



## Full Length Article

# Actual mercury speciation and mercury discharges from coal-fired power plants in Inner Mongolia, Northern China



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## HIGHLIGHTS

- Mercury emissions from coal combustion are in the dominant form of  $\text{Hg}^0$  (>85%).
- Direct and indirect speciated Hg discharge factors of coal-fired power plants were obtained.
- The maximum of Hg emissions from coal-fired power plants of Inner Mongolia is 24 Mg/y.
- The largest direct Hg emissions may be the utilization industry of fly ash and gypsum.

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## ABSTRACT

Mercury species distribution in the flue gas from three typical coal-fired power plants have been investigated using a C-5000 sampler for Ontario Hydro Method (OHM) to evaluate specified Hg emission inventories in the largest coal-production province of China, Inner Mongolia. The feed coal, bottom ash, fly ash and gypsum have also been sampled in the field. Mercury emissions are in the dominant form of  $\text{Hg}^0$  (>85%). The  $\text{Hg}^{2+}$  (<15%) and the  $\text{Hg}^{\text{p}}$  (<2%) emissions are minor fractions of  $\text{Hg}^{\text{t}}$  in the flue gas. The wet limestone flue gas desulfurization device (WLFSD) showed much higher removal efficiency for  $\text{Hg}^{2+}$  (87–95%) than for the other two Hg species. The input Hg/output Hg varied from 92% to 115% for the tested 3 coal-fired utility boilers during sampling time. We obtained comprehensive Hg discharge factors, including direct atmospheric Hg emission factors and indirect discharge factors of Hg associated with bottom ash, fly ash and gypsum, to the environment, designating the fates of Hg in coal. We estimated the Hg discharges from coal-fired power plants in Inner Mongolia in 2008–2014 and expanded to China. The maximum of direct Hg emissions from coal-fired power plants of Inner Mongolia was 24 Mg in 2012. The Chinese coal-fired power plants emitted directly 100 Mg Hg to the atmosphere every year at the nationwide air control actions. The maximum discharges of Hg associated with fly ash and gypsum of Inner Mongolia was 81 Mg and 11 Mg in 2012, respectively. The national Hg discharges with fly ash and gypsum every year are respectively about 300 Mg and 82 Mg, majority of which may be reemitted to the atmosphere by the utilization industry. Therefore, mercury emissions from coal-fired power plants are not the largest single source of Hg to the atmosphere in normal operation of the current efficient denitrification, particles control and desulfurization devices. Instead, the utilization industry of fly ash and gypsum would be emitting more Hg to the atmosphere.

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## 1. Introduction

Mercury (Hg) is a global pollutant because of the long-range Hg transportation and deposition from anthropogenic sources, its bioaccumulation as methylmercury in the environment and its

neurological health impacts [1]. It has been found in Arctic biota [2] at concentrations so high that it presents a threat to human health. The modern model of atmosphere Hg circulation has revealed that Hg budget had tripled since pre-industrial times. The increased part of Hg is mainly from anthropogenic sources, especially from coal-fired power plants. It has been demonstrated that burning of fossil fuels (primarily coal) is the largest Hg source of emissions accounting for about half of anthropogenic Hg emissions of the total anthropogenic emissions with an annual emission

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Hg flux of 700–900 Mg to the atmosphere [3–6], and power plants are considered to be the largest single source in most countries [3].

Mercury emitted from natural sources is believed to be mainly the elemental mercury ( $\text{Hg}^0$ ), whereas anthropogenically emitted Hg has a significant portion in gaseous oxidized mercury ( $\text{Hg}^{2+}$ ) and particulate-phase mercury ( $\text{Hg}^p$ ) depending on the specifically conditions [7]. It has been well-documented that different physicochemical forms of Hg influence its environmental transport, fates, and in some cases, impacts. Elemental mercury is volatile, relatively inert, and virtually insoluble. As a result, it can pass through conventional scrubbers and particulate control devices, such as electrostatic precipitators (ESP) and fabric dust collector (FDC) and flue gas desulfurization (FGD) and contributes to the global mercury emissions inventory [8–10]. In contrast, oxidized mercury is water-soluble, thus more apt to react with particles to form  $\text{Hg}^p$ , and part of  $\text{Hg}^{2+}$  can be captured in scrubbers while the  $\text{Hg}^0$  may be transported a few hundred kilometers away from the source. Particulate-phase mercury is likely to deposit at an intermediate distance depending on the aerosol diameter. In the atmosphere, elemental mercury has a residence time of approximately 1 year [11,12], which is significantly longer when compared to the other forms which have atmospheric residence time of a few hours to several months. Consequently,  $\text{Hg}^p$  and  $\text{Hg}^{2+}$  are expected to be deposited closer to emission sources by dry or wet deposition. Therefore, some developed countries have been studying and using dedicated mercury-control technologies to regulate mercury emissions from coal-fired power plants [13–16].

Increasing attention has been paid on the Hg pollution problem in China because of the considerable amount of Hg emissions [3,17,18]. Streets et al. [17] estimated Hg emissions from China in 1999 where 537 ( $\pm 236$ ) Mg, and 38% of the Hg comes from coal combustion. Wu et al. [18] estimated Hg emissions from coal combustion increased from 202 Mg in 1995 to 257 Mg in 2003 at an average annual rate of 3.0%. Pacyna et al. [3] concluded that about two-thirds of global anthropogenic releases of Hg to the atmosphere appear to come from Asian sources, with China as the largest contributor worldwide for 2005. Obviously, coal-fired power plants are one of the largest anthropogenic sources of Hg emissions in China, but the above results have large uncertainties because comprehensive field investigations to characterize Hg emissions from coal-fired power plants are only available for developed countries [19–21], and have been gone for at least ten years.

However, with the increasing trend of air pollution in recent years, especially characterized by regional photochemical smog and haze in rapidly developing regions such as the North China Plain, the Yangtze River Delta and the Pearl River Delta, the Chinese government has implemented a series of national control policies to reduce the emissions of air pollutants since 2005 [22,23]. The 11th Five-Year Plan (2006–2010) for national environmental protection required the reduction of annual emissions of sulfur dioxide ( $\text{SO}_2$ ) in 2010 by 10% from its 2005 level. Besides stressing on primary particles control (PPC), FGD and nitrogen oxide control ( $\text{NO}_x\text{C}$ ), the Hg control had been listed in “Emission standard of air pollutants for thermal power plants” as Chinese national standard (GB 13223-2011) and implemented in 2015. In 2013, the Chinese government has promulgated and implemented the feasible “Air Pollution Prevention and Control Actions”. Therefore, with the above nationwide control actions, a large reduction in ambient  $\text{SO}_2$  level,  $\text{NO}_x$  emission and primary particles has been observed by ground monitors and satellite monitoring instruments [22,24]. In view of the above nationwide air control actions, mercury emissions from coal-fired plants in China would or will be reduced largely but lack of the actual measurements of mercury species, concentration in flue gases and capture of Hg through emission control devices in China.

The coal production of Inner Mongolia has surpassed Shanxi province and becomes the largest coal production province in China since 2007, and the coal consumption has also increased greatly. Coal resources in Inner Mongolia are divided into two areas: the first is the low metamorphic bituminous coal region in Erdos City possessing  $4.3 \times 10^{11}$  Mg of proven reserves, accounting for 53% of the provincial coal reserves and 13% of the national coal reserves. The second is the lignite area in eastern Inner Mongolia owning  $3.7 \times 10^{11}$  Mg of proven reserves, accounting for 45% of the provincial coal reserves and more than 3/4 of the national lignite reserves. Therefore, many advanced thermal power plants and coal chemical enterprises were constructed around the Ordos and the eastern Inner Mongolia.

In view of the coal distribution characteristics of Inner Mongolia, we chose three typical power plants, two of which have similar generating process, flue gas treatment process except for PPC and same generating capacity but burn bituminous coal and lignitous coal, respectively, and conducted three direct sampling and Hg analyzing campaigns. The subjects of this work aim to (1) directly determine the Hg species in flue gases from the 3 typical coal-fired plants in Inner Mongolia, Northern China, (2) study the fates of Hg in coal, the Hg discharge factors and the resulting discharges through the Hg mass balance verification, (3) estimate the Hg discharges from coal-fired power plants in Inner Mongolia in 2008–2014 and expand to China.

## 2. Method

### 2.1. Site description

Inner Mongolia has an abundance of resources especially coal, natural gas and rare earth elements, etc. It is an important coal production base, with more than a quarter of the world's coal reserves located in the province. The coal reserve has exceeded more than  $8 \times 10^{11}$  Mg in 2014 in Inner Mongolia.

