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ORIGINAL PAPER

Atmospheric emission inventory of cadmium from anthropogenic sources

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Abstract To demonstrate the atmospheric emission characteristics of cadmium (Cd), which is considered an important contaminant to human health and environment, a comprehensive emission inventory of Cd has been established by applying the best available emission factors and activity data for the first time. This inventory covers major anthropogenic sources in China and a bottom-up approach is adopted to compile the inventory for the sources where possible. The total emissions of Cd are estimated at about 743.77 metric tons for the year 2009, of which the contributions of industrial processes and combustion sources are approximately 56.6 and 43.4 %, respectively. Nonferrous metals smelting including copper, lead, and zinc, ranks as the leading source accounting for about 40.6 % of the total. The high contribution results from the rapid growth of nonferrous metallurgical industry that reflects a new focus of Cd emission pollution in China. Cd emissions from coal combustion are estimated at approximately 273.69 metric tons, with a share of 36.8 %, in which industrial coal-burning sector is thought to be the primary source. Moreover, Cd emissions are spatially allocated onto grid cells with a resolution of 0.5° × 0.5°, indicating that the emissions are mainly distributed among the regions of eastern, central and southern China. In addition, the uncertainties in the inventory are quantified by using a Monte Carlo simulation, and the overall uncertainty falls within a range of −15 to 48 %. It implies that more field tests for industrial coal combustion and metals smelting process are very necessary.

Keywords Anthropogenic emissions · Cadmium · Coal combustion · Nonferrous metals smelting · Spatial distribution · Uncertainty analysis

Introduction

Because of its potential harm, cadmium (Cd) has aroused a special concern of environmental and human exposure, which causes it to be one of the priority contaminants to be controlled within various programs (European Monitoring and Evaluation Programme (EMEP) 2006). Cd mainly resides in the kidneys of the human body and, when it accumulates to a critical threshold, it can lead to kidney failure (World Health Organization (WHO) 2010).

Cadmium mainly occurs in the crust of earth associated with zinc ores. The average content is generally between 0.1 and 0.5 μg/g although much higher levels can also be found in sedimentary rock and marine phosphates and phosphorites (Cook and Morrow 1995). Cd usually exists as the solid-state form of Cd^{2+} compounds when the temperature is below 900 K under oxidizing conditions and is considered hazardous to human health (International Agency for Research on Cancer (IARC) 1993). Once

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released from the ores, it can attach to fine particles that could easily pass through conventional air pollution control devices into the atmosphere (Mukherjee 1998). Ambient air Cd concentrations have generally been estimated to range from 0.1 to 5 ng/m^3 in rural areas, 2.0 to 15 ng/m^3 in urban areas, and 15 to 150 ng/m^3 for industrialized areas (International Cadmium Association (ICdA) 2011). The Cd-containing particles may transport a long distance before finally settling onto soil and aqueous systems through wet and dry deposition (Sakata et al. 2008).

The atmospheric emissions from anthropogenic categories are thought to be the primary sources of contamination of atmospheric, terrestrial and aquatic environments. These categories include fossil fuel combustion, metallurgical smelting, municipal solid waste (MSW) incineration, and biomass (BM) burning (Nriagu 1989). Pacyna and Pacyna (2001) reported nonferrous (NF) metals smelting was the largest emission source of Cd to the atmosphere with a contribution of 73 % among all anthropogenic sources.

China plays an important role in global anthropogenic Cd emissions and its geochemistry cycle. Recently, there is a considerably increasing concern about Cd pollution because anthropogenic activities have led to an increasing concentration of Cd in the environment. Increasing concentration of Cd in the aerosols of urban areas has been reported (Han et al. 2006; Nguyen et al. 2010). The investigation conducted by Nanjing Agricultural University indicates the proportion of rice production with excessive Cd content is nearly 10 % in China (Zhen et al. 2008). Cd poisoning accidents have happened with an increasing tendency.

To restrain the increasing emission and pollution risk of typical heavy metals (mainly including mercury, arsenic, cadmium, chromium, and lead) from fuels combustion and industrial processes, the Ministry of Environmental Protection of China (MEP) proposed a specific comprehensive prevention plan on heavy metals pollution (CPPHMP) for the 12th five-year-plan (2011–2015) in the early 2011. However, the Chinese government has not specifically regulated Cd discharge from industrial production and residential sources to date.

By now, the understanding on the situation of anthropogenic atmospheric emissions of Cd in China is quite limited compared with some other trace elements such as mercury and antimony, and there have been few published estimates to date of Cd emissions in China (Tian et al. 2010, 2012a, b). The development of a complete emission inventory is an important step in an air quality management process. Emission inventory can be applied to help determine significant sources of air pollutants, target regulatory actions, and estimate air quality through computer dispersion modeling. On the basis of atmospheric emission inventory of Cd from anthropogenic sources, researchers can apply air quality simulation to assess the environmental effects and long-range trans-boundary transportation of Cd emissions. Up to now, the atmospheric emissions of Cd in European countries have been presented (Pacyna et al. 2007, 2009). However, it is little known about the current situation of Cd emissions in China as well as its spatial and source contribution characteristics until now.

Thus, an integrated emission inventory of Cd with highly spatial resolution information is urgently needed in China to know the current status and source allocation characteristics of Cd discharge, which will be benefit for the Chinese policymakers in formulating effective control programs and policies to combat the increasing stress on urban and regional air heavy metals pollution and poisoning accidents. The main objectives of this study are to establish the detailed algorithms to compile an integrated atmospheric emission inventory of Cd from identified anthropogenic sources and to explore the spatial characteristics of Cd emissions in China during 2009. This research work was carried out in the year 2011 at the State Key Joint Laboratory of Environmental Simulation and Pollution Control in School of Environment, Beijing Normal University of China.

