

1 Mercury emission and speciation of coal-fired power 2 plants in China

3 S. Wang¹, L. Zhang¹, G. Li¹, Y. Wu¹, J. Hao¹, N. Pirrone², F. Sprovieri², M. P. Ancora²

4 ¹Department of Environmental Science and Engineering, and State Key Joint Laboratory of
5 Environment Simulation and Pollution Control, Tsinghua University, Beijing 100084, China

6 ²CNR – Institute of Atmospheric Pollution Research, Via Salaria Km 29.300-CP10, 00015
7 Monterotondo St., Rome, Italy

8 *Correspondence to:* S. Wang (shxwang@tsinghua.edu.cn)

9 Abstracts

10 Comprehensive field measurements are needed to understand the mercury emissions from
11 Chinese power plants and to improve the accuracy of emission inventories. Characterization
12 of mercury emissions and their behavior were measured in six typical coal-fired power plants
13 in China. During the tests, the flue gas was sampled simultaneously at inlet and outlet of
14 Selective Catalytic Reduction (SCR), electrostatic precipitators (ESP), and flue gas
15 desulfurization (FGD) using the Ontario Hydro Method (OHM). The pulverized coal, bottom
16 ash, fly ash and gypsum were also sampled in the field. Mercury concentrations in coal
17 burned in the measured power plants ranged from 17 to 385 $\mu\text{g}/\text{kg}$. The mercury mass
18 balances for the six power plants varied from 87 to 116% of the input coal mercury for the
19 whole system. The total mercury concentrations in the flue gas from boilers were at the range
20 of 1.92–27.15 $\mu\text{g}/\text{m}^3$, which were significantly related to the mercury contents in burned coal.
21 The mercury speciation in flue gas right after the boiler is influenced by the contents of
22 halogen, mercury, and ash in the burned coal. The average mercury removal efficiencies of
23 ESP, ESP plus wet FGD, and ESP plus dry FGD-FF systems were 24%, 73% and 66%,
24 respectively, which were similar to the average removal efficiencies of pollution control
25 device systems in other countries such as US, Japan and South Korea. The SCR system
26 oxidized 16% elemental mercury and reduced about 32% of total mercury. Elemental mercury,
27 accounting for 66–94% of total mercury, was the dominant species emitted to the atmosphere.
28 The mercury emission factor was also calculated for each power plant.

1

2 **1 Introduction**

3 Mercury (Hg) is one of the most important environmental contaminants that has aroused
4 a global concern due to its toxicity, long range transport, persistence and bioaccumulation in
5 the environment. Coal combustion is believed to be the main source of mercury emissions to
6 the atmosphere, accounting for 60%, or even more, of the total mercury emissions (Pacyna et
7 al., 2006). Streets et al. (2009) suggested that the change of global anthropogenic Hg
8 emissions may range anywhere from -4% to +96% by 2050, depending on future
9 implementation of best available technology (BAT) in coal-fired utilities and energy demand.

10 Mercury is present in coal in trace amounts (0.01–0.5 mg/kg). At the high temperatures
11 in combustion zone of boilers, combustion releases the Hg in coal into the exhaust gas as
12 elemental mercury (Hg^0). This vapor may then be oxidized by HCl, SO_2 , and fly ash in flue
13 gas due to thermo-chemical processes (Meij et al., 2002; Niksa et al., 2004; Lee et al., 2006;
14 Park et al., 2008). Oxidized mercury (Hg^{2+}) is soluble and has a tendency to associate with the
15 particles in flue gas to form particulate-bound mercury (Hg_p). Therefore, emissions of Hg^{2+} ,
16 may be efficiently controlled by typical air pollution control devices (APCD), such as
17 electrostatic precipitators (ESP), fabric filter (FF), and flue gas desulfurization (FGD) systems
18 (US EPA, 1997, 2002a, 2000b). However, because the relative proportions of Hg^{2+} , Hg_p and
19 Hg^0 can vary widely, the corresponding reductions in total mercury achieved by APCD vary
20 (Pavlish et al., 2003; Srivastava et al., 2006; Lee et al., 2008; Cao et al., 2008a). For example,
21 the removal efficiency of Hg from the flue gas by a combination of cold side ESP and wet
22 FGD range from 24 to 70%. Emission speciation is an important source of uncertainty when
23 assessing the atmospheric fate of mercury because Hg^{2+} , Hg_p and Hg^0 have very different
24 physico-chemical characteristics and, consequently, different atmospheric lifetimes.

