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

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

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

1 Introduction

Heavy Metals (HMs) is a general collective term which applies to the group of metals (e.g. Hg, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu, Zn, etc.) and metalloids (e.g. As, Se. etc.) with atomic density greater than 4.5 g cm^{-3}. Although these elements are present in only trace levels in feed coals and raw materials, the huge coal consumption and enormous output of various industrial products have resulted in significant emissions of HMs into the atmosphere. As a result, the mean atmospheric concentration of As, Cd, Ni, and Mn are reported at 51.0 $\pm$ 67.0, 12.9 $\pm$ 19.6, 29.0 $\pm$ 39.4, and 198.8 $\pm$ 364.4 ng m^{-3} in China respectively, which are much higher than the limit ceilings of 6.6, 5, 25, and 150 ng m^{-3} for WHO guidelines, respectively (Duan and Tan, 2013). Mukherjee et al. (1998) and Song et al. (2003) indicate that various HMs can remain in the atmosphere for 5–8 days and even for 30 days when discharged from elevated stacks associated with fine particles. Therefore, these toxic substances can be transported for long distances before they finally settle down through wet and dry deposition into soil and aqueous systems, causing widespread adverse effects and even trans-boundary environmental pollution disputes. In particular, 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$_2$O$_3$, and Co along with its compounds are suspected of being probable carcinogens (IARC, 2014).

Since 1980s, the United States, the United Kingdom, Australia and several 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). Further, the quantitative assessments of global contamination of air by HMs from anthropogenic sources have been estimated in previous studies (Nriagu, 1979; Nriagu and Pacyna, 1988; Pacyna and Pacyna, 2001; Streets et al., 2011; Tian et al., 2014b). With the increasing environmental pollution associated with economic growth, some researchers have paid special attention to estimating China's HM emission inventory, especially for Hg, which is regarded as a global pollutant (Fang et al., 2002; Streets et al., 2005; Wu et al., 2006). Streets et al. (2005) and Wu et al. (2006) have developed Hg emission

77 inventory from anthropogenic activities of China for the year 1999 and 1995 to 2003,

78 respectively. The research group led by Tian have established the integrated emission

79 inventories of eight HMs (Hg, As, Se, Pb, Cd, Cr, Ni and Sb) from coal combustion or

80 primary anthropogenic sources on the provincial level during 1980 to 2009 (Cheng et

81 al., 2015; Tian et al., 2010, 2012a–c, 2014a, b). However, comprehensive and detailed

82 studies on anthropogenic atmospheric emissions of 12 typical toxic HMs with highly

83 resolved temporal and spatial distribution information in China are still quite limited.

84 Moreover, we have little knowledge on what the past and accelerated emission levels

85 of HMs are like from anthropogenic sources during the historical period since the

86 founding of the People's Republic of China in 1949 to the reformation and opening

87 policy (1978).

88   In this study, for the first time, we have evaluated the historical trend and spatial

89 distribution characteristics by source categories and provinces of atmospheric

90 emissions of 12 typical HMs (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn)

91 from primary anthropogenic activities during the period of 1949–2012. Particularly,

92 we have attempted to determine the temporal variation profiles of emission factors for

93 several significant sources categories (e.g. nonferrous metal smelting, ferrous metal

94 smelting, cement production, MSW incineration, etc.) during the long period of 1949

95 to 2012, which include the technological upgrade of industrial process and the

96 progress of the application rate for various air pollutant control devices (APCDs).

97 **2   Methodologies, data sources and key assumptions**

98   We estimate the atmospheric emissions of the targeted 12 HMs (Hg, As, Se, Pb,

99 Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) from primary anthropogenic sources by

100 combining the specific annual activities and dynamic emission factors by source

101 category in this study. Table S1 in the separate Supplementary Material file lists the

102 targeted heavy metal species and the associated emission sources. Generally, we

103 classify all sources into two major categories: coal combustion sources and non-coal

104 combustion sources.

105 **2.1 Methodology of HM emissions from coal combustion sources**

106   Currently, coal plays a dominant role in China's energy consumption, making up

107 about 70 percent of its total primary energy consumption (Tian et al., 2007; Tian et al.,

108 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 at parts per million (ppm) levels.

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

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

where E is the atmospheric emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn; C is the averaged concentration of each HM in feed coals in one province; A is the amount of annual coal consumption; R is the fraction of each heavy metal released with flue gas from varied coal combustion facilities; η_{PM}, η_{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 province (autonomous region or municipality); j represents the sub-category emission source which is classified by different sectors of the economy and combustion facilities, as well as the installed PM, SO$_2$ and NO$_X$ control devices (the detailed source classification can be seen in Supplement Table S2); k represents the type of coal as consumed (raw coal, cleaned coal, briquette, and coke); and t represents the calendar year.

2.1.1. Average concentrations of varied HMs in feed coals

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

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

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

2.1.2.   HM emission factors from coal combustion sources

In this study, various coal combustion facilities are separated into five sub-categories: pulverized-coal boilers, stoker fired boilers, fluidized-bed furnaces, coke furnaces, and domestic coal-fired stoves. Therein, pulverized-coal boilers are predominant in coal-fired power plants in most of the provinces in China, representing over 85.0% of the total installed capacities. The remaining share is divided between fluidized-bed furnaces and stoker fired boilers, which are mainly used in relatively small unit-size coal-fired power plants. Different from the thermal power plants sector, stoker fired boilers make up a large proportion of the coal-fired industrial sector and other commercial coal-fired sectors. The release rates of HMs in flue gas from various boiler categories vary substantially due to the different combustion patterns and operating conditions, as well as their genetic physical and chemical characteristics (Reddy et al., 2005). Therefore, it is necessary to develop a detailed specification of the methods by which the coals are fed and burned in China. In this study, we have compiled the release rates of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn for different combustion boilers from published literatures (see Supplement Table S10). The arithmetic mean values of release rates of these 12 HMs from different combustion boilers reported in the literature are adopted to calculate the final emissions (see Table 1).

Besides, the conventional APCDs used to reduce criteria air pollutants (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 of approximately 94% of the total, followed by about 6 percent for fabric filters (FFs) or FFs plus ESPs. Meanwhile, the

173   wet flue gas desulfurization (WFGD) and selective catalytic reduction (SCR) have

174   been increasingly used in coal-fired power plants to reduce SO_2 and NO_X emissions in

175   recent years, and the installed capacity proportion of FGD and SCR have amounted to

176   about 86.2% and 25.7% of the total capacity, respectively (MEP, 2014a, b). However,

177   compared with coal-fired power plant boilers, there are still many small and medium

178   scale industrial boilers which are equipped with cyclones and wet dust collectors to

179   reduce fly ash emissions, and fewer FGD and de-NO_X devices have been installed to

180   abate SO_2 and NO_X emissions. In this study, we adopt the arithmetic mean values of

181   those reported in the available literature as the average synergistic removal

182   efficiencies by different APCD configurations, as shown in Table 1 and Supplement

183   Table S11.

184   The residential sector is another important coal consumer in China. The

185   traditional cook stoves and improved cook stoves are major combustion facilities for

186   residential cooking and heating, both of which are normally without any PM and SO_2

187   control devices. There is little information about the real-world test results of HM

188   emissions through residential coal use of China. Hence, we choose to use the

189   averaged emission factors for coal/briquette combustion provided by AP42 (US EPA,

190   1993), NPI (DEA,1999) and NAEI (UK, 2012), and the assumed emission factors of

191   Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn by residential coal use are also

192   listed in Table 1.

193   **2.2 Methodology of HM emissions from non-coal combustion sources**

194   HM emissions from non-coal categories are calculated as a product of annual

195   activity data (e.g., fuel consumption, industrial products yields, etc.) and specific

196   emission factors of varied HMs. The basic calculation can be described by the

197   following equation:

198   $$E(t) = \sum_i \sum_j (A_{i,j} \times EF_j) \quad (2)$$

199   where E is the atmospheric emissions of each heavy metal; A is the annual production

200   yield of industrial producing processes, volume of municipal solid wastes incineration,

201   or liquid fuel and biofuel consumption, etc.; EF is the assumed average emission

202   factors; and j is the emission source classified by source sub-categories (see

203   Supplement Table S1).

204   Notably, atmospheric emissions of Pb have significantly dropped in China, as a

205 result of unleaded gasoline introduction since the early 2000s. The proportion of lead

206 in leaded gasoline emitted to the air is estimated at about 77% (Biggins and Harrison,

207 1979) or 75% (Hassel et al., 1987), and thus this parameter is assumed at about 76%

208 for the period before 2000 in this study. Consequently, for leaded gasoline used by

209 motor vehicles in China, the total Pb emitted to the atmosphere is calculated

210 according to the following equation:

211
$$E(t) = \sum_i \left(0.76 \times C_{Pb} \times A_i\right) \quad (3)$$

212 where $E(t)$ is the emissions of Pb from motor vehicle gasoline combustion in calendar

213 year t; C_{Pb} is the average content of lead in gasoline; A_i is annual gasoline

214 consumption in one province, autonomous region or municipality i.

215   For brake and tyre wear, the atmospheric emissions of several HMs are estimated

216 by the following equation:

217
$$E(t) = \sum_i \sum_j \sum_k (P_{i,j} \times M_j \times EF_{j,k} \times C_k) \quad (4)$$

218 where $E(t)$ is the atmospheric emissions of As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu or

219 Zn in calendar year t; $P_{i,j}$ is the population of vehicles in category j (passenger car, bus

220 and coach, light-duty truck, and heavy-duty vehicle) in province, autonomous region

221 or municipality i; M_j is the average annual mileage driven by vehicle in category j;

222 $EF_{j,k}$ is the emission factor of TSP (total suspended particles) for brake lining or tyre k

223 by vehicle category j; C_k is the averaged concentration of each heavy metal in brake

224 lining or tyre k . Relevant parameters are summarized in the Supplement Table

225 S12−S13.

226 **2.2.1. Algorithm for determination of dynamic emission factors**

227   Because remarkable changes in products, devices, processes as well as practices

228 (technology improvement) have imposed positive effects on emission reductions of

229 pollutants with the growth of the economy and the increasing awareness of

230 environment protection, the resulting pollutant emission level at any given time is a

231 competition between technology improvement and production growth. Consequently,

232 one of the major challenges in this study is to develop a reasonable representation of

233 the time-varying dynamic emission factors of HMs associated with each primary

234 industrial activity.

235   Taking into consideration the updated air pollutant control technologies, and

236 outdated enterprises that have shut down, the HM emission factors show a gradually

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

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

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

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

269 of unabated emission factor in pre-1900 and the best emission factor achieved at
270 present for each industrial process in China. In addition, several values of *s* are cited
271 from Street et al. (2011) if only limited information about the emission level for
272 certain processes can be gained.

