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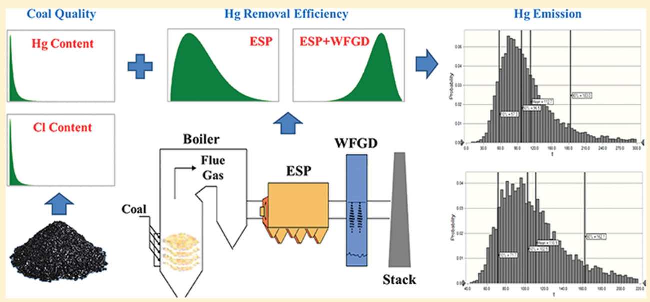
Influence of Mercury and Chlorine Content of Coal on Mercury Emissions from Coal-Fired Power Plants in China

Lei Zhang, Shuxiao Wang,* Yang Meng, and Jiming Hao

State Key Joint Laboratory of Environment Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, China

Supporting Information

ABSTRACT: China is the largest mercury emitter in the world and coal combustion is the most important mercury source in China. This paper updates the coal quality database of China and evaluates the mercury removal efficiency of air pollution control devices (APCDs) based on 112 on-site measurements. A submodel was developed to address the relationship of mercury emission factor to the chlorine content of coal. The mercury emissions from coal-fired power plants (CFPPs) in China were estimated using deterministic mercury emission factor model, nonchlorine-based and chlorine-based probabilistic emission factor models, respectively. The national mercury emission from CFPPs in 2008 was calculated to be 113.3 t using the deterministic model. The nonchlorine-based probabilistic emission factor model, which addresses the log-normal distribution of the mercury content of coal, estimates that the mercury emission from CFPPs is 96.5 t (P50), with a confidence interval of 57.3 t (P10) to 183.0 t (P90). The best estimate by the chlorine-based probabilistic emission factor model is 102.5 t, with a confidence interval of 71.7 to 162.1 t. The chlorine-based model addresses the influence of chlorine and reduces the uncertainties of mercury emission estimates.



1. INTRODUCTION

Coal combustion is generally considered as the dominant mercury emission source for the global mercury emission inventory. It is reported that fossil fuel combustion, primarily coal combustion, emitted 878 tons of atmospheric mercury in 2005, accounting for 46% of the total anthropogenic emission.[1] Coal-fired power plants are estimated to account for 25% of global anthropogenic mercury emission to the atmosphere, and industrial and residential heating boilers account for another 20%.

As the largest coal producer and consumer in the world, China accounts for 48.2% of world coal combustion and releases large amounts of Hg that are getting more and more attention. Mercury emissions from coal-fired power plants in China have been growing at an annual growth rate of 5.9% during 1995–2003, much higher than the average growth rate of all coal consumption sectors.[2] By 2010, the coal consumption by power generation in China has increased to 1.6 billion tons, indicating an even higher annual growth rate during 2004–2010.

Large uncertainties exist in these mercury emission estimates. Based on a preliminary uncertainty analysis, approximately ±40% for power plants, ± 60% for industrial coal use, and even larger uncertainty ranges for other sources were estimated for mercury emissions in China in 1999.[3] A new approach was adopted recently to analyze the uncertainty in the mercury inventory for coal-fired power plants.[4] The best estimate for total Hg emissions from coal-fired power plants in China in 2003 was 90.5 t, with the uncertainty range of −37%/+71%. The mercury content of coal and the removal efficiency of APCDs were identified as the two key factors in the uncertainty in the mercury inventory.[5] The chlorine content of coal has a significant influence on mercury speciation, resulting in a wide range of mercury removal efficiencies in APCDs.[5]

Data on mercury content of Chinese coal are quite limited. Wang et al.[6,7] and Zhang et al. [8] used 0.22 mg/kg as a national mean value, which was derived from coal analysis in 14 provinces. The values varied from 0.02–1.92 mg/kg. Other researches yielded estimated values of 0.15 mg/kg [9] and 0.16 mg/kg.[10] All these results came from very limited raw coal samples taken from coal mines. The United States Geological Survey (USGS) did further studies after analyzing 305 samples from all provinces in China and got an average mercury content of 0.16 mg/kg.[11] Based on data from USGS and other research, Streets et al. [3] presented a complete mercury content database by province for China, and got a value of 0.19 mg/kg for the mercury content of raw coal in China. Ren et al.[12] did a more detailed data investigation and summarized previous results of 619 samples in their book. Zheng et al.[13,14] analyzed 62 samples, summarized 1699 samples from previous studies, and reported the national average to be 0.19 mg/kg. There were also previous studies on chlorine in Chinese coal. The USGS[11]