Materials and methods

A bottom-up approach is adopted in this study for estimating Cd emissions from different anthropogenic sources where detailed activity level data and emission factors are available.

The anthropogenic sources are classified into two categories first: industrial processes and combustion sources. For industrial processes, Cd emissions are mainly produced from the calcination of raw materials and ores including NF metals smelting (including copper, lead, and zinc production), iron and steel manufacturing (ISM), and construction materials (CM) production. For combustion sources, Cd emissions come from the burning of fuels such as coal combustion, liquid fuels (LF) combustion, BM burning, and MSW incineration. Since coal dominates the primary energy consumption of China and the emission performances from different patterns of coal combustion facilities show substantial variability, coal combustion sources are further classified into power plants (PP), industrial coal use sector (IS), residential coal use sector (RS), and other coal use sectors (OS). Notably, Cd emissions from fuel consumption during industrial production are considered in combustion sources.

The specific procedures for compiling the emission inventory by source categories are elucidated in the following sections.

Calculation of Cd emissions from industrial process sources

Nonferrous metals smelting

Cadmium is often a by-product of smelting zinc, lead and copper, which can be released from the ores during high-temperature extraction (International Cadmium Association (ICdA) 2011). Cd in the off-gas can be released into the atmosphere through the stack after the combustion exhaust passes through particulate and gaseous control equipments. Emissions from NF metals smelting industry are considered to contribute most to the worldwide emissions of Cd (Nriagu 1989). Here, smelting sources are divided into primary and secondary production process, and the algorithms of Cd emission estimation can be expressed with Eqs. (1) and (2).

$$E_{\mathrm{NF}_i} = \sum F_{\mathrm{P}_i}\mathrm{EF}_{\mathrm{P}_i} + \sum F_{\mathrm{S}_i}\mathrm{EF}_{\mathrm{S}_i}, \quad (1)$$

$$E_{\mathrm{NF}_T} = \sum E_{\mathrm{NF}_i}. \quad (2)$$

Where E_{NF} is the atmospheric emissions of Cd from NF metals smelting; F_{P} is the yield of primary copper, lead, or zinc production; F_{S} is the yield of secondary copper, lead, or zinc production; EF_{P} and EF_{S} are the emission factor of Cd to the atmosphere from primary and secondary smelting processes, respectively; i is the province (autonomous region or municipality); and T is the national totals. The activity data of the NF metallurgical industry are obtained from provincial statistical yearbooks (Editorial Committee of the Yearbook of Nonferrous Metals Industry of China (ECNMI) 2010), and the emission factors assumed are shown in Table 1.

Iron and steel manufacturing

The iron and steel industry is a highly energy-intensive sector. More than half of the mass input becomes output in the form of off-gases and solid waste or by-products. The emissions from sinter plants dominate the overall emissions for most of the pollutants. The contribution of this sector to the total air emissions in the EU is considerable for a number of pollutants, especially for some heavy metals (European Environment Agency (EEA) 2009). Cd emissions from this sector can be calculated with the following equations:

$$E_{\mathrm{ISM}_i} = \sum F_{\mathrm{PI}_i}\mathrm{EF}_{\mathrm{PI}_i} + \sum F_{\mathrm{ST}_i}\mathrm{EF}_{\mathrm{ST}_i}, \quad (3)$$

$$E_{\mathrm{ISM}_T} = \sum E_{\mathrm{ISM}_i}. \quad (4)$$

Where E_{ISM} is the atmospheric emissions of Cd during pig ISM; F_{PI} is the amount of pig iron production; F_{ST} is the amount of steel production; $\mathrm{EF}_{\mathrm{PI}}$ is the average emission factor of Cd to the atmosphere from pig iron production; $\mathrm{EF}_{\mathrm{ST}}$ is the average emission factor of Cd to the atmosphere from steel production. The activity data of pig iron production and steel production are obtained from provincial statistical yearbooks, and the emission factors used are listed in Table 1.

Construction materials production

Cadmium within ash and exit gases from producing CM comes from raw material sintering and combustion processes. This sector includes cement, flat glass, and brick production, which are classified as key sources of various air pollutants (European Environment Agency (EEA) 2009). The emissions estimation is based on Eqs. (5) and (6):

$$E_{\mathrm{CM}_i} = \sum F_{\mathrm{MP}_i}\mathrm{EF}_{\mathrm{MP}_i}, \quad (5)$$

$$E_{\mathrm{CM}_T} = \sum E_{\mathrm{CM}_i}. \quad (6)$$

Where E_{CM} is the atmospheric emissions of Cd from cement, flat glass, or brick production; F_{MP} is the production volume of cement, flat glass, or brick; EF_{MP} is the average emission factor of Cd to the atmosphere from cement, flat glass, or brick production.

Here, to avoid double counting with the emissions from coal combustion category, coal-related emissions are excluded when calculating Cd emissions from the above categories, i.e., NF metals smelting, pig iron and steel smelting processes, and CM production.