2.2.2. Dynamic HM emission factors of nonferrous metals smelting

274 By 2010, bath smelting (e.g. Ausmelt smelting, Isa smelting, etc.), flash smelting
275 and imperial smelting process (ISP) represent the three most commonly used
276 techniques for copper smelting, for about 52%, 34% and 10% of Chinese copper
277 production, respectively. For lead smelting, sintering plus blast furnace technique
278 (traditional technique) and bath smelting (e.g. oxygen side-blowing, oxygen
279 bottom-blowing, etc.) plus blast furnace technique (advanced technique) are the two
280 most commonly used techniques in China, accounting for about 48% and 47% of lead
281 production, respectively. With respect to zinc smelting, hydrometallurgy is the
282 predominant technique in China, for about 77% of the zinc production capacity. The
283 remaining share is divided among vertical retort (VR) pyrometallurgy (~10%),
284 imperial smelting process (ISP) pyrometallurgy (~7%) and other pyrometallurgy
285 (~6%). Especially, VR pyrometallurgy is regarded as an outdated technique which is
286 mandated to be shut down gradually and will be totally eliminated in the near future.

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

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

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

2.2.3.   Dynamic HM emission factors of ferrous metal smelting

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

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

336   industry in China with those in certain European Union countries (e.g. United

337   Kingdom, Germany, Netherlands, Austria, etc.), we choose to use the emission factors

338   of HMs for the iron smelting industry obtained from emission factors database of

339   NAEI in 2000 as the national average emission factors for iron smelting of China in

340   2015. This is mainly because the PM emission limits of existing facilities for iron

341   smelting of China in 2015 (20 mg m^{-3}) is approximately comparable to these of

342   European Union countries in the early 2000s (IRIS, 2005; MEP, 2012). With respect

343   to steel smelting, the emission factors of HMs with higher abatement in Eastern

344   Europe, Caucasus and Central Asia countries are chosen as the national average

345   emission factors of this sector in China at the same calendar year (see Fig. 1b). The

346   unabated emission factors of HMs for pig iron and steel production are determined by

347   using the similar method discussed above for the nonferrous metals smelting industry.

348   Please see Supplement Table S16 and Table S17 for more details about specific

349   emission factors.

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

351   Cement, glass and brick manufacturing are the major mineral commodity

352   industries. During the manufacturing process, various HMs vaporing from raw

353   materials and feed fuels associated with fine particulate matters are emitted from the

354   kiln system at high temperatures.

355   Currently, the new dry rotary kiln process is the dominant technology in cement

356   manufacturing factories of China, representing over 92% of the national total cement

357   output. The emission ceilings of air pollutants for cement, glass or brick

358   manufacturing specified in the present standards of China (e.g., GB 4915−2013, GB

359   26453−2011, GB 29620−2013, etc.) are less stringent compared with those of

360   developed countries (see Supplement Table S18). By contrasting the emission limits

361   of air pollutants from non-metallic minerals (cement, glass and brick) manufacturing

362   between China and developed countries, we presume the best emission factors of air

363   pollutants achieved in China today are approximately identical to the average

364   emission factors of developed countries in the end of 1990s. With respect to cement

365   production, the unabated emission factors of HMs can be obtained from the Web

366   Factor Information Retrieval System (WebFIRE) (US EPA, 2012). Moreover, the

367   average emission factors for glass and brick manufacturing are assumed to remain

368 unchanged pre-1996. Subsequently, atmospheric emission factors of HMs from these
369 two sub-source categories decrease gradually with the implementation of gradually
370 tightened emission limits from above mentioned Emission Standards of Pollutants
371 from non-metallic mineral manufacturing industry. Specific emission factors of
372 various HMs from non-metallic mineral manufacturing can be seen in Supplement
373 Table S16.

374 **2.2.5.   HM emission factors of biomass burning**

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

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

394 **2.2.6.   HM emission factors of liquid fuels combustion**

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

398   Historically, leaded gasoline combustion by vehicles has been recognized as the
399 most significant contributor for the increase of human blood lead level (Robbins et al.,

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

2.2.7.   Dynamic HM emission factors of municipal solid waste incineration

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

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

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

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incineration from published literature (Nriagu, 1979; Pacyna, 1984; Nriagu and Pacyna, 1988) and certain emission factors of HMs with uncontrolled technology from *AP42, Fifth Edition, Volume I, Chapter 2: Solid Waste Disposal* (US EPA, 1996), the unabated emission factors of HMs from this source category are determined. Specific emission factors of various HMs from MSW incineration can be seen in Supplement Table S16.

2.2.8.   HM emission factors of brake and tyre wear

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

In addition to steel as brake pad support material, the agents present in brake linings usually consist of Sb, Cu, Zn, Ba, Sn and Mo (Bukowiecki et al., 2009). Further, antimony is presented in brake linings as Sb_2S_3 that serves as a lubricant and filler to improve friction stability and to reduce vibrations. Then, Sb_2S_3 is oxidized to Sb_2O_3 (possibly a carcinogenic substance) during the braking process, which have been proved to be partially soluble in physiological fluids (Gao et al., 2014; von Uexküll et al., 2005). Because of the excellent characteristic of thermal conductivity, copper or brass are widely used for automotive braking as a major ingredient in friction materials (Österle et al., 2010). Additionally, although zinc is a less specific marker for brake wear than antimony and copper, it has also been reported to be another important constituent of brake wear (Johansson et al., 2009). Hence, the HMs (especially for Sb and Cu) associated with particulate matter are mainly emitted from brake wear due to relatively higher average contents of HMs in brake lining, compared to those from tyre wear (EEA, 2013).

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

466 the foreign-invested transnational vehicle companies, we presume the composition of
467 worn materials from brake and tyre wear in term of HMs are consistent with foreign
468 countries (see Supplement Table S13).

469 **2.3 Activity data**

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

480 **2.4 Evaluation of Potential Uncertainties**

481   It is necessary to examine the potential uncertainty in emissions by sources and
482 regions to quantify the reliability and identify improvements space of emission
483 inventories in the future. A detailed uncertainty analysis is conducted by combining
484 uncertainties of both activity levels and emission factors, through adopting Monte
485 Carlo simulation (Zhao et al., 2011; Tian et al., 2014a; Tian et al., 2014b). Streets et al.
486 (2003) indicate that there is no way to judge the accuracy of activity data estimates.
487 Furthermore, uncertainties are still inevitable when representative values are selected
488 for specific emission sources, countries and regions in spite of emission factors
489 adopted from detailed experiments.

490   Most of the input parameters of specific activity levels and emission factors, with
491 corresponding statistical distribution, are specified on the basis of the data fitting, or
492 referred to the related published references (Wu et al., 2010; Zhao et al., 2011; Tian et
493 al., 2012a, b). Besides, for parameters with limited observation data, the probability
494 distributions such as normal distribution and triangular distribution are assumed by
495 the authors for corresponding sources. Further details about the probability
496 distribution for each source discussed in this study are listed in Table S20. Finally, all
497 of the input parameters are placed in a Monte Carlo framework, 10 000 times of

498　simulations are run to estimate the uncertainty ranges of varied HM emissions with a
499　95% confidence interval.

3　Results and discussion

3.1　Temporal trend of HM emissions by source categories

502　The historical trend of atmospheric emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb,
503　Mn, Co, Cu and Zn by different source categories from 1949 to 2012 are illustrated in
504　Fig. 2. The total emissions of HMs from primary anthropogenic sources since 1949
505　have shown substantial shifts among varied source categories that reflect
506　technological and economic trends and transition during this over 60 years long
507　period. Within the year after the establishment of the People's Republic of China in
508　1949, the total emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn from
509　anthropogenic sources are estimated at about 11.5–312.6 t (see Table 2). The
510　discharges of HMs on a national scale have increased by 3–20 times from 1949 to
511　1960 due to the increasing demands for energy consumption and industrial production
512　(especially for the period of the Great Leap Forward from 1958 to 1960 resulting in a
513　remarkable increasing output of industrial products), then, a substantial decrease in
514　1961 and 1962 of 27.6–55.7% compared to 1960 on account of the serious imbalance
515　of economic structure and the Great Leap Forward Famine caused by policy mistakes
516　together with natural disaster (Kung and Lin, 2003). In spite of the negative growth of
517　heavy metal emissions in individual years such as 1967, 1974 and 1976, the annually
518　averaged growth rates of national emissions of HMs from primary anthropogenic
519　sources are still as high as 0.2–8.4% during the periods from 1963 to 1977.

520　Subsequently, the policy of openness and reformation was issued by the Chinese
521　central government. With the implementation of this policy from 1978 to 2012,
522　China's GDP has been growing at an average annual growth rate of about 9.8%
523　resulting in tremendous energy consumption and enormous output of industrial
524　products. As can be seen from Fig. 2, historically there have been two periods during
525　which the total emissions of HMs (except Pb) increased rapidly after 1978. The first
526　one is the period of 1978 to 2000, except for one remarkable fluctuation from 1998 to
527　1999, which reflects a decrease in input of raw materials and output of industrial
528　products mainly owing to the influence of Asian financial crisis (Hao et al., 2002).
529　The second one is the period of the 10th Five-Year Plan (10th FYP, from 2001 to
530　2005), a sharp increase of emissions of Hg, As, Se, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn

531 have occurred, with the emissions increasing from about 268.0–11308.6 t in 2001 to

532 about 378.9–15987.9 t in 2005, at an annually average growth rate of 4.8–12.0%,

533 respectively (see Table 2).

534   In terms of the lead content requirement in gasoline, the past 64 years since the

535 foundation of the PR China (1949 to 2012) can be divided into two phases: the leaded

536 gasoline period (1949 to 1990: gasoline with high lead content (0.64 g L^{-1}); 1991–

537 2000: gasoline with low lead content (0.35 g L^{-1}) and the unleaded gasoline period

538 (2001 to 2012, 0.005 g L^{-1}). As a result, the discharge of Pb from primary

539 anthropogenic sources has experienced two fluctuations over the 64 year period. The

540 first sharp emission decline occurs in 1991, and the total emissions have decreased by

541 26.2% from 17 644.0 t in 1990 to 13 029.6 t in 1991, mainly because the average Pb

542 content in leaded gasoline regulated by GB 484–89 is decreased about 45.3%

543 compared to that in GB 484–64. The other sharp decline occurs in 2001, and the total

544 Pb emissions from primary anthropogenic sources are reduced abruptly by about 61.6%

545 in 2001. Subsequently, along with the rapid increase of vehicle volume and oil

546 consumption, a substantial increase is once again experienced from 7747.2 t in 2001

547 to 14 397.6 t in 2012, at an annual average growth rate of about 5.8%.

