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Anthropogenic atmospheric nickel emissions and its distribution characteristics in China

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ABSTRACT

Nickel and its compounds are considered as potential human carcinogens, and atmospheric nickel is one of the major routes for human exposure. By applying the best available fuel-based or product-based emission factors and annual activity levels, a multiple-year comprehensive inventory of anthropogenic atmospheric nickel emissions in China is presented with temporal trend and spatial resolutions for the period of 1980–2009 from both fuels combustion sources and industrial producing processes. We estimate that the total atmospheric nickel emissions from all the sources have increased from 1096.07t in 1980 to 3933.71t in 2009, at an average annual growth rate of 4.5%. Therein, coal combustion is the leading source, attributing 63.4% of the national total nickel emissions in 2009; liquid fuels consumption ranks the second, contributing 12.4% of the totals; biofuels burning accounts for 8.4% and the remaining sources together contribute 15.8% of the totals. Significant spatial variations are demonstrated among provincial emissions and the most concentrated regions are the highly industrialized and densely populated areas like the Yangtze River Delta, the Pearl River Delta and the Beijing-Tianjin-Hebei region. Moreover, the overall uncertainties are estimated at −32.6%–37.7% by using Monte Carlo simulation, most of which come from non-ferrous metals smelting category, implying the urgent need for further investigation and field tests. This article may help to combat the increasing stress on air heavy metals pollution in China and provide useful information to calculate global mass balance models for hazardous trace elements.

1. Introduction

Hazardous trace elements (HTEs) in the environment have aroused widely concerns recently because of their potential harm to human health and eco-environment. The adverse effects of HTEs on public health are well-documented (Fishbein, 1981; Swaine and Goodarzi, 1995; Denkhaus and Salnikow, 2002; Lenz and Lens, 2009). Nickel (Ni) is one of the HTEs designated as an acute toxic substance by many governmental agencies and international organizations, such as the US EPA, the European Union (EU), the Health Ministry of Japan, and the World Health Organization (WHO). The International Agency for the Research on Cancer (IARC) has concluded that nickel compounds are human carcinogens (Group 1), and elemental nickel is also a possible human carcinogen (Group 2B) (IARC, 1990).

Nickel occurs naturally in the earth's crust and is ubiquitous in the air, water, soil and the biosphere. The average concentration of nickel in the earth's crust is 0.008% (ATSDR, 2005). Nickel compounds presented in soils are in both insoluble forms, such as sulfides and silicates, and in a number of soluble forms (Garrett, 2000); in aquatic sources, divalent nickel is the predominate form; however, in atmosphere, the species of nickel present is highly dependent on the source or origin. Nickel particulates emitted from high temperature processes, such as smelting furnaces and fuels combustors, are primarily found to be nickel oxides and other metals (primarily iron), followed by lesser amounts of metallic nickel (US EPA, 1984; Schroeder et al., 1987). In addition, windblown dusts may contain mineral species of nickel, which are often in the form of sulfides.

Remarkable natural sources of atmospheric Ni include windborne dust particles, volcanoes, vegetation, sea salt, and forest fires (Nriagu, 1989). Although nickel is ubiquitous, anthropogenic activities have increased its flux into the environment. It is reported that nickel levels in the ambient air range from 1 $ng \cdot m^{-3}$ to 10 $ng \cdot m^{-3}$ in urban areas, while the concentration range is 110–180 $ng \cdot m^{-3}$ in industrialized areas and large cities (WHO, 2000). Anthropogenic nickel finds its way into the ambient air as a result of fossil fuels combustion, the ferrous and non-ferrous metals smelting, the incineration of waste, and other miscellaneous sources (Cempel and Nikel, 2006). At high temperatures, nickel is released from anthropogenic sources

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both as suspended particulate matter and in a gaseous form. Once released into the air, nickel can attach itself to fine particles (Song et al., 2003), which could easily pass through conventional air pollution control devices (APCDs), and may stay in the atmosphere for 5–8 days normally and even 30 days for very small particles (Mukherjee, 1998). These nickel-containing particulates may transport over long distance before they finally settle down through wet and dry deposition into soil and aqueous systems (Pacyna and Ottar, 1985; Lee et al., 2008; Cong et al., 2010).

Although nickel is not the major pollutants in the atmosphere, its toxicological and environmental impacts can't be ignored. Exposure to nickel compounds can cause a variety of adverse effects on human health (Oller et al., 1997; Denkhaus and Salnikow, 2002; Grimsrud et al., 2003). Among them the most commons are skin allergies, lung fibrosis, and cancer of the respiratory tract (Kasprzak and Sunderman, 2003). Doll (1990) found that not only water-insoluble nickel components of the dusts (e.g., Ni_3S, NiO) were carcinogenic, but also water-soluble nickel compounds (e.g., Ni(II) sulfate) were carcinogenic to human respiratory tract. When the released nickel meets with carbon monoxide (CO) in the air, nickel carbonyl might be generated. It has been reported that nickel carbonyl is the most toxic nickel compound, which may cause respiratory tract irritation and neurological effects and even lead to infertility and death (Shi, 1994; Foxall, 2009). Human exposure to nickel occurs primarily via inhalation and ingestion and is particularly high among nickel metallurgy workers (ATSDR, 2005). Increased risks of cancer of the lungs and nasal passages have been reported in workers exposed to nickel compounds (oxidic and sulphidic nickel) during roasting, sintering and calcining processes, in refineries in the UK, Norway and Canada (Foxall, 2009).

Emissions of Ni from anthropogenic sources to the atmosphere in Europe as well as global emissions have been calculated and reported (Nriagu and Pacyna, 1988; Mukherjee, 1998; Pacyna and Pacyna, 2001; Pacyna et al., 2007). However, the comprehensive and detailed studies on the anthropogenic atmospheric Ni emissions in China are quite limited. Although there have been some emission inventories about other metals like Hg, As, Se, and Sb published (Streets et al., 2005; Wu et al., 2006; Tian et al., 2010; 2011a), a comprehensive emission inventory of Ni with highly resolved temporal and spatial information is also urgently needed in China in order to combat the increasing stress on urban and regional air heavy metals pollution and poisoning accidents.

With the increase of fossil fuels consumption and large amounts of industrial products produced, a considerable amount of Ni will be emitted into the environment in China. Therefore, it is quite necessary to know the situation and distribution characteristics of anthropogenic atmospheric nickel emissions. In this study, a multiple-year comprehensive inventory is presented with temporal and spatial resolutions for the period of 1980–2009 from both fuels combustion processes and industrial producing processes in China. Temporal trend and its distribution characteristics by sectors and provinces are analyzed in details. In addition, the uncertainties are assessed with Monte Carlo simulation.