Calculation of Cd emissions from combustion sources

Coal combustion

As furnace temperature increases during coal burning, trace elements incorporated in coal will volatilize into the flue gas and react with surrounding gases. The release rate of Cd greatly depends on coal combustion technologies and operating conditions (Zhang et al. 2010), as well as the performance of PM and SO_2 control devices downstream. The statistical data of coal consumption and detailed emission factors are adopted to calculate the atmospheric emissions of Cd from coal burning. In this study, the methodologies for determining the average content of Cd in coals as produced and consumed at provincial levels are consistent with the previous detailed analysis, the detail algorithms for determining Cd content in coals as consumed, cleaned coals, coal briquettes, and cokes as produced can be referred to the previous studies (Tian et al. 2010, 2011, 2012a, b). The data sources and final Cd content in coal products as consumed are listed in Table S1–S4 of the Supplemental Information (SI). By compiling the available data about Cd-related release rate (R) of different combustor types (pulverized coal boilers, stoker

Table 1 Assumed emission factors of Cd from different anthropogenic sources

Category	Sub-category	Emission factor (g/t)[a]
Coal combustion	Pulverized coal boiler	0.09 (0.06–0.14)
	Stoker fired boiler	0.17 (0.10–0.25)
	Fluidized bed furnace	0.28 (0.17–0.42)
	Coke furnace	0.07 (0.04–0.12)
	Traditional cook stoves	0.11
	Improved cook stoves	0.028
Nonferrous smelting	Primary copper product	50 (17–150)
	Secondary copper product	2.3 (1.1–4.6)
	Primary lead product	5 (3–7)
	Secondary lead product	1.1 (0.7–2.9)
	Primary zinc product	35 (15–35)
	Secondary zinc product	2.8 (1.6–4.1)
Iron and steel manufacturing	Pig iron	0.1 (0.02–0.4)
	Steel	0.07 (0.05–0.08)
Municipal waste incineration	Municipal waste	0.1 (0.01–1)
	Crude oil	0.05 (0.03–0.1)
	Fuel oil for stationary sources	0.05 (0.03–0.1)
	Gasoline	0.01
Liquid fuel combustion	Diesel for stationary sources	$5.04 \times e^{-4}$
	Diesel for transportation	0.04
	Kerosene for stationary sources	$5.04 \times e^{-4}$
	Kerosene for transportation	0.01
Construction materials production	Cement	0.01
	Flat glass	0.15
	Brick	0.075
Biomass burning	Crop residue	0.05 (0.01–0.09)
	Wood	0.08

[a] Cited references used to compile the emission factors are in Table S4 of Supplementary Information (SI)

fired boilers, fluidized bed furnaces, and coke furnaces) and the removal efficiencies of air pollution control devices [including electrostatic precipitators (ESPs), fabric filters (FFs), cyclones, wet scrubbers, as well as wet flue gas desulfurization (FGD) system], the comprehensive emission factors (CEF) of Cd from coal combustion by sectors were determined (see Table 1). The algorithms of emissions estimation can be described by the following equations:

$$\mathrm{CEF}_{\mathrm{coal}_{i,j}} = C_{\mathrm{coal}_{i,j}} R_{\mathrm{coal}_{i,j}} (1 - \eta_{\mathrm{PM}_{i,j}})(1 - \eta_{\mathrm{FGD}_{i,j}}), \tag{7}$$

$$E_{\mathrm{coal}_{i,j}} = F_{\mathrm{coal}_{i,j}} \mathrm{CEF}_{\mathrm{coal}_{i,j}}, \tag{8}$$

$$E_{\mathrm{coal}_i} = \sum E_{\mathrm{coal}_{i,j}}, \tag{9}$$

$$E_{\mathrm{coal}_T} = \sum E_{\mathrm{coal}_i}. \tag{10}$$

Where C_{coal} is the average content of Cd in coals as consumed; R_{coal} is the release rate of Cd from coal burning facilities; η_{PM} and η_{FGD} are the removal efficiency of Cd by PM and SO_2 control devices, respectively; $\mathrm{CEF}_{\mathrm{coal}}$ is the CEF of Cd to the atmosphere of coal combustion; E_{coal} is the atmospheric emission of Cd; F_{coal} is the amount of coal consumption; and j is the emission source classified by economic sectors, combustion facilities, and PM and SO_2 control devices.

Because coal resources are very unevenly distributed in China and only some provinces produce coal, the annual average Cd content of specific province might change as the coal comes from different provinces with varied proportion. No significant difference of Cd content in coal samples among different years has been reported. Thus, by assuming the averaged Cd content of raw coals as produced did not change with year, the weighted average Cd content in coals as consumed was estimated by using the average content in coal as produced and the annual inter-province matrix of coal transportation in the year 2009. In addition, the uncertainties during the determination of Cd content in coals and the calculation of atmospheric Cd emissions have been considered by applying Monte Carlo simulation.

Liquid fuels combustion

The most significant factors determining atmospheric releases from oil combustion include the Cd levels in the oil and the amount of fuel burned. The content of Cd in oil is normally several orders of magnitude lower than that in coal. The content of Cd in oil and its products in China has been investigated (Zong and Huang 2003; Guan 2007). Here, LF are classified into crude oil, fuel oil, gasoline, diesel, and kerosene, the assumed emission factors of different oil utilization and the cited references are also listed in Table 1. Equations (11) and (12) are used to calculate the emissions of Cd during LF combustion:

$$E_{\mathrm{LF}_i} = \sum F_{\mathrm{FC}_{i,j}} \mathrm{EF}_{\mathrm{FC}_{i,j}}, \tag{11}$$

$$E_{\mathrm{LF}_T} = \sum E_{\mathrm{LF}_i}. \tag{12}$$

Where E_{LF} is the atmospheric emissions of Cd during LF combustion; F_{FC} is the volume of liquid fuel consumption by category; $\mathrm{EF}_{\mathrm{FC}}$ is the average emission factor of Cd to the atmosphere for different types of fuel combustion.

