and 25 % to national productions in 2003 and 2010, respectively). 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. In Guizhou and Shaanxi province, Hg emissions from mercury smelting took the majority, with about 70.7 and 54.8 %, respectively, due to the high emission factor of Hg from this sub-category source and huge production of mercury in these two provinces (the outputs of mercury of Guizhou and Shaanxi in 2010 were about 986 and 599 t, accounting for about 62.2 and 37.8 % of total national mercury output, respectively). In Shandong, coal consumption by industrial boiler ranked as the largest emitter (32.9 %), followed by coal combustion by power plants (30.3 %). In Henan province, the contributions of coal consumption by industrial boiler and nonferrous metals smelting sector were dominant (both at about 30 %). Regarding nonferrous metals smelting emissions from Henan, the primary-Pb smelting industries and primary-Zn smelting industries were found to be the primary sub-category sources which occupied 12.9 and 9.9 % of the total Hg emissions in Henan mainly due to the high production of primary-Pb smelting (accounting for about 34.0 % of the total national production) and relatively lower removal efficiency of mercury through conventional APCDs for nonferrous metals smelting sector. Because of high production of primary-Zn (accounting for about 23.5 % of the total national production), Hunan was dominated by this subsector as the primary contributing source, which accounted for about 44.5 % of the provincial Hg emissions.

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3.3.2 Arsenic (As)

The major sources of As emission were found to be coal consumption by industrial boilers, coal consumption by other sectors, coal combustion by power plants and nonferrous metals smelting, accounting for 35.4, 20.9, 17.5 and 14.6 % of the total emissions, respectively. As for nonferrous metals smelting industrial processes, the subsector of primary-Cu smelting industry, accounting for about 89.5 %, represented the major contributor to the arsenic emission.

Shandong, Inner Mongolia and Hebei ranked as the top three largest provinces with As emissions, accounting for about 10.6, 7.6 and 6.7 % of the national emissions, respectively. As can be seen from Fig. 4b, the combined As emissions from coal consumption by industrial boilers, coal consumption by other sectors and coal combustion by power plants took the majority in these three provinces, contributing about 77.4, 83.6 and 81.7 % of each provincial emission, respectively.

3.3.3 Selenium (Se)

As can be seen from Fig. 4c, the major sources of Se emissions in China in 2010 were coal consumption by industrial boilers, non-metallic mineral manufacturing sector and coal combustion by power plants, which occupied 33.5, 25.8 and 18.7 % of the national emissions, respectively. 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 decolorising agent in glass production process and huge output of glass production.

In terms of provincial level emissions, the key provinces were as follow: Shandong (294.5 t, 10.2 % of the national emissions), Hebei (239.6 t, 8.3 % of the national emissions) and Henan (224.1 t, 7.8 % of the national emissions). Hence, atmospheric Se release from the glass production industry and coal consumption by industrial boilers in these three provinces should be emphasized in priority when designing control and reduction regulations.

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3.3.4 Lead (Pb)

For Pb emissions, coal consumption by industrial boilers and nonferrous metals smelting sector represented the two major contributors, accounting for 41.3 and 12.1 %, respectively. Regarding nonferrous metals smelting emissions, primary-Cu smelting industry and primary-Pb smelting industry were demonstrated to be the dominant subcategory sources, which occupied 37.3 and 36.5 % of the total nonferrous metals smelting emissions in 2010, respectively, mainly due to their high emission factors as well as huge volume of production yields.

Hebei was found as the province producing largest lead emissions throughout China, with a total Pb emissions of about 1220.5 t in 2010, accounting for 9.3 % of the national emissions (see Fig. 4d), mainly due to huge coal consumption by coal consumption by industrial boilers (accounting for about 50.8 % of total provincial emissions) and prosperous steel production (accounting for about 19.5 % of total provincial emissions). Simultaneously, Shandong and Henan generated 1160.2 and 815.1 t of the Pb emissions, respectively. Besides, the local government (especially for Henan) also should pay more attention to the emission reduction of Pb from primary-Pb smelting industry due to the high output of lead ore in this province (0.95 Mt, 34.0 % of the national lead ore production) and the elevated exposure risk of Pb for exceedance of Children's blood.