548   Due to the technological progress resulting in relatively low emission factors of

549 HMs and economic development bringing about high coal consumption and industrial

550 products output, the trends of total atmospheric emissions for different HMs in China

551 are diverse during the period of 2006 to 2012 (Cheng et al., 2015). Generally speaking,

552 the national atmospheric emissions of Hg, Pb, Cd, Cr, Sb, Cu and Zn have increased

553 at an annual average growth rate of 1.5–7.2% from 2006 to 2012. In spite of the

554 remarkable growth in coal consumption and gross industrial production, the national

555 As, Se, Ni, Mn and Co emissions are well restrained in this period. These are mainly

556 due to the different volatility of these 12 elements during high temperature process

557 resulting in diverse release rates of furnaces and synergistic removal efficiencies of

558 control measures (Xu et al., 2004).

559   Due to limited information about historical ground-level concentrations of

560 twelve HMs in different cities in China, the temporal characteristics of atmospheric

561 concentrations of four HMs (As, Pb, Cr and Cu) in Beijing during 2000 to 2012 are

562 used as valid index to verify whether or not the trend of historical HM emissions are

563 reasonable (see Supplement Fig. S6). The data sources and specific values about

564 atmospheric concentrations of As, Pb, Cr and Cu in Beijing during 2000 to 2012 are

listed in Supplement Table S21. It should be acknowledged that this verification method applied in this study has certain limitations on account of sampling discrepancies, including sampling time, sampling site and detection method, etc. Therefore, the historical variation trends of HM emissions may be inconsistent with those of ambient concentrations of HMs in some years.

As can be seen from Fig. S6, minimum values of the atmospheric concentrations of As, Pb, Cr and Cu occur in 2008. This is mainly because most of aerosol samples compiled from published papers are collected during August in that year, the time during which China hosted the Beijing Olympics under which a series of strict measures about energy-saving and pollution reduction were implemented, such as suspending production of high polluting industries in the Beijing and neighboring municipalities, restricting vehicle driving on alternate days under an even–odd license plate system, limiting pollutant emissions from coal combustion facilities in Beijing and the surrounding provinces, etc. Consequently, the variation trends of atmospheric concentrations of As, Pb, Cr and Cu have some discrepancies with those of historical emissions of the above four HMs in Beijing in 2008. However, the historical emission trends of As, Pb, Cr and Cu are consistent with those of atmospheric concentrations of the above four HMs during 2000 to 2012 in general (see Fig. S6), which indicate that the historical trend of HM emissions estimated by this study are reasonable.

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

Overall, the estimated Hg emissions from fuel combustion (except for the subcategory of coal consumption by residential sectors) in this work are substantially consistent with those reported by Streets et al. (2005) and Wu et al. (2006), although the values calculated for the same year are somewhat different. This may be mainly attributed to the difference in the averaged provincial content of Hg in raw coal. In our study, according to a comprehensive investigation of published literature, we determine the national averaged Hg content in China to be 0.18 mg kg^{-1} by using a

bootstrap simulation method, a little lower than those used by above two studies (0.19 mg kg^{-1}). Another important factor influencing the result is the difference of removal effectiveness of Hg through traditional APCDs. Nevertheless, the estimated Hg emissions from coal consumption by residential sectors by Streets et al. (2005) and Wu et al. (2006) are higher than our estimation in the same year. This is mainly because the emission factor of Hg from coal consumption by residential sectors is cited from Australia NPI in this paper, which is only approximately half of that which EPA adopted in the above two studies. In terms of Hg emissions from industrial processes, the estimated Hg emissions in this study are generally lower than those in other Hg emission inventories in the same year. This may be because we have adopted S-shaped curves to quantify the positive effects on emission reduction of pollutants by technology improvement, so that the emission factors adopted in this study are generally lower than those used in studies of Streets et al. (2005), Wu et al. (2006) and Wu et al. (2012) in the same year. Besides, some anthropogenic sources with high uncertainties are not taken into account in this work due to the lack of detailed activity data for the long period. Certain natural sources (e.g., forest burning, grassland burning, etc.) are also not included in this study. Consequently, our estimated total Hg emissions are lower than those in inventories estimated by Streets et al. (2005) and Wu et al. (2006).

3.1.1. HM emissions from coal combustion by power plants

The power plant sector represents the largest consumer of coal in China. The thermal power generation has increased from 3.6 TWh in 1949 to 3925.5 TWh in 2012 (NBS, 2013a). Meanwhile, coal burned by power plants has increased from 5.2 to 1785.3 Mt (NBS, 2013b), with an annual growth rate of 9.9% and a percentage share of the total coal consumption increasing from 22.7 to 50.6%. For the period of 1949 to 2005, the emissions of HMs from coal combustion by power plants have increased in rough proportion to coal consumption. However, this trend began to change after 2006 due to the implementation of policies of energy-saving and pollution reduction, especially the strengthening of SO$_2$ emission control for coal-fired power plants (Zhu et al., 2015).

Presently, the combination of pulverized-coal boilers plus ESPs plus WFGD is the most common APCDs configuration in coal-fired power plants of China. By the end of 2012, the installed capacities of FGD in power plants have increased by nearly

632   14 times compared with those in 2005, reaching about 706.4 GWe, accounting for

633   approximately 86.2% of the installed capacity of total thermal power plants (MEP,

634   2014a). Of all of the units with FGD installation, approximately 89.7% adopt

635   limestone gypsum WFGD process. The discharges of Hg, As, Se, Pb, Cd, Cr, Ni, Sb,

636   Mn, Co, Cu and Zn from coal combustion by power plants in 2012 are estimated at

637   about 15.2–3038.9 t (see Fig. 2), which have decreased by 1.7–11.8% annually since

638   2006. Moreover, the distinction of integrated co-benefit removal efficiencies of these

639   elements for the typical APCD configurations is the primary reason for the obvious

640   variations of the declining rates among varied HMs, as illustrated in Table 1 and Fig.

641   2.

3.1.2.   HM emissions from coal consumption by industrial boilers

643   In general, coal combusted by industrial boilers is used to provide hot water and

644   heating for industrial production processes. With the development of China's

645   economy (GDP increased from CNY (Chinese Yuan) 46.6 billion in 1949 to CNY 51

646   894.2 billion in 2012), coal consumption by industrial boilers has increased at a

647   relatively lower growth rate than the power sector, from 11.5 Mt in 1949 to 1205.6 Mt

648   in 2012 (NBS, 2013b). According to the statistical data from China Machinery

649   Industry Yearbook, the combination of stoker fired boiler plus wet scrubber and

650   cyclone is the most common configuration in coal-fired industrial sectors of China,

651   especially for the small and medium scale boilers (CMIF, 2013).

652   As can be seen from Fig. 2, the emission trends of HMs from coal consumption

653   by industrial boilers are consistent with the national total emissions trends between

654   1949 and 1997, and negative growths appear in 1998 and 1999 due to the decreased

655   coal consumption resulting by the Asian financial crisis (Hao et al., 2002; Tian et al.,

656   2007, 2012b). Subsequently, the emissions of different toxic HMs from coal

657   consumption by industrial boilers have distinct variation tendencies mainly due to the

658   different removal efficiencies of HMs through typical APCDs. Generally, Hg and Pb

659   emissions from coal consumption by industrial boilers have increased almost

660   monotonically from 85.1 and 3717.8 t in 2000 to 179.0 and 5770.0 t in 2012, with an

661   annual growth rate of about 6.4 and 3.7%, respectively. However, the discharges of

662   Mn from coal consumption by industrial boilers have decreased to about 1.2 times

663   from 5866.0 to 4951.8 t during this period (2000–2012). Moreover, the discharges of

664   other nine HMs (As, Se, Cd, Cr, Ni, Sb, Co, Cu and Zn) from coal consumption by

21

665 industrial boilers present a trend of first an increase and then a decrease overall with

666 the implementation of policies of saving-energy and pollution reduction in coal-fired

667 industrial boilers sector, especially the growing application of high-efficiency dust

668 collectors and various types of combined dust and SO_2 removal devices.

3.1.3. HM emissions from metal smelting and other primary sources

670 Historically, a sharp fluctuation of Hg discharges from nonferrous metals

671 smelting sector has occurred in the period of Great Leap Forward to Great Leap

672 Forward Famine (increase from 92.6 t in 1957 to 221.7 t in 1959, then decrease

673 rapidly to 104.0 t in 1963), this is mainly due to the rapid increase or decline of

674 mercury mining outputs in this period (increase from 1060 t in 1957 to 2684 t in 1959,

675 then decrease rapidly to 1345 t in 1963). Subsequently, a sharp increase of emissions

676 of Hg has occurred, with the emission from about 60.6 t in 1998 increasing to about

677 218.6 t in 2012, at an annually averaged growth rate of 9.6%. Simultaneously, the

678 primary contributor of Hg emissions from the nonferrous metals smelting sector has

679 changed to the subsector of primary-Zn smelting, which makes up about 36.9–52.7%

680 of the sector during 1998 to 2012. Unlike Hg emissions, the emissions of As, Se, Pb,

681 Cd, Ni, Sb, Cu and Zn from nonferrous metals smelting sector have increased by

682 approximately 7–15 times to 442.3, 1856.4, 251.8, 412.7, 140.6, 1240.9 and 4025.6 t

683 in 2012, respectively. This is mainly because the reduced shares of HM emissions

684 from nonferrous metals smelting sector, caused by increasing advanced pollutants

685 control devices installation, have been partly counteracted by the rapid growth of

686 nonferrous metals production.

687 A steady increase of HM emissions from the pig iron and steel industry

688 accompanying by certain undulations has occurred from 1949 to 1999 (see Fig. 2).

689 Specifically, because of the emphasis on the backyard furnaces for steel production in

690 the period of the Great Leap Forward Movement, a sharp fluctuation of emissions has

691 occurred during the period of 1958 to 1963, with the emissions of Hg, As, Se, Pb, Cd,

692 Cr, Ni, Sb, Mn, Cu and Zn almost doubling (NBS, 2013b). Although emission factors

693 have leveled off between 2000 and 2012, the output of pig iron and steel has rapidly

694 increased from 131.0 and 128.5 Mt in 2000 to 663.5 and 723.9 Mt in 2012 and, as a

695 result, the emissions of Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Cu and Zn from this

696 sector have quadrupled or quintupled in the past twelve years. Especially, the share of

697 Zn emissions from ferrous metals smelting sector to the national emissions has

increased from 13.1 to 32.2%. Therein, the steel making industry represents the dominant contributor to the Zn emissions, accounting for about 60.9–62.9% during this period.

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

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

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

As the largest coal consumer in China, coal consumption by power plants is identified as the second largest contributor and accounts for about 14.0% in national total emission of twelve HMs. In order to achieve the emission reduction of PM, SO_2 and NO_X for satisfying the national or local emission reduction goals for the year 2010 (the end year of 11th FYP) (NBS, 2011; Tian et al., 2014a), control policies have been implemented, including replacement of small coal-fired plant units with large and high efficiency units and the continuously increasing installation rate of advanced APCDs systems (e.g., ESP, FFs, WFGD, SCR, etc.). Consequently, the final discharge rates of HM from power plants have decreased obviously even though the volume of coal consumption has grown substantially (see Fig. 2 and Fig. S1).