2. Methodologies and data sources

Anthropogenic atmospheric emissions of nickel are calculated by using fuels consumption (or industrial products yield) data and detailed Ni emission factors. The basic formulas can be expressed as follows:

$$E_t = \sum_i \sum_j \left[ef_{i,j,t} A_{i,j,t} F_{REL,j,t} \left(1 - F_{REM,j,t}\right) \right] \tag{1}$$

where E_t is the Ni emission; $ef_{i,j,t}$ is the average content of Ni in coals as burning or the emission factor for other fuels combustion or industrial producing processes; $A_{i,j,t}$ is the amount of fuel consumption or production yield of industrial producing processes; $F_{REL,j,t}$ is the fraction of Ni released from combustion facilities; $F_{REM,j,t}$ is the fraction of Ni removed by the conventional air pollution emission (PM, SO_2, NO_x, etc.) control devices; j is the combustor type with/without emission control devices; i is the province and t is the calendar year.

2.1. Nickel content in coals and coal products

Although the contents of HTEs in coals are trace levels, it could lead to tons of pollutants released into the environment, and from an environmental point of view, they can provide useful information to the pollution control during coal combustion and utilization. Some studies have reported the content of Ni in raw coals as mined in China and it varies substantially due to the differences of coal-forming plants and coal-forming geological environments (Zhao, 1997; Tang et al., 2002; Bai, 2003; Ren et al., 2006; Dai et al., 2006; Song, et al., 2007). Here, we have compiled and summarized the provincial-level data of Ni content from published literature up-to-date, and obtained a national averaged Ni content of 17.14 mg/kg (See details in Table 1). The content we obtained is within the range (0.5–50 mg/kg) of Ni concentration in most of the world coals (Swaine, 1990; Dale and Lavrencic, 1993; Spears and Zheng, 1999).

To obtain reliable estimates of Ni emissions, it is essential to know the Ni content of coals as burned, not just as mined. Because

Table 1
Averaged content of Ni in raw coals as produced and consumed by province in China, 2009 (mg/kg).

Province[a]	Raw coal production (Mt)[b]	Raw coal consumption (Mt)[b]	Ni_P	Ni_C
Beijing	0.64	26.65	17.14[c]	13.23
Tianjin	0	41.20	0.00[d]	13.04
Hebei	84.95	265.16	12.19	13.20
Shanxi	593.54	277.62	15.31	15.10
Inner Mongolia	600.58	240.473	6.34	6.68
Liaoning	66.24	160.33	28.47	20.04
Jilin	44.01	85.89	20.38	13.63
Heilongjiang	87.49	100.50	9.60	9.19
Shanghai	0	53.05	0.00[d]	13.38
Jiangsu	23.97	210.03	20.84	14.98
Zhejiang	0.13	132.76	9.95	14.89
Anhui	128.49	126.66	19.64	18.93
Fujian	24.66	71.09	16.42	13.52
Shandong	143.78	347.95	23.13	19.63
Jiangxi	29.82	53.56	20.01	18.70
Henan	230.18	244.45	11.88	12.07
Hubei	10.58	110.99	15.92	15.13
Hunan	65.73	107.51	13.25	17.88
Guangdong	0	136.47	24.90	12.48
Guangxi	5.20	51.99	22.53	22.51
Hainan	0	5.37	0.00[d]	10.17
Chongqing	42.91	57.82	20.90	21.70
Sichuan	89.97	121.47	29.02	27.76
Guizhou	136.91	109.12	22.73	22.75
Yunnan	55.71	88.86	24.38	24.37
Shaanxi	296.11	94.97	16.21	14.66
Gansu	38.76	44.79	19.30	17.34
Qinghai	12.84	13.10	12.20	14.98
Ningxia	55.10	47.81	11.01	8.59
Xinjiang	76.46	74.18	8.28	8.25
Arithmetic average	–	–	17.14	15.63

Ni_P stands for raw coal as produced; Ni_C stands for raw coal as consumed.

[a] Xizang, Taiwan province, Hong Kong and Macau Special Administrative Region are not included in this table due to lack of data.

[b] The data come from China energy statistical yearbook 2010.

[c] No Ni contents data reported in Beijing, we use the national average value as the replacement.

[d] No raw coal produced in Tianjin, Shanghai, and Hainan, thus the values of Ni content are assumed to be zero.

geographical distribution of coal resources in China is extremely unbalanced, a great quantity of coals mined has to be transported from producing regions to the other coal shortage areas. Therefore, it is necessary to relate the coal mined in particular provinces to its consumption in each province. Coal transportation matrix (by coal types and by sectors) is used to quantify in-province coal use and inter-provinces coal flows (Streets et al., 2005; Wu et al., 2006; Tian et al., 2010; 2011a). According to the statistical data obtained from China Energy Statistical Yearbooks (1997–2010) and China Coal Industry Yearbooks (2005–2009), annual coal flow matrixes among 30 provinces are established. Then, combined with the average content of Ni in raw coals as mined by province, the weighted-average content of Ni in raw coals as consumed by province are calculated and also illustrated in Table 1. As can be seen, the national average content of Ni in coals as consumed (15.63 mg/kg) is some lower than that as produced (17.14 mg/kg), primarily owing to the lower content of Ni in coals as mined in the coal-exporting provinces, such as Inner Mongolia, Shanxi, and Ningxia.

In China, coal cleaning is a major way to reduce ash and SO_2 emission before coal burning. Meanwhile, concentration of HTEs can also be reduced during the washing process. The removal efficiency of Ni content through coal cleaning vary significantly from ~20% to ~80% (DeVito et al., 1984; Akers, 1995; Quick and Irons, 2002; Han and Xu, 2003; Wang, 2007). In view of the application situation and the operation characteristics of coal cleaning processes in China, we presume an averaged removal efficiency of 58.49% independent of Ni content in coals. The methodologies for calculating the average content of Ni in cleaned coals, coke and briquettes can be referred in previous studies (Tian et al., 2010; 2011a). We assume 90.25% of Ni contained in a given coal remains in coke after the coking process (Helble et al., 1996; Zajusz-Zubek and Konieczynski, 2003).