3.3.5 Cadmium (Cd)

In sum, the major sub-category sources for Cd emissions in China in 2010 were nonferrous metals smelting sector, coal consumption by industrial boilers and other non-coal sources, which accounted for 44.0, 22.8 and 8.4 % of the total emissions, respectively (see Fig. 4e) In term of nonferrous metals smelting emissions, primary-Cu smelting industry was thought to be the dominant sub-category emission source, which occupied 74.8 % nonferrous metals smelting emissions in 2010.

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In terms of provincial emissions, the top three provinces were as follow: Shandong (37.1 t, 8.1 % of the national emissions), Jiangxi (32.5 t, 7.1 % of the national emissions) and Yunnan (31.6 t, 6.9 % of the national emissions). Primary-Cu smelting industry ranked as the largest emitter in these three provinces, accounting for about 42.8, 46.0 and 80.0 %, respectively, of each provincial emission.

3.3.6 Chromium (Cr)

The national atmospheric Cr emissions from anthropogenic sources in 2010 reached 7465.2 t, of which about 5317.6 t were emitted from coal consumption by industrial boilers (Fig. 4f).

Yunnan, Shandong and Hebei were the three largest provinces, accounting for about 7.8, 7.7 and 7.1 % of the national emissions, respectively. In particular, the contribution of coal consumption by industrial boiler was dominant (about 76.6 %) in Yunnan, mainly due to high concentration of chromium in feed coals. For instance, the averaged concentration of chromium in coals as consumed in Yunnan is about 71.7 $\mu g\, g^{-1}$, which is two times higher than the national averaged concentration of chromium in coal as consumed in China (see Table S8).

3.3.7 Nickel (Ni)

For Ni emissions, coal consumption by industrial boilers, coal combustion by power plants, nonferrous metals smelting sector and liquid fuels combustion sector were the major source contributors, accounting for 32.0, 17.1, 13.5 and 13.4 %, respectively (see Fig. 4g). Within nonferrous metals smelting emissions, primary-Cu smelting industry, primary-Al smelting industry and nickel smelting industry represented the dominant sub-category sources, accounting for 38.7, 38.4 and 17.2 % of the total nonferrous metals smelting emissions in 2010, respectively, mainly due to the huge productions of copper ore and aluminum ore as well as the high emission factors of Ni in smelting pro-

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cess. With respect to liquid fuels combustion emissions, fuel oil combustion contributed over 72.4 % of this category in 2010.

Shandong was the province producing highest Ni emissions throughout China, with a total Ni emission of 328.8 t in 2010, which accounting for 10.5 % of the national emissions. Therein, coal consumption by industrial boilers (30.2 %) and coal combustion by power plants (23.1 %) were regard as the major contributors of Ni emission in Shandong. Simultaneously, provinces of Henan and Liaoning generated 173.3 and 171.0 t of the Ni emissions, respectively. In Henan, the contribution of coal consumption by industrial boiler and primary-Al smelting industry were dominant, accounting for about 38.7 and 21.5 % of the total provincial emission. Whereas in Liaoning, the contributions of coal consumption by industrial boilers, coal combustion by power plants and fuel oil combustion subsector were dominant, accounting for about 29.7, 22.4 and 17.5 % of the total provincial emissions.

3.3.8 Antimony (Sb)

Brake and tyre wear sector, coal consumption by industrial boilers and nonferrous metals smelting sector were top three major sources, with 39.9, 20.1 and 11.5 % of the total Sb emissions, respectively. Within brake and tyre wear emissions, brake wear is the absolutely dominant sub-contributor, which occupied over 99.9 % of brake and tyre wear emissions in 2010. Regarding nonferrous metals smelting emission, Sb emissions from primary-Pb smelting, primary-Zn smelting and primary-Cu smelting were dominant with a share of 36.0, 25.6 and 25.0 %, respectively.

The top four provinces with largest Sb emissions were found in Guizhou (77.2 t), Shandong (70.9 t), Jiangsu (65.4 t) and Guangdong (62.4 t). As can be seen from Fig. 4h, the total discharges of Sb from Shandong, Jiangsu and Guangdong were characterized by the outstanding contribution of brake wear, accounting for 49.7, 40.9 and 53.4 % of the provincial emissions, respectively. This was mainly because these three provinces are all economically developed and populous provinces with explosive increase of vehicles and huge requirement of citizen's trip. In Guizhou province, the

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contributions of coal consumption by other sectors and coal consumption by industrial boiler sector were dominant, which accounted for 50.4 and 27.1 %, respectively. This was mainly due to high concentration of antimony in feed coals of Guizhou and low application rate of APCDs in coal consumption by other sectors. For instance, the bootstrap weighted average concentration of Sb in coal as consumed in Guizhou was calculated at about 6.0 $\mu g\,g^{-1}$, which was approximately four times higher than the national averaged concentration of Sb in coal as consumed in China (see Table S8).