Biomass burning

In China, biomass burning (including crop residues and wood) is a common practice in rural regions especially remote villages. Biomass is burned outdoors or for energy supplied by low efficiency uncontrolled stoves (European Environment Agency (EEA) 2009). Accordingly, Cd in biomass is discharged into the atmosphere with smoke. The estimation equations can be expressed as below:

$$E_{\mathrm{BM}_i} = \sum F_{\mathrm{C}_i} \mathrm{EF}_{\mathrm{C}_i} + \sum F_{\mathrm{W}_i} \mathrm{EF}_{\mathrm{W}_i}, \tag{13}$$

$$E_{\mathrm{BM}_T} = \sum E_{\mathrm{BM}_i}. \tag{14}$$

Where E_{BM} is the atmospheric emissions of Cd from biomass burning; F_{C} is the volume of crop residues burning; EF_{C} is the emission factor of Cd to the atmosphere from crop residue burning; F_{W} is the amount of wood burning; EF_{W} is the emission factor of Cd to the atmosphere from wood burning.

Municipal solid waste incineration

Municipal solid waste is the unwanted materials collected from households and commercial organizations. It consists of a mix of combustible and noncombustible materials such as paper, plastics, food waste, glass, defunct household appliances and other nonhazardous materials. In this study, the emission factor of Cd from MSW incineration is listed in Table 1 and the amount of MSW incineration is obtained from Chinese statistics yearbooks (National Bureau of Statistics of China (NBS) 2001–2010) to estimate Cd emissions. The following two equations are applied to estimate Cd emissions from MSW incineration (Tian et al. 2012c):

$$E_{\mathrm{MSW}_i} = \sum F_{\mathrm{WI}_i} \mathrm{EF}_{\mathrm{WI}_i}, \tag{15}$$

$$E_{\mathrm{MSW}_T} = \sum E_{\mathrm{MSW}_i}. \tag{16}$$

Where E_{MSW} is the atmospheric emissions of Cd from MSW incineration; F_{WI} is the amount of MSW incineration; E_{FWI} is the emission factor of Cd to the atmosphere from MSW incineration.

Results and discussion

In this paper, the atmospheric Cd emissions from anthropogenic sources are calculated on a basis of annual activity level for the year 2009. Table 2 presents the final results of Cd emissions province wise in China. The national total emissions of Cd from anthropogenic sources are estimated to be about 743.77 metric tons (t) in 2009. Moreover, to describe the spatial distribution characteristics of Cd emissions, the provincial level emissions are further spatially allocated into grid cells with a resolution of $0.5° \times 0.5°$.

Cadmium emissions by source category

The contributions of various anthropogenic sources are presented in Fig. 1. The emission proportion of industrial processes and combustion sources are 56.6 and 43.4 %, respectively, among which NF metals smelting and coal combustion are the two largest sources, responsible for 40.6 and 36.8 % of the total emissions. The emissions from pig iron and steel production and MSW incineration are also very high, with shares of 12.6 and 5.1 % of the total, followed by CM production with a contribution of 3.4 %. The emissions from other sources, such as LF combustion and biomass burning are relatively limited with a combined contribution of 1.5 %. Further analysis of the major anthropogenic sources is presented as follows.

Nonferrous metals smelting

Nonferrous metallurgical industry has experienced a rapid development during the past decade in China. The yield of copper, lead, and zinc production had increased sharply from 1.32, 1.10 and 1.91 million tons (Mt) in 2000 to 4.03, 3.77 and 4.29 million tons (Mt) in 2009, with an annual growth rate of 13.2, 14.7, and 9.4 %, respectively (National Bureau of Statistics of China (NBS) 2001–2010). The atmospheric Cd emissions from these three products are estimated at about 140.39 t for copper production, 14.39 t for lead production, and 147.10 t for zinc production, with a combined contribution of 40.6 %, the largest source of anthropogenic Cd emissions in 2009. In addition, the

Table 2 Anthropogenic atmospheric emissions of Cd by province in China, 2009 (t/a)