2.2. Coal consumption, combustor types and emission control by sectors

Coal consumption data by different sectors (power plants, industry sector, residential use and other uses) and produced coal types (raw coal, cleaned coal, briquettes, coke) at provincial-level are compiled from China Energy Statistical Yearbooks from 1980 to 2010 (DITS, 1992, 1998; NBS, 2001, 2004; NBS and NDRC, 2005–2010). According to the statistic data, by the end of 2009, coal consumption (2158.77 Mtce) has accounted for 70.4% of the total primary energy consumption (3066.47 Mtce). Among the main coal consuming sectors, coal-fired power plants is the fastest increasing coal combusting sector, with an annual growth rate of 9.2% (by 2009), followed by industry sector at a rate of 5.9% (by 2009) annually since 1980. Coal consumption for other uses has a moderate increase, 3.0% (by 2009) annually. However, coal for residential use has been slightly decreasing (−0.3% annually, 1980–2009) due to energy transitions to cleaner gaseous fuels and electricity in many regions of China especially in urban areas.

Presently, the major coal combustion facilities in coal-fired plants are pulverized-coal boilers in most of the provinces in China, taking a share over 90%; Stoker fired boilers take a relatively small proportion and the proportion decline annually due to the energy-saving and pollution reduction policies issued by the Chinese government (National Development and Reform Commission, NDRC, 2011). However, stoker fired boilers are the dominant boiler types used in industry and other use sectors. The release rate of nickel from various boiler types varies substantially. Several studies (Nodelman et al., 2000; Han et al., 2002; Tolvanen, 2004) indicate that about 36%–75% of Ni release into atmosphere for pulverized-coal boilers, while the ratio may reduce to approximately 5%–22% for stokers (Wang et al., 1996; Zhang et al., 2003; Li et al., 2005) and 53%–94% for fluidized-bed furnaces (Klika et al., 2001; Reddy et al., 2005; Bartoňová and Klika, 2009). The detailed release rates of Ni from different combustion boilers are compiled and listed in Table 2. Here, we use the arithmetic mean of reported release rates as input in our estimation.

Table 2
The release rates of Ni from coal combustion facilities.

Boiler type	Release rate (%)	Literature cited
Pulverized-coal boiler	36.78	Han et al., 2002
Pulverized-coal boiler	75	Nodelman et al., 2000
Pulverized-coal boiler	57.8	Tolvanen, 2004
Stoker fired boiler	21.8	Wang et al., 1996
Stoker fired boiler	5.5	Zhang et al., 2003
Stoker fired boiler	10, 7, 8	Li et al., 2005
Fluidized-bed furnace	54.8	Reddy et al., 2005
Fluidized-bed furnace	81, 94	Klika et al., 2001
Fluidized-bed furnace	59, 53	Bartoňová and Klika, 2009
Coke furnace	5	Helble et al., 1996
Coke furnace	14.5	Zajusz-Zubek and Konieczynski, 2003
In this study		
Pulverized-coal boiler	57.06	Averaged value
Stoker fired boiler	10.46	
Fluidized-bed furnace	68.36	
Coke furnace	9.75	

Air pollution control devices are utilized on the downstream of coal-fired utility boilers or industrial boilers for diminishing NO$_X$, SO_2 and PM, and they could also be effective in reducing the final Ni emissions from the exhaust. ESPs can achieve a Ni removal efficiency of 79%–100%, while the Ni removal efficiency of fabric filters (FFs) range from 82% to 100% (Helble, 2000; Nodelman et al., 2000; Klika et al., 2001; Tolvanen, 2004; Ito et al., 2006; Meij and Te Winkel, 2007; Nyberg et al., 2009). Cyclones show relatively low Ni removal efficiency with about 40% (Gogebakan and Sel Uk, 2009). In addition, the removal efficiency of wet flue gas desulfurization (WFGD) is reported at about 80% in flue gas removing process (Meij and Te Winkel, 2007). Table 3 presents the minutely assumed Ni removal efficiencies for different types of control devices.

Residential use is also an important coal-consuming sector in China. However, there is very little information about Ni emissions through residential uses in China. Here, we choose to use an average emission factor for residential coal consumption obtained from NPI (1999) (1.4×10^{-4} kg/t) and NAEI (2008) (5.0×10^{-4} kg/t), and thus the mean emission factor is assumed at 3.2×10^{-4} kg/t.

2.3. Other fuels consumption, material yields and Ni emission factors

Besides coal combustion, there are other sources (liquid fuels consumption, biofuels burning, ferrous and non-ferrous metals smelting,

Table 3
Removal efficiency of Ni by various PM and SO_2 control devices.

Control device	Removal efficiency (%)	Literature cited
ESP	79.02	Han et al., 2002
ESP	97.6	Helble, 2000
ESP	79.1	Brooks, 1989
ESP	99.6	Szpunar, 1993
ESP	80.6	Ito et al., 2006
ESP	99.4	Meij and Te Winkel, 2007
ESP	99.1, 97.2	Nyberg et al., 2009
ESP	98, 99.6	Tolvanen, 2004
FF	98	Nodelman et al., 2000
FF	99.8, 99.5	Nyberg et al., 2009
FF	82	Klika et al., 2001
Cyclone	17.86	Wang et al., 1996
Cyclone	62	Gogebakan and Sel Uk, 2009
In this study		
ESP	93.52	Averaged value
FF	94.83	
Cyclone	39.93	
Wet scrubber	70.9	Sandelin and Backman, 2001
WFGD	80	Meiji and Te Winkel, 2007

etc.) contributing to atmospheric Ni emissions in China. Multiple-year liquid fuels and biofuels consumption data are estimated and complied at provincial-level from the China Energy Statistical Yearbooks (DITS, 1992, 1998; NBS, 2001, 2004; NBS and NDRC, 2005–2010). Material-yield data (e.g., non-ferrous metals, pig iron and steel, cement, etc.) related to industrial producing processes are obtained from China Statistical Yearbooks (National Bureau of Statistics of China, NBS, 1981–2011) and professional year-books such as the Yearbooks of Nonferrous Metals Industry of China (ECNMI, 1991–2011).

Total consumption of liquid fuels has increased from 68.61 million tons in 1980 to 294.38 million tons in 2009, at an annual growth rate of 5.2%. Among the major liquid fuels, gasoline, diesel oil, and kerosene contributed the major increment. In this study, we assume that all the gasoline is consumed by vehicles; diesel oil is consumed by both vehicles and stationary combustors; kerosene consumption is divided into stationary combustion and transportation use; and all the fuel oil is used for stationary combustion. Notably, both the ratio of vehicles and stationary combustors for diesel oil consumption and the ratio of stationary combustion and transportation use for kerosene use are varying with different calendar year and province, and are compiled from energy balance tables in the annual China Energy Statistical Yearbooks (DITS, 1992, 1998; NBS, 2001, 2004; NBS and NDRC, 2005–2010).