3.3.9 Manganese (Mn)

The three major Mn sources were coal consumption by industrial boilers, coal combustion by power plants and coal consumption by other sectors, accounting for 37.2, 25.6 and 17.7 % of the total emissions, respectively. As for non-coal combustion sources, ferrous metals smelting sector represented the major contributor, with a share of 11.9 % of the total.

Shandong, Hebei and Inner Mongolia were thought to be the three largest provinces with Mn emissions, accounting for about 9.7, 9.3 and 8.6 % of the national Mn emissions, respectively. As can be seen from Fig. 4i, the coal combustion sources (coal consumption by industrial boilers, coal combustion by power plants and coal consumption by other sectors) should be emphasized in priority when designing control and reduction regulations for Mn emission in Inner Mongolia and Shandong, which almost contributed about 94.4 and 82.9 % of each provincial emission, respectively. Nevertheless, in Hebei province, the sector of coal consumption by industrial boilers and ferrous metals smelting represented the dominant sources, which occupied approximately 41.3 and 27.9 % of the provincial emissions, respectively. This was mainly due to the high coal consumption by coal consumption by industrial boilers and huge output of steel production in Hebei (144.6 Mt, accounting for about 22.7 % of the national steel production in 2010).

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3.3.10 Cobalt (Co)

As can be seen from Fig. 4j, the major sources of Co emissions in China in 2010 were coal consumption by industrial boilers, coal consumption by other sectors and coal combustion by power plants, accounting for about 56.3, 23.8 and 17.9 % of the national total Co emissions, respectively.

In terms of provincial-level emissions, the key provinces were as follow: Shanxi (69.1 t, 7.5 % of the national emissions), Shandong (65.1 t, 7.1 % of the national emissions) and Guizhou (59.9 t, 6.5 % of the national emissions). 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.

3.3.11 Copper (Cu)

Brake and tyre wear sector, coal consumption by industrial boilers, coal combustion by power plants and nonferrous metals smelting sector were dominant sources, with a share of 26.3, 24.1, 17.8 and 11.9 % of total Cu emissions, respectively. Regarding brake and tyre wear emissions, brake wear was the dominant contributor, which almost occupied 99.6 % brake and tyre wear emissions in 2010 on accounting of the high content of Cu in the brake linings (about 117.94 $mg\,g^{-1}$ for brake linings front and 92.20 $mg\,g^{-1}$ for brake linings rear, Hjortenkrans et al., 2007) and the explosive expansion of vehicle population in China (see Fig. S5). With respect to nonferrous metals smelting emissions, primary-Cu smelting industry accounted for approximately 76.6 % of the nonferrous metals smelting sector's emissions.

The top three provinces with largest Cu emissions were found in Shandong (763.5 t), Hebei (558.1 t) and Henan (517.4 t). As can be seen from Fig. 4k, the total discharges of Cu from brake wear plus coal consumption by industrial boilers plus coal combustion by power plants were dominant in the above three provinces, which occupied about 65.4, 73.8 and 85.6 % of each provincial emission, respectively.

3.3.12 Zinc (Zn)

The national atmospheric Zn emissions from anthropogenic sources in 2010 were estimated at 20 503.7 t, of which about 31.3, 21.7, 19.3 and 11.5 % were emitted from ferrous metals smelting sector, coal consumption by industrial boilers, nonferrous metals smelting sector and coal combustion by power plants, respectively. In terms of ferrous metals smelting emissions, the pig iron production industry and steel production industry were responsible for 37.8 and 62.2 %, respectively. With respect to nonferrous metals smelting emissions, the Primary-Cu smelting industry and Primary-Zn smelting industry were the dominant subsectors, responsible for 22.6 and 65.9 % of the total nonferrous metals smelting sector's emissions, respectively.