25 As the largest coal producer and consumer in the world, China releases amounts of Hg
26 that have been increasing rapidly in recent years and are getting more and more attention (Wu
27 et al., 2006; Pirrone et al., 2009). Wu et al. (2006) estimated mercury emissions from
28 coal-fired power plants in China have been growing at an annual growth rate of 5.9% during
29 1995–2003, much higher than the average growth rate of all coal consumption sectors. By

1 2007, the coal consumption by power generation in China increased to 1.49 billion tons,
2 indicating an even higher annual growth rate during 2004–2007.

3 However, mercury emissions for China have large uncertainties because comprehensive
4 field tests to characterize Hg emissions from coal-fired power stations are only available for
5 the developed countries such as Netherlands (Meij and Winkel, 2006), United States (US EPA,
6 2002b) and Japan (Yokoyama et al., 2000; Ito et al., 2006). Due to the paucity of information
7 on Hg emission rates, speciation profiles from Chinese utility boilers and the capture of Hg in
8 Chinese air pollution control devices, the uncertainty of total Hg emissions was estimated to
9 be approximately –40%/+70% for coal-fired power plants in China (Streets et al., 2005; Wu et
10 al., 2009). There are even higher uncertainties for the speciation profiles. Therefore there has
11 been increasing needs to characterize the Hg emissions from coal-fired power plants in China
12 (Niksa and Fujiwara, 2009; Clack, 2009).

13 Up to now, mercury emission tests have been conducted only for a few power plants in
14 China (Chen et al., 2007; Zhang et al., 2008; Tang et al., 2007). Chen et al. (2007) and Zhang
15 et al. (2008) reported Hg speciation data based on flue gas monitoring with the Ontario Hydro
16 protocol from 6 plants at the inlets and outlets to the particle collection devices. They found
17 that the average mercury removal efficiency of the ESP systems was 11%, and that of the FF
18 systems was 52%, much lower than the average removal efficiencies of pollution control
19 devices in US plants. The tests also indicated that share of Hg⁰ vs. total Hg in Chinese boilers
20 is much higher than that found in US boilers. For example, the share of Hg⁰ is 26% on
21 average for the outlet of ESPs tested in the US, while such ratio increases to 56% on average
22 for Chinese boilers, which may be mainly because the compositions of Chinese coals differ
23 from those of US coals. At the end of 2008, about 48% of Chinese coal-fired power plants
24 were equipped with FGD. Considering that FGDs are going to be installed in all new units
25 (according to the 11th five-year plan), the application rate of FGDs will reach up to 60% in
26 2010 and will keep increasing during 2010–2020 (Zhao et al., 2008). However, the test data
27 for Hg emissions from coal-fired power plants with ESPs plus FGD are scarce in China.
28 Therefore, more field tests are needed on more Chinese power plants to understand the full
29 details of mercury partitioning and emissions from Chinese power plants, especially those
30 with ESPs plus FGD.

1 In this paper, we present a comprehensive analysis of onsite measurements for mercury
2 emission and behavior in six Chinese coal-fired power plants. The Ontario Hydro Method was
3 used to sample the mercury in flue gases, at the inlet of the APCDs and at the stack, in order
4 to understand the change in chemical forms of mercury. The fate of Hg in coal-fired power
5 plants, including its removal by APCDs was quantified by collecting and analyzing gaseous
6 samples as well as solid samples such as coal, fly ash, bottom ash, gypsum (by-product from
7 FGD), and effluents. The assessment of mercury emission and total mercury mass balance
8 was estimated from the gathered sample data.

9 10 **2 Experimental methods**

11 **2.1 Power plants tested**

12 Onsite tests were carried out in six typical coal-fired power plants across China,
13 covering the most common unit types in terms of boiler variety, coal quality, and emission
14 control device. As shown in Table 1, all the tested units are pulverized coal boilers ranging
15 from 100 to 600 MW. Among these units, three of them burn bituminous coal, two burn
16 lignite coal and one burns anthracite coal. All tested units have ESP or FF systems for
17 removing particles in flue gases. Five of six tested units install wet FGD while plant 5 uses
18 CFB-FGD, a type of dry FGD, to control SO₂ emissions. Plant 6 installs Selective Catalytic
19 Reduction system (SCR) to control NO_x emissions. During the test period, all of the power
20 units were operating under normal conditions.