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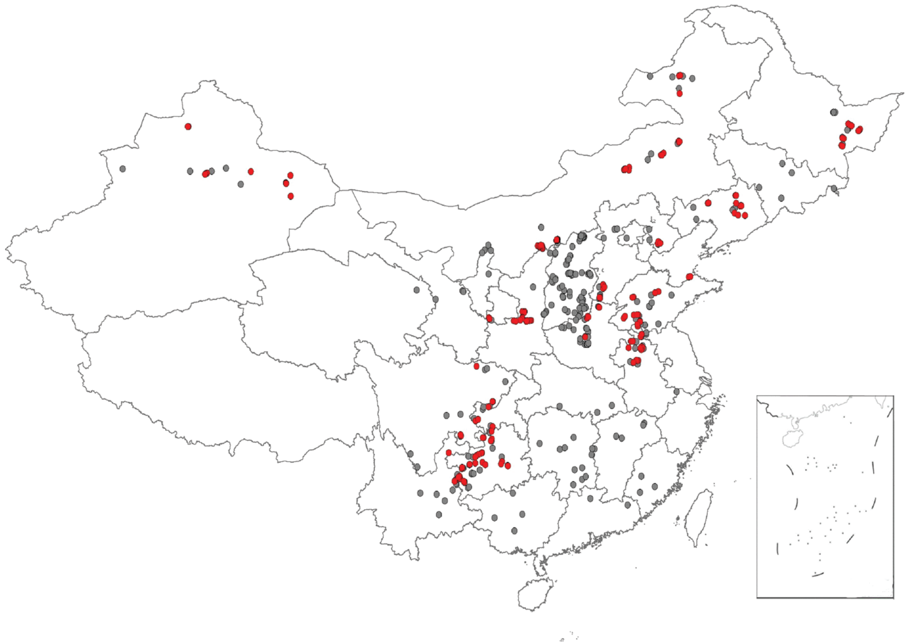

Figure 1. Geographic distribution of coal sampling locations: red dots – this study; gray dots – USGS database.

analyzed more samples and also covered more provinces, which have been the most reliable data source so far. According to their results, the average chlorine content of coal in China is 436 mg/kg. Although the number of samples is quite large in Ren et al. and Zheng et al.'s studies, most of their data were derived from earlier studies before 2000. The database they established might not be applicable for the inventory since the coal exploitation in China has changed substantially since 2000. The USGS database is the latest database for Chinese coal so far. However, there is still a lack of data for some provinces and data for certain provinces with large coal production or some typical provinces are not sufficient.

This study has collected and analyzed 177 Chinese coal samples so as to obtain a more complete coal database, developed a submodel on mercury emission factor to address the mercury behavior throughout APCDs regarding the coal quality, based on which a more precise mercury emission inventory has been developed for coal-fired power plants in China.

2. METHODOLOGY

2.1. Coal Sampling, Preparation, and Analysis. In this study, samples were collected from 177 coal mines in 15 provinces in China (see Table S1). Figure 1 shows the locations of all the sampled coal mines both from this study and the USGS database. The coal mines we sampled were selected based on the coal production by province in China and the existing USGS database which includes 305 samples. The final coal database, with information of 482 samples, covers almost all the large coal basins in China. Shanxi and Inner Mongolia, the largest two coal producers in China, have 88 and 46 samples, respectively. For other large coal producers, such as Shaanxi, Henan, Shandong, Anhui, and Heilongjiang, over 20 samples were obtained. Besides the quantity of coal production, the variation range of mercury content of coal was also taken into consideration. Guizhou, always considered as the province with the largest uncertainty in the mercury content of coal, has 46 samples. For other provinces with a large variation in the range of coal mercury content, such as Yunnan, Sichuan, and Hebei, over 15 samples were taken.

The samples were initially air-dried to constant weight, and then pulverized into 80 meshes (200 μm in particular diameter). The ASTM D6722-01, also known as Direct Combustion Method, was used for mercury analysis in this study with the Milestone DMA-80 Direct Mercury Analyzer. For mercury content analysis, twenty of the samples were also analyzed with the traditional Wet Digestion Method based on the U.S. EPA method 7470A for comparison. The chlorine content of coal was analyzed with the Chinese National Standard Method GB/T 3558-1996, the techniques of which are mainly based on hydrolysis and potentiometry. Eighteen of the samples were also analyzed with ASTM D7359-08, which is based on oxidative pyrohydrolytic combustion and ion chromatography for chlorine content analysis. The methods for coal sampling, preparation, and analysis are consistent with those adopted for the USGS database. Details for coal sampling, preparation, and analysis are given in Table S2 of the Supporting Information.