Hebei, Shanxi and Shandong ranked the three largest provinces with Zn emissions, accounting for about 11.3, 7.2 and 7.1 % of the national emissions, respectively. As can be seen from Fig. 4l, the Zn emissions from ferrous metals smelting sector took the majority, with about 63.0 and 40.0 % in Hebei and Shandong, respectively, mainly due to the explosive increase of production of pig iron and steel in these two provinces along with rapid economic growth in China (see Fig. S3). Furthermore, the coal consumption by industrial boilers was thought to be the dominant subsectors in Shanxi with 53.9 % of the total provincial emissions due to the booming coke making industry of this province.

3.4 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 were identified as large point sources and their emissions are precisely allocated at their latitude/longitude coordinates (the geographical distribution of 2496

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point sources in China is shown in Fig. S6). It should be noted here, the emissions from point sources of nonferrous metals smelting industry and ferrous metals smelting industry contain two parts: emissions originated from fuel combustion and emissions emitted from industrial production processes. Except the emissions from point sources discussed above, the remaining anthropogenic sources in provincial level were 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, c).

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 were 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 was that the HM emission intensities were much higher in the central and eastern China than those in the western China, and the coastal regions had been zoned as most polluted areas of varied HMs. The emissions of HMs from Hebei, Shandong, Henan, Jiangsu, Shanxi, and Liaoning provinces almost accounted for about 40 % of the total emissions of these HMs. These above six provinces were characterized by extensive economy growth mode, large volume of coal consumption and various industrial products output, and 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 played 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 were flourishing, especially the copper and zinc smelting industries. Consequently, nonferrous metals smelting sector was 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 had been reviewed comprehensively by Duan and Tan (2013). Their results indicated 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 were also 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 were reasonable and representative of the real situation of these HM pollutions.

3.5 Uncertainty analysis

Emissions of varied HMs from primary anthropogenic sources with uncertainties were summarized in Fig. 6 and Table S21. As can be seen, the overall uncertainties of the total emissions in our inventories quantified by Mote Carlo simulation are 32.2–50.8 %. Among all the coal combustion sectors, uncertainties for thermal power plants emissions were smallest, whereas those for coal-fired residential sectors and coal-fired other sectors were considerable. These were 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 could be 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 could be mainly attributed to imprecise statistics information, poor source understanding, as well as lacking adequate field test data in China.

Generally speaking, emission inventories are never complete and perfect, and most emissions estimates possess a significant associated uncertainty mainly owing to the

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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 sources. Consequently, more detailed investigation and long-term field tests for all kinds of coal-fired facilities and industrial production processes are in great demand.

3.6 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) 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), (2) promote coal washing before combustion (the removal efficiencies of coal preparation for heavy metals can reach as

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high as approximately 30.0–60.0 %, see 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, amounting to about 79 570.0 t 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.) had 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 were closely related with the unbalanced regional economic development and population density in China. One notable characteristic was that the HM emission intensities are much higher in the central and eastern China than those in western China, and the coastal regions had been zoned as most polluted areas of HMs. Notably, because of the flourishing of nonferrous metals smelting industry, the southwestern and central-southern provinces also played a prominent role in HM emissions.

The overall uncertainties in our bottom-up inventories were 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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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
	Fabric filters	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

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Table 2. HM emissions from primary anthropogenic sources in China, 1949–2012 ($t\,yr^{-1}$).

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	12 922.5	123.7	2353.5	1250.0	250.6	5736.8	478.8	2194.9	4896.5
1990	261.3	1311.7	1546.4	17 644.0	156.2	3374.7	1667.5	337.3	7607.8	624.0	2880.5	6541.9
1995	351.1	1699.7	2179.8	17 620.3	223.3	5155.0	2354.2	499.4	9454.9	778.7	4131.5	9564.5
2000	316.1	1673.2	2113.0	20 193.5	255.9	4928.7	2407.0	566.1	10 034.7	842.7	4733.0	10 788.6
2005	492.3	2454.4	3058.1	10 887.1	378.9	6828.5	3246.4	797.9	12 195.4	1075.8	7101.1	15 987.9
2006	509.3	2501.2	3146.8	11 250.2	398.5	7179.0	3356.7	826.2	12 181.6	1042.8	7201.1	16 895.0
2007	533.8	2407.2	3067.2	11 729.0	420.8	7445.2	3369.6	822.8	12 528.9	1064.5	7600.0	18 147.6
2008	564.8	2489.7	3136.1	12 213.6	442.4	7755.7	3248.3	962.9	12 499.8	1056.5	8208.7	18 337.4
2009	589.7	2325.8	2936.1	12 519.9	453.7	7810.2	3250.8	1006.0	12 195.4	1010.7	8428.6	19 035.8
2010	672.0	2322.9	2880.5	13 194.5	455.8	7465.2	3138.6	1068.1	12 015.9	919.2	8318.8	20 503.7
2011	688.4	2422.8	3062.4	14 032.4	493.9	7733.0	3440.1	1172.8	12 657.3	981.2	9115.5	21 876.0
2012	695.1	2529.0	3061.7	14 397.6	526.9	7834.1	3395.5	1251.7	13 006.6	1004.6	9547.6	22 319.6