21 **2.2 Sampling and analysis methods**

22 The APCD configuration and all the sampling locations in power plants are shown in
23 Fig. 1. The Ontario Hydro Method (ASTM, 2002) was performing onsite tests for total
24 mercury and speciation profile at inlet/outlet of SCR (if applicable), ESP, and FGD. The
25 samples were withdrawn from the flue gas stream isokinetically through a probe/filter system
26 maintaining the flue gas at 120 °C, which is followed by a series of impingers in an ice bath.
27 The particulate-bound mercury is collected on the quartz fiber filter. The Hg²⁺ is collected in
28 the first three impingers with 1.0 mol/L potassium chloride (KCl) solution and Hg⁰ is
29 collected in subsequent impingers, of which one impinger containing a 5% nitric acid (HNO₃)
30 and 10% peroxide (H₂O₂) solution and three impingers with a solution of 10% sulfuric acid

1 (H₂SO₄) and 4% potassium permanganate (KMnO₄), as shown in Fig. 2.

2 Liquid and solid samples were collected in the field and analyzed in accordance with US
3 EPA 7470A for liquid samples and 7473 for solid samples. The impinger solutions are
4 recovered and analyzed with Cold Vapor Atomic Absorption Spectrophotometry (CVAAS)
5 type mercury analyzer with a detection limit of 0.005 µg/m³. The samples of coal, fly ash,
6 bottom ash and gypsum were analyzed with Direct Mercury Analyzer (Milestone DMA-80,
7 Italy) with a detection limit of 0.05 µg/g.

8 **2.3 Quality assurance and quality control (QA/QC)**

9 All sampling tests and analysis were carried out in triplicate or more to obtain parallel
10 results and reduce uncertainties. The parallel tests were found to be reproducible. Differences
11 of tests in each sampling site are within a range of ±20%, which is acceptable for onsite tests.
12 Most of the differences came from the fluctuation of flue gas because of the time difference of
13 sampling. The error in the analytical procedure is less than 5%. The data obtained from tests
14 at the same conditions were averaged to get the final results.

15 Each of the seven impingers in the sampling train of Ontario Hydro Method was
16 recovered and analyzed separately. Thereby the success of the sample collection can be
17 evaluated. For example, if the first KCl impinger collected over 85% of the Hg²⁺ and the last
18 one collected less than 5%, we could have a reasonable degree of confidence that the Hg²⁺
19 had been successfully collected. Otherwise we would hypothesize that a considerable
20 breakthrough of mercury species had occurred and the sample collection was not successful.

21 The removal efficiencies of APCDs can be calculated either by the mercury
22 concentration in flue gas at inlet/outlet of APCDs or by the mass balance. The removal
23 efficiency based on the mercury concentration in flue gas at inlet/outlet of APCDs and that
24 based on the mass balancing were compared and their differences were less than 20%.

26 **3 Results and discussion**

27 **3.1 Properties of feed-coal**

28 The six selected plants are located in different parts of China, and thus the coal collected
29 from each plant has different qualities. Differences in coals quality may lead to a different
30 behavior of mercury species in the flue gas. The results of proximate and ultimate analysis of

1 feed-coals were presented in Table 2. The contents of mercury, chlorine (Cl) and ash in coal
2 have significant impacts on Hg speciation. The mercury content in these coals varies from 17
3 to 385 $\mu\text{g}/\text{kg}$, which agrees with mercury contents of 10–570 $\mu\text{g}/\text{kg}$ in Chinese coals found by
4 other researchers (USGS, 2004; Zheng et al., 2007a,b). The chlorine content in feed-coal
5 varies from 63–318 mg/kg , which is much lower than the average value of US coals, 628
6 mg/kg (Ren et al., 2006). The ash content of tested coals varies from 7.42 to 36.32% and
7 sulfur content ranges from 0.44 to 4.03%. The ash and sulfur content of coals used in plant
8 1–5 is much higher than that in US coals. To identify the impacts of bromine (Br) and fluorine
9 (F) on Hg emissions, we also analyzed the content of Br and F in tested coals. The results
10 indicate that the fluorine in coal ranges from 114 to 235 mg/kg and bromine from 34 to 63
11 mg/kg .

12 **3.2 Mercury concentration and speciation in flue gas**

13 Table 3 gives the concentrations of total Hg, Hg^0 , Hg^{2+} and Hg_p across APCDs in 6
14 power plants. All the data are normalized to dry flue gas in standard conditions.