Biofuels are sorted into two types: agricultural residues and firewood. The mass of biofuels burning in this study is estimated based on the statistical data of crop production, residue/crop ratio, and the percentage of burning (National Bureau of Statistics of China, NBS, 1981–2011; Tian et al., 2011b). Total consumption of biofuels increased slightly from 438.39 million tons to 660.92 million tons during the period of 1980–2009.

The amount of municipal solid waste (MSW) incineration has increased annually since the first incinerator was established in Shenzhen City in 1988, reaching 20 million tons in 2009. With the development of Chinese economy, China is experiencing greatly demand for building materials. Consequently, the production of cement, iron and steel, glass and non-ferrous metals each has increased significantly in China during the past decades.

Emission factors for these sources are listed in Table 4. However, due to limited information and lack of field experimental tests on Ni emissions in these categories in China, some of emission factors for these source types are cited from developed countries (e.g. US, UK), with only nationally averaged level.

3. Results and discussion

3.1. Emission trends by sectors

Trends of total atmospheric Ni emissions by sectors from 1980 to 2009 are presented in Fig. 1. We estimate that the national total emissions of Ni in China have increased from 1096.07t in 1980 to 3933.71t in 2009, at an average annual growth rate of 4.5%. As can be seen from Fig. 1, coal combustion is the biggest contributor to Chinese anthropogenic Ni emissions, followed by liquid fuels consumption and biofuels combustion, but by 2009, the non-ferrous metals smelting category has become the third largest Ni emitting sources instead of biofuels burning. Furthermore, we can observe that Ni emissions from coal consumption were generally increasing during past decades while those from liquid fuels and biofuels combustion have no discernible increase, with an average annual growth rate less than 1%. The remaining sources (excluding coal, liquid fuels and biofuels combustion sources) together take up a small share of total atmospheric Ni emissions but their contributions have kept increasing from 4.9% in 1980 to 15.8% in 2009, indicating that the control of atmospheric Ni emissions from industrial producing processes has become more and more urgent, especially for non-ferrous metals smelting.

Table 4
Emission factors for Ni emissions from other anthropogenic sources.

	Source category	Emission factor	Literature cited
1	Crude oil	10.6 g/t oil	US EPA, 1995
2	Fuel oil for stationary sources	10.6 g/t oil	US EPA, 1995
3	Gasoline	0.04 g/t oil	UK NAEI, 2008
4	Diesel oil		
	Diesel oil for stationary sources	0.06 g/t oil	US EPA, 1995
	Diesel oil for transportation	0.04 g/t oil	UK NAEI, 2008
5	Kerosene		
	Kerosene for stationary sources	0.06 g/t oil	US EPA, 1995
	Kerosene for transportation	0.03 g/t oil	UK NAEI, 2008
6	Non-ferrous metal smelting		
	Zinc	1.36 g/t Zn	Skeaff and Dubreuil, 1997
	Copper	50 g/t Cu	EMEP/EEA, 2009
	Lead	5.0 g/t Pb	Pacyna and Pacyna, 2001
	Nickel	900 g/t Ni	Nriagu and Pacyna, 1988
7	Cement production	0.074 g/t cement[a]	US EPA, 1995
8	Glass manufacturing	0.35 g/t glass[b]	UK NAEI, 2008
9	Brick production	0.71 g/10^4 bricks[c]	NPI, 1998
10	Ferrous smelting		
	Steel	0.05 g/t steel	UK NAEI, 2008
	Pig iron	0.1 g/t pig iron	UK NAEI, 2008
11	Biofuels combustion		
	Agricultural residue	0.31 g/t residue	NPI, 1999
	Firewood	1.0 g/t firewood	UK NAEI, 2008
12	MSW incineration	0.7 g/t waste	Pacyna and Pacyna, 2001

[a] Coal related Ni emissions for cement production are excluded from this category. Energy intensity of 0.12t coal per ton cement produced (Zhou, 2007) is used here to adjust emission factor of 0.09 g/t cement to 0.074 g/t cement produced.

[b] Coal related Ni emissions for this category are excluded. We assumed an energy intensity of 0.4t coal per ton glass produced, and the emission factor here is adjusted to 0.35 g/t from 0.4 g/t glass produced.

[c] Coal related Ni emissions for brick production are also excluded. The emission factor of 0.9 g/10^4bricks is adjusted to 0.71 g/10^4bricks with an evaluated energy intensity of 1.5t coal per 10^4 bricks produced.

3.1.1. Ni Emissions from coal combustion sources

Fig. 2 illustrates the emissions of Ni by sectors from coal combustion. As can be seen, the emissions of Ni from coal combustion in China have been growing steadily during the past years. In 1980, the national total emissions from coal combustion are estimated at 310.53t, while in 2009, it has increased to 2492.29t, growing by 7.5% annually.

Among all the coal consuming sub-sectors, industrial coal combustion is the largest single sector for Ni emissions, increasing from 165.07t in 1980 to 1637.46t in 2009, at an annual growth rate of 8.2%. However, Ni emissions from the power plants sector grow fastest, at a rate of 9.0% annually, reaching at 701.29t in 2009. Compared to industrial and power generation sectors, emissions from other coal

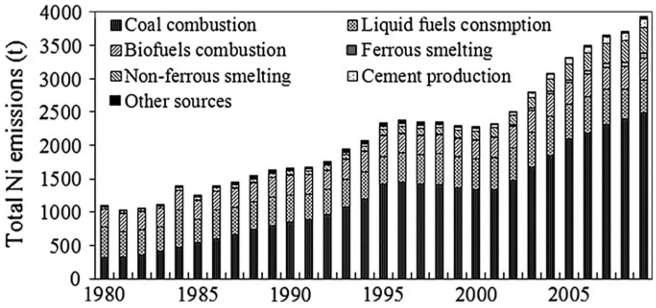

Fig. 1. Trend of total Ni emissions by sources in China, 1980–2009.