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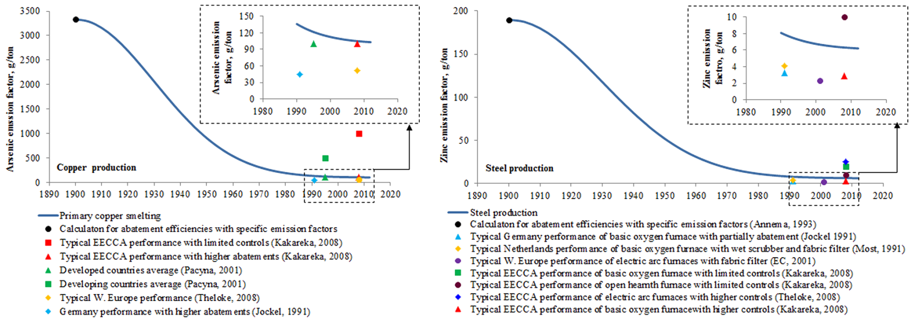

Figure 1. Time variation of arsenic emission factors for copper production and zinc emission factors for steel making in China (for instance).

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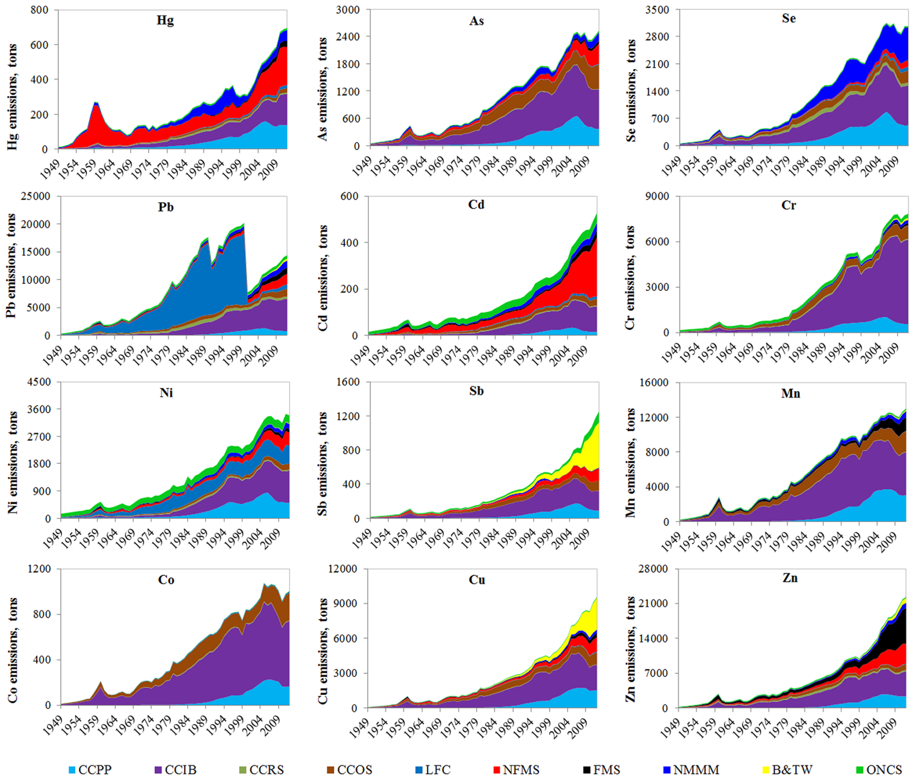

Figure 2. Historical trends of atmospheric HMs (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) emissions from primary anthropogenic sources in China, 1949–2012. CCPP, coal consumption by power plants; CCIB, coal consumption by industrial boilers; CCRS, coal consumption by residential sectors; CCOS, 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).