Province	Coal combustion				Nonferrous smelting			ISM	MSW	CM	LF	BM
	PP	IS	RS	OS	Cu	Pb	Zn					
Anhui	0.38	2.90	0.09	0.06	22.04	1.00	0.13	2.84	0.03	0.93	0.15	2.36
Beijing	0.14	1.40	0.16	0.14	0.01	0.00	0.00	0.75	0.07	0.13	0.17	0.13
Chongqing	0.38	11.42	0.10	0.14	1.66	0.08	0.00	0.56	0.04	0.48	0.13	0.91
Fujian	0.31	3.97	0.08	0.05	0.91	0.08	0.01	1.07	0.13	0.74	0.28	0.57
Gansu	0.13	0.63	0.24	0.05	20.95	0.19	6.87	1.03	0.00	0.27	0.09	0.73
Guangdong	0.96	7.71	0.03	0.03	0.11	0.62	8.79	1.51	0.41	1.68	1.19	1.63
Guangxi	0.31	6.38	0.01	0.05	0.00	0.66	12.69	1.64	0.01	0.82	0.19	2.01
Guizhou	0.82	6.39	0.36	0.46	0.01	0.04	0.55	0.63	0.00	0.32	0.11	1.74
Hainan	0.17	0.28	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.10	0.07	0.20
Hebei	0.58	25.07	0.64	0.23	0.43	0.00	0.00	22.39	0.01	2.16	0.27	2.20
Heilongjiang	0.56	1.28	0.07	0.08	0.00	0.00	0.00	0.87	0.02	0.34	0.48	2.70
Henan	1.57	14.91	0.62	0.06	1.42	5.50	10.35	3.53	0.03	2.87	0.25	2.83
Hubei	0.69	11.42	0.31	0.29	10.35	0.18	0.01	3.34	0.00	1.31	0.43	2.01
Hunan	0.47	10.43	0.22	0.35	0.08	3.07	34.33	2.39	0.00	1.12	0.24	1.51
Inner Mongolia	1.03	2.55	0.52	0.60	8.81	0.10	7.65	2.28	0.00	0.59	0.34	1.09
Jiangsu	1.46	9.85	0.04	0.05	9.49	0.19	0.08	8.31	0.39	1.91	0.43	1.70
Jiangxi	0.33	4.86	0.06	0.02	23.21	0.32	0.15	2.53	0.00	0.72	0.13	0.93
Jilin	0.50	1.30	0.09	0.20	0.02	0.00	0.00	1.32	0.03	0.54	0.17	1.41
Liaoning	1.37	5.47	0.21	0.18	1.96	0.10	12.35	8.31	0.01	0.87	0.58	1.53
Ningxia	0.72	2.72	0.04	0.02	0.00	0.17	0.00	0.04	0.00	0.11	0.04	0.15
Qinghai	0.01	0.08	0.06	0.03	0.00	0.03	3.79	0.19	0.00	0.13	0.04	0.11
Shaanxi	1.40	7.53	0.19	0.15	0.07	0.39	13.38	0.86	0.00	0.56	0.26	1.16
Shandong	2.66	20.88	0.18	0.55	13.84	0.05	0.00	8.68	0.11	2.40	0.87	2.79
Shanghai	0.31	3.02	0.03	0.04	3.21	0.02	0.00	3.15	0.11	0.08	0.64	0.02
Shanxi	3.10	23.22	0.57	0.28	3.30	0.00	0.02	4.94	0.03	0.41	0.24	0.72
Sichuan	0.89	34.02	0.40	0.06	0.06	0.00	8.28	2.55	0.07	1.46	0.28	2.25
Tianjin	0.38	2.87	0.04	0.05	0.56	0.00	0.01	3.19	0.05	0.14	0.20	0.19
Xinjiang	0.45	2.26	0.15	0.10	0.00	0.01	0.00	1.17	0.00	0.22	0.18	0.70
Yunnan	0.89	9.49	0.19	0.12	14.67	1.59	26.65	2.00	0.04	0.55	0.20	1.27
Zhejiang	1.16	5.08	0.02	0.02	3.23	0.01	1.04	1.53	0.40	1.43	0.53	0.45
Total	24.13	239.36	5.72	4.48	140.39	14.39	147.10	93.62	2.02	25.38	9.18	38.00

majority of Cd emissions come from the primary production processes (297.42 t), far more than those emitted from the secondary production processes (4.47 t). These results are closely consistent with those reported by Pacyna and Pacyna (2001) and Pacyna et al. (2009), in which the emissions of NF metals smelting is considered to be the primary source of anthropogenic atmospheric Cd emissions in Asia and the world.

In recent years, the production technologies and equipments of the NF metallurgical industry have been greatly improved to save energy and abate toxic air pollutants discharge. However, a large portion of smelting enterprises is still small-scale plants with outdated technologies. This results in high-energy consumption (≤750 kgtce/t for primary copper production; ≤460 kgtce/t for primary lead production; ≤1,850 kgtce/t for hydro-zinc smelting, and ≤2,200 kgtce/t for pyro-zinc smelting) and heavy pollution. These production facilities are the most noteworthy problems in the metallurgical industry (Standardization Administration of the People's Republic of China (SAPRC) 2007). Because copper, lead, and zinc are always associated with sulfide in the ores, air pollutants like mercury, arsenic, cadmium and their compounds are released into the flue gas along with dust and sulfide under high temperature process conditions. By now, the Chinese government has issued some policies to control the air pollution from the NF metallurgy industry. Dust removal devices with high efficiency are strongly required to