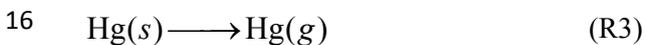
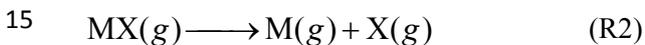
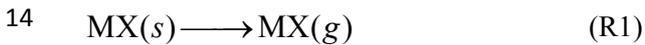
15 **3.2.1 Mercury release from coal combustion**

16 The total mercury concentration in flue gas at inlet of ESP (at inlet of SCR for plant 6)
17 varies over a large range, from 1.92 to 27.15 $\mu\text{g}/\text{m}^3$. There is significant correlation between
18 the mercury content of coal and the total mercury concentration in flue gas released from the
19 tested boilers (as shown in Fig. 3), with a correlation coefficient of 0.98 for bituminous and
20 lignite coal-fired boilers. The anthracite coal-burning unit emitted higher concentration of
21 total mercury than the bituminous and lignite coal-fired boilers, which is in line with a
22 previous study in Korea (Park et al., 2008). Further study is necessary to investigate the
23 mechanism of Hg release from anthracite.

24 During combustion, most of the Hg in coal is first released in Hg^0 form. With the
25 existence of Cl, Br, and particles in flue gas, part of the Hg^0 is oxidized into Hg^{2+} either by gas
26 phase oxidation or catalytic oxidation (Galbreath and Zygarlicke, 2000). As the flue gas
27 temperature decreases, part of the Hg^0 and Hg^{2+} in the gas phase condenses on or is adsorbed
28 by fly ash particles. According to Table 3, the speciation profile varies a lot among the tested
29 plants. Generally the share of Hg^0 to total Hg in flue gas released from lignite coal-burning
30 boilers (80% on average) is significantly higher than that from the bituminous coal-fired

1 boilers (30% on average). By contrast, the share of Hg^{2+} to total Hg in flue gas released from
2 lignite coal-burning boilers is significantly lower than that from the bituminous coal-fired
3 boilers. The share of Hg_p to total Hg varies from 2 to 22%, which is significantly lower than
4 that from US tests.

5 Halogen in coal can be a key factor influencing Hg speciation. We collected data from
6 over twenty onsite tests and analyzed the effect of chlorine content in coal on mercury
7 speciation in the flue gas released from the boilers, as shown in Fig. 4a. We found that, with
8 three sample points excluded, the correlation coefficient reached 0.75, indicating that chlorine
9 content of coal may have significant effect on distribution of different mercury species. This
10 is in line with previous studies (Yang et al., 2007; Chen et al., 2007). The follow reactions
11 show the mechanism of mercury changing from elemental form to oxidized form with the
12 presence of halogens (Cl and Br). In the reactions, M stands for metal and X stands for
13 halogen.



18 The three exceptional sample points in Fig. 4a are probably because of the bromine
19 content of coal. There is evidence that bromine species are capable of enhancing the
20 conversion of Hg^0 to Hg^{2+} (Liu et al., 2007; Cao et al., 2008b; Niksa et al., 2009). We found
21 there was significant correlation between the Hg^{2+} percentage in flue gas released from the
22 tested boilers and the bromine content of coal (see Fig. 4b), with a correlation coefficient of
23 0.83. The bromine content of coal eventually determines the Hg^{2+} percentage in the flue gas
24 more than chlorine.

25 The particulate concentration in flue gas is largely affected by the ash content in coal
26 burned. Particles tend to be the adsorbents in flue gas. Mercury adsorption onto the
27 particulates in flue gas can be considered as mono-molecule-layer adsorption. Therefore,
28 Langmuir's adsorption isotherm formula (see Eq. 1) can be applied in this case.

1
$$\gamma = \frac{Kbp}{1+bp} \quad (1)$$

2 In Eq. (1), γ is the total amount of adsorption; K and b are constants; p is the partial pressure
3 of the adsorbate. Mercury is a trace element in flue gas, which means $bp \ll 1$. Accordingly,
4 Eq. (1) can be rewritten as Eq. (2):

5
$$\gamma = Kbp \quad (2)$$

6 For a certain amount of adsorbent, more mercury leads to higher mercury partial
7 pressure, and higher partial pressure leads to larger amount of adsorption. In other words, the
8 higher ratio of mercury content to ash content of coal (M/A ratio) contributes to higher
9 adsorption rate, i.e. the Hg_p percentage in flue gas. The correlation between M/A ratio and
10 Hg_p percentage was tested in Fig. 5. We found that the correlation coefficient was 0.79 when
11 we removed two exceptional sample points. The exception might have something to do with
12 the temperature, which is another sensitive variable in the adsorption process.