2.2. Emission Factor Model Description. Most of the existing mercury emission inventories were based on a deterministic emission factor approach, which can be described by eq E1. Mean values were used for all the parameters.

$$E = \sum_i \sum_j \left[M_i \cdot A_{i,j} \cdot (1 - Q \cdot w) \cdot R_j \cdot \left(1 - \sum_k P_{j,k} \cdot \eta_{j,k} \right) \right] \tag{E1}$$

where E is the mercury emission from coal-fired power plants, t/yr; M is the mercury content of coal as burned, mg/kg; A is the amount of coal consumption, Mt/yr; Q is the percentage of washed coal in the power plants; w is the mercury removal efficiency of coal washing; R is the release factor of mercury from boiler; P is the application rate of a certain combination of APCDs; η is the mercury removal efficiency of one combination of APCDs; i is the province; j is the combustor type; and k is the type of APCD combinations.

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Table 1. Mercury Removal Efficiencies of Air Pollution Control Devices[a]

	bituminous		anthracite		lignite		subbituminous	
PC+CS-ESP	29%	(42)	22%	(4)	38%	(6)	27%	(11)
PC+CS-ESP+WFGD	63%	(14)	81%	(1)	65%	(1)	50%	(3)
PC+FF	66%	(8)					73%	(2)
PC+SCR+CS-ESP+WFGD	67%	(3)						
PC+FF+WFGD	90%	(2)	79%	(1)				
PC+SDA+FF	99%	(1)			66%	(1)	13%	(1)
PC+SDA+CS-ESP							70%	(1)
PC+CS-ESP+CFB-FGD+FF	68%	(1)						
PC+SCR+CS-ESP+SW-FGD	74%	(1)						
PC+SCR+SDA+FF	98%	(2)						
PC+NID+CS-ESP			90%	(1)				
PC+SNCR+CS-ESP	83%	(1)						
CFB+CS-ESP	99%	(1)			66%	(2)		
CFB+FF	100%	(2)			59%	(1)		
CFB+SNCR+FF	89%	(1)					79%	(1)

[a]Numbers in brackets are number of onsite measurements. PC − pulverized coal boiler; CFB − circulating fluidized bed boiler; CS-ESP − cold-side electrostatic precipitator; FF − fabric filter; FGD − flue gas desulfurization; WFGD − wet FGD; CFB-FGD − circulating fluidized bed FGD; SW-FGD − seawater FGD; NID − novel integrated desulfurization; SDA − spray dryer absorber; SCR − selective catalytic reduction; SNCR − selective non-catalytic reduction.

In this study, a probabilistic emission factor model was adopted from our recent study[4] to assess the mercury emission from coal-fired power plants in China by province. This model can be described by eq E2 (details are given in the Supporting Information):

$$E(x_i, y_{j,k}) = \sum_i \sum_j \left[M_i(x_i) \cdot A_{i,j} \cdot (1 - Q \cdot w) \cdot R_j \times \left(1 - \sum_k P_{j,k} \cdot \eta_{j,k}(y_{j,k})\right)\right] \quad \text{(E2)}$$

where $E(x,y)$ is the probability distribution of the mercury emission from coal-fired power plants; $M(x)$ is the probability distribution of the mercury content of coal as burned; and $\eta(y)$ is the probability distribution of the mercury removal efficiency of APCD combination.

2.3. Coal Transport Matrix. The mercury content of coal in eq E2 is for the coal consumed in coal-fired power plants. The provinces with large coal consumption are not the same as the provinces with large coal production, so there is inter-provincial coal transport (see Figure S1). To get the provincial mercury content of coal as consumed in power plants from the raw coal database, a coal transport matrix was developed in this study. The coal transport matrix can be described as follows:

$$\mathbf{m}_c = \mathbf{A}\mathbf{m}_p$$

$$\mathbf{m}_c = [m_{c1}, m_{c2}, \cdots, m_{cn}]^T$$

$$\mathbf{A} = \{a_{ij}\}_{n\times n}$$

$$\mathbf{m}_p = [m_{p1}, m_{p2}, \cdots, m_{pn}]^T \quad \text{(E3)}$$

where vector $\mathbf{m}_c$ is the mercury content of coal as consumed in all the provinces; $\mathbf{m}_p$ is the mercury content of coal as produced in all the provinces; $\mathbf{A}$ is the coal transport matrix, and a_{ij} is the percentage of the amount of coal transported from province j to province i; n is the number of provinces. The detailed methodology and the coal transport matrix are given in Table S3 in the Supporting Information.