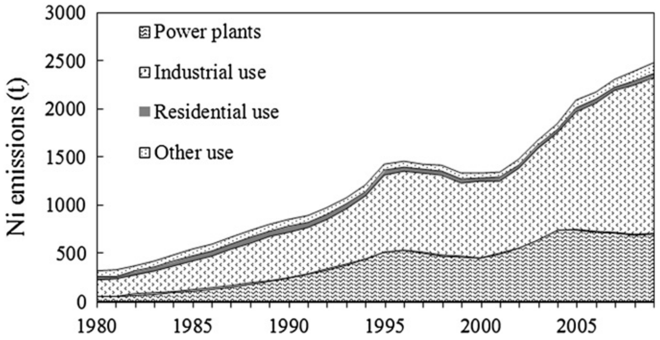

Fig. 2. Trend of Ni emission by sectors from coal combustion in China, 1980–2009.

combustion sources have been increasing slowly, at an annual growth rate of 3.0%. Residential coal uses are estimated to emit 34.36t Ni in 2009, contributing only 1.4% of total Ni emissions in the coal-combustion category. We find that Ni emissions from residential coal consumption have dropped down during the period (1980–2009), which is mainly because of substitution with more clean energy such as natural gas, liquefied petroleum gas, as well as electricity.

The total atmospheric Ni emissions from coal combustion present a mounting tendency in most of the years over the past decades (see Fig. 2) except during the period of 1997 to 1999, which could be mainly attributed to lower coal consumption during the Asian financial crisis (Hao, et al., 2002). As can be seen, Ni emissions from coal combustion in China began to grow at a more moderate pace (4.4% annually) in spite of continuously rapid coal consumption growth since 2005. This is mainly due to two reasons: (1) the implementation of various APCDs,especially the request for widely installation and operation of FGD to reduce SO_2 emissions in coal-fired power plants (SEPA, 2008), and (2) suspension of small-scale thermal power plants during the 11th-five-year-plan period (NDRC, 2011).

The annual increase/decrease of Ni emissions from industrial coal use is basically consistent with the trend of total Ni emissions from coal combustion. Notably, Ni emission from industrial coal combustion basically shows a rapid increase trend from 1980 to 2009 except a large fluctuation in the years of 1997–1999. However, the emissions of Ni from power generation sector have declined substantially since 2005 (see Fig. 2). This could be attributed to the co-benefit removal effects by the existing and newly installed PM and SO_2 control devices in coal-fired power plants. In addition, Ni emissions from power sector in 2009 are a little higher than that in 2008, increased by 7t, which can be explained by much more coal burning in power sector in 2009 (especially in some provinces with high installed capacity of coal-fired power plants, like Inner Mongolian and Shandong). This shows that the declined share of Ni emissions in power sector, caused by increasing advanced PM and SO_2 control devices installation, has offset by the added coal combustion and this also indicates the further control of Ni emissions from power generation sector in the future might be more and more difficult.

3.1.2. Ni Emissions from liquid fuels and biofuels combustion sources

Besides the biggest Ni emission category mentioned above, liquid fuels consumption, biofuels burning are also major contributors to atmospheric Ni emissions. It was reported that combustion of liquid fuels in electric power plants and industrial, commercial, and residential burners was the most important source of atmospheric Ni emissions in Europe (Pacyna and Ottar, 1985), because liquid fuels are the dominating energy source in Europe rather than coals. However, liquid fuels are not the primary energy source in China, and they only take up about 10% of the total primary energy production and account for nearly 19% of total energy consumption in 2009 (NBS and NDRC 2010). As a result, the atmospheric Ni emission from liquid fuels consumption is far less than those from coal combustion in China (see Fig. 1).

In this study, we estimate that the accumulated Ni emitted into atmosphere from gasoline, diesel oil, and kerosene consumption during the period of 1980–2009 is about 36.85t, 73.33t, and 8.31t, respectively. Fuel oil combustion has become one of the major contributors to atmospheric Ni emissions due to the relatively high content of Ni, attributing over 75% of total liquid fuels consumption category in 2009. As can been seen from Fig. 1, total Ni emissions from liquid fuels consumption category have increased slightly (less than 1% annually) during the past decades despite of the rapid growth of distillate oils (gasoline, diesel oil, and kerosene) consumption, which is because of the lower Ni content in distillate oils and relatively constant supply of fuel oil in China in the past decades.

In China, biofuels are combusted in low efficiency domestic stoves or burned in open air without any control devices. Accordingly, hazardous air pollutants are easily discharged into atmosphere with the exhaust. We estimated that 478.76 million tons agricultural residues and 182.16 million tons firewood were burned in China in 2009, which resulted in 330.77t atmospheric Ni emissions. In addition, as can be seen from Fig. 1, the emissions of Ni from biofuels combustion have no discernible increase (0.8% annually). This because the increase portion of Ni emitted from open air agricultural residues burning has offset by the reduction of firewood combustion during the past decades, which is mainly due to the fuel transitions to cleaner gaseous fuels and electricity in rural areas in China.

3.1.3. Ni emissions from other anthropogenic sources

Other anthropogenic sources emitting Ni into the atmosphere include ferrous and non-ferrous metals smelting; municipal solid waste (MSW) incineration; cement and brick production; and glass manufacturing. In these categories, we strip out the share of Ni emissions of fuels combustion during these industrial processes (as mentioned above) by using product-based emission factors that are excluding fuels combustion portion. However, due to limited information on these industrial processes and lack of sufficient field test samples, our estimation in these categories may be subject to higher uncertainties than those from fuels combustion.

Total Ni emissions from non-ferrous metals smelting category increased rapidly at an annual rate of 9.0%, from 30.64t in 1980 to 375.47t in 2009. In this category, as can be seen from Fig. 3, copper smelting is the largest single sector of total Ni emissions, reaching 202.57t in 2009 and attributing 53.9% of the totals, which mainly results from much higher Ni content in copper concentrate ore and large amount of copper produced in China. Total Ni emissions from lead smelting have increased to 18.86t in 2009, at an annual rate of 11.1%. Nickel smelting emit 148.29t atmospheric Ni in 2009, less than those from copper smelting, because the output of nickel is much less than other nonferrous metals productions. In addition, the accumulated total Ni emissions from zinc smelting are estimated

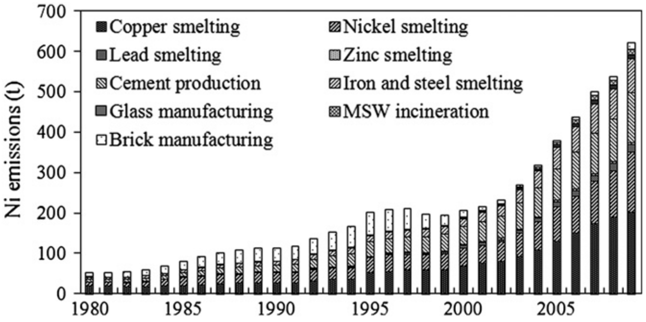

Fig. 3. Trend of Ni emissions from non-combustion sources in China, 1980–2009.

at 58.4t during the period of 1980–2009. Although non-ferrous smelting category contributes a small share of national total Ni emissions, compared with coal burning, it is easily to cause human health problems in these industry smelting processes, which is mainly because workers are normally long-time exposure to relative higher local Ni concentration in metals smelting plants compared to the widespread Ni release from fuels combustion (Denkhaus and Salnikow, 2002; Grimsrud et al., 2003).