China has been the world's largest producer of pig iron and steel by a rapidly growing margin. By the end of 2012, the output of steel has amounted to 723.9 Mt, accounting for about 46% of worldwide steel production (CISA, 2013). Despite the

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

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

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

764 Although the non-metallic mineral manufacturing sector is not the dominant

source for most of HMs, the discharge of Se from this sector makes it the largest contributor to the total. Within this category, the glass production sector discharges about 92.9% of the total Se emissions due to the widespread application of selenium powder as decolorizing agent in the glass production process and the huge output of glass production (Kavlak and Graedel, 2013).

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

3.3 Spatial variation characteristics of HM emissions

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

798   from fuel combustion and emissions emitted from industrial production processes.

799   Except for the emissions from point sources discussed above, the remaining

800   anthropogenic sources in the provincial level are all treated as regional area sources.

801   The specific method of geographical location for area sources has been discussed in

802   our previous studies (Tian et al., 2012b; Tian et al., 2012c).

803   The spatial variation is closely related with the unbalanced economic

804   development and population density in the Chinese mainland, so that these twelve

805   typical HM emissions are distributed very unevenly from one area to another, with the

806   annual As emissions at the province level ranging from 0.009 kg km^{-2} in Qinghai to

807   1.6 kg km^{-2} in Shandong, for instance. One notable characteristic of the spatial

808   distribution of China's HM emissions is that the HM emission intensities are much

809   higher in the central and eastern China than those in the western China, and the

810   coastal regions are zoned as the most polluted areas of varied HMs. The emissions of

811   HMs from Hebei, Shandong, Henan, Jiangsu, Shanxi, and Liaoning provinces almost

812   account for about 39.4% of the total emissions of these HMs. These above six

813   provinces are characterized by extensive economy growth mode, large volume of coal

814   consumption and various industrial products output, as well as a high population

815   density. Therefore, more energy consumption and higher travel demand characterize

816   these six provinces, compared to other provinces and districts, resulting in higher HM

817   emission intensity.

818   Moreover, several provinces in the southwestern and central-southern regions

819   also play a prominent role for these twelve HM emissions, especially for Guizhou,

820   Sichuan, Yunnan, Hubei and Hunan provinces. In general, Guizhou province starts

821   out with high emissions of HMs from coal consumption by other sectors mainly

822   owing to both the high HM contents in the feed coals and the large magnitude of coal

823   consumption by this sector. In addition, the nonferrous industries of Hunan and

824   Yunnan provinces are flourishing, especially the copper and zinc smelting industries.

825   Consequently, the nonferrous metals smelting sector is seen as one of major source of

826   Cu and Zn emissions in these two provinces.

827   The situations of atmospheric HM concentrations in the aerosols of 44 major

828   cities in China during the last 10 years have been reviewed comprehensively by Duan

829   and Tan (2013). Their results indicate that the ambient concentrations of HMs (As, Pb,

830   Cd, Cr, Ni, Mn, Cu and Zn) is high in some cities, including Beijing, Tianjin,

831   Shijiazhuang, Shenyang, Harbin, Jinan, Zhengzhou, Hangzhou, Nanjing, Hefei, Xian,

832 Yinchuan, Urumqi, Wuhan, Changsha, Chongqing, Guangzhou, Shenzhen, Foshan,

833 Shaoguan, and others. For HM emissions on the urban scale in 2010, these twenty

834 cities with high HMs concentrations also represent the cities with the high HM

835 emissions in China (see Fig. 5). In general, the spatial distribution characteristics of

836 gridded HM emissions from primary anthropogenic sources for the year 2010 in this

837 study are reasonable and representative of the real situation of these HM pollutions.

838 **3.4 Uncertainty analysis**

839 Emissions of varied HMs from primary anthropogenic sources with uncertainties

840 in 2010 are summarized in Fig. 6 and Supplement Table S22. As can be seen, the

841 overall uncertainties of the total emissions in our inventories quantified by Mote Carlo

842 simulation are -39.1−50.8%. Among all the coal combustion sectors, uncertainties for

843 thermal power plants emissions are smallest, whereas those for coal-fired residential

844 sectors and coal-fired other sectors are considerable. These are mainly attributed to

845 the relatively poor resolution of coal burning technologies and emission control

846 devices in these two sub-categories. In contrast, relatively higher uncertainties are

847 observed in the non-coal combustion categories, particular for non-metallic mineral

848 manufacturing and brake and tyre wear emissions. These high uncertainties of HM

849 emissions can be mainly attributed to imprecise statistics information, poor source

850 understanding, as well as the absence of adequate field test data in China.

851 The earlier statistical data for activity levels are considered to have high

852 uncertainty for developing countries (including China) with less developed statistical

853 systems. Unfortunately, we have to acknowledge that it is quite difficult to accurately

854 assess the specific uncertainty of activity data from China's earlier official statistics.

855 Akimoto et al. (2006) argue that the data of energy consumption of China during

856 1996–2003 is not recommended for use in the study of emission inventories due to the

857 probable underestimates. However, the discrepancies in coal consumption from the

858 power sector are considered to be less than ±5%, which do not dominate the emission

859 uncertainties (Wu et al., 2010; Zhao, et al., 2008). In order to approximately quantify

860 the uncertainty of activity data, we divide the whole period of 1949 to 2012 into three

861 stages with respect to economic development and emission control: before reform and

862 opening (1949–1978), intermediate stage (1979–2005), and the substantial control

863 stage of atmospheric pollutants (2006–2012). For the activity level of anthropogenic

864 sources obtained from official statistics after 2006, we assume normal distributions

865 with sector-dependent uncertainties (see Supplement Table S20). On the basis of

866 above discussion and consideration, the uncertainty of activity data from official

867 statistics during the two early periods of 1949–1978 and 1979–2005, are assumed to

868 be about 2 and 1.5 times of those in the period of 2006–2012, respectively.

869   The combined uncertainty bounds for the national emissions of twelve HMs

870 during the historical period are shown in Fig. S8. In general, the range of uncertainty

871 has gradually diminished over time. For example, we calculate an uncertainty level of

872 -90.1–125.7% (95% confidence interval) in the estimate of national Hg emissions in

873 1949, which is higher than those of the other eleven HM emissions (between -90.0%

874 and 119.3%). This is mainly attributed to remarkable emissions from several Hg

875 sources that have the largest uncertainty in both activity levels and emission factors,

876 such as gold smelting and mercury mining. Since then, the relative uncertainties have

877 gradually decreased from the beginning to the end of the period. This is primarily

878 because more reliable activity data with a smaller coefficient of variation (CV) from

879 related yearbooks and reports became available. The uncertainty range of national Hg

880 emissions is estimated to -40.6–55.8% by 2003, which compares well with estimates

881 of ±44% for China's Hg emissions by Wu et al. (2006). By the end of 2012, the

882 overall uncertainty level has been reduced to -39.0–47.0% for the national HM

883 emissions. Particularly, it should be acknowledged that emission trends of HMs are

884 probably more uncertain than indicated. This is mainly because dynamic emission

885 factor curves of certain sectors are set between two very distant points (e.g., 1890 and

886 1990 in Fig. 1), which means that the timing and rate of the decreased emission

887 factors are really unconstrained. Nevertheless, no data are available to improve the

888 confidence presently, which merits further investigation in the future.

889   Generally speaking, emission inventories are never complete and perfect, and

890 most emissions estimates possess a significant associated uncertainty mainly owing to

891 the lack of representativeness of specific emission factors and the reliability of

892 each-source specific activity data. In this study, we have made great efforts to

893 evaluate the historical trend of these HM emissions by collecting detailed activity

894 levels for various source categories, adopting the best available dynamic emission

895 factors for various anthropogenic sources in China today, and integrating publication

896 literature and reports from developed countries and districts. Nevertheless,

897 considerable uncertainties are still present, and this may lead to under- or over-

898 estimation of HM emissions from some source categories. Consequently, more

899 detailed investigation and long-term field tests for all kinds of coal-fired facilities and

900 industrial production processes are in great demand.

901 **3.5 Proposals for future control policies**

902 Presently, control of atmospheric HM emissions still has not received sufficient

903 attention by the government and public in spite of the frequent occurrence of HM

904 pollution in China (especially for provinces with high point sources of HM emissions).

905 The implementation of more rigorous emission standards on primary anthropogenic

906 sources (thermal power plant, coal-fired boiler, nonferrous metallurgy, pig iron and

907 steel production, etc.) and national ambient air quality standards (NAAQS) are

908 regarded as the important triggers to promote enterprises with diminished HM

909 emissions. Therefore, the MEP should speed up the revision of the system of

910 hazardous air pollutant (including HM) emission standards, and strengthen the

911 amendment of NAAQS. Especially, brake wear has been confirmed to be the main

912 source of HM emissions from traffic, particularly in urban areas. However, there is no

913 related emission standard of air pollutants for brake wear. In the near future, the

914 promulgation of emission standards of brake wear should be expected, which will

915 further strengthen the control of atmospheric HM emissions in China.

916 In addition, some specific actions are suggested as follows: (1) lower or stop

917 mining and burning of coal with high HM concentrations in certain provinces where

918 the coals are mainly mined from by small coal mines such as Zhejiang and Guangxi

919 (or lower or stop using high-sulfur coal in corresponding provinces due to the high

920 affinity between HMs and pyrite in coal) (Yuan et al., 2013; Zhu et al., 2015); (2)

921 promote coal washing before combustion (the removal efficiencies of coal preparation

922 to lower heavy metals can reach as high as approximately 30.0−60.0%, see

923 Supplement table S9); (3) increase the application rate of advanced APCDs

924 configurations in newly built or retrofitted coal-fired boilers; (4) initiate pilot-tests or

925 demonstration projects for specified mercury control (SMC) technologies in some

926 sectors with high Hg emissions and develop comprehensive HM control technologies

927 capable of simultaneously removing multiple heavy metals; (5) strengthen energy

928 conservation and boost electricity and/or heat generation using cleaned energy and

929 renewable energy, such as nuclear, wind and solar energy; (6) suspend small-scale

930 coal-fired boilers and industrial production plants with backward emission control

931 technologies (e.g., cement plants, ferrous smelting plants, nonferrous smelting plants,

932 etc.); (7) eliminate outdated production technology, such as VR pyrometallurgy and
933 ISP pyrometallurgy; (8) improve cyclic utilization rate of nonferrous metals and
934 ferrous metals during the period of 12th FYP; (9) etc.

935 **4   Conclusions**

936   We have calculated the historical emissions of 12 typical HMs from primary
937 manmade activities during the period of 1949−2012, based on the detailed statistical
938 data at provincial level from various statistical yearbooks and adopting
939 comprehensive time-varying dynamic emission factors from relevant research and
940 literature. Undoubtedly, taking consideration of the economic transition and emission
941 control technology improvement, the dynamic emission factors used in this study will
942 enhance the accuracy and reliability of the estimation of HM emissions.