2.4. Mercury Removal Efficiency. Besides the mercury content of coal, the mercury removal efficiency of APCDs is another key parameter in the model. Table S4 in Supporting Information shows the installation rate of WFGD and SCR by province in China in 2008 which is the basic data for inventory development. The results of the 112 on-site measurements from existing studies[5,17−44] were summarized and analyzed to achieve a comprehensive understanding of mercury removal across APCDs (see Table S5 in Supporting Information). Most of these test results were from China and the United States, and some also came from Canada, Japan, South Korea, The Netherlands, and Australia. Table 1 shows the mercury removal efficiencies for 15 different APCD combinations (including boiler type). There are sufficient data for the first three combinations: pulverized coal boiler (PC) with cold-side electrostatic precipitator (CS-ESP), PC with CS-ESP and wet flue gas desulfurization (WFGD), and PC with fabric filter (FF). The mean values of mercury removal efficiency for these three combinations are 29%, 62%, and 67%, respectively. The influence of coal type on mercury removal efficiency is not significant.

PC+CS-ESP and PC+CS-ESP+WFGD are two dominant APCD combinations in China, accounting for over 95% of the coal-fired power plants in China. Now that there is enough data for these two combinations, 64 results for PC+CS-ESP and 19 for PC+CS-ESP+WFGD, we can use Crystal Ball to find a statistical distribution to fit these data. As a result, the mercury removal efficiencies of PC+CS-ESP and PC+CS-ESP+WFGD both comply with the Weibull distribution (Figure 2). The P50 value for the mercury removal efficiency of PC+CS-ESP turns out to be 26%, lower than the mean value (29%). That of PC+CS-ESP+WFGD is 65%, which is higher than the mean value (62%).

2.5. Submodel for the Mercury Emission Factor in Relation to the Chlorine Content of Coal. Both coal quality and operational conditions affect the mercury removal efficiency of APCD. Previous study indicates that fuel characteristics are more important than the operation conditions of APCD.[17] This submodel mainly describes the effect of coal quality, primarily chlorine content, on the mercury speciation,

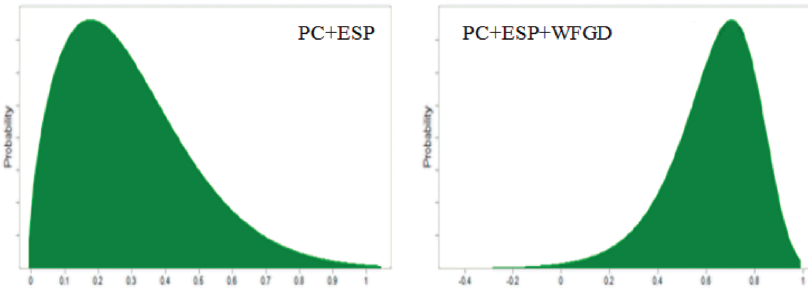

Figure 2. Probabilistic distribution profile of mercury removal efficiency.

transformation, and removal in flue gas. Mercury in flue gas includes gaseous elemental mercury (Hg^0), gaseous oxidized mercury (Hg^{2+}), and particulate mercury (Hg_p). The boiler in a typical Chinese coal-fired power plant is usually followed by ESP and WFGD. The mercury speciation after the boiler and before the ESP, i.e., at location a, is determined mainly by the chlorine content of coal and the ratio of mercury content of coal to ash content of coal, or the M/A ratio. The chlorine content in coal affects the percentage of Hg^{2+} in flue gas, while the M/A ratio influences the percentage of Hg_p in flue gas. Our previous study[5] has found the relationship between the chlorine content of coal and the percentage of Hg^{2+} in flue gas as well as the relationship between the M/A ratio and the percentage of Hg_p in flue gas. The mathematical expressions for the relationships are as follows:

$$\mathrm{Hg}_a^{2+}\% = (0.0785\cdot \mathrm{Cl}_0 + 1.7202)\% \tag{E4}$$

$$\mathrm{Hg}_a^{p}\% = \left(1.2333\cdot\frac{\mathrm{Hg}_0}{\mathrm{Ash}_0} + 1.7561\right)\% \tag{E5}$$

$$\mathrm{Hg}_a^{0}\% = 100\% - \mathrm{Hg}_a^{2+} - \mathrm{Hg}_a^{p} \tag{E6}$$

$$\mathrm{Hg}_a^{2+} = \mathrm{Hg}_0\cdot r\cdot \mathrm{Hg}_a^{2+}\% \tag{E7}$$

$$\mathrm{Hg}_a^{0} = \mathrm{Hg}_0\cdot r\cdot \mathrm{Hg}_a^{0}\% \tag{E8}$$

$$\mathrm{Hg}_a^{p} = \mathrm{Hg}_0\cdot r\cdot \mathrm{Hg}_a^{p}\% \tag{E9}$$

where Cl_0 is the Cl content of coal; Hg_0 is the Hg content of coal; Ash_0 is the ash content of coal; and r is mercury release rate from the boiler (99% for power plants).