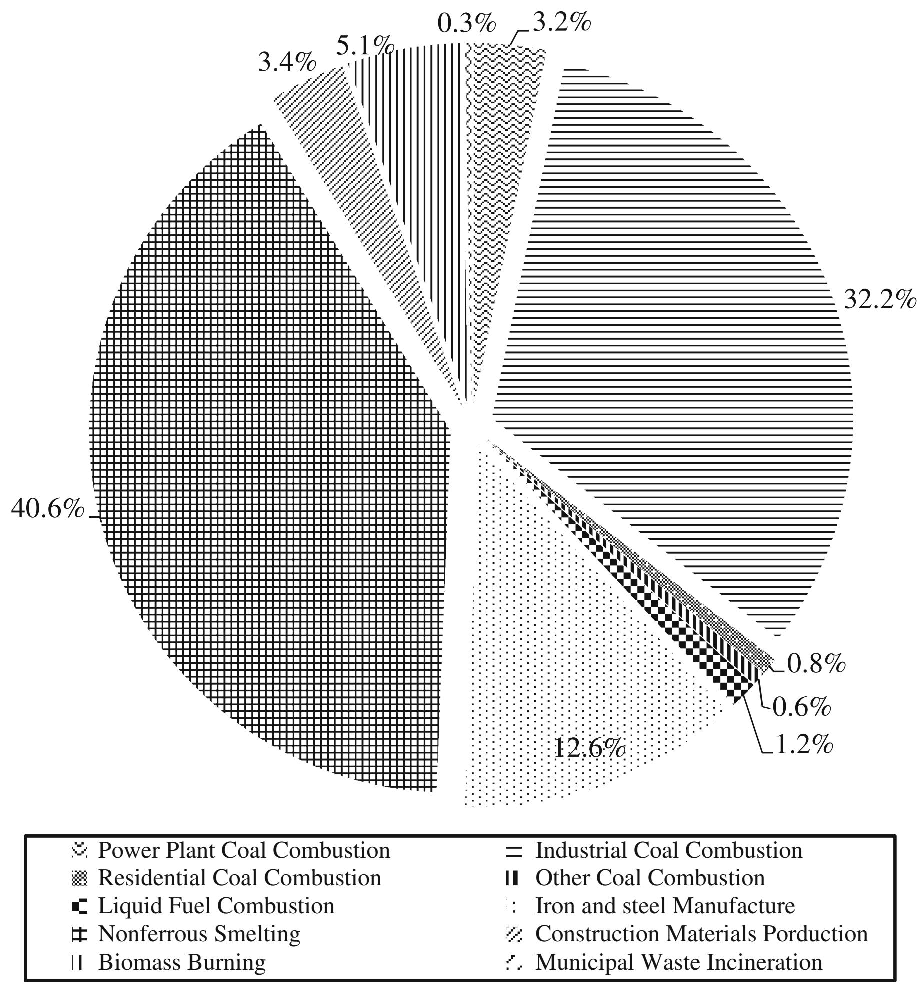

Fig. 1 Composition of Cd emissions by anthropogenic sources in China, 2009

control air pollution of the industry, and ESPs and FFs have been commonly used in the ventilation and dust collection processes (China Nonferrous Metals Industry (CNMI) 2011).

To reduce the atmospheric Cd emissions from the NF metallurgical industry, our suggested initiatives include controlling the total production capacity of the industry, eliminating outdated technologies and backward enterprises, improving the manufacturing technologies and pollution control equipments, and encouraging large-scale enterprises with best available control technologies (BACT).

Iron and steel manufacturing and CM production

Since the expansion of the country's infrastructure construction intensified during the past decades, the production of the iron and steel metallurgical industry and CM industry has experienced a rapid growth. In 2009, the yields of pig iron and steel production are reported at 552.83 and 572.18 Mt, respectively; for the CM industry, the production of cement, flat glass, and brick are 164.21 Mt, 585.74 million weight cases, and 610.89 Mt, respectively (National Bureau of Statistics (NBS) and National Development and Reform Commission (NDRC) 2001–2010). The contributions of Cd emissions from these two source categories are 12.6 and 3.4 %, respectively. Cd in raw materials and fuels will be released during ISM and CM production, but only the part of Cd emissions associated with raw material smelting or calcination is considered by referenced emission factors and official statistical yearbooks in this section.

Before the coal can be served for the ISM, some pretreatment processes such as coke making process, also contribute Cd emission. In this study, the Cd emissions related to coke making process are considered in the industrial coal use sector as a whole, including those coke production used for ISM. The average content of Cd in cleaned coal for coking furnace is assumed at 0.48 μg/g, and the caused Cd emissions from coking are estimated at 56.53 t.

For ISM, the primary process of pollutant emissions is the sinter plant, and the common pollution control devices are ESPs and FFs for particle collection. For CM production processes, heavy pollution of fugitive particulates during raw material calcinations is common; therefore, advanced smoke and dust control equipment with high PM removal efficiency will facilitate the abatement of atmospheric Cd emissions.

Coal combustion

In China, coal consumption always accounts for the majority of total primary energy consumption, with a proportion of 70.4 % of the total by the end of 2009. The national total coal consumption has reached about 3,621 Mt, and the amount of coal consumed by the industrial use sector and PP are 1,762.95 and 1,631.73 Mt, respectively (National Bureau of Statistics (NBS) and National Development and Reform Commission (NDRC) 2001–2010). The total emissions of atmospheric Cd from coal combustion are estimated at about 273.69 t in 2009, accounting for 36.8 % of the total emissions from anthropogenic sources (Fig. 1).

The industrial use sector is found to be the leading source of Cd emissions from coal combustion sources, accounting for about 87.5 % of Cd emissions from coal and 32.2 % of the total from anthropogenic sources. As a result of high coal consumption and low penetration of advanced air pollution control devices, Cd emissions from the industrial sector (IS) are still experiencing rapid growth. To reduce atmospheric Cd emissions from coal combustion, more effective emission control equipments (such as ESPs/FFs and FGD) are urgently needed for the enterprises in this sector.

The share of PP sector is approximately 3.2 % of the total. Due to the wide penetration of high-efficiency air pollution control devices such as ESPs, FFs, and FGD systems, the final discharge of Cd from PP has decreased, while coal consumption has grown (State Environmental Protection Administration (SEPA) 2008, 2010). The contribution of residential and other sectors (OSs) is very small with a combined proportion of 1.4 % of the total. The substitution of cleaner energy forms like natural gas, liquefied petroleum gas (LPG) and electricity will be very effective to further reduce the direct Cd emissions from these sectors.

Liquid fuel combustion

According to the end consumption and emission factors by liquid fuel type, the atmospheric Cd emissions by liquid fuel combustion are calculated at 9.18 t in 2009, altogether. The specific composition is 5.94 t for diesel, 1.79 t for fuel oil, 0.84 t for gasoline, 0.46 t for fuel oil, and 0.15 t for kerosene, respectively. Although the exhaust pollution caused by gasoline vehicles has aroused more concerns by the public, the very low Cd content and advanced exhaust emission control devices (like the three-way catalytic converter) result in low emissions compared to other LF. Due to the high consumption and Cd content, diesel and fuel oil are identified as the main contributors; these are usually used in heavy duty trucks and power generation and heating, which should be given priority attention.