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

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

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

964   The overall uncertainties in our bottom-up inventories are thought to be

965 reasonable and acceptable with the adequate data availability. Nevertheless, to
966 achieve the more reliable estimations of HM emissions in China, much more detailed
967 investigation and long-term field tests for all kinds of coal-fired facilities and
968 industrial process are still in greatly needed in the future.

975 **References**

976 Akimoto, H., Ohara, T., Kurokawa, J, and Horii, N.: Verification of energy consumption in China
977 during 1996–2003 by using satellite observational data, Atmos. Environ., 40, 7664–7667,
978 doi:10.1016/j.atmosenv.2006.07.052, 2006.
979 Annema, J. A.: SPIN document "Productie van secundair staal", RIVM rapportnr, the Netherlands,
980 1993.
981 Biggins, P. D., and Harrison, R. M.: Atmospheric chemistry of automotive lead, Environ. Sci.
982 Technol., 13, 558−565, doi:10.1021/es60153a017, 1979.
983 Bond, T. C., Bhardwaj, E., Dong, R., Jogani, R., Jung, S., Roden, C., Streets, D. G., and
984 Trautmann, N. M.: Historical emissions of black and organic carbon aerosol from energy‐
985 related combustion, 1850 − 2000, Global Biogeochem. Cycles, 21, 1 − 16,
986 doi:10.1029/2006GB002840, 2007.
987 Bukowiecki, N., Lienemann, P., Hill, M., Figi, R., Richard, A., Furger, M., Rickers, K.,
988 Falkenberg, G., Zhao, Y., and Cliff, S. S.: Real-world emission factors for antimony and other
989 brake wear related trace elements: size-segregated values for light and heavy duty vehicles,
990 Environ. Sci. Technol., 43, 8072−8078, doi:10.1021/es9006096, 2009.
991 Chang, M. B., Huang, C. K., Wu, H. T., Lin, J. J., and Chang, S. H.: Characteristics of heavy
992 metals on particles with different sizes from municipal solid waste incineration, J. Hazard.
993 Mater., 79, 229−239, doi:10.1016/S0304-3894(00)00277-6, 2000.
994 Cheng, H. F., and Hu, Y. A.: Municipal solid waste (MSW) as a renewable source of energy:
995 Current and future practices in China, Bioresour. Technol., 101, 3816−3824,
996 doi:10.1016/j.biortech.2010.01.040, 2010.
997 Cheng, K., Wang, Y., Tian, H. Z., Gao, X., Zhang, Y. X., Wu, X. C., Zhu, C. Y., Gao, J. J.:
998 Atmospheric emission characteristics and control policies of five precedent-controlled toxic
999 heavy metals from anthropogenic sources in China, Environ. Sci. Technol., 49, 1206−1214,
1000 doi:10.1021/es5037332, 2015.
1001 Cheng, Z., Wang, S. X., Fu, X., Watson, J. G., Jiang, J. K., Fu, Q., Chen, C., Xu, B., Yu, J., Chow,
1002 J. C., and Hao, J. M.: Impact of biomass burning on haze pollution in the Yangtze River delta,
1003 China: a case study in summer 2011, Atmos. Chem. Phys., 14, 4573−4585,
1004 doi:10.5194/acp-14-4573-2014, 2014.
1005 China Iron and Steel Association (CISA), P. R. China: China Steel Yearbook, China Steel Industry
1006 Press, Beijing, 2013 (in Chinese).
1007 China Machinery Industry Federation (CMIF), P. R. China: China Machinery Industry Yearbook,
1008 China Machine Press, Beijing, 2013.
1009 Department of Environment of Australia (DEA): Emissions estimation technique manual for
1010 aggregated emissions from domestic solid fuel burning, National Pollutant Inventroy (NPI),
1011 1999.
1012 Duan, J. C., and Tan, J. H.: Atmospheric heavy metals and arsenic in China: situation, sources and
1013 control policies, Atmos. Environ., 74, 93−101, doi:10.1016/j.atmosenv.2013.03.031, 2013.
1014 European Commission (EC): Integrated Pollution Prevention and Control (IPPC), Best available
1015 techniques reference document on the production of iron and steel, 2001.
1016 European Environment Agency (EEA): EMEP/EEA air pollutant emission inventory guidebook
1017 2009, available at:
1018 http://www.eea.europa.eu/publications/emep-eea-emission-inventory-guidebook-2009 (last
1019 access: 24 December 2013), 2009.
1020 European Environment Agency (EEA): EMEP/EEA air pollutant emission inventory guidebook
1021 2013, available at: http://www.eea.europa.eu/publications/emep-eea-guidebook-2013 (last
1022 access: 12 November 2013), 2013.
1023 Fang, F. M., Wang, Q. C., Ma, Z. W., Liu, R. H., and Cao, Y. H.: Estimation of atmospheric input
1024 of mercury to South Lake and Jingyue Pool, Chinese Geog. Sci., 12, 86−89,
1025 doi:10.1007/s11769-002-0076-y, 2002.
1026 Feng, X.: Mercury pollution in China—an overview, Springer Publishers, 657–678, doi:
1027 10.1007/0-387-24494-827, 2005.
1028
1029 Gao, J. J., Tian, H. Z., Cheng, K., Lu, L., Wang, Y. X., Wu, Y., Zhu, C. Y., Liu, K. Y., Zhou, J. J.,
1030 Liu, X. G., Chen, J., and Hao, J. M.: Seasonal and spatial variation of trace elements in

33

multi-size airborne particulate matters of Beijing, China: Mass concentration, enrichment characteristics, source apportionment, chemical speciation and bioavailability, Atmos. Environ., 99, 257−265, doi:10.1016/j.atmosenv.2014.08.081, 2014.

Grübler, A., Nakićenović, N., and Victor, D. G.: Dynamics of energy technologies and global change, Energy policy, 27, 247−280, doi:10.1016/S0301-4215(98)00067-6, 1999.

Hao, J. M., Tian, H. Z., and Lu, Y. Q.: Emission inventories of NOx from commercial energy consumption in China, 1995−1998, Environ. Sci. Technol., 36, 552−560, doi:10.1021/es015601k, 2002.

Hassel, D., Jost, P., and Dursbeck, F.: Das Abgas-Emissionsverhalten von Personenkraftwagen in der Bundesrepublik Deutschland im Bezugsjahr, 1985, UBA-Berichte, 7, 1987.

Hjortenkrans, D. S., Bergbäck, B. G., and Häggerud, A. V.: Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005, Environ. Sci. Technol., 41, 5224−5230, doi:10.1021/es070198o, 2007.

Hulskotte, J. H. J., Schaap, M., and Visschedijk, A. J. H.: Brake wear from vehicles as an important source of diffuse copper pollution, 10th International specialized conference on diffuse pollution and sustainable basin management, 18−22, 2006.

International Agency for Research on Cancer (IARC): Agents classified by the iarc monographs, volumes 1-111, oline availiable at: http://monographs.iarc.fr/ENG/Classification/index.php (last access: 23 October 2014), 2014.

Industial emissions Reporting Information System (IRIS), European Commission, available at: http://iris.eionet.europa.eu/ippc/reporting-period-2003-2005/elv-reports/key-results/ (last access: 18 September 2014), 2005.

Jockel W., and Hartje J.: Datenerhebung Ÿber die emissionen umweltgefŠhrdender schwermetalle, forschungsbericht 91-104 02 588, T†V Rheinland e.V. Kšln, 1991.

Johansson, C., Norman, M., and Burman, L.: Road traffic emission factors for heavy metals, Atmos. Environ., 43, 4681−4688, doi:10.1016/j.atmosenv.2008.10.024, 2009.

Kavlak, G., and Graedel, T. E.: Global anthropogenic selenium cycles for 1949–2010, Resour. Conserv. Recycl., 73, 17-22, doi:10.1016/j.resconrec.2013.01.013, 2013.

Kung, J. K. s., and Lin, J. Y.: The Causes of China's Great Leap Famine, 1959–1961, Econ. Dev. Cultural Change, 52, 51−73, doi:10.1086/380584, 2003.

Li, J. F., Song, Y., Mao, Y., Mao, Z. C., Wu, Y. S., Li, M. M., Huang, X., He, Q. C., and Hu, M.: Chemical characteristics and source apportionment of PM2.5 during the harvest season in eastern China's agricultural regions, Atmos. Environ., 92, 442−448, doi:10.1016/j.atmosenv.2014.04.058, 2014.

Lu, B., Kong, S. F., Han, B., Wang, X. Y., and Bai, Z. P.: Inventory of atmospheric pollutants discharged from biomass burning in China continent in 2007, Chin. Environ. Sci., 31, 186−194, 2011 (In Chinese with English abstract).

Ministry of Environmental Protection of the People's Republic of China (MEP), P. R. China: Emission standard of air pollutants for iron smelt industry, Beijing, 2012 (in Chinese).

Ministry of Environmental Protection of the People's Republic of China (MEP), P. R. China: The list of desulfurization facilities equipped by coal-fired boiler in China, available at: http://www.mep.gov.cn/gkml/hbb/bgg/201407/W020140711581927228220.pdf (last access: 8 July 2014), 2014a.

Ministry of Environmental Protection of the People's Republic of China (MEP), P. R. China: The list of denitration facilities equipped by coal-fired boiler in China, available at: http://www.mep.gov.cn/gkml/hbb/bgg/201407/W020140711581927393439.pdf (last access: 8 July 2014), 2014b.

Mukherjee, A. B.: Nickel: a review of occurrence, uses, emissions, and concentration in the environment in Finland, Environ. Rev., 6, 173−187, doi:10.1139/a99-001, 1998.

National Bureau of Statistics (NBS), P. R. China: Report on "12th Five-Year Plan" of the electric power industry. National Bureau of Statistics of China, Beijing, China, 2011 (in Chinese).

National Bureau of Statistics (NBS), P. R. China: China Energy Statistical Yearbook, China Statistics Press, Beijing, 2013b.

National Bureau of Statistics (NBS), P. R. China: China Statistical Yearbook, China Statistics Press, Beijing, 2013a.

Nie, Y. F.: Development and prospects of municipal solid waste (MSW) incineration in China, Front. Environ. Sci. Engin. China, 2, 1−7, doi:10.1007/s11783-008-0028-6, 2008.

Nriagu, J. O.: Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere, Nature, 279, 409−411, doi:10.1038/279409a0, 1979.

Nriagu, J. O., and Pacyna, J. M.: Quantitative assessment of worldwide contamination of air, water and soils by trace metals, Nature, 333, 134−139, doi:10.1038/333134a0, 1988.