Inner Mongolia is not only rich in bituminous coal also accounts for about 3/4 of lignite resources of China. However in the past, the exploitation and utilization of resources were rather inefficient, which resulted in poor returns from rich resources. With the implementation of series of national strategy, such as “The development campaign of the western regions”, “West-East electricity transmission project” and “West-East natural gas transmission project”, it has grown up mainly around coal, power generation. In 2007, the coal production in Inner Mongolia has surpassed Shanxi Province as the largest coal production province in China. The provincial coal production has increased to 1080 million Mg in 2012 from 457 million Mg in 2002 and slightly decreased from 908 million Mg in 2014 in Inner Mongolia. Consequently, many large-scale coal-fired power plants ( $\geq 300$  WM) have been built with high efficiency of  $\text{NO}_x\text{C}$ , PPC and FGD device. Therefore, the Hg investigation of the coal-fired plants in Inner Mongolia is particularly urgent for China with the nationwide air control and reduction actions situation.

In this study, three typical of coal-fired power plants are chosen to conduct three directly measuring campaigns of Hg species in flue gas and Hg in the by-products of the flue gas treatment in Inner Mongolia. The first one is Jinshan bitumite-fired power plant (JSBFPP,  $2 \times 300$  MW) of Hohhot Municipality, the provincial capital of Inner Mongolia, which represents to the type of bituminous coal-fired power plants. The second is Xilinhot lignite-fired power plant (XLLFPP,  $2 \times 300$  MW), the prefectural capital of Xilinguole located in the eastern Inner Mongolia, which represents to the type of lignite-fired power plants. The third is named as a gangue-fired power plant, in fact, which is a lignite-fired power plant during our

investigating period (LFPP,  $2 \times 135$  MW). All the three power plants consume prepared pulverized coal.

## 2.2. Sampling and analysis

The first campaign was conducted in JSBFPP through April 5–9 in 2015 to directly sample the flue gas outlet of wet limestone flue gas desulfurization (WLFGD) due to the smaller platform of the preset gas sampling port before the WLFGD for our C-5000 sampler installation. The WLFGD is a typical vertical spray tower which consists of a tower with spray nozzles that generate the droplets of lime slurry for surface contact with flue gas. JSBFPP generates electricity using subcritical pressure burning boiler and air cooling generator, and the flue gas undergoes ammonia injection for Selective Catalytic Reduction (SCR) denitrification, then passes through the FDC, and eventually releases into the atmosphere after WLFGD by a 210 m high smokestack. It consumes bituminous coal from Dongsheng coal mine of Erdos coal basin.

The second campaign was conducted in XLLFPP through April 11–16 in 2015 to directly sample the flue gas inlet and outlet of WLFGD that is as same as the WLFGD of JSBFPP. Its generation technology and the flue gas treatment process are similar to the JSCFPP except for coal consuming type and the PPC device. XLLFPP is a coal mine mouth power plant, which consumes lignitous coal from its strip coal mine 7 km away, and uses ESP control device to reduce primary particles emissions. Xilinhot is one of the two main lignite production basins and accounts for more than half of lignite production in Inner Mongolia.

The third campaign was conducted in LFPP through April 24–27 in 2015 to directly sample the flue gas inlet and outlet of WLFGD that is similar to the WLFGD of the aforementioned power plants. The generation electricity uses circulating fluidized bed burning boiler and water cooling generator, and the flue gas undergoes urea denitrification in furnace, then passes through ESP + FDC device, and finally releases into the atmosphere after WLFGD by a 110 m higher smokestack. It consumes pulverized lignite. The above 3 coal-fired power plants all install Continuous Emission monitoring (CEM) with concentrations of PP, NO<sub>x</sub> and SO<sub>2</sub> on-line to prefectural, provincial and national environmental protection department for air pollutant monitoring. Our directly flue gas sampling sites are the same as the sites of CEM.

The sampling method was based on U.S. Environmental Protection Agency method 5 and Ontario Hydro Method (OHM) to collect the speciated Hg in flue gas. The OHM is the D3874-02 standard method of American Society for Testing and Materials and has been validated as a mercury speciation measurement method in a full-scale test program at power plant [25–28]. The sampling equipment is the C-5000 source sampling system for stack sampling professionals, which was made in Environmental Supply Company of U.S. Nearly one particulate Hg (Hg<sup>p</sup>) was collected on a 47 mm diameter glass fiber filter, and gas phase Hg (Hg<sup>2+</sup>, Hg<sup>0</sup>) was collected in seven impingers solutions that connected in a series. Hg<sup>2+</sup> was collected in the first three impingers containing KCl solution (1 mol/dm<sup>3</sup>) and Hg<sup>0</sup> was collected in the fourth impinger containing H<sub>2</sub>O<sub>2</sub>–HNO<sub>3</sub> (10% v/5% v) solution and the last three impingers containing KMnO<sub>4</sub>–H<sub>2</sub>SO<sub>4</sub> (4%/10%v) solution. The sampling lines and the Glass Filter Holder were heated to 120 °C to prevent flue gas condensation. The eighth impinger containing silica gel was used to remove the moisture from the sampling line before entering the gas meter. All impingers were placed in an ice bath to prevent evaporation of the sampling solutions. Due to the power plants in the PPC control efficiency is very high (>99.8%), the primary particulate concentrations are general in 10–60 mg/N m<sup>3</sup> in flue gas after PPC device. We can't collect enough primary particles samples to analyze Hg because our sampling sites are located in the flue gas outlet of PPC facilities, such as the flue gas inlet and

outlet of WLFGD device which is EPA CEM sites. In addition, the OHM requirements of the constant speed sampling are for primary particles and too much primary particles on the filter membrane in Glass Filter Holder will absorb mercury in the flue gas and impact the flue gas mercury collection. Therefore, we modified the sampling velocity of OHM required constant sample rate with flue gas in chimney. The Hg<sup>p</sup> concentration in flue gas will be obtained by the following method. The collected flue gas samples were salvaged according to OHM and transferred to 250 ml of higher boron silicon glass bottle, capping, labeling packaging with self sealing bag, and preserved in the refrigerator at the same day for waiting lab Hg analysis. Preliminary Hg concentrations of the residual samples were analyzed with Lumex R915 made in Russia in-situ to determine the flue gas sampling velocity of flow and the sampling time.

During the flue gas directly sampling, samples of the feed coal and the byproducts of flue gas control, such as bottom ash, fly ash, gypsum and process circulating water, were collected. The sampling frequency is determined according to the sampling time of the flue gas with duration of 4–5 days for every investigated power plant, generally 2–3 times a day. These solid samples were dried by natural air in the laboratory ventilated kitchen, and then milled, sieved to 200 meshes for digestion. For coal, 1.5000g samples were put into a 45 ml centrifugal tube, and then added 10 ml reverse aqua regia (HNO<sub>3</sub>:HCl = 3:1) because of much organic matter, shaking and placing for the night. For the byproducts samples, 1.5000g samples were put into a 45 ml centrifugal tube, and then added 10 ml aqua regia (HNO<sub>3</sub>:HCl = 1:3), shaking and placing for the night. The next day, the centrifuge tubes with sample and reagent were water bathed at 50 °C for half an hour, and then heated to 95 °C to water bath for 2 h. After the tubes cooling to room temperature, it was filtrated into a new 45 ml centrifugal tube with disposable syringe and Millex Syringe-driven Filter Unit (PVDF, D33 mm, 0.45 μm), capping, labeling and waiting for Hg analysis. For process water, 10 ml supernatant water was put into a 45 ml centrifugal tube, and then added 100 μl BrCl to digest 2 h for analysis.

Mercury in the prepared flue gas samples, digested solid samples and process water samples were ultimately analyzed with Brooks Rand Model III of cold vapor atomic fluorescence spectrometry (CVAFS) technique in the laboratory following our previous studies [27,29].

## 2.3. Quality control

Due to the low concentration of mercury in flue gas, the main reagents of flue gas sampling were lower Hg blanks, such as KMnO<sub>4</sub> (Hg = 0.004 mg/kg) was ACS reagent grade from Charlotte, NC, U.S., H<sub>2</sub>SO<sub>4</sub> (AR, 95–98%), KCl (GR, 99.8%), H<sub>2</sub>O<sub>2</sub> (Ph, Eur, Bp, usp, 30–31%) and HNO<sub>3</sub> (Semiconductor grade, 70%) were purchased from Aladdin Industrial Corporation (Shanghai, China). The Hg blanks in main reagents of flue gas sampling are lower and basically equivalent of the distilled water (Table A.1 of Appendices). Another main objective of our sampling campaigns is to study the mercury isotope composition in flue gas and the byproducts, so, mercury concentrations in the samples need to be 2–5 ng/ml or even higher for MC-ICP-MS analysis. The concentrations of Hg in flue gas samples were measured initially by Lumex R915 M for adjusting the appropriate sampling flow rate and the sampling time.