The removal efficiencies of Hg^0 and Hg^{2+} were found to be related to the percentage of Hg^0 and Hg^{2+}, respectively (Figure 3). Over 99% of Hg_p is removed inside the ESP. Mercury removal efficiency in ESP (from location a to location b) can be calculated by the following equations:

$$\mathrm{RemHg}_{a-b}^{2+} = (0.3834\cdot \mathrm{Hg}_a^{2+}\% + 0.0115)\cdot 100\% \tag{E10}$$

$$\mathrm{RemHg}_{a-b}^{0} = (0.724\cdot \ln \mathrm{Hg}_a^{0}\% + 0.6076)\cdot 100\% \tag{E11}$$

$$\mathrm{RemHg}_{a-b}^{p} = 99\% \tag{E12}$$

where RemHg is the Hg removal efficiency.

Then the mercury speciation after the ESP (location b) can be obtained:

$$\mathrm{Hg}_b^{2+} = \mathrm{Hg}_a^{2+}\cdot(100\% - \mathrm{RemHg}_{a-b}^{2+}) \tag{E13}$$

$$\mathrm{Hg}_b^{0} = \mathrm{Hg}_a^{0}\cdot(100\% - \mathrm{RemHg}_{a-b}^{0}) \tag{E14}$$

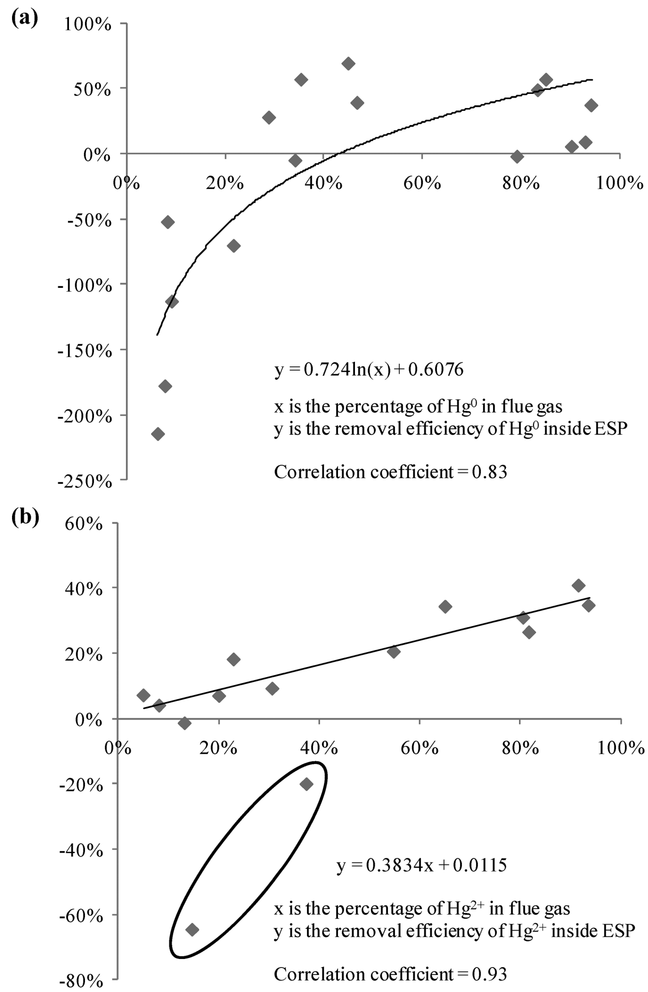

Figure 3. Relationship (a) between the percentage of Hg^0 in flue gas and the removal efficiency of Hg^0 inside ESP; and (b) between the percentage of Hg^{2+} in flue gas and the removal efficiency of Hg^{2+} inside ESP.

$$\mathrm{Hg}_b^{p} = \mathrm{Hg}_a^{p}\cdot(100\% - \mathrm{RemHg}_{a-b}^{p}) \tag{E15}$$

$$\mathrm{Hg}_b^{T} = \mathrm{Hg}_b^{2+} + \mathrm{Hg}_b^{0} + \mathrm{Hg}_b^{p} \tag{E16}$$