The trend of Ni emissions from ferrous smelting category (pig iron and steel) is much similar to non-ferrous metals smelting category (see Fig. 3), increased rapidly at an annual growth rate of 9.7%, reaching at 83.89t in 2009. Total Ni emissions from cement production increased rapidly from 5.91t in 1980 to 121.52t in 2009, at an annual growth rate over 10%. Brick and glass manufacturing together emit 27.33t atmospheric Ni in 2009. MSW incineration contributes a little share of Chinese atmospheric Ni emissions, emitting 14.15t in 2009. However, with the rapid increasing installation of MSW incineration devices throughout China especially since this century, the emissions of Ni from this category have been increasing sharply, at an annual rate as high as 31.9%. It might be an emerging important source of atmospheric Ni in future of China, especially for the several metropolitans such as Beijing, Shanghai, and Guangzhou, and much attention should be paid to this category.

3.2. Distribution characteristics of Ni emissions in 2009

For a specific Ni emission source category, both the magnitude and composition of Ni emissions can be quite different from one province to another. Table 5 shows the detailed provincial inventory of atmospheric Ni in China in 2009. As can be seen, Shandong, Liaoning and Hebei are the highest Ni emitting provinces, emitting 425.65t, 253.94t and 245.77t, respectively. The reasons include large amount of coal consumption and high Ni content of raw coals in these provinces. Obviously, liquid fuels combustion in Guangdong and Shanghai, and non-ferrous smelting in Gansu and Jiangxi, both contribute nearly half of total Ni emissions, rank the top one source category in each province, though in most provinces, coal combustion still accounting for the largest source. For Shanghai and Guangdong, large amount consumption of liquid fuels due to their energy supply system and industry structure results in relatively high Ni emissions. Gansu is the largest nickel smelting province, attributing nearly 80% of the national total nickel production, and emits 138.45t atmospheric Ni in 2009. Jiangxi is one of the biggest non-ferrous metals smelting provinces in China, leading to 56.74t atmospheric Ni emission. Henan and Shandong are two of biggest Ni emitters from biofuels burning, because these provinces are major grain production areas in China and have a huge amount of rural populations relying on mainly biofuels burning for cooking and heating.

Fig. 4 shows out the spatial distribution characteristics of the total Ni emissions intensity (unit: kg/km^2) in China for the year of 2009. It can be seen clearly that Ni emissions in China are very unevenly allocated: the high emission density areas are mainly concentrated in the Beijing-Tianjin-Hebei Region (BTHR), the Yangtze River Delta (YRD) and the Pearl River Delta (PRD), which are highly industrialized and densely populated areas; while the rest areas of China show relatively lower density below 1.0 kg/km^2; the Ni density in Northwest China (except Gansu province) is even lower than 0.2 kg/km^2.

At provincial level, the trends of total Ni emissions show significant differences. Some provinces (Shandong, Inner Mongolia, Yunnan, etc.) present much higher Ni emission growth rates while some other provinces (Beijing and Hainan) demonstrate negative growth during the period of 2000–2009 (see Fig. 5). Ni emissions reductions in Beijing (−6.0% annually) are primarily due to the fast penetration of high-efficiency PM and SO_2 control technologies in power plants and industrial sectors and the shut down of some heavy polluting industries, for improving urban air quality to hold the 2008 Olympic Game successfully; while the reduction of Ni emissions in Hainan (−1.1% annually) results from the substitution with more cleaner energy such as electricity and natural gas for its tourist industry purpose; the large increase in Ni emissions (Shandong, Inner Mongolia, Yunnan, etc.), over 10% growth

Table 5
Sources composition of provincial Ni emissions in China, 2009 (t/a).

Provinces	Coal burning	Liquid fuels burning	Biofuels burning	Non-ferrous smelting	Ferrous smelting	Cement production	Other sources	Total Ni
Beijing	14.34	1.52	1.05	0.12	0.68	0.80	0.56	19.07
Tianjin	25.55	12.04	1.75	1.44	2.83	0.52	0.56	44.69
Hebei	184.27	8.29	18.37	3.81	20.09	7.91	3.02	245.77
Shanxi	180.66	1.61	5.69	3.35	4.49	2.04	0.59	198.43
Inner Mongolia	77.23	3.98	8.28	9.43	2.07	3.21	0.43	104.62
Liaoning	179.38	44.23	13.70	4.24	7.50	3.48	1.41	253.94
Jilin	66.97	6.16	10.48	0.02	1.18	2.72	0.83	88.36
Heilongjiang	51.28	51.55	18.87	0.03	0.78	1.93	0.32	124.76
Shanghai	27.14	79.38	0.16	4.51	2.80	0.56	0.74	116.29
Jiangsu	120.13	24.79	11.65	11.95	7.37	10.71	3.88	190.49
Zhejiang	71.32	25.18	4.14	11.50	1.35	8.01	3.78	125.28
Anhui	95.78	1.88	19.02	30.25	2.55	5.39	0.90	155.76
Fujian	38.52	18.06	6.28	0.99	0.94	4.05	1.38	70.23
Shandong	299.49	57.59	20.08	28.39	7.82	10.40	3.88	425.65
Jiangxi	50.66	2.09	8.78	56.74	2.26	4.59	0.31	125.43
Henan	124.35	5.10	22.13	8.02	3.13	8.79	6.30	177.81
Hubei	95.04	13.27	17.67	13.90	2.99	5.18	1.92	149.97
Hunan	87.72	8.08	14.53	6.32	2.14	5.66	1.18	125.64
Guangdong	60.28	96.24	17.45	3.48	1.32	7.43	4.53	190.74
Guangxi	59.36	3.20	21.20	9.17	1.47	4.76	0.70	99.86
Hainan	3.06	0.97	2.09	0.00	0.01	0.69	0.04	6.86
Chongqing	57.79	1.54	8.27	3.35	0.50	2.69	0.39	74.52
Sichuan	141.02	1.54	20.94	0.39	2.29	6.66	2.26	175.11
Guizhou	89.59	1.58	19.14	0.06	0.57	2.13	0.11	113.18
Yunnan	114.25	0.83	13.37	19.40	1.82	3.73	0.40	153.80
Shaanxi	75.70	7.76	10.95	0.97	0.77	3.33	0.45	99.94
Gansu	35.82	1.96	6.50	138.45	0.93	1.37	0.35	185.38
Qinghai	8.37	0.17	0.83	0.18	0.17	0.45	0.12	10.30
Ningxia	19.11	0.10	0.99	0.17	0.04	0.79	0.00	21.21
Xinjiang	39.12	7.58	6.41	4.83	1.06	1.51	0.11	60.02
China	2492.29	488.29	330.77	375.47	83.89	121.52	41.48	3933.71