The analyzing quality control was conducted to new analytical standard curve, standard coal samples, parallel samples and random sampling. The new analytical standard curve was made of new mercury standard solution with the new commercial raw standard solution (100 μg/ml), and the standard deviation is reached to more than 99%. Two standard coal samples of NIST

SRM 2692C and 2693 were analyzed using the same digestion with coal samples, the analytical results were shown in (Table A.2 of Appendices). Each sample was digested and analyzed two times, and used geometric mean of Hg content as the Hg concentration in the sample. The results of some parallel samples were shown in Table A.3 of Appendices.

### 3. Results and discussion

#### 3.1. Mercury speciation in flue gases

The 2 × 300 MW JSBFPP is a typical bituminous coal-fired power plant with the combination of ammonia SCR + FDC + WLFGD devices. Mercury speciation in the cleaned flue gases at the outlet of WLFGD of JSBFPP is summarized in Table 1. The range of total mercury (Hg<sup>t</sup>) concentrations in flue gas varies between 0.18 μg/N m<sup>3</sup> and 1.08 μg/N m<sup>3</sup> with the mean value of 0.57 μg/N m<sup>3</sup>. It reflects that Hg in coal is inconsistent. Mercury in flue gas of bituminous coal-fired power plant of JSBFPP emits in the dominant form of Hg<sup>0</sup> and the average Hg<sup>0</sup> concentration is 0.53 μg/N m<sup>3</sup>, accounting for 93% of all Hg species in flue gas. The percentage of Hg<sup>2+</sup> and Hg<sup>p</sup> are very lower. The average Hg<sup>2+</sup> concentration is 29 ng/N m<sup>3</sup> accounting for 5% of all Hg species. The average Hg<sup>p</sup> concentration is 10 ng/N m<sup>3</sup> accounting for 2% of all Hg species. These results are very lower than that of Guiyang coal-fired power plants with only ESP by our previous study [27] in a decade ago and lower than that of two bitumite-fired power plants with ESP + WLFGD devices by another Chinese research group [28]. It is also far lower than that of Hg emission limitation of 30 μg/N m<sup>3</sup> specified by GB13223-2011. It implies that most of the Hg, especially in Hg<sup>p</sup> and Hg<sup>2+</sup>, are removed from flue gas by SCR + FDC + WLFGD devices. The amount of Hg removed across a WLFGD depends largely on how much Hg<sup>2+</sup> is present at the scrubber inlet [30]. SCR systems have been observed to oxidize Hg in coal-fired power plants [31] and the range of Hg oxidation observed in plants firing bituminous coals was 30–98%. The combination of an SCR and a WLFGD scrubber can remove 90% or more of the Hg (from input to stack), if there is sufficient Hg<sup>2+</sup> at the scrubber inlet. Withum [32] measured Hg removal on eight bituminous coal-fired boilers with SCR + WLFGD and average Hg removal (coal to stack) on these boilers varied from 65% to 97%.

The 2 × 300 MW XLLFPP is a typical lignite-fired power plant with the combination of ammonia SCR + ESP + WLFGD devices. Mercury speciation in the flue gases at the outlet of WLFGD of XLLFPP in eastern Inner Mongolia, is summarized in Table 2. There are significantly different in Hg species concentrations in flue gas compared with JSBFPP. The Hg<sup>t</sup> and Hg<sup>0</sup> concentrations emitted to the atmosphere are 6–7 times of JSBFPP. The range of Hg<sup>t</sup> concentrations in cleaned flue gas at outlet of WLFGD varies between 2.47 μg/N m<sup>3</sup> and 4.81 μg/N m<sup>3</sup> with average concentration of 3.

80 μg/N m<sup>3</sup>. The Hg<sup>0</sup> is also dominant forms with the mean Hg<sup>0</sup> concentration of 3.39 μg/N m<sup>3</sup> accounting for 89% of all Hg species in flue gas. Although the percentage of Hg<sup>2+</sup> is a fraction of Hg<sup>t</sup> in the flue gas, which accounts for 11% of all Hg species with the average Hg<sup>2+</sup> concentration of 0.42 μg/N m<sup>3</sup>, it is still 14.5 times of Hg<sup>2+</sup> in flue gas of JSBFPP. The average Hg<sup>p</sup> concentration is 3.0 ng/N m<sup>3</sup> accounting for 0.08% of all Hg species, and can be almost negligible. The Hg<sup>0</sup> and Hg<sup>t</sup> concentrations emitted to the atmosphere are far lower than that of previous studies [27,28] and still far lower than that of the mercury limitation of 30 μg/N m<sup>3</sup> specified by GB13223-2011.

For comparison, we investigate the Hg species in flue gas at inlet of WLFGD of the XLLFPP (Table 2). Although the average Hg<sup>t</sup> concentrations in flue gas at inlet of WLFGD are higher to 17.75 μg/N m<sup>3</sup> with the mean value of 11.65 μg/N m<sup>3</sup>, it is also below the mercury limitation specified by GB13223-2011. The distribution of mercury speciation in flue gas at inlet of WLFGD has significant difference with that of flue gas at outlet of WLFGD. The main forms of Hg in flue gas at inlet of WLFGD are Hg<sup>2+</sup> and Hg<sup>0</sup>, and the Hg<sup>2+</sup> content is much higher than Hg<sup>0</sup> content. The average Hg<sup>2+</sup> concentration in flue gas at inlet of WLFGD is 7.68 μg/N m<sup>3</sup> with range of 1.69–13.28 μg/N m<sup>3</sup>, which accounts for 66% of Hg<sup>t</sup>. The Hg<sup>2+</sup> content at inlet of WLFGD is 18–22 times of Hg<sup>2+</sup> content at outlet of WLFGD by comparison. The mean Hg<sup>0</sup> concentration in flue gas at inlet of WLFGD is 4.82 μg/N m<sup>3</sup> with the range of 2.73–8.25 μg/N m<sup>3</sup>, which accounts for 41% of Hg<sup>t</sup>. The average Hg<sup>p</sup> concentration is 9 ng/N m<sup>3</sup> accounting for 0.07% of all Hg species, and also can be almost negligible. Our results indicate that the Hg<sup>t</sup> removals of the WLFGD are 67%, among them the WLFGD device has very higher removal efficiency for Hg<sup>2+</sup> reaching 94% and the removal effect of the WLFGD device for Hg<sup>0</sup> is not obvious and only 30%. These mercury removal rates are higher than that in Holland [19], Japan [21] and are about similar to the USA [33].

In order to confirm the mercury speciation and relative distributions in flue gas from lignite-fired power plants, the LFPP with urea SCR + ESP + FDC + WLFGD devices has been investigated. The mercury speciation and relative distributions in flue gas at the outlet and inlet of LFPP are about similar to that of XLLFPP. The differences are reflected in the concentrations of Hg species (Table 3) because of low mercury in feed coal. For cleaned flue gas, in general, it emits also mainly in the form of Hg<sup>0</sup> accounting for 88% of all Hg species. The Hg<sup>2+</sup> accounts for 15% of all Hg species and Hg<sup>p</sup> also can be almost negligible. For flue gas at inlet of WLFGD, the main forms of Hg in flue gas are Hg<sup>2+</sup> and Hg<sup>0</sup>, and the Hg<sup>2+</sup> content is much higher than Hg<sup>0</sup> content. The Hg<sup>2+</sup> accounts for 59% of Hg<sup>t</sup> with average concentration of 1.19 μg/N m<sup>3</sup> and 7.8 times of Hg<sup>2+</sup> content in cleaned flue gas by comparison. The Hg<sup>0</sup> accounts for 41% of Hg<sup>t</sup> with mean Hg<sup>0</sup> concentration of 0.83 μg/N m<sup>3</sup> and Hg<sup>p</sup> also can be almost negligible. The WLFGD system has very