Österle, W., Prietzel, C., Kloß, H., and Dmitriev, A. I.: On the role of copper in brake friction materials, Tribol. Int., 43, 2317−2326, doi:10.1016/j.triboint.2010.08.005, 2010.

Pacyna, E. G., Pacyna, J. M., Steenhuisen, F., Wilson, S.: Global anthropogenic mercury emission inventory for 2000, Atmos. Environ., 40, 4048−4063, doi:10.1016/j.atmosenv.2006.03.041, doi:10.1016/j.atmosenv.2006.03.041, 2006.

Pacyna, J. M.: Estimation of the atmospheric emissoins of trace elements from anthropogenic sources in Europe, Atmos. Environ., 18, 41−50, doi:10.1016/0004-6981(84)90227-0, 1984.

Pacyna, J. M., and Pacyna, E. G.: An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide, Environ. Rev., 9, 269−298, doi:10.1139/a01-012, 2001.

Pirrone, N., Cinnirella, S., Feng, X., Finkelman, R. B., Friedli, H. R., Leaner, J., Mason, R., Mukherjee, A. B., Stracher, G. B., Streets, D. G., Telmer, K.: Global mercury emissions to the atmosphere from anthropogenic and natural sources. Atmos. Chem. Phys, 10, 5951–5964, doi:10.5194/acp-10-5951-2010, 2010.

Qin, J. F.: Estimation of lead emission to atmospheric from gasoline combustion, Guangdong Trace Ele. Sci., 17, 27−34, 2010 (in Chinese).

Reddy, M. S., Basha, S., Joshi, H. V., and Jha, B.: Evaluation of the emission characteristics of trace metals from coal and fuel oil fired power plants and their fate during combustion, J. Hazard. Mater., 123, 242-249, doi:10.1016/j.jhazmat.2005.04.008, 2005.

Ren, D. Y., Zhao, F. H., Dai, S., and Zhang, J.: Geochemistry of trace elements in coal, Science Press, Beijing , 2006 (in Chinese).

Robbins, N., Zhang, Z. F., Sun, J., Ketterer, M. E., Lalumandier, J. A., and Shulze, R. A.: Childhood lead exposure and uptake in teeth in the Cleveland area during the era of leaded gasoline, Sci. Total Environ., 408, 4118−4127, doi:10.1016/j.scitotenv.2010.04.060, 2010.

Song, D. Y., Qin, Y., and Wang, W. F.: Burning and migration behavior of trace elements of coal used in power plant, J. China Univ. Min. Technol., 32, 316−320, 2003 (in Chinese with English abstract).

Streets, D. G., Bond, T. C., Lee, T., and Jang, C.: On the future of carbonaceous aerosol emissions, J. Geophys. Res., 109, 1−19, doi:10.1029/2004JD004902, 2004.

Streets, D. G., Bond, T. C., Carmichael, G. R., Fernandes, S. D., and Fu, Q.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, J. Geophys. Research policy, 108, 8809, doi:10.1029/2002JD003093, 2003.

Streets, D. G., Hao, J. M., Wu, Y., Jiang, J. K., Chan, M., Tian, H. Z., and Feng, X. B.: Anthropogenic mercury emissions in China, Atmos. Environ., 39, 7789−7806, doi:10.1016/j.atmosenv.2005.08.029, 2005.

Streets, D. G., Devane, M. K., Lu, Z., Bond, T. C., Sunderland, E. M., and Jacob, D. J.: All-time releases of mercury to the atmosphere from human activities, Environ. Sci. Technol., 45, 10485−10491, doi:10.1021/es202765m, 2011.

Tang, X. Y., Zhao, J. Y., and Huang, W. H.: Nine metal elements in coal of China, Coal Geol. China, 14, 43−54, 2002 (in Chinese).

Theloke, J., Kummer, U., Nitter, S., Geftler, T., and Friedrich, R.: Überarbeitung der Schwermetallkapitel im CORINAIR Guidebook zur Verbesserung der Emissionsinventare und der Berichterstattung im Rahmen der Genfer Luftreinhaltekonvention. Report for Umweltbundesamt, 2008.

Tian, H. Z., Hao, J. M., Hu, M. Y., and Nie, Y. F.: Recent trends of energy consumption and air pollution in China, J. Energy Eng., 133, 4−12, doi: 10.1061/(ASCE)0733-9402(2007)133:1(4), 2007.

Tian, H. Z., Wang, Y., Xue, Z. G., Cheng, K., Qu, Y. P., Chai, F. H., and Hao, J. M.: Trend and characteristics of atmospheric emissions of Hg, As, and Se from coal combustion in China, 1980−2007, Atmos. Chem. Phys., 10, 11905−11919, doi:10.5194/acp-10-11905-2010, 2010.

Tian, H. Z., Cheng, K., Wang, Y., Zhao, D., Chai, F. H., Xue, Z. G., and Hao, J. M.: Quantitative assessment of variability and uncertainty of hazardous trace element (Cd, Cr, and Pb) contents in Chinese coals by using bootstrap simulation, J. Air Waste Manage. Assoc., 61,

1145   755−763, doi:10.3155/1047-3289.61.7.755, 2011a.

1146 Tian, H. Z., Zhao, D., and Wang, Y.: Emission inventories of atmospheric pollutants discharged
1147   from biom ass burning in China, Acta Sci. Circumstantiae, 31, 349−357, 2011b (in Chinese
1148   with English abstract).

1149 Tian, H. Z., Cheng, K., Wang, Y., Zhao, D., Lu, L., Jia, W. X., and Hao, J. M.: Temporal and
1150   spatial variation characteristics of atmospheric emissions of Cd, Cr, and Pb from coal in
1151   China, Atmos. Environ., 50, 157−163, doi:10.1016/j.atmosenv.2011.12.045, 2012a.

1152 Tian, H. Z., Lu, L., Cheng, K., Hao, J. M., Zhao, D., Wang, Y., Jia, W. X., and Qiu, P. P.:
1153   Anthropogenic atmospheric nickel emissions and its distribution characteristics in China, Sci.
1154   Total Environ., 417, 148−157, doi:10.1016/j.scitotenv.2011.11.069, 2012b.

1155 Tian, H. Z., Zhao, D., Cheng, K., Lu, L., He, M. C., and Hao, J. M.: Anthropogenic atmospheric
1156   emissions of antimony and its spatial distribution characteristics in China, Environ. Sci.
1157   Technol., 46, 3973−3980, doi:10.1021/es2041465, 2012c.

1158 Tian, H., Lu, L., Hao, J. M., Gao, J. J., Cheng, K., Liu, K. Y., Qiu, P. P., and Zhu, C. Y.: A review
1159   of key hazardous trace elements in Chinese coals: Abundance, occurrence, behavior during
1160   coal combustion and their environmental impacts, Energy Fuels, 27, 601−614,
1161   doi:10.1021/ef3017305, 2013.

1162 Tian, H., Liu, K. Y., Zhou, J. J., Lu, L., Hao, J. M., Qiu, P. P., Gao, J. J., Zhu, C. Y., Wang, K., and
1163   Hua, S. B.: Atmospheric emission inventory of hazardous trace elements from China's
1164   coal-fired power plants−Temporal trends and spatial variation characteristics, Environ. Sci.
1165   Technol., 48, 3575−3582, doi:10.1021/es404730j, 2014a.

1166 Tian, H. Z., Gao, J. J., Lu, L., Zhao, D., Cheng, K., and Qiu, P. P.: Temporal trends and spatial
1167   variation characteristics of hazardous air pollutant emission inventory from municipal solid
1168   waste incineration in China, Environ. Sci. Technol., 46, doi:10364−10371,
1169   10.1021/es302343s, 2012d.

1170 Tian, H. Z., Zhou, J. R., Zhu, C. Y., Zhao, D., Gao, J. J., Hao, J. M., He, M. C., Liu, K. Y., Wang,
1171   K., and Hua, S. B.: A Comprehensive global inventory of atmospheric antimony emissions
1172   from anthropogenic activities, 1995−2010, Environ. Sci. Technol., 48, 10235−10241,
1173   doi:10.1021/es405817u, 2014b.

1174 United Kingdom (UK): emission factor databases of NAEI, 1970−1995, availiable at:
1175   http://naei.defra.gov.uk/data/ef-all-results?q=14774, (last access: 10 August 2014), 1995.

1176 United Kingdom (UK): emission factor databases of NAEI, available at:
1177   http://naei.defra.gov.uk/data/ef-all-results?q=15354 (last access: 11 September 2014), 2012.

1178 US Environmental Protection Agency (US EPA): AP 42, fifth edition, volume I, chapter 1, section
1179   1.1: bituminous and subbituminous coal combustion, availabe at:
1180   http://www.epa.gov/ttn/chief/ap42/ch01/index.html (last access: 12 October 2014), 1993.

1181 US Environmental Protection Agency (US EPA): Web Factor Information Retrieval System
1182   (WebFIRE), availabe at:
1183   http://cfpub.epa.gov/webfire/index.cfm?action=fire.FactorsBasedOnDetailedSearch (last
1184   access: 21 September 2014), 2012.

1185 US Environmental Protection Agency (US EPA): AP 42, fifth edition, volume I, chapter 2, section
1186   2.1: refuese combustion, availiable at: http://www.epa.gov/ttn/chief/ap42/ch02/index.html
1187   (last access: 23 July 2014), 1996.

1188 Van der Most, P. F. J. and Veldt, C.: Emission factors Manual PARCOM-ATMOS, TNO-MEP,
1189   Apeldoorn, the Netherlands, 1991.

1190 von Uexküll, O., Skerfving, S., Doyle, R., and Braungart, M.: Antimony in brake pads-a
1191   carcinogenic component?, J. Cleaner Prod., 13, 19−31, doi:10.1016/j.jclepro.2003.10.008,
1192   2005.

1193 Wu, Q. R., Wang, S. X., Zhang, L., Song, J. X., Yang, H., and Meng, Y.: Update of mercury
1194   emissions from China's primary zinc, lead and copper smelters, 2000−2010, Atmos. Chem.
1195   Phys., 12, 11153−11163, doi:10.5194/acp-12-11153-2012, 2012.

1196 Wu, Y., Streets, D. G., Wang, S. X., and Hao, J. M.: Uncertainties in estimating mercury emissions
1197   from coal-fired power plants in China, Atmos. Chem. Phys., 10, 2937−2946,
1198   doi:10.5194/acp-10-2937-2010, 2010.

1199 Wu, Y., Wang, S. X., Streets, D. G., Hao, J. M., Chan, M., and Jiang, J. K.: Trends in
1200   anthropogenic mercury emissions in China from 1995 to 2003, Environ. Sci. Technol., 40,
1201   5312−5318, doi:10.1021/es060406x, 2006.

Wu, Y. Y., Qin, Y., Yi, T. S., and Xia, X. H.: Enrichment and geochemical origin of some trace elements in high-sulfur coal from Kaili, eastern Guizhou Province, Geochimica, 37, 615-622, 2008 (in Chinese with English abstract).