The removal efficiencies of Hg^{2+}, Hg^0, and Hg_p inside the WFGD (from location b to location c) are more stable. Therefore, we use the average values for WFGD:

$$\mathrm{RemHg}_{b-c}^{2+} = 77.1\% \tag{E17}$$

$$\mathrm{RemHg}_{b-c}^{0} = 3.94\% \tag{E18}$$

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Table 2. Mercury and Chlorine Content in Chinese Coals

province	mercury content in coal (mg/kg)				chlorine content in coal (mg/kg)			
	this study				this study			
	mean	min	max	USGS	mean	min	max	USGS
Anhui	0.204	0.08	0.406	0.194	190	80	310	585
Beijing				0.55				160
Chongqing	0.411	0.155	0.776	0.147	348	100	660	700
Fujian				0.074				211
Gansu	0.183	0.038	0.328	0.047	40	40	40	248
Guangdong				0.062				162
Guangxi				0.346				166
Guizhou	0.213	0.009	2.248	0.2	272	70	780	251
Hainan								
Hebei	0.172	0.039	0.45	0.141	407	190	720	749
Heilongjiang	0.032	0.014	0.049	0.062	229	70	390	402
Henan	0.135	0.055	0.26	0.208	344	140	550	500
Hubei				0.16				160
Hunan				0.141				558
Inner Mongolia	0.18	0.009	1.527	0.163	209	30	3280	435
Jiangsu	0.178	0.106	0.297	0.345	262	190	380	235
Jiangxi				0.27				608
Jilin				0.069				324
Liaoning	0.104	0.045	0.16	0.186	227	90	340	271
Ningxia				0.208				546
Qinghai				0.044				170
Shaanxi	0.248	0.009	1.134	0.142	214	40	690	1132
Shandong	0.163	0.051	0.386	0.131	344	40	1010	392
Shanghai								
Shanxi				0.152				361
Sichuan	0.335	0.206	0.541	0.09	325	200	450	478
Tianjin								
Xinjiang	0.023	0.008	0.057	0.032	233	60	730	392
Xizang								
Yunnan	0.076	0.018	0.264	0.142	246	90	410	196
Zhejiang								
national average	0.17	0.008	2.248	0.159	260	30	3280	436

$$\mathrm{RemHg}_{b-c}^{p} = 80\% \quad \text{(E19)}$$

Then the mercury speciation after the WFGD (location c) can be obtained:

$$\mathrm{Hg}_c^{2+} = \mathrm{Hg}_b^{2+} \cdot (100\% - \mathrm{RemHg}_{b-c}^{2+}) \quad \text{(E20)}$$

$$\mathrm{Hg}_c^{0} = \mathrm{Hg}_b^{0} \cdot (100\% - \mathrm{RemHg}_{b-c}^{0}) \quad \text{(E21)}$$

$$\mathrm{Hg}_c^{p} = \mathrm{Hg}_b^{p} \cdot (100\% - \mathrm{RemHg}_{b-c}^{p}) \quad \text{(E22)}$$

$$\mathrm{Hg}_c^{T} = \mathrm{Hg}_c^{2+} + \mathrm{Hg}_c^{0} + \mathrm{Hg}_c^{p} \quad \text{(E23)}$$

The submodel for the mercury emission factor in relation to the chlorine content of coal was thus established based on the relationships and the assumptions above. Not only the total mercury removal efficiency, but also the mercury speciation, is determined by the submodel.

3. MERCURY AND CHLORINE IN CHINESE COALS

3.1. Spatial Distribution of Mercury and Chlorine in Coal in China. The mercury content of coal was analyzed with two different methods to validate the results, as was the chlorine content. Figure S2 shows the comparison for mercury content and chlorine content and indicates that the results for the mercury and chlorine content from the two methods are consistent. The mercury and chlorine concentrations in coal in China by province obtained from this study are listed in Table 2. The coal from Chongqing has the highest mercury concentration, while Xinjiang and Heilongjiang have the lowest values. The mercury content of coal for Southwest China is higher than that of any other areas in China, which is probably related to the dense mercury mines in Northeast Guizhou. The national average mercury content of coal from this study is 0.17 mg/kg, slightly higher than that from the USGS database (0.16 mg/kg). For the chlorine content of coal, Hebei Province takes the lead, and Chongqing, Henan, Shandong, and Sichuan Provinces also have relatively high mean values. However, the chlorine content of coal for China is much lower than that for the United States in general. Most of the coal in China is extra-low-chlorine coal, whose chlorine content is less than 500 mg/kg. The national average chlorine content of coal from this study is 260 mg/kg, lower than that from the USGS database (436 mg/kg). The average mercury content of coal for Guizhou from this study (0.21 mg/kg) and the USGS database (0.20 mg/kg) is much lower than that from several previous studies.[9,10,15] The depth of the coal seam tends to be the most plausible reason for this. From 1980s to the present, coal mining has gone deeper and deeper with the development of technology and the depletion of the superficial coal mines.