**Table 1**  
Mercury speciation and relative distributions in flue gas from JSBFPP consuming bituminous coal.

Sampling site	Sampling time	Hg <sup>p</sup>		Hg <sup>2+</sup>		Hg <sup>0</sup>			Hg <sup>t</sup>	
		ng/N m <sup>3</sup>	%	ng/N m <sup>3</sup> (KCl)	%	ng/N m <sup>3</sup> (H <sub>2</sub> O <sub>2</sub> -HNO <sub>3</sub> )	ng/N m <sup>3</sup> (KMnO <sub>4</sub> -H <sub>2</sub> SO <sub>4</sub> )	%	ng/N m <sup>3</sup>	
Outlet of WLFGD	April-4	10.0	0.9	8.6	0.8	–	1065	98.3	1083	
		12.0	2.7	22.6	5.2	–	404	92.1	438	
		10.4	1.4	16.2	2.2	6.0	691	96.3	724	
	April-6	9.9	1.1	20.7	2.3	13.1	847	96.6	891	
		8.9	1.0	82.1	9.1	3.0	811	89.9	905	
		9.0	2.1	35.9	8.3	6.0	383	89.7	434	
	April-7	9.8	3.1	41.9	13.3	5.0	260	83.6	316	
		8.6	4.8	12.1	6.8	1.2	157	88.4	179	
		8.0	4.4	20.7	11.3	1.7	152	84.3	182	
	Average (ng/N m <sup>3</sup> )	10 ± 1	2	29 ± 16	5	5 ± 3	530 ± 290	93	570 ± 290	
							530 ± 290			

**Table 2**  
Mercury speciation and relative distributions in flue gas from XLLFPP consuming lignituous coal.

Sampling sites	Sampling time	Hg <sup>p</sup>		Hg <sup>2+</sup>		Hg <sup>0</sup>			Hg <sup>t</sup>
		ng/N m <sup>3</sup>	%	ng/N m <sup>3</sup> (KCl)	%	ng/N m <sup>3</sup> (H <sub>2</sub> O <sub>2</sub> –HNO <sub>3</sub> )	ng/N m <sup>3</sup> (KMnO <sub>4</sub> –H <sub>2</sub> SO <sub>4</sub> )	%	
Outlet WLFGD	April-11	3.0	0.12	285	11.5	13.6	2172	88.4	2473
	April-12	3.4	0.07	574	12.4	63.3	3971	87.5	4612
		3.4	0.08	501	11.3	10.8	3914	88.6	4429
	April-13	2.6	0.05	255	5.3	28.7	4518	94.6	4805
		2.6	0.07	236	6.7	18.7	3283	93.3	3540
		2.6	0.09	673	22.5	36.8	2277	77.4	2989
	Average (ng/N m <sup>3</sup> )	3 ± 1	0.08	420 ± 160	11	30 ± 14	3330 ± 780	89	3800 ± 810
Inlet WLFGD	April-14	8.5	0.10	1689	20.3	–	6609	79.6	8307
		7.8	0.09	–	–	580	7670	99.9	8258
	April-15	8.2	0.07	8724	73.0	326	2900	27.0	11958
		9.4	0.08	7551	64.0	239	4008	36.0	11807
		8.7	0.07	8558	65.4	270	4240	34.5	13077
		9.4	0.09	8192	74.9	224	2506	25.0	10931
	April-16	8.3	0.05	13278	74.8	277	4182	25.1	17746
		9.1	0.09	4800	49.3	358	4570	50.6	9737
		8.7	0.07	8650	66.3	274	4112	33.6	13045
	Average (ng/N m <sup>3</sup> )	9 ± 1	0.07	7680 ± 2250	66	320 ± 80	4530 ± 1170	41	11650 ± 2090
						4820 ± 1190			

**Table 3**  
Mercury speciation and relative distributions in flue gas from LFPP consuming lignite.

Sampling sites	Sampling time	Hg <sup>p</sup>		Hg <sup>2+</sup>		Hg <sup>0</sup>			Hg <sup>t</sup>
		ng/N m <sup>3</sup>	%	ng/N m <sup>3</sup> (KCl)	%	ng/N m <sup>3</sup> (H <sub>2</sub> O <sub>2</sub> –HNO <sub>3</sub> )	ng/N m <sup>3</sup> (KMnO <sub>4</sub> –H <sub>2</sub> SO <sub>4</sub> )	%	
Outlet WLFGD	April-24	2.7	0.2	303	26.3	35.6	810	73.5	1152
		2.4	0.2	196	14.7	7.5	1130	85.1	1336
	April-25	2.5	0.3	–	–	–	766	99.7	769
		3.2	0.3	73	7.1	6.4	958	92.6	1041
	Average (ng/N m <sup>3</sup> )	2.9	0.4	33	4.7	3.6	653	94.9	692
		3 ± 1	0.3	150 ± 100	15	13 ± 11	860 ± 150	88	1000 ± 210
					870 ± 140				
Inlet WLFGD	April-26	5.6	0.1	2976	72.6	71.5	1049	27.3	4102
		10.8	0.5	1451	60.9	60.3	861	38.7	2382
	April-27	8.2	0.4	968	50.9	57.2	868	48.7	1902
		6.4	0.6	372	36.2	39.1	610	63.2	1028
		5.6	0.4	681	51.0	50.6	598	48.6	1336
	Average (ng/N m <sup>3</sup> )	6.4	0.5	660	48.7	48.2	642	50.9	1357
		7 ± 2	0.4	1190 ± 690	59	55 ± 8	770 ± 160	41	2020 ± 820
						830 ± 160			

higher removal efficiency of 87% for Hg<sup>2+</sup>. The relatively consistent results of the two lignite-fired power plants show that our mercury speciation and relative distributions in flue gas are reproducible. In addition, we find an interesting fact that the Hg<sup>0</sup> concentration in flue gas at inlet of WLFGD is lower than that at outlet of WLFGD (Table 3). Through the investigation, we conjecture the reason some desulfurization synergists would or will be added into process water for desulfurization by the LFPP due to the desulfurization effects are not very good. The desulfurization synergistic agents are favorable for desulfurization, but it is not conducive to remove mercury. It would be transformed the Hg<sup>2+</sup> in process water removed from flue gas to Hg<sup>0</sup> into flue gas and result in the above fact. Further studies are necessary to confirm this reason.

### 3.2. Mercury in feed coal and the byproducts of flue gas control device

Mercury in feed bitumite and the byproducts of the flue gas, such as bottom ash, fly ash and gypsum from JSBFPP are listed in Table 4. The mean value of Hg in the feed bitumite, which is the low metamorphic bituminous coal from Dongsheng coal mine in Erdos during sampling period, is 0.16 µg/g ( $n = 7$ ) with the range of 0.11–0.23 µg/g and agrees with Hg content of 0.19 µg/g ( $n = 4$ ) in Inner Mongolia [34,35]. The Dongsheng coal mine is one part

of Chinese and the world's largest coal field named Shengfu-Dongsheng coalfield, which is located in the northwest of Shaanxi province and south of the Inner Mongolia. It is formed early-middle Jurassic, has been proven D grade reserves of about  $8 \times 10^{10}$  Mg. Its coal seam thickness is generally 16–20 m and its ash is generally less than 10%. The consuming coal of bitumite-fired power plants constructed mainly in west Inner Mongolia is from Dongsheng coal Basin. So, the Hg concentration in the bituminous coal in our study represents the Hg content of the coal consuming in the bitumite-fired power plant of Inner Mongolia.

Mercury in bottom ash is very little by comparison of Hg in the feed bitumite, which is  $1.86 \times 10^{-3}$  µg/g ( $n = 11$ ) accounting for 1.1% of Hg in feed coal, which agrees with the results by another Chinese research group [28]. It shows that the mercury in bitumite by high temperature burning is almost released into the flue gas, which is expected to be in the vapor phase according to equilibrium calculations [36,37]. Mercury in fly ash removed by FDC is higher to 0.64 µg/g ( $n = 11$ ) with the range of 0.51–0.90 µg/g, which is about 3–5 times of Hg in feed bitumite. It indicates that Hg is highly enriched in the fly ash after passing through the FDC relative to Hg in the feed coal. It also indicates that FDC has a remarkable Hg removal effect relative to other particles remover (e.g., ESP). Mercury concentration in WLFGD gypsum is nearly equal to the