Xu, H. M., Cao, J. J., Ho, K. F., Ding, H., Han, Y. M., Wang, G. H., Chow, J. C., Watson, J. G., Khol, S. D., Qiang, J., and Li, W. T.: Lead concentrations in fine particulate matter after the phasing out of leaded gasoline in Xi'an, China, Atmos. Environ., 46, 217−224, doi:10.1016/j.atmosenv.2011.09.078, 2012.

Xu, M. H., Yan, R., Zheng, C. G., Qiao, Y., Han, J., Sheng, C. D.: Status of trace element emission in a coal combustion process: a review. Fuel Process. Technol., 85, 215-23, doi:10.1016/S0378-3820(03)00174-7, 2004.

Yuan, X. L., Mi, M., Mu, R. M., and Zuo, J.: Strategic route map of sulphur dioxide reduction in China, Energy Policy, 60, 844–851, doi:10.1016/j.enpol.2013.05.072, 2013.

Zhang, J. L., and Wang, G. S.: Energy saving technologies and productive efficiency in the Chinese iron and steel sector, Energy, 33, 525−537, doi:10.1016/j.energy.2007.11.002, 2008.

Zhao, Y., Nielsen, C. P., Lei, Y., McElroy, M. B., and Hao, J. M.: Quantifying the uncertainties of a bottom-up emission inventory of anthropogenic atmospheric pollutants in China, Atmos. Chem. Phys., 11, 2295−2308, doi:10.5194/acp-11-2295-2011, 2011.

Zhu, C. Y., Tian, H. Z., Cheng, K., Liu, K. Y., Wang, K., Hua, S. B., Gao, J. J., and Zhou, J. R.: Potentials of whole process control of heavy metals emissions from coal-fired power plants in China, J. Cleaner Prod., doi: 10.1016/j.jclepro.2015.05.008, 2015 (in Press).

1222   **Table 1.** Averaged release rates and removal efficiencies of various HMs from coal-fired facilities and the installed APCDs.

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

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

| Year	Hg	As	Se	Pb	Cd	Cr	Ni	Sb	Mn	Co	Cu	Zn
1949	12.7	45.2	53.7	312.6	15.5	158.6	147.3	16.3	212.1	11.5	74.0	226.8
1978	144.1	593.6	607.6	7206.2	82.5	1021.2	891.9	151.1	3616.5	295.3	1356.8	3396.0
1980	163.1	791.3	825.8	9744.8	98.0	1481.4	1101.5	193.9	4637.4	387.2	1745.6	4128.4
1985	209.7	1055.5	1168.7	12922.5	123.7	2353.5	1250.0	250.6	5736.8	478.8	2194.9	4896.5
1990	261.3	1311.7	1546.4	17644.0	156.2	3374.7	1667.5	337.3	7607.8	624.0	2880.5	6541.9
1995	351.1	1699.7	2179.8	17620.3	223.3	5155.0	2354.2	499.4	9454.9	778.7	4131.5	9564.5
2000	316.1	1673.2	2113.0	20193.5	255.9	4928.7	2407.0	566.1	10034.7	842.7	4733.0	10788.6
2005	492.3	2454.4	3058.1	10887.1	378.9	6828.5	3246.4	797.9	12195.4	1075.8	7101.1	15987.9
2006	509.3	2501.2	3146.8	11250.2	398.5	7179.0	3356.7	826.2	12181.6	1042.8	7201.1	16895.0
2007	533.8	2407.2	3067.2	11729.0	420.8	7445.2	3369.6	822.8	12528.9	1064.5	7600.0	18147.6
2008	564.8	2489.7	3136.1	12213.6	442.4	7755.7	3248.3	962.9	12499.8	1056.5	8208.7	18337.4
2009	589.7	2325.8	2936.1	12519.9	453.7	7810.2	3250.8	1006.0	12195.4	1010.7	8428.6	19035.8
2010	672.0	2322.9	2880.5	13194.5	455.8	7465.2	3138.6	1068.1	12015.9	919.2	8318.8	20503.7
2011	688.4	2422.8	3062.4	14032.4	493.9	7733.0	3440.1	1172.8	12657.3	981.2	9115.5	21876.0
2012	695.1	2529.0	3061.7	14397.6	526.9	7834.1	3395.5	1251.7	13006.6	1004.6	9547.6	22319.6
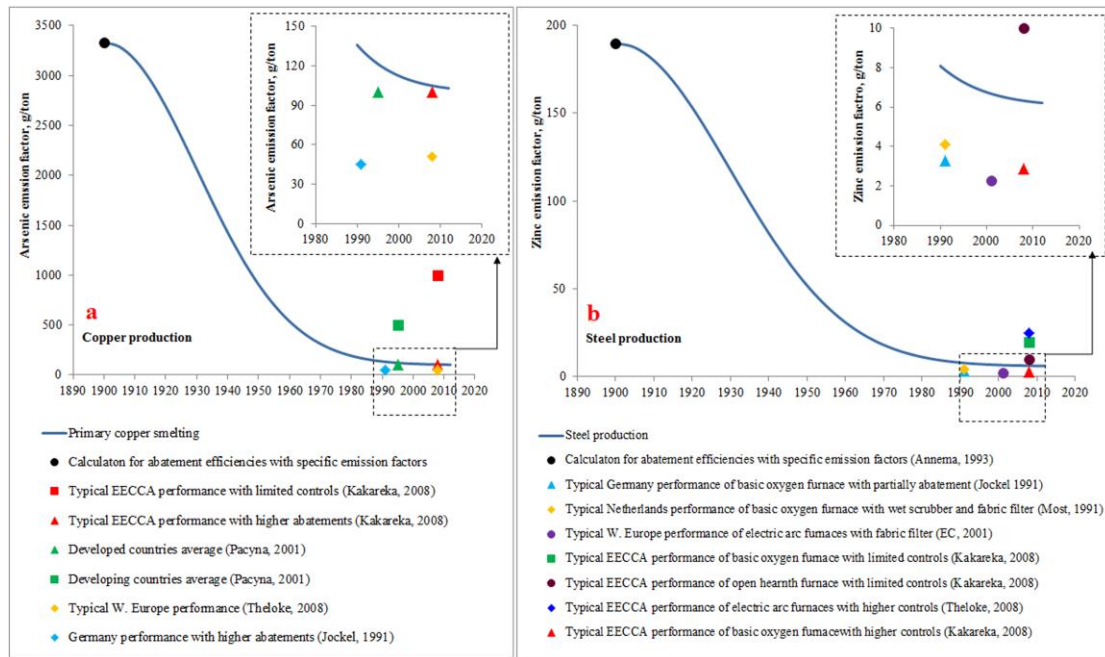
Figure 1. Time variation of arsenic emission factors for copper production and zinc emission factors for steel making in China (an example)
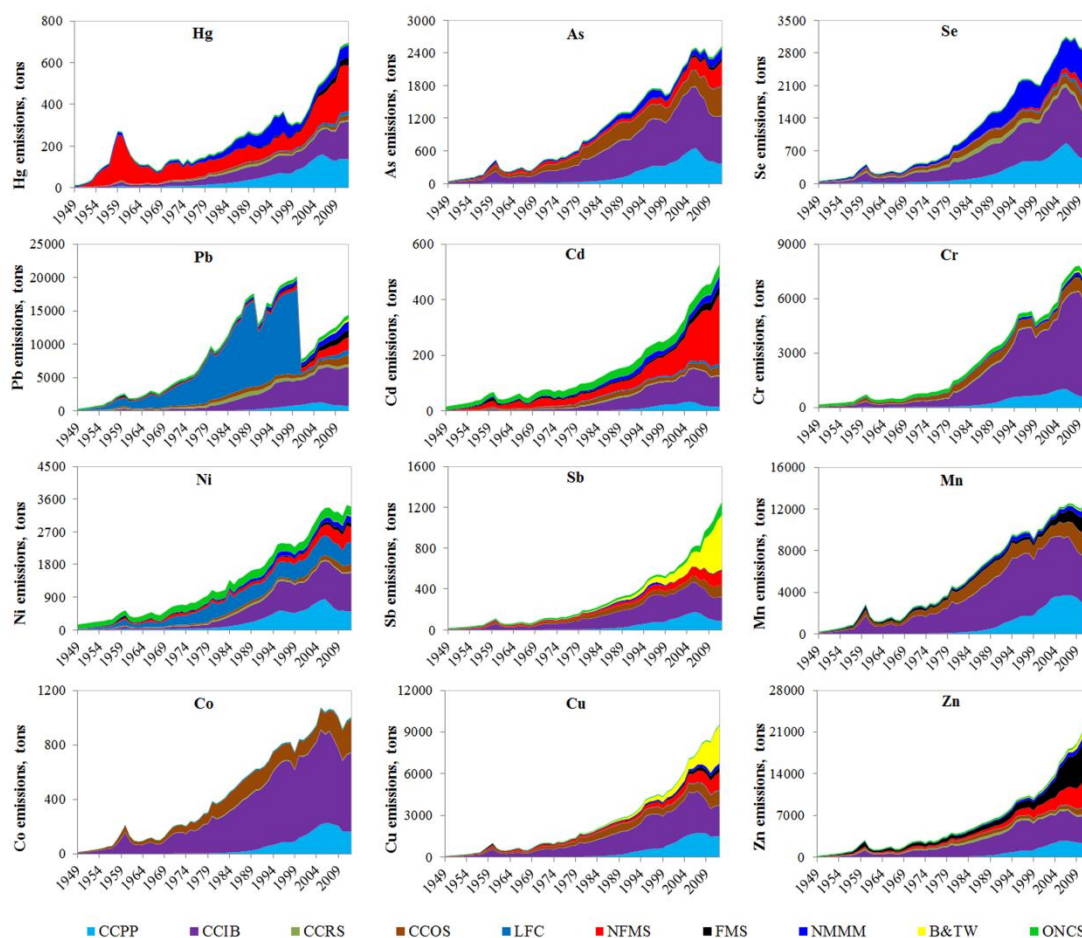
Figure 2. Historical trends of atmospheric HMs (Hg, As, Se, Pb, Cd, Cr, Ni, Sb, Mn, Co, Cu and Zn) emissions from primary anthropogenic sources in China, 1949−2012. CCPP, coal consumption by power plants; CCIB, coal consumption by industrial boilers; CCRS, coal consumption by residential sectors; CCOS, 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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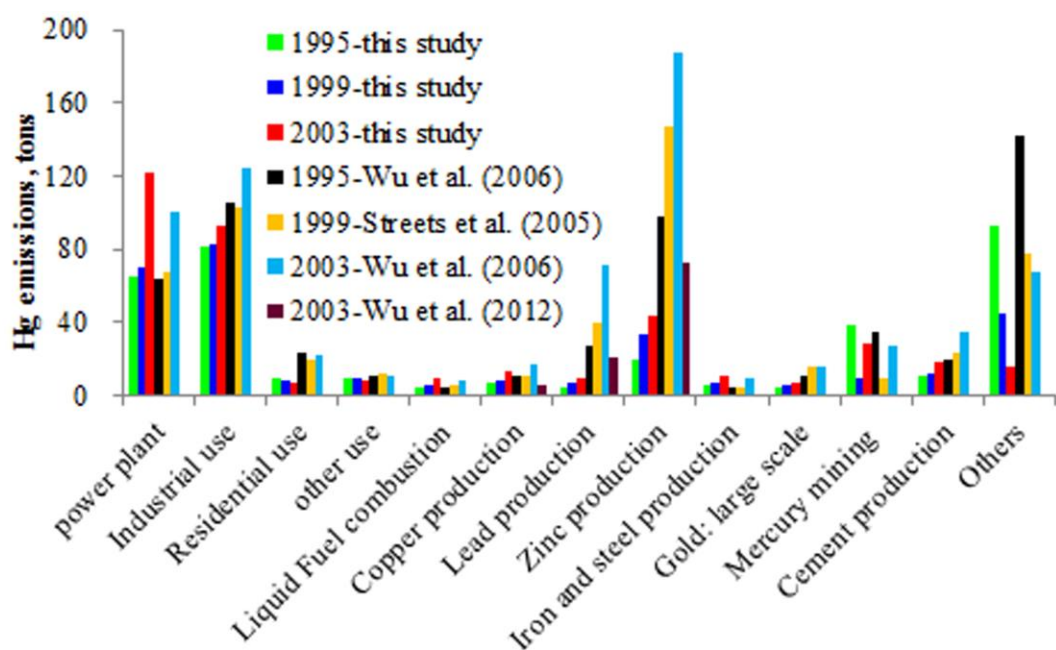
1236 **Figure 3.** Estimate of annual Hg emissions from primary anthropogenic sources among various