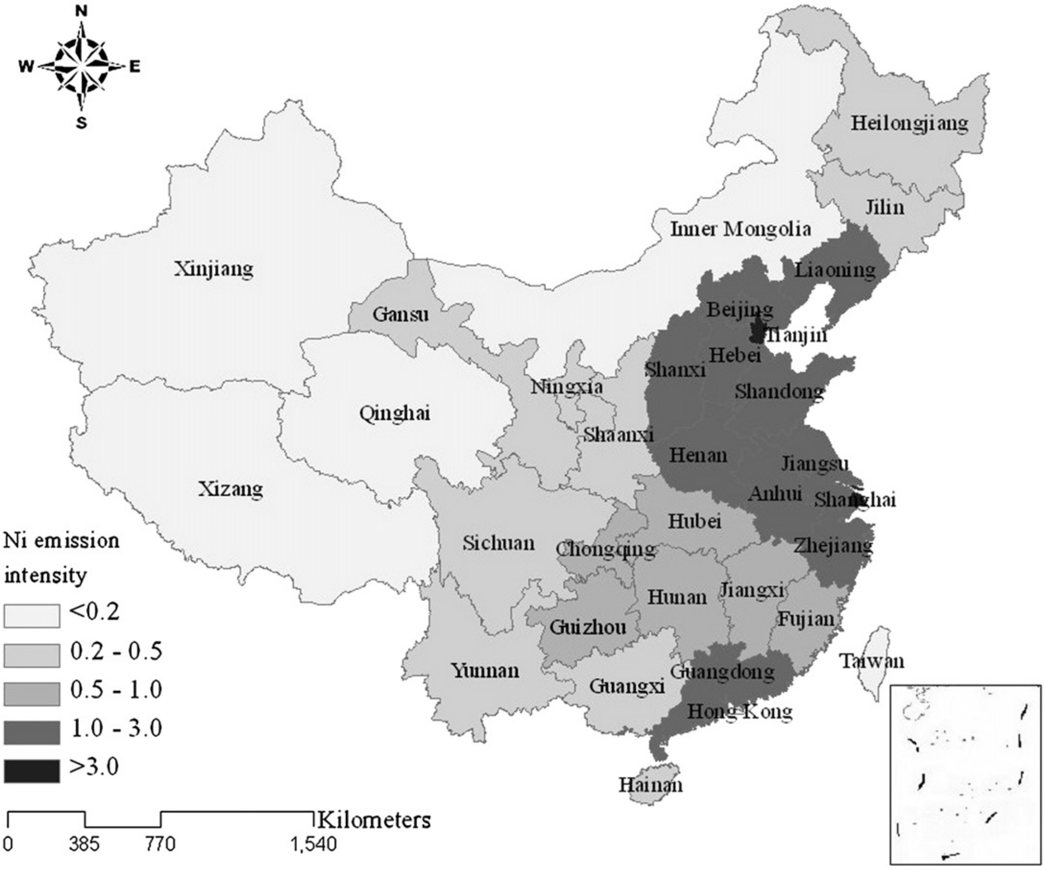

Fig. 4. Spatial distribution of Ni emission intensity in China in 2009, kg/km^2.

rate annually, is primarily attributed to greatly increased coal consumption in industrial use; the 1.4% annually increase rate in Shanghai City is mainly driven by the increased use of liquid fuels. Generally speaking, Ni emissions for each province are strongly affected by specific source-related variation trends.

Fig. 5. also presents the annual average growth rate of the total Ni emissions in fuels combustion source category and the other non-combustion sources category. As can be seen, Ni emissions from the industrial producing category have increased in all the provinces except Beijing and Shanghai. During the period of 2000–2008, lots of polluting industries in Beijing and Shanghai were closed down or moved out in preparing for holding the 2008 Beijing Olympic Game and the 2010 Shanghai World Expo. However, some provinces in the Western and Northwestern China (Inner Mongolia, Shaanxi provinces, etc.) present much higher Ni emission growth rates (about 20% annually) from the industrial producing sources due to their high speed development of local manufacturing industry, with the motivating policies of west development strategies issued by the central and local government. We can clearly see that the trend of Ni emissions from fuels combustion category coincides well with the trend of total Ni emissions in China, hence, it can be concluded that the total Ni emissions in China is mainly affected by the volume of fossil fuels consumption. Thus, except for controlling Ni discharge from industrial process such as metals smelting, much attention should be paid to atmospheric Ni emissions during fuels combustion processes.

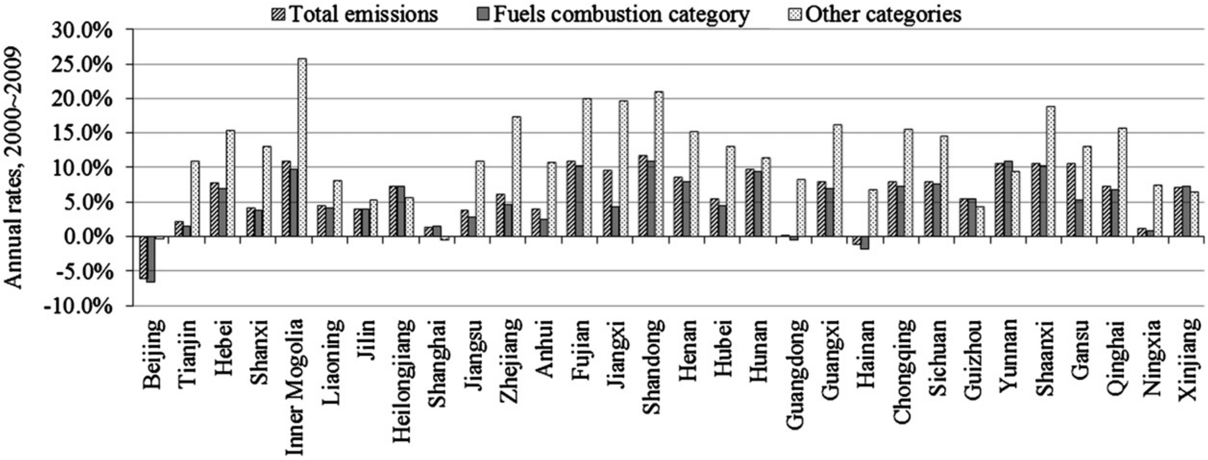

Fig. 5. Annual growth rates of Ni emissions at provincial level, 2000–2009.