**Table 4**  
Mercury in feed bitumite, bottom ash, fly ash, gypsum in JSBFPP.

Sampling time	Fired coal ( $\mu\text{g/g}$ )	Bottom ash ( $\times 10^{-3} \mu\text{g/g}$ )	Fly ash ( $\mu\text{g/g}$ )	Gypsum ( $\mu\text{g/g}$ )
April-4		$2.52 \pm 0.09$	$0.65 \pm 0.06$	
April-5	$0.16 \pm 0.00$ $3.25 \pm 0.62$	$1.66 \pm 0.12$ $0.67 \pm 0.05$	$0.77 \pm 0.08$	
April-6	$0.23 \pm 0.00$ $1.53 \pm 0.02$	$2.04 \pm 0.16$ $0.57 \pm 0.00$	$0.64 \pm 0.05$	
April-7	$0.18 \pm 0.00$ $2.18 \pm 0.44$	$1.28 \pm 0.02$ $0.63 \pm 0.08$	$0.58 \pm 0.04$	$0.19 \pm 0.00$
April-8	$0.22 \pm 0.02$ $0.12 \pm 0.00$	$1.38 \pm 0.11$ $1.33 \pm 0.15$	$0.90 \pm 0.01$ $0.59 \pm 0.01$	$0.15 \pm 0.00$ $0.21 \pm 0.00$
April-9	$0.12 \pm 0.00$ $0.16 \pm 0.00$ $0.11 \pm 0.01$	$1.33 \pm 0.07$ $1.96 \pm 0.13$	$0.55 \pm 0.01$ $0.51 \pm 0.05$	$0.15 \pm 0.04$ $0.17 \pm 0.03$ $0.16 \pm 0.01$
Average	$0.16 \pm 0.04$ ( $n = 7$ )	$1.86 \pm 0.48$ ( $n = 11$ )	$0.64 \pm 0.08$ ( $n = 11$ )	$0.17 \pm 0.02$ ( $n = 7$ )

concentration of Hg in fired bitumite. It also implies that WLFGD system not only desulfurizes and Hg removes, especially  $\text{Hg}^{2+}$  removal.

Mercury in feed lignite and the byproducts from the XLLFPP are listed in Table 5. The Hg in the feed lignite from Shengli coal mine in Xilinhot city of Xilinguole League, which is 7 km away from the XLLFPP, is slightly higher than Hg in bituminous coal and the mean value is  $0.19 \mu\text{g/g}$  ( $n = 11$ ) with the range of  $0.10$ – $0.34 \mu\text{g/g}$ , which also agree with the Hg content of other studies [34,35]. Xilinguole has abundant lignitous coal with the proven reserves of  $1.4 \times 10^{11}$  Mg which is in the first place in the country. Mercury in bottom ash is higher than that in bituminous coal and the mean value is  $0.021 \mu\text{g/g}$  ( $n = 10$ ) accounting for 11.1% of Hg in feed lignite, which is about 11 times in bituminous coal. It shows that Hg in lignite cannot be released entirely into flue gas by high temperature burning. It also elucidates that Hg occurrence in lignite combined partly with inorganic substances and perhaps in silicate-bound Hg [35]. Mercury in fly ash removed by ESP is  $0.22 \mu\text{g/g}$  ( $n = 7$ ), which is a little higher than Hg in lignite. It indicates that Hg in lignite is also enriched in the fly ash after passing through the ESP but the enrichment degree is not obviously with FDC fly ash. It implies that ESP has a certain Hg removal effect relative to FDC. Mercury concentration in WLFGD gypsum is higher of 2–3 times of Hg in feed lignite. It states clearly that the WLFGD system possesses obvious Hg removal efficiency, especially  $\text{Hg}^{2+}$  removal.

Mercury in feed lignite and the byproducts from the LFPP are showed in Table 6. The Hg in the feed lignite is  $0.09 \mu\text{g/g}$  ( $n = 20$ ) with range of  $0.05$ – $0.14 \mu\text{g/g}$ , which comes from three small local lignite mine nearby the LFPP. The mean Hg concentration in bottom ash is  $2.12 \times 10^{-3} \mu\text{g/g}$  ( $n = 7$ ) accounting for 2.4% of Hg in feed lignite. Mercury in fly ash removed by ESP + FDC is  $0.22 \mu\text{g/g}$  ( $n = 7$ ), which is higher to 2.5 times Hg in feed coal. By comparison with

the above investigated FDC and ESP device, we believe that FDC plays a major role in the enrichment of mercury. It indicates that Hg in lignite is also enriched in the fly ash after passing through the ESP + FDC which has obvious Hg removal effect. Mercury concentration in WLFGD gypsum is very lower to  $6.16 \times 10^{-3} \mu\text{g/g}$  ( $n = 7$ ) and the reason may be as same as our above discussions.

Our results clearly show that the fly ash from coal-fired power plants of Inner Mongolia can capture Hg in flue gas efficiently whether it is from bitumite-fired power plants or from lignite-fired power plants. From the perspective of power generation, fly ash is a waste material, while from a coal utilization perspective, fly ash is a resource yet to be fully utilized. The cement industry has been used it as a raw material for the production of concrete. Some of the utilization processes, which include high temperature procedures, can lead to all Hg reemissions [38] and emit considerable amount of Hg emissions to the atmosphere. Further researches should focus on these secondary Hg pollution problems.

Our results also clearly show that the Hg capture efficiency by fly ash is mainly related to the particles removal device. To cope with the mercury emission problem, efforts have been made to remove various types of mercury from the flue gas of utility boilers [18,19,21]. The relationships between Hg capture and fly ash composition and properties, such as carbon in the fly ash, the temperature of the flue gas at the point of ash collection, the form of the fly ash carbon, the chemistry of the coal, fly ash carbons from low-rank coals, bituminous coals and anthracites, all have been proved to capture Hg from flue gas and widely studied in response to concerns about Hg emissions to the atmosphere and potential new regulations related to these emissions [39–46]. Due to technical and economic limitations, no process has been commercially utilized beyond pilot scale tests [47]. However, our results have a little relation with the coal types or coal rank, the fly ash from

**Table 5**  
Mercury in feed lignite, bottom ash, fly ash, gypsum in XLLFPP.

Sampling time	Fired coal ( $\mu\text{g/g}$ )	Bottom ash ( $\times 10^{-3} \mu\text{g/g}$ )	Fly ash ( $\mu\text{g/g}$ )	Gypsum ( $\mu\text{g/g}$ )
April-12	$0.10 \pm 0.00$ $0.23 \pm 0.02$ $0.08 \pm 0.00$	$5.60 \pm 0.91$ $10.82 \pm 1.96$	– –	$0.50 \pm 0.04$ $0.42 \pm 0.03$
April-13	$0.18 \pm 0.00$ $0.18 \pm 0.02$	$19.24 \pm 1.54$ $17.27 \pm 1.13$	$0.26 \pm 0.04$ $0.27 \pm 0.02$	$0.34 \pm 0.02$ $0.36 \pm 0.00$
April-14	$0.34 \pm 0.01$ $0.26 \pm 0.07$	$69.49 \pm 16.71$ $23.52 \pm 1.22$	$0.19 \pm 0.02$ $0.18 \pm 0.00$	$0.37 \pm 0.04$ $0.41 \pm 0.03$
April-15	$0.14 \pm 0.02$ $0.19 \pm 0.01$	$42.65 \pm 7.34$ $7.38 \pm 0.20$	– $0.21 \pm 0.01$	$0.57 \pm 0.05$ $0.45 \pm 0.02$
April-16	$0.18 \pm 0.00$ $0.18 \pm 0.04$	$10.96 \pm 0.10$ $3.39 \pm 0.29$	$0.19 \pm 0.01$ $0.21 \pm 0.01$	$0.44 \pm 0.02$ $0.42 \pm 0.01$
Average	$0.19 \pm 0.05$ ( $n = 11$ )	$21.03 \pm 14.51$ ( $n = 10$ )	$0.22 \pm 0.03$ ( $n = 7$ )	$0.43 \pm 0.05$ ( $n = 10$ )