Biomass burning

The average Cd content of biomass in China is about 0.41 mg/kg (dry biomass basis) for the crop residues and 0.58 mg/kg (dry biomass basis) for wood, and it has significantly different elemental characteristics compared with that of coal (Liao and Wang 2004; Tian et al. 2012b). In 2009, Cd emissions from biomass burning are estimated at approximately 38.99 t, of which the shares of crop residues and wood burning are 61.7 and 38.3 %, respectively. Part of biomass is open burned in the farmland as a means of clearing the land rapidly and inexpensively, and allowing tillage practices to proceed unimpeded; however, open burning of biomass can cause serious pollution and visibility problems. To control the pollution from fugitive burning, the practice has been banned by the Chinese central and local government.

Municipal solid waste incineration

With the continuous improvement of residents' living standards, MSW incineration has become a new significant source of atmospheric emissions in urban areas (Tian et al. 2012c). Cd emissions from MSW incineration in 2009 are estimated at about 2.02 t in this study. Owing to lack of available field test results from domestic plants, the average Cd emission factor of MSW incineration was assumed at about 0.1 g/t according to EEA report (European Environment Agency (EEA) 2009), which can be regarded as a preliminary estimate for the common MSW incinerators of China at present. Thus, it should be noted that when the incineration materials and their components changed (such as the amount of dry battery with different Cd content are separated or incinerated), the related emission factor and the final emissions will have a large fluctuation.

At present, Chinese MSW incineration enterprises are mainly located at Guangdong, Jiangsu, and Zhejiang province; thus, the emission controls for this source should be concentrated in these regions. However, MSW has become a serious problem in nearly all the urban areas in China, especially the largest cities, as the pressure of waste reduction and disposal prompts more cities to adopt MSW incineration. The resulting toxic pollutants discharge including Cd from MSW incineration may raise more environmental health issues. Although the current volume of MSW incineration is still very small, it needs to be highlighted and control strategies need to be promulgated in advance. Further, due to the complex composition of municipal waste, investigations are needed to reduce Cd emissions and diminish its potential health risks.

Spatial distribution characteristics of Cd emissions

On the basis of the specific features of anthropogenic sources, different spatial allocation methods are applicable for the atmospheric emission inventory of Cd. In this study, PP, large-scale metallurgical enterprises, and municipal waste

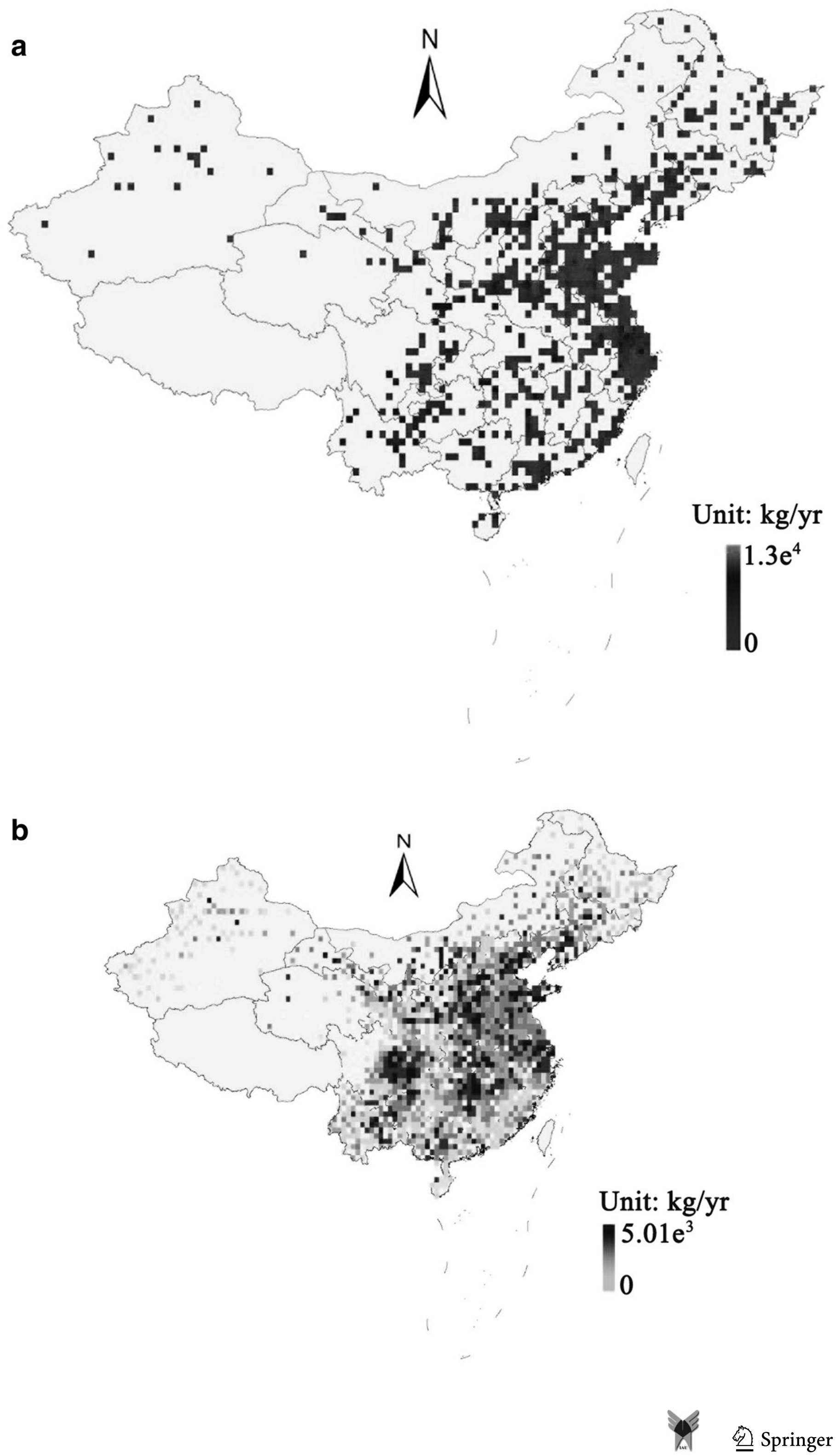

Fig. 2 Spatial distribution of Cd emissions with a solution of 0.5° × 0.5° in China, 2009