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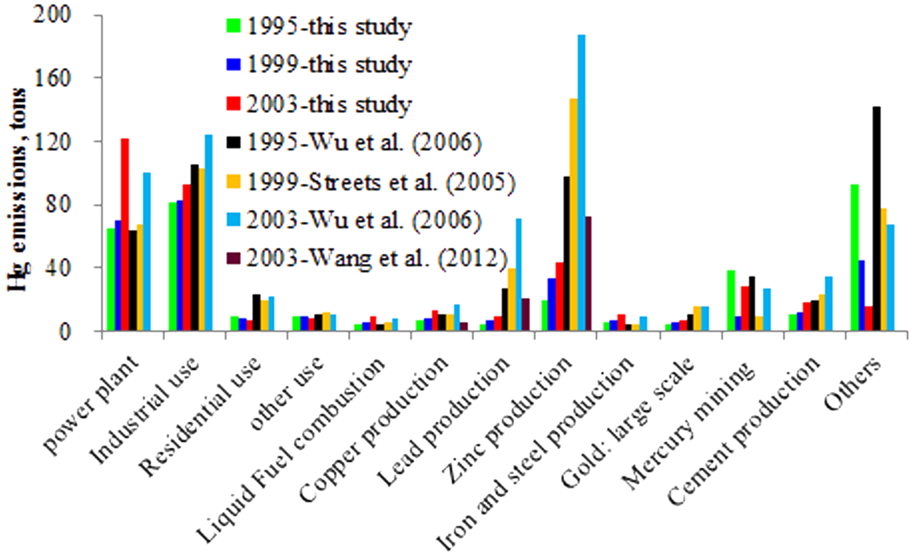

Figure 3. Estimate of annual Hg emissions from primary anthropogenic sources among various studies ($t\,yr^{-1}$).

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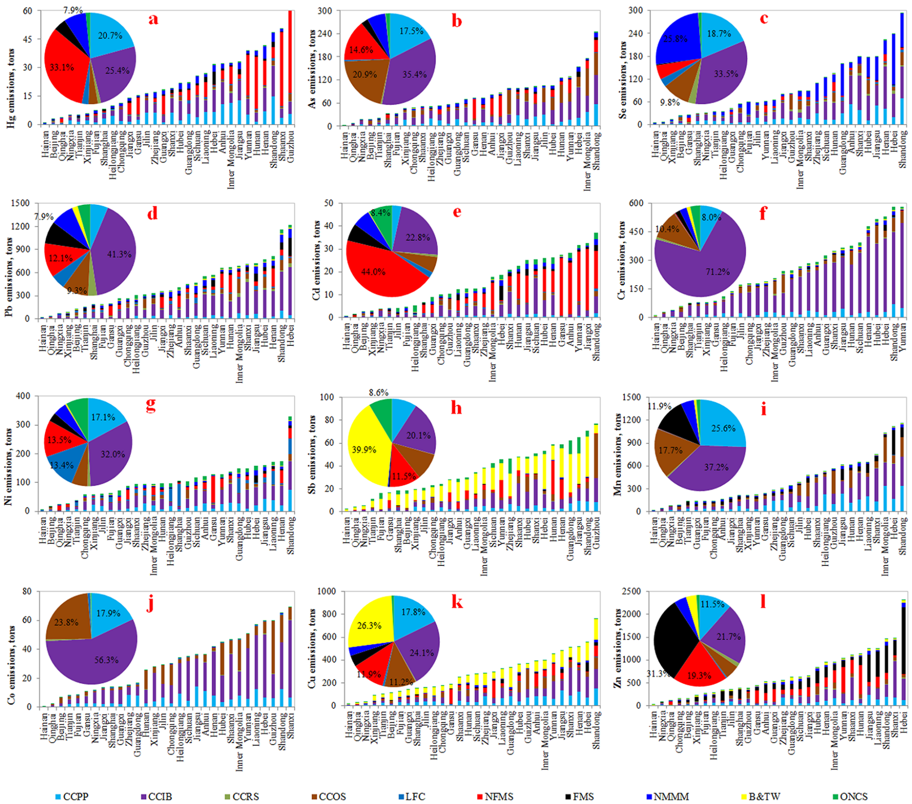

Figure 4. Provincial HM emissions from anthropogenic sources and national composition by source categories in 2010.