**Table 6**  
Mercury in feed lignite, bottom ash, fly ash, gypsum in LFPP.

Sampling time	Fired coal ( $\mu\text{g/g}$ )	Bottom ash ( $\times 10^{-3} \mu\text{g/g}$ )	Fly ash ( $\mu\text{g/g}$ )	Gypsum ( $\times 10^{-3} \mu\text{g/g}$ )
April-24	0.08 $\pm$ 0.01	1.65 $\pm$ 0.28	0.18 $\pm$ 0.02	8.57 $\pm$ 1.46
	0.11 $\pm$ 0.01			
	0.07 $\pm$ 0.00	1.01 $\pm$ 0.46	0.16 $\pm$ 0.00	4.21 $\pm$ 1.21
	0.09 $\pm$ 0.00			
April-25	0.06 $\pm$ 0.01	3.48 $\pm$ 0.33	0.17 $\pm$ 0.00	7.28 $\pm$ 0.53
	0.10 $\pm$ 0.01			
	0.05 $\pm$ 0.00			
	0.10 $\pm$ 0.01	2.26 $\pm$ 0.06	0.21 $\pm$ 0.02	7.59 $\pm$ 1.27
	0.08 $\pm$ 0.01			
April-26	0.08 $\pm$ 0.00	1.84 $\pm$ 0.05	0.20 $\pm$ 0.01	4.54 $\pm$ 0.16
	0.12 $\pm$ 0.01			
	0.11 $\pm$ 0.03			
	0.11 $\pm$ 0.01	2.00 $\pm$ 0.05	0.39 $\pm$ 0.01	4.24 $\pm$ 0.02
	0.10 $\pm$ 0.01			
	0.07 $\pm$ 0.00			
April-27	0.13 $\pm$ 0.01	2.57 $\pm$ 0.47	0.23 $\pm$ 0.00	6.70 $\pm$ 0.63
	0.14 $\pm$ 0.01			
	0.07 $\pm$ 0.00			
Average	0.09 $\pm$ 0.02 (n = 20)	2.12 $\pm$ 0.56 (n = 7)	0.22 $\pm$ 0.05 (n = 7)	6.16 $\pm$ 1.57 (n = 7)

Inner Mongolia may be the further commercial utilization and need further research.

### 3.3. Mercury mass balance to mercury fates in coal and mercury discharge factors from coal-fired power plants

In order to decide mercury fates in coal and check the reliability of our OHM sampling method, sampling equipment and the Hg analytical accuracy of flue gas, coal and the byproducts, mercury mass balance are carried out with the three sampling and analytical campaigns in Fig. 1. The consumption data of coal, fresh water and limestone consumptions, and the discharge data of bottom ash, fly ash and gypsum for every studied power plant every year are obtained from actual statistical results of the power plants in recent years. The flue gas emissions are from CEM on-line to the local and provincial environmental protection networking. The principal Hg input stream to a coal-fired boiler is the coal. In fact, mercury input to the coal combustion and subsequent flue gas control devices include little Hg in ammonia or urea for denitration, Hg in fresh water and limestone powder for desulfurization besides Hg in coal. Mercury in ammonia and fresh water are below 0.5  $\mu\text{g}/\text{dm}^3$  and the Hg in limestone powders are 4.0–5.0  $\mu\text{g}/\text{kg}$  in general. Mercury output to the coal combustion and subsequent flue gas control devices include bottom ash discharges, fly ash discharges by FDC or ESP or ESP + FDC, gypsum discharges by WLFGD and the Hg emissions with cleaned flue gas. We calculate the Hg in the process water for desulfurization according to the fresh water consuming and not to take it as one Hg discharge source because it is always circulating. Mercury concentration in process water after WLFGD in XLLFPP is 5.93  $\mu\text{g}/\text{dm}^3$  (n = 1).

After passing through ammonia SCR, FDC and WLFGD, the ratio of Hg input/output of the JSBFPP is 94% for April 9 and the Hg mass balance during the sampling period is 114% (Fig. 1A). For XLLFPP, the ratio of Hg input/output is 92% for April 13 and the Hg mass balance in sampling period is 110% (Fig. 1B). For LFPP, after passing through urea SCR, ESP + FDC and WLFGD, the ratio of Hg input/output of this combustion is 112% for April 25 and the Hg mass balance during our sampling period is 115% (Fig. 1C). Our Hg mass balance calculations show that our sampling method, sampling equipments, analysis method and research method are more reliable and reach a certain accuracy.

We can deduce consequentially Hg fates and Hg discharge factors for bitumite-fired power plants with SCR + FDC + WLFGD device (Fig. 2A) from JSBFPP. Almost all mercury in bituminous coal (99.95%) is transferred to the form of gaseous mercury and entered into high temperature flue gas after high temperature (–1600 K) combustion. With the flue gas outflows the furnace, then followed by SCR and FDC, mercury in the flue gas is most enriched in fly ash (90.85%) which is discharged to environment or as a raw material of the construction industry. Then, the Hg in flue gas is reduced considerably and entered into the WLFGD system with the flue gas, and a part of Hg in the flue gas is transferred to desulfurization gypsum (3.46%) and the process water (1.85%). Eventually, a fraction of Hg (3.80%) in coal finally emits to the atmosphere with flue gas through the chimney. The Hg emitted to the atmosphere include 93.23% of Hg as  $\text{Hg}^0$  contributing to the global cycling, 5.06% of Hg as  $\text{Hg}^{2+}$  and 1.71% of Hg as  $\text{Hg}^p$  deposited in the vicinity area of the bitumite-fired power plants (Fig. 2A).

There are obvious differences in the fates and Hg discharges factors of Hg in lignite with SCR + ESP + WLFGD and that of bitumite with SCR + FDC + WLFGD device after power plants. 99.59% of Hg in lignituous coal is released to the flue gas byproducts including 65.51% enriched notably in fly ash, 9.58% transferred in gypsum and 1.56% circulated in process water, and 22.26% of Hg in lignite is emitted to the atmosphere including 88.88% of Hg as  $\text{Hg}^0$  contributing to the global cycling, 11.05% of Hg as  $\text{Hg}^{2+}$  and 0.08% of Hg as  $\text{Hg}^p$  deposited in the vicinity area of the lignite-fired power plants after SCR, ESP and WLFGD (Fig. 2B).

For Hg fates in lignite and Hg discharge factors of lignite-fired power plants with urea SCR + ESP + FDC + WLFGD after power plants burning, 99.90% of Hg in lignite is released to the flue gas by-products including 90.84% enriched significantly in fly ash, 0.04% entered in gypsum and 1.33% circulated in process water, and 7.70% of Hg in lignite is emitted to the atmosphere including 85.01% of Hg as  $\text{Hg}^0$  contributing to the global cycling, 14.72% of Hg as  $\text{Hg}^{2+}$  and 0.27% of Hg as  $\text{Hg}^p$  deposited in the vicinity area of the lignite-fired power plants after SCR + ESP + FDC + WLFGD (Fig. 2C). It is quite unexpected that Hg in gypsum from LFPP is very lower but the desulfurization effect is very good. We speculate the reason as same as the above discussions (see Section 3.1).

Our Hg discharge factors include not only Hg species emission factors which emit directly to the atmosphere from coal-fired power plants, also the Hg discharge factors with bottom ash, fly ash and