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Table 3. Mercury Emission from Coal-Fired Power Plants in China in 2008 (t) Using Different Calculation Models[a]

	deterministic model	nonchlorine probabilistic model			chlorine-regarded probabilistic model		
province	mean	P50	P10	P90	P50	P10	P90
Anhui	4.79	3.67	1.93	8.99	4.08	2.32	9.57
Beijing	0.61	0.42	0.19	1.29	0.47	0.23	1.31
Chongqing	1.77	1.27	0.58	3.02	1.57	0.78	3.33
Fujian	1.78	1.47	0.83	2.95	1.78	1.17	3.13
Gansu	0.97	1.07	0.56	2.26	1.10	0.62	2.25
Guangdong	7.24	5.80	2.97	14.69	6.42	3.58	14.96
Guangxi	1.55	1.44	1.01	2.14	1.44	1.29	2.01
Guizhou	3.88	1.75	0.36	10.00	1.96	0.43	9.93
Hainan	0.29	0.17	0.06	0.69	0.18	0.06	0.64
Hebei	6.40	4.50	1.85	12.02	5.37	2.40	12.97
Heilongjiang	2.15	1.53	0.67	3.56	1.50	0.71	3.41
Henan	8.58	6.71	2.83	14.32	8.16	3.80	15.69
Hubei	2.38	2.03	1.08	3.88	2.37	1.39	4.14
Hunan	1.99	1.77	0.81	3.67	2.11	1.06	3.91
Inner Mongolia	13.43	5.66	1.38	24.98	5.97	1.50	24.33
Jiangsu	10.70	8.64	4.91	17.57	10.35	6.70	18.65
Jiangxi	2.69	2.32	1.19	4.36	2.64	1.46	4.49
Jilin	2.13	1.51	0.86	3.31	1.51	0.97	3.28
Liaoning	5.31	4.00	1.92	9.21	3.99	2.13	8.67
Ningxia	2.31	1.67	0.48	4.58	1.91	0.61	4.65
Qinghai	0.18	0.17	0.11	0.26	0.16	0.12	0.23
Shaanxi	2.99	1.30	0.39	7.20	1.32	0.43	5.82
Shandong	8.70	7.29	3.60	15.91	8.36	4.51	16.99
Shanghai	2.93	2.03	1.05	4.69	2.21	1.27	4.98
Shanxi	6.07	3.47	1.17	14.19	4.02	1.48	14.27
Sichuan	1.99	1.42	0.56	4.20	1.62	0.71	4.44
Tianjin	1.70	1.30	0.73	3.18	1.47	0.97	3.25
Xinjiang	0.57	0.45	0.21	0.79	0.43	0.23	0.71
Xizang	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Yunnan	1.55	1.03	0.40	3.39	1.11	0.47	3.49
Zhejiang	5.70	4.23	2.21	10.91	4.76	2.80	11.44
national	113.3	96.5	57.3	183.0	102.5	71.7	162.1
Hg^0	72%	71%			76%		
Hg^{2+}	27%	28%			24%		
Hg_p	1%	1%			1%		

[a]P10 values mean that there is a probability of 10% that the actual result would be equal to or below the P10 values; P50 values mean that there is a probability of 50% that the actual result would be equal to or below the P50 values; and P90 values mean that there is a probability of 90% that the actual result would be equal to or below the P90 values.

Our current research (unpublished) indicates that the mercury content of coal will probably get lower as coal mining goes deeper.

3.2. Variation of Mercury and Chlorine Concentration in Coal. There is a broad range of values for the mercury content of coal from Guizhou, Inner Mongolia, and Shaanxi, resulting in a significant difference between the arithmetic mean and the geometric mean. The case for the chlorine content of coal is not as significant, but the range of chlorine content for Inner Mongolia, Shaanxi, Xinjiang, and Shandong is still quite large. Therefore, the average mercury or chlorine concentration in coal cannot totally reflect the whole picture, and there might be an overestimation in mercury or chlorine concentration when an extremely large value occurs, e.g. the Guizhou case as mentioned above. To examine the variation of mercury and chlorine concentrations in coal, a statistical software package named Crystal Ball was used.[45] With Crystal Ball, a statistical distribution was fit to a portion of the data points from both this study and the USGS database for each province. The log-normal distribution was found to fit the data for all the provinces (see Figures S3 and S4 in the Supporting Information).