Table 3 Uncertainty in the emission inventory of Cd in China for the year 2009

Category	Sub-category	Uncertainty range (%)	
		Lower	Upper
Coal combustion	Power plants (PP)	−10	35
	Industrial sector (IS)	−22	153
	Residential sector (RS)	−65	75
	Other sector(OS)	−114	81
Nonferrous metals smelting	Cu	−61	76
	Pb	−45	52
	Zn	−45	46
Iron and steel manufacturing (ISM)		−55	54
Municipal solid waste incineration (MSW)		−93	92
Construction materials production (CM)		−43	50
Liquid fuel combustion (LF)		−52	55
Biomass burning (BM)		−93	84
Total		−15	48

incineration plants are considered to be point sources, and the associated Cd emissions are allocated into the grid cells directly according to their latitude and longitude coordinates (Fig. 2a). Other anthropogenic sources and miscellaneous small-scale ISs are treated as area sources. According to the proportion of population and industrial gross domestic product (GDP) by county in each province, the Cd emissions of area sources are allocated into the $0.5° \times 0.5°$ grid cells (Fig. 2b).

As can be seen, the atmospheric emissions of Cd from anthropogenic sources in China show very uneven distribution owing to the remarkable difference in economic and energy consumption structure, degree of development, density of population, as well as regional area magnitude of each province. Cd emissions are mainly concentrated around the coastal provinces in the eastern, central and southern areas, accounting for approximately 50 % of the national emissions. For most provinces in these regions, coal combustion in PP and industrial enterprises are identified to be the primary emission sources; however, for Hunan, Anhui, and Jiangxi province, the most significant sources come from NF metallurgical enterprises. Cd emissions in the southwestern region contribute nearly 18 % of the national emissions. The high content of Cd in coals consumed by ISs in this region causes heavy emissions, and NF smelting is the main cause of a large proportion of emissions in Yunnan province. Rapid growth of coal consumption by ISs and PP has led to substantial Cd emissions in the northern region which accounts for approximately 17 % of the total emissions.

Uncertainty analysis

For better understanding of the possible uncertainties in atmospheric pollutants emissions, different methods have been proposed to quantify the variation of the emission inventory (Zheng et al. 2009; Zhao et al. 2011). Based on the results of variability analysis of Cd content in coals by bootstrap simulation (Tian et al. 2011, 2012a, b), the Monte Carlo simulation is used to quantify the uncertainty of Cd emissions depending on available activity data and emission factors distribution. The emissions of anthropogenic sources with uncertainty (95 % confidence interval around the arithmetic mean value) are shown in Table 3. The overall uncertainties in this inventory are estimated at −15 to 48 %.

As shown in Table 3, estimates of PP (−10 to 35 %) have the lowest uncertainty compared to other sources due to the detailed activity data of coal consumption, the release rate of boilers, and removal efficiencies of pollutant control devices.

For the industrial coal combustion sources and metallurgical sources, there are relatively higher uncertainties in the emission estimates compared to PP because these sources involve various industries and production processes. The uncertainty sources are mainly attributed to the lack of detailed information including manufacturing processes and facility parameters for boilers/smelting processes and emission control equipment downstream, as well as localized emissions factors.

The highest uncertainty estimation occurs in the sources of residential and other coal combustion sectors, MSW incineration, and biomass burning. Few studies have been conducted on the real release features of Cd from these sources to date. In this study, the average emission factors of such sources are mainly referenced from limited domestic and nondomestic studies. Therefore, it is inevitable that there is uncertainty during the determination.

In summary, to better understand the characteristics of atmospheric Cd emissions from anthropogenic sources in China, more detailed investigation and field tests of atmospheric Cd emission for all the anthropogenic sources are required in future research.

Conclusion

A highly spatial resolved atmospheric emission inventory of Cd in China for the year 2009 is developed by using a bottom-up approach. The results of this study demonstrate that the total Cd emissions from anthropogenic sources in China are about 743.77 t. The contributions of industrial processes and combustion sources are 56.6 and 43.4 %, respectively. Therein, NF metals smelting is considered to be the leading source while industrial coal use sectors are considered to be the main contributor in the coal combustion category.

The spatial distribution pattern shows that Cd emissions are mainly concentrated in the eastern, central and southern regions of China. For provinces in these regions, metallurgical enterprises and coal combustion by PP and the IS are thought to be the dominant contributors.

By using Monte Carlo simulation, the overall uncertainty of this Cd inventory is estimated at −15 to 48 %, implying that there is relatively low uncertainty in the estimates. However, due to the shortage of detailed source information and localized emissions factors, there is likely a large uncertainty for the emissions of residential and other coal combustion sectors, municipal waste incineration, and biomass burning.

In short, to improve the reliability of the emission inventory, continuous long-term field testing and monitoring of different anthropogenic sources in China are necessary. Potential future improvements include the enhancement of localized emission factors determination, more detailed classification of emission sources, and comprehensive collection of activity data.

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