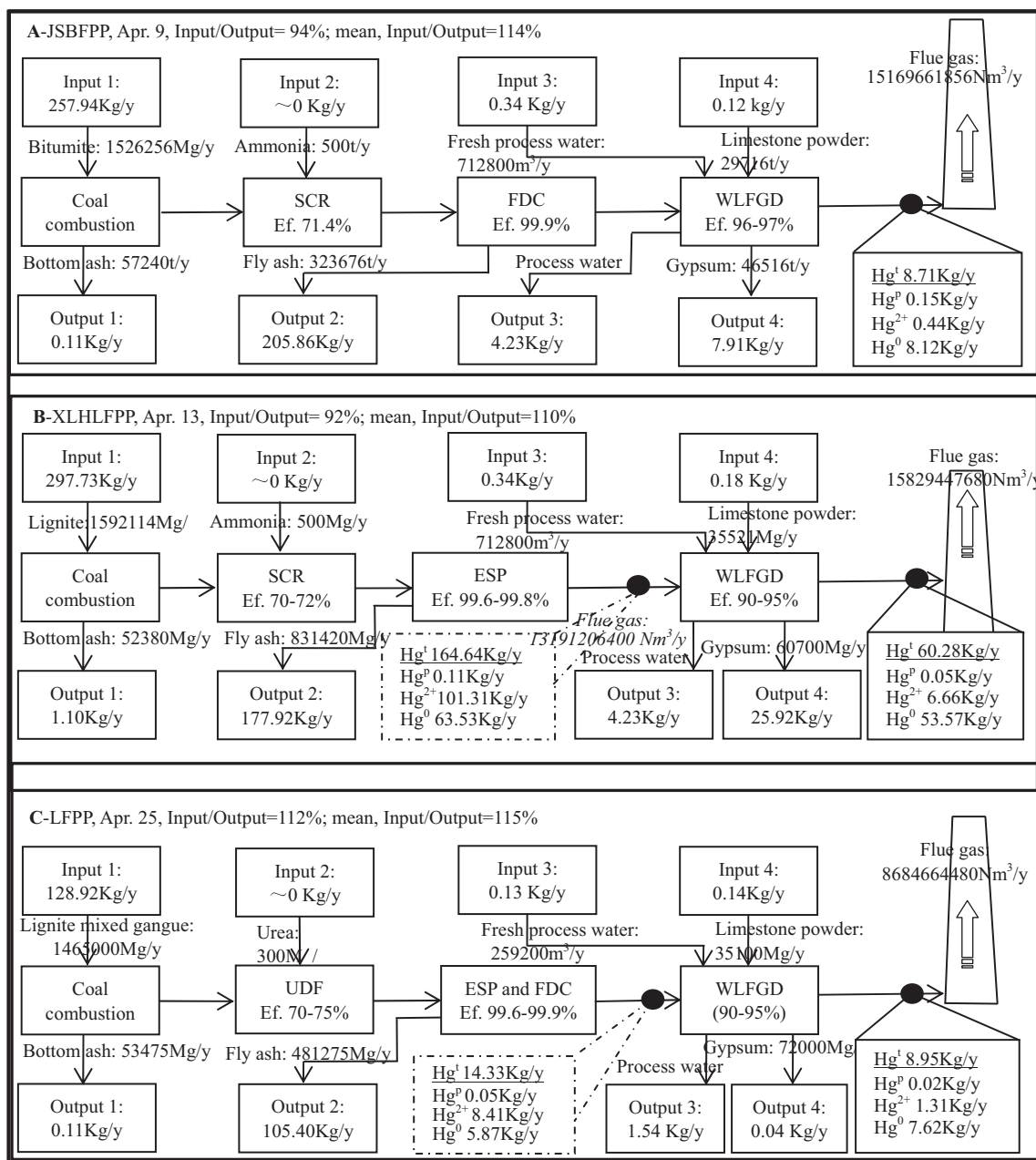


Fig. 1. Mercury mass balance and fates of coal-fired power plants in Inner Mongolia.

gypsum and Hg cycling in process water which may indirectly emit to the atmosphere by other combustion. Our direct Hg emission factors plus the indirect Hg discharge factors respectively are same as Streets et al. [5], Pacyna et al. [3,48] and Pirrone et al. [4].

By comparison, we conclude that the Hg fates and Hg discharge factors for a pulverized coal-fired boiler just installed FDC devices are similar to each other (see Fig. 2A and C) whether it consumes bituminous coal or lignitous coal except for Hg with gypsum discharges. Because FDC has a high removal efficiency of mercury in flue gas, it is the best choice to reduce the emission of mercury to the atmosphere. The direct Hg species emission factors in cleaned flue gas are similar to each other with the consuming coal type (see Fig. 2B and C). The relatively consistent discharge factors also show their credibility and can be expanded to more extensive coal-fired power plants. Therefore, the Hg discharge factors of pulverized coal-fired power plants with SCR + FDC (or FDC + ESP) + WLFGD are same as that of JSBFPP and the Hg discharge factors

of pulverized coal-fired power plants with SCR + ESP + WLFGD are same as that of XLFPF.

### 3.4. Mercury emissions from coal-fired power plants in Inner Mongolia

The coal consuming in power plants including bitumite and lignite in Inner Mongolia from 2007 to 2014 [49] are listed in Table A.4 of Appendices. With the nationwide air control actions, all of the coal-fired power plants were required to install reliable and efficient NO<sub>x</sub>C, PPC and FGD device. NO<sub>x</sub>C was mainly ammonia injection SCR. However, only 10% of PPC is installed with FDC and 90% of the PPC is installed with ESP [28]. The FGD devices are all of WLFGD. Therefore, the Hg discharges are based on the weight of the PPC and take the corresponding Hg release factors for calculation. The calculation methods are the same as that of our previous studies on mercury emission from Guizhou coal-fired power plants [27]. In light of the above calculation and



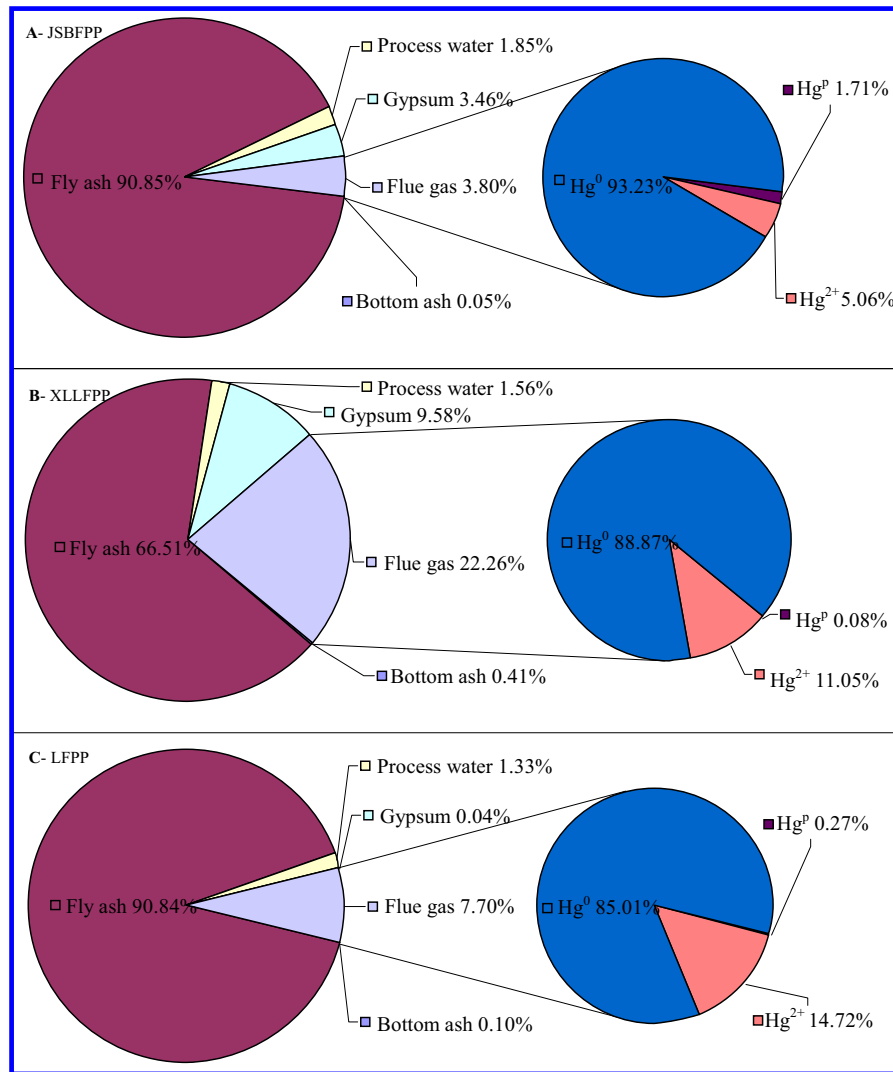


Fig. 2. Mercury discharge factors from pulverized coal-fired power plants in Inner Mongolia.

discussions, we estimate the yearly Hg discharges from coal-fired power plants from 2007 to 2014 (Fig. 3).

Mercury in coal including bitumite and lignite is almost all released into flue gas through higher temperature burning of coal-fired power plants. With the flue gas go through the NO<sub>x</sub>C and PPC, mercury in flue gas is greatly reduced and enriched mostly in the fly ash by FDC or ESP, which the mercury enrichment degree in fly ash is higher than that by ESP. Subsequently, the Hg in the flue gas is further reduced by WLFGD system and the Hg in the flue gas is transferred to the gypsum and process water. At last, mercury in cleaned flue gas is a rare part of Hg in coal.