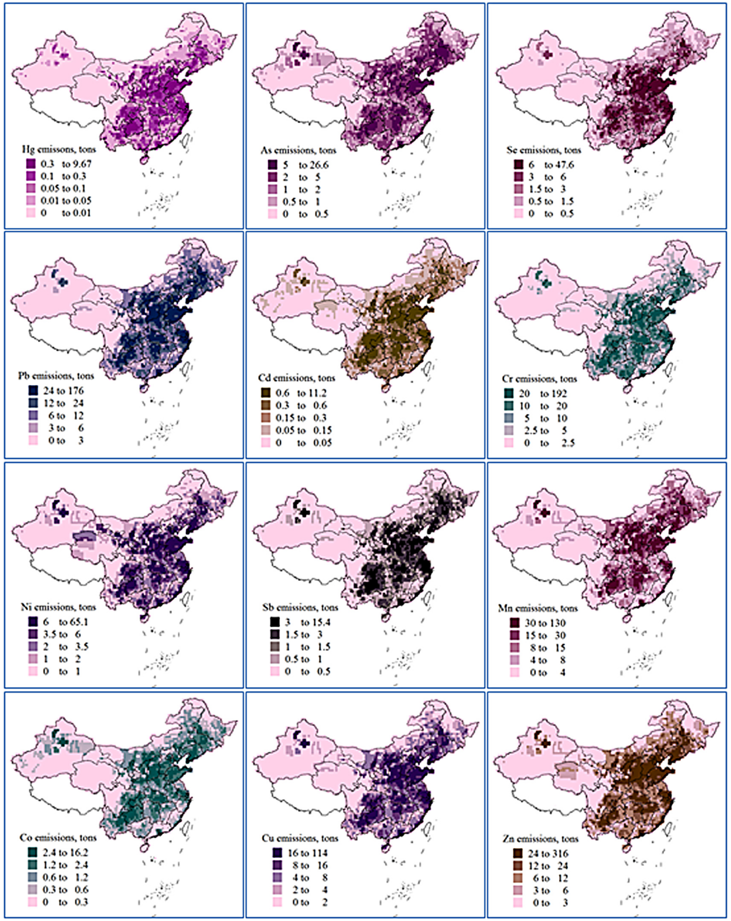

Figure 5. Gridded HM emissions from anthropogenic sources for the year 2010 ($0.5^{\circ} \times 0.5^{\circ}$ resolution; units, $\mathrm{kg\,yr^{-1}}$ (grid cell)$^{-1}$).

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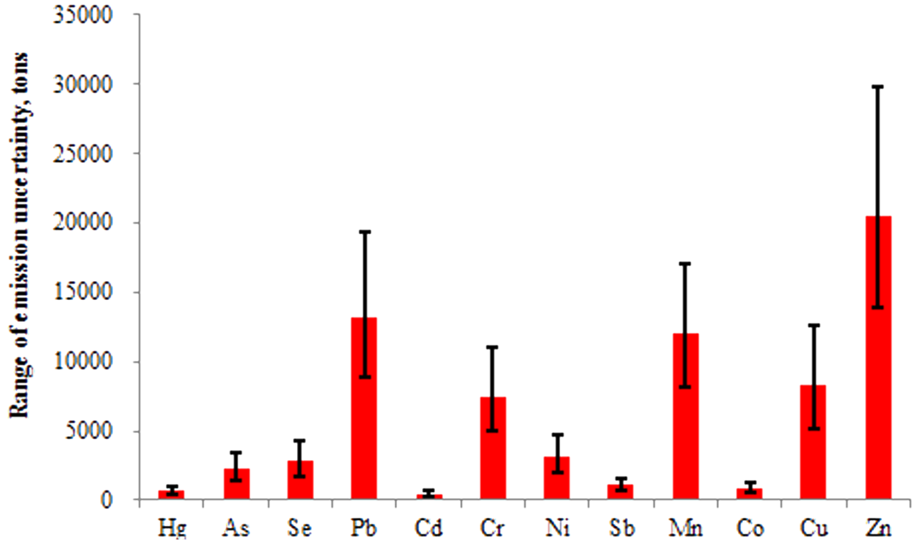

Figure 6. Uncertainties in the total emissions of HMs in China in 2010 (Uncertainties in the emissions of HMs by source categories in China in 2010 can be seen Table S21).