4. MERCURY EMISSION INVENTORY FOR COAL-FIRED POWER PLANTS IN CHINA

4.1. Influence of the Mercury Content of Coal on the Inventory. Using the deterministic model, the national mercury emission from coal-fired power plants in 2008 was calculated to be 113.3 t (as shown in Table 3). Elemental mercury and oxidized mercury make up 72% and 27%, respectively, of the total mercury emission. Based on the probabilistic emission factor model without considering the chlorine content, i.e., the nonclorine probabilistic model, the best estimate of the total mercury emission from coal-fired power plants is 96.5 t (P50), with a confidence interval of 57.3 t (P10) to 183.0 t (P90) (see Table 3 and Figure S5). The national mercury emission estimate is 17% higher by the conventional deterministic model compared with that by the nonclorine probabilistic model. The provincial emission estimates for Guizhou, Inner Mongolia, and Shaanxi were 122%, 137%, and 130% higher, respectively. This arises because the mercury content of coal fits a log-normal distribution, and the mean value is considerably higher than the median value.

The P50 values for elemental mercury and oxidized mercury are 68.5 and 26.7 t, accounting for 71% and 28% of the total mercury, respectively. The proportional distribution of the mercury species is almost the same as that using the deterministic model. A considerable amount of oxidized mercury was removed by WFGD. The best guess for particulate mercury is 1.0 t. The total mercury emission fits the log-normal distribution. Jiangsu, Shandong, Henan, Guangdong, and Inner Mongolia are the top five mercury emitters in coal power sector, whose emissions were higher than 5 t in 2008 (Table 3). The P90 value for Guizhou is 471% higher than the P50 value due to the broad range of mercury content of coal in Guizhou.

4.2. Influence of the Chlorine Content of Coal on the Inventory. The mercury emission was also estimated using the chlorine-based probabilistic emission factor model. The chlorine-based model was developed by replacing the mercury removal efficiency in the probabilistic emission factor model with the submodel regarding chlorine content of coal (Section 2.5). The best estimate of the total mercury emission from coal-fired power plants is 102.5 t (P50) in this inventory, with a confidence interval of 71.7 t (P10) to 162.1 t (P90). The uncertainty range of the emission inventory by chlorine-based probabilistic emission factor model is lower compared with that by the nonchlorine model. For provinces such as Chongqing, Fujian, Hebei, Henan, Hunan, and Jiangsu, the provincial emission estimates from chlorine-based probabilistic emission factor model are over 15% higher than that by the nonchlorine model. The cause of the difference lies in the mercury removal efficiency of ESP+WFGD. The average efficiency for the ESP+WFGD in the nonchlorine model was 62%, while that in the chlorine-based model was only 50%. The average mercury removal efficiencies of ESP in these two models were 29% and 28%, respectively, which were almost the same. As a result, the total mercury emission estimate for coal-fired power plants in China is lower when the chlorine content of coal is not considered. Because the coal consumed in China is mostly extra-low-chlorine coal, the mercury removal efficiency of ESP+WFGD is likely to be overestimated if average value is used. If the average chlorine content of coal were raised to 1000 mg/kg, the average mercury removal efficiency of ESP+WFGD would go up to 69%. Therefore, adding halogen addition in coal will help on the mercury removal. Elemental mercury and oxidized mercury account for 76% and 24%, respectively. The proportion of elemental mercury is slightly higher than that from the nonchlorine probabilistic model.

The chlorine-based probabilistic model in this paper addresses the distribution of the mercury content of coal and the influence of chlorine content of coal on emissions. According to the chlorine-based model, the total mercury emission from Chinese coal-fired power plants is 102.5 t (P50), with a confidence interval of 71.7 t (P10) to 162.1 t (P90). The mercury emission estimates by the chlorine-based model have lower uncertainties compared with that by the nonchlorine model. Based on our evaluation of the influence of coal quality on the emission inventory, the use of low-mercury coal and halogen addition to coal could be possible options for the mercury emission control in Chinese coal-fired power plants. The bromine content of coal, the compositions of fly ash such as CaO, Na_2O, K_2O, and Fe_2O_3, as well as the temperature of ESP also affect the mercury removal efficiency of APCDs. More tests shall be conducted to quantify the influence of these factors on mercury emissions.

ASSOCIATED CONTENT

Supporting Information

Details on coal sampling and analysis, comparison of analytical methods, probabilistic model, coal transport matrix, installation rates and mercury removal efficiencies of APCDs, and probabilistic distribution profile of key parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Phone: +86-10-62771466; fax: +86-10-62773597; e-mail: shxwang@tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

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