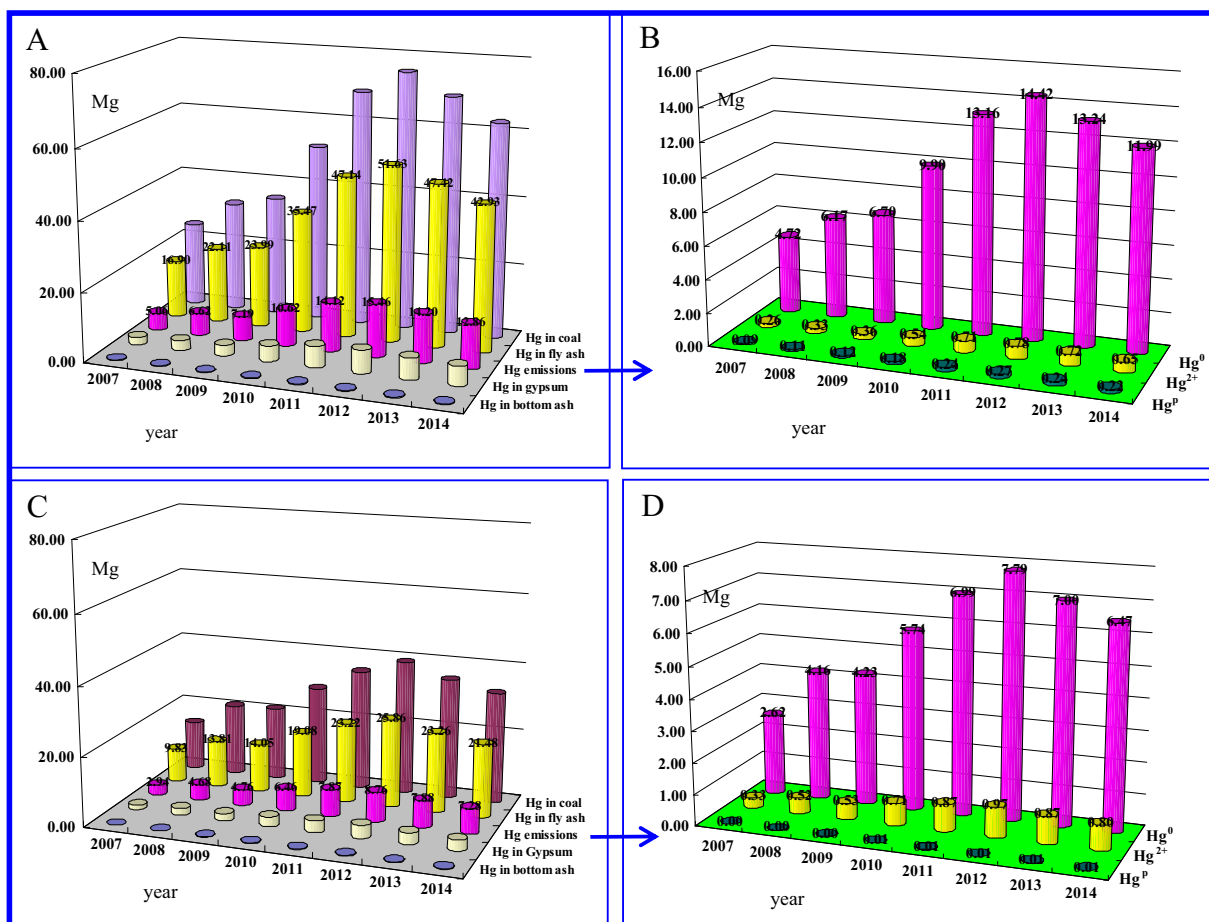
The maximum discharge source of Hg for bitumite-fired power plants (BFPPs) in Inner Mongolia is fly ash by FDC or ESP instead of Hg emitted with flue gas into the atmosphere. Mercury discharges from fly ash of BFPPs increased sharply from 19.90 Mg to the maximum of 54.63 Mg from 2007 to 2012 and decrease to 42.98 Mg in 2014. The maximum of mercury emissions to the atmosphere is 15.46 Mg in 2012 where 14.42 Mg Hg emitted as Hg<sup>0</sup>, 0.78 Mg as Hg<sup>2+</sup> and 0.27 Mg as Hg<sup>p</sup>. In addition, the maximum of mercury transferred into gypsum is 6.79 Mg in 2012.

For lignite-fired power plants (LFPPs) in Inner Mongolia, the maximum discharge source of Hg is also fly ash by FDC or ESP instead of Hg emitted with flue gas into the atmosphere. Mercury

discharges from fly ash of LFPPs increased sharply from 9.83 Mg to the maximum of 25.86 Mg from 2007 to 2012 and decrease to 24.48 Mg in 2014. The maximum of mercury emissions to the atmosphere is 8.76 Mg in 2012 where 7.79 Mg Hg emitted as Hg<sup>0</sup>, 0.97 Mg as Hg<sup>2+</sup> and 0.01 Mg as Hg<sup>p</sup>. In addition, the maximum of mercury transferred into gypsum is 3.77 Mg in 2012.

According to our above results and discussion, mercury emitted directly to the atmosphere with flue gas is much less than that of Hg enriched in fly ash and Hg transferred to the desulfurization gypsum. Our results state clearly that mercury emissions from coal-fired power plants are not the largest source of mercury to the atmosphere in normal operation of the current efficient denitrification, dust removal and desulfurization facilities. The largest mercury emissions to the atmosphere can or may be the utilization industry of fly ash and gypsum, such as cement industry and brick industry because the fly ash and gypsum is acquisitive for raw materials of cement industry and brick industry.

In summary, the coal-fired power plants of Inner Mongolia emit directly 21% of the Hg in coal to the atmosphere, the maximum of mercury emissions is 24.22 Mg in 2012. Because of the coal production of Inner Mongolia accounting for more than 1/4 of national coal production, we rough estimate that the Chinese thermal power plants emit directly less than 100 Mg Hg to the atmosphere



**Fig. 3.** Mercury discharges from coal-fired power plants in Inner Mongolia ((A) Hg discharges from bitumite-fired power plants; (B) Hg speciation and emissions from bitumite-fired power plants; (C) Hg discharges from lignite-fired power plants; (D) Hg speciation and emissions from lignite-fired power plants).

every year at the nationwide air control actions, which is far less than the previous estimation by other researchers. The maximum of Hg discharges with fly ash and gypsum of Inner Mongolia is 80.49 Mg and 10.56 Mg t in 2012, respectively. The national Hg discharges with fly ash and gypsum every year is about 300 Mg and 82 Mg, respectively and it may be re-emitted mostly to the atmosphere by the utilization industry every year.

#### 4. Conclusion

Actual mercury speciation in flue gas has been comprehensively measured from coal-fired power plants in the largest coal production province of China, Inner Mongolia. Mercury emission is in the dominant form of  $\text{Hg}^0$  (>85%), the  $\text{Hg}^{2+}$  (<15%) and the  $\text{Hg}^p$  (<2%) is a fraction of  $\text{Hg}^t$  in the flue gas. The WLFGD device has very higher removal efficiency for  $\text{Hg}^{2+}$  reaching 87–95%.

The Hg discharge factors of pulverized coal-fired power plants with SCR + FDC (or FDC + ESP) + WLFGD are same as that of JSBFPP. All mercury in pulverized coal is transferred to the form of gaseous mercury. For indirect Hg discharge factors, 99.95% of Hg in pulverized feed coal is released to the flue gas by-products including 90.85% enriched notably in fly ash, 3.46% transferred in gypsum and 1.85% circulated in process water. 3.80% of Hg in pulverized coal is emitted directly to the atmosphere including 93.22% of Hg as  $\text{Hg}^0$  contributing to the global cycling, 5.06% of Hg as  $\text{Hg}^{2+}$  and 1.71% of Hg as  $\text{Hg}^p$  deposited in the vicinity area of the bitumite-fired power plants.

The Hg discharge factors of pulverized coal-fired power plants with SCR + ESP + WLFGD are same as that of XLLFPP. All mercury

in pulverized coal is transferred to the form of gaseous mercury. For indirect Hg discharge factors, 99.59% of Hg in pulverized coal is released to the flue gas byproducts including 66.51% enriched notably in fly ash, 9.58% transferred in gypsum and 1.56% circulated in process water. 22.26% of Hg in pulverized coal is emitted directly to the atmosphere including 88.88% of Hg as  $\text{Hg}^0$  contributing to the global cycling, 11.05% of Hg as  $\text{Hg}^{2+}$  and 0.08% of Hg as  $\text{Hg}^p$  deposited in the vicinity area of the lignite-fired power plants.

The maximum of mercury emissions from coal-fired power plants of Inner Mongolia is 24.22 Mg in 2012. The Chinese coal-fired power plants emit directly less than 100 Mg Hg to the atmosphere every year at the nationwide air control actions. The maximum of Hg discharges with fly ash and gypsum from coal-fired power plants of Inner Mongolia is 81 Mg and 11 Mg in 2012, respectively. The national Hg discharges with fly ash and gypsum from coal-fired power plants every year is about 300 Mg and 82 Mg, respectively and it may be re-emitted mostly to the atmosphere by the utilization industry every year. Mercury emissions from coal-fired power plants are not the largest source of mercury to the atmosphere in normal operation of the current efficient denitrification, dust removal and desulfurization facilities. The largest mercury emissions to the atmosphere can be the utilization industry of fly ash and gypsum.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2016.04.037>.

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