Table 6
Uncertainties in atmospheric Ni emission by sectors in China, 2009 (t).

Categories	Uncertainties[a]	Categories	Uncertainties[s]
Coal combustion	2492.29 (−34.2%, 48.7%)	Non-ferrous smelting	375.47 (−73.7%, 102.7%)
Liquid fuels	488.29 (−68.9%, 58.6%)	Cement production	121.52 (−64.9%, 84.5%)
Biofuels burning	330.77 (−83.4%, 67.1%)	Other category	41.48 (−70.5%, 95.1%)
Ferrous smelting	83.89 (−84.7%, 91.9%)	Total emissions	3933.71 (−32.6%, 37.7%)

[a] Expressed as the lower and upper bounds of a 95% confidence interval around a central estimate.

In general, the anthropogenic atmospheric emissions of Ni at provincial level are decided by the economic and energy consumption structure, degree of economic development, as well as the population density. All provinces emitting large amounts of Ni is relatively developed economically and/or densely populated, which causes much higher fossil fuels consumption in industrial sector or power generation and large amount of industrial products yield or consumed.

3.3. Uncertainty analysis

Several factors influence the estimation of atmospheric Ni emissions including emission factors and activity levels. In this study, Monte Carlo simulation is used to quantify the uncertainties in the anthropogenic atmospheric Ni emission inventory based on available activity data and emission factors distribution. Most of the input parameters of activity levels and emission factors, with corresponding statistical distribution, are determined depended on the authors' judgment, or referred to the related references (Wu et al., 2010; Zhao et al., 2010; 2011). Table 6 shows the uncertainties (95% confidence interval around the arithmetic mean value) in Chinese anthropogenic atmospheric Ni emissions by sectors in 2009. Due to relatively much lower Ni emissions, Ni emissions from brick production, glass manufacturing, and MSW incineration are aggregated into a single category as other category for calculating the uncertainties.

The overall uncertainties of national total Ni emissions from all the categories are estimated as −32.6%–37.7%. As can be seen from Table 6, among fuels combustion sources, biofuels burning (−83.4%–67.1%) contributes the largest uncertainties, because there are very few estimates of Ni emission factors of Chinese combustion of biofuels and the statistics of firewood and agricultural residues for biofuels may be inadequate. However, the uncertainties in the rest categories (ferrous smelting −84.7%–91.9%, non-ferrous metals smelting −73.7%–102.7%, cement production −64.9%–84.5%, other category −70.5%–95.1%) are even larger than those in biofuels burning, and non-ferrous metals smelting category is found to be with the largest uncertainties of Ni emissions. These high Ni emission uncertainties mainly resulted from poor source investigation and inadequate field test data during industrial producing processes in China. In addition, the imprecise output statistics of industrial products (non-ferrous metals, cement, etc.) may also attribute to these large uncertainties.

Among all the coal combustion sectors, the largest uncertainty is found in the residential sector, ranging from −75.3% to 90.6%, and the uncertainty of industrial sector and other coal uses sector is estimated to be −45.9%–87.4% and −62.6%–64.6%, respectively. Due to poor resolution of coal combustion and control technologies in these three sectors, the differences of combustion and control efficiencies are ignored, and this inevitably yields higher uncertainties. However, due to relatively lower variations for the distribution of available activity data, release rates of different boiler types, and removal efficiencies of different control devices, the coal-fired power plants (−43.3%–48.9%) is found to be with least uncertainty among all the coal combustion sectors.

Till now, actual measurement of atmospheric Ni emission rates and species profiles from Chinese combustion facilities and industrial processes are still very limited, as well as the capture performance of Ni in Chinese emission control devices. As a result, some emission factors used in our study are cited from developed countries such as the US and the UK. The release rates of Ni in these developed countries are relatively lower than developing countries due to their best available technologies application and higher control efficiencies of APCDs. Using these emission factors may lead to underestimate of the total Ni emissions in China. In addition, there are some other Ni emission sources not considered in this study due to lack of detailed information about emission factors and activity data, for example, nickel-metal hydride batteries manufacturing, stainless steel manufacturing, electrode consumption and electroplating process. For a better reliable estimation of anthropogenic atmospheric Ni emissions from anthropogenic sources, long-term field testing and continuously monitoring for all kinds of combustion facilities and industrial processes in China, deserve further investigation.

4. Conclusions

The national total atmospheric nickel emissions are estimated increasing from 1096.07t in 1980 to 3933.71t in 2009. Fuels combustion category (e.g. coal, liquid fuels and biofuels combustion) dominate the atmospheric Ni emissions in China, with a share over 80% of totals in 2009. Coal combustion is the leading source of Ni emissions among all the categories, contributing 63.4% of the total Ni emissions, and among all the coal combustion sectors, industrial use ranks the biggest single sector for Ni emissions, followed by power generation sector. Ni emissions from other industrial producing categories are increasing rapidly, at an annual growth rate of 8.8%.

The regional distribution of Ni emissions is mainly concentrated in the Yangtze River Delta, the Pearl River Delta and the Beijing-Tianjin-Hebei region, which are all highly industrialized and densely populated areas. At provincial level, the trends of total Ni emissions represent significant variation, the top 3 provinces with the heaviest nickel emissions in 2009 are Shandong (425.65t), Liaoning (253.94t), and Hebei (245.77t). All of the provinces show positive growth rate of Ni emission except Beijing and Hainan during the period of 2000–2009, leading to a national average annual growth rate of 6.1%.

The overall uncertainties of Ni emission in 2009 are estimated as −32.6%–37.7% by using Monte Carlo simulation. To achieve a more reliable estimation of Ni emissions in China, long-term field testing and continuously monitoring for all kinds of combustion facilities and industrial processes in China are urgently required.

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