1237 studies (t yr^{-1}).
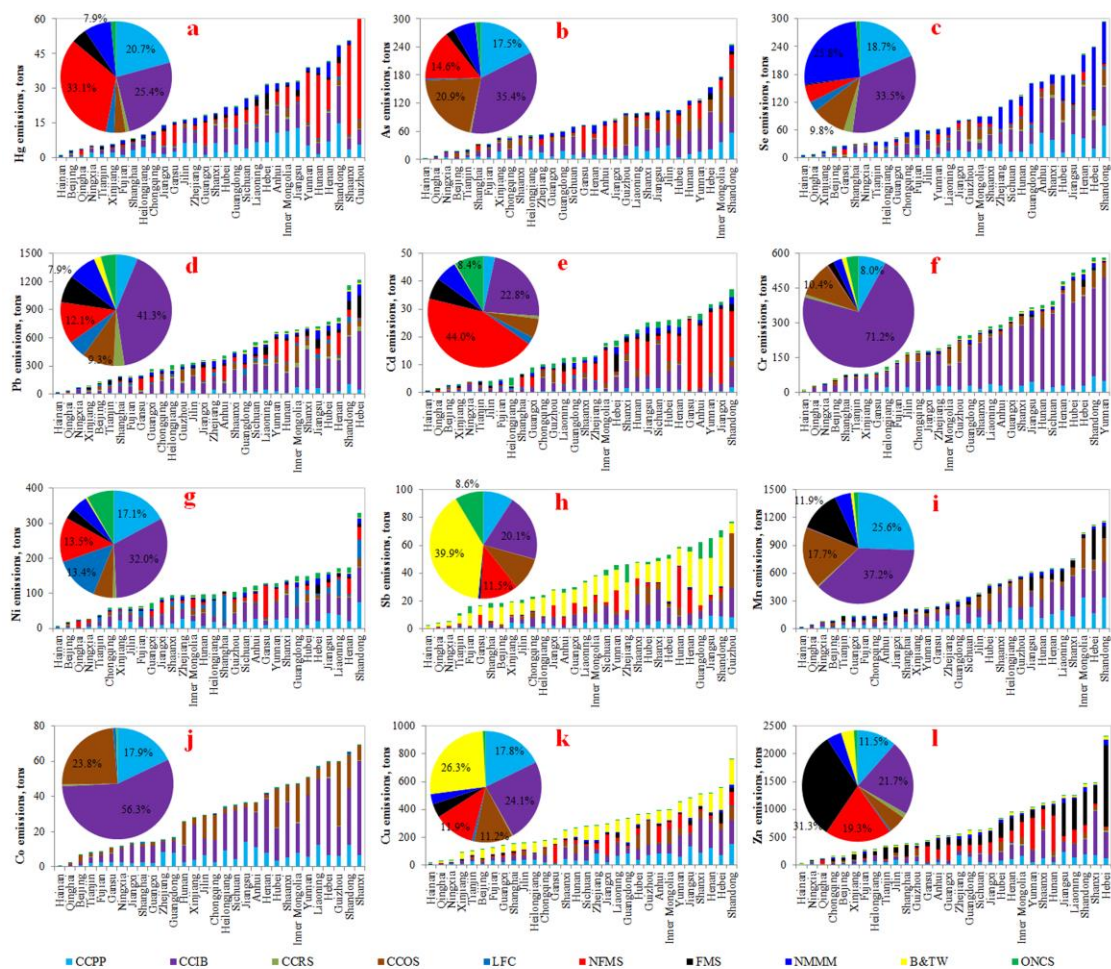
Figure 4. Provincial HM emissions from anthropogenic sources and national composition by source categories in 2010.
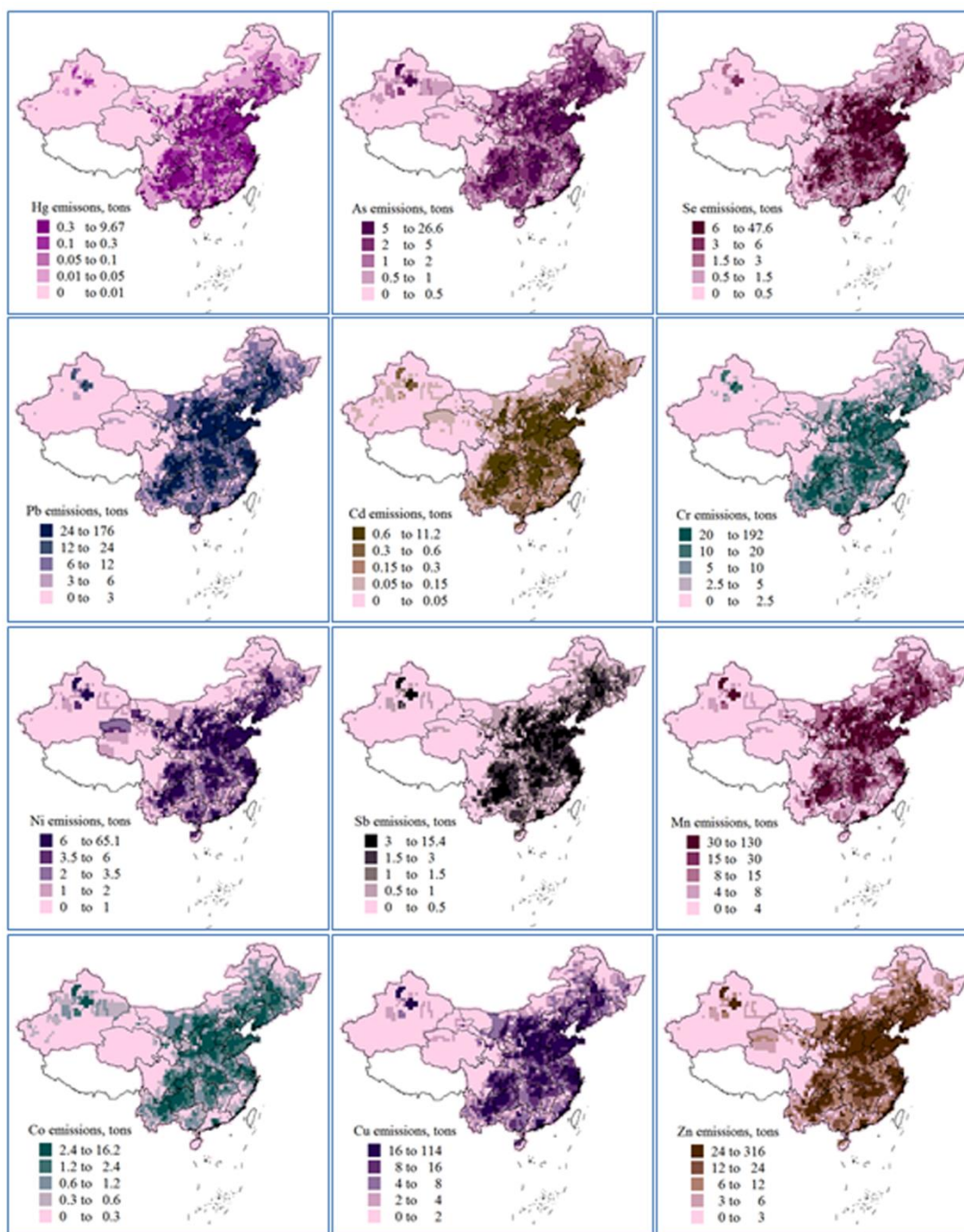
Figure 5. Gridded HM emissions from anthropogenic sources for the year 2010 ($0.5° \times 0.5°$ resolution; units, kilograms per year per grid cell).
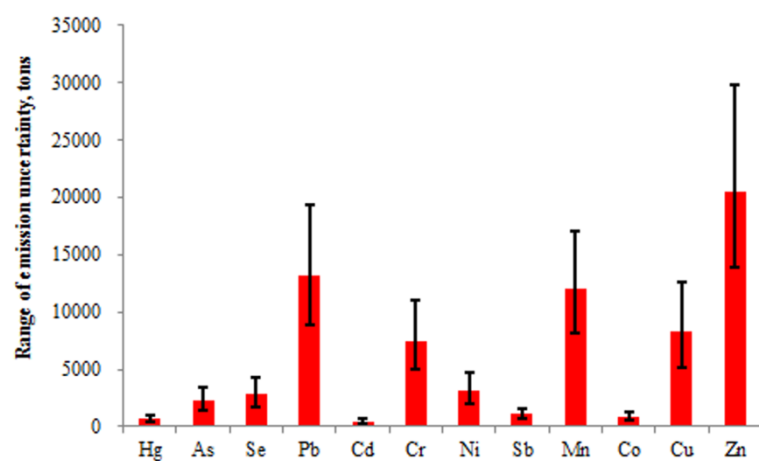
Figure 6. Uncertainties in the total emissions of HMs in China in 2010 (Uncertainties in the emissions of HMs by source categories in China in 2010 can be seen Supplement Table S22).