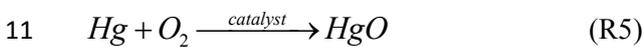
13 **3.2.2 Mercury behavior across APCDs**

14 ESP is the most commonly used APCD in coal-fired power plants. In China, more than
15 90% of total installed power capacity has ESPs. Particulate-bound mercury is simultaneously
16 removed when the particles are captured by ESP. ESPs can capture nearly all Hg_p , as shown in
17 Table 3. Although gas phase mercury is barely removed by ESPs, it does transform
18 continuously across the ducts and devices. Oxidized mercury with positive charge, on the
19 other hand, will move forward along with the flue gas. Therefore, Hg^{2+} is unlikely to be
20 adsorbed onto particles to transform to Hg_p . However, some of the Hg^0 will be adsorbed or
21 oxidized into Hg_p or Hg^{2+} when cooling to 400 °C, which explains the fact that total gaseous
22 mercury decreased when going through ESP in some tests (plant 1, 2 and 5). The
23 concentration of total gaseous mercury at outlet of ESP was 18–30% lower than that at inlet
24 of ESP for plant 1, 2 and 5. Another process taking place inside ESP is the transformation of
25 Hg^{2+} to Hg^0 . If no Hg^{2+} was supposed to be adsorbed to particles, then all the Hg^{2+} reduction
26 occurred across the ESP because all Hg^{2+} was transformed into Hg^0 . The balance between
27 Hg^{2+} and Hg^0 was broken when some of the Hg^0 was adsorbed onto the particles and removed
28 by ESP. To build up a new balance, some Hg^{2+} converts into Hg^0 . The rate is kinetically

1 controlled and the concentration of Hg^{2+} played important role, as shown in Fig. 6. As a result,
2 the share of Hg^0 at outlet of ESP was 46% on average, which was much higher than that at
3 outlet of ESPs tested in the United States (26% on average).

4 Wet FGD is also widely used in Chinese coal-fired power plants. Due to the solubility of
5 Hg^{2+} in water, 67–98% of Hg^{2+} was absorbed in the scrubber solution and retained in the FGD
6 gypsum. Higher concentration of Hg^{2+} in the flue gas led to higher removal efficiency in wet
7 FGD (see Fig. 7). The reduction of Hg^0 in flue gas across wet FGD was less than 30%.

8 Plant 6 is the only tested plant installing SCR. According to Table 3, the three mercury
9 species were redistributed across SCR. The oxidability of flue gas was enhanced in SCR due
10 to the existence of the catalyst. The catalyst can accelerate Reaction (5):



12 Part of the Hg^0 was thus transformed to Hg^{2+} . The share of Hg^{2+} in flue gas increased from
13 8% before SCR to 21% after SCR. On the contrast, the share of Hg^0 in flue gas decreased
14 from 81% before SCR to 54% after SCR. Ammonia injection before SCR might have positive
15 effect on the adsorption of mercury onto the particulate matter. That could be the reason why
16 the Hg_p concentration increased. More tests are needed to confirm the effects of SCR and its
17 catalysts on mercury speciation.

18 Plant 5 is the only plant with CFB-FGD plus FF system. The sticky Hg^{2+} in flue gas
19 tends to adsorb on the particles when flue gas goes through CFB-FGD and then be captured
20 by FF system. Due to the high percentage of Hg^{2+} in flue gas after ESP, the removal efficiency
21 of CFB-FGD+FF for Hg^{2+} is over 80%.

22 Final emission from stack to the atmosphere varied from 1.22 to 9.60 $\mu\text{g}/\text{m}^3$, and was
23 dominated by Hg^0 . For the boilers with wet FGD systems, the share of Hg^0 to total Hg in
24 stack gas to the atmosphere was 75–94%. For the boiler with ESP+CFB-FGD+FF system, the
25 share of Hg^0 to total Hg in stack gas to the atmosphere was 67%.

26 **3.3 Mercury removal efficiencies of APCDs**

27 In this study, the average mercury removal efficiencies of the ESP, ESP+WFGD, and
28 ESP+CFB-FGD+FF systems were 24%, 73% and 66%, respectively, as shown in Fig. 8. The
29 removal efficiencies of ESP for tested power plants, including the results from US, Japan and

1 South Korea, varied significantly from 6 to 52%. The mercury removal efficiencies of
2 ESP+WFGD were around 70% for bituminous coal-fired power plants. The Hg removal
3 efficiency for anthracite coal-burning unit is higher than that for bituminous coal. The lignite
4 coal-burning plants have lowest Hg removal efficiencies.

5 The overall mercury removal efficiency was in a logarithmic correlation with the total
6 mercury concentration in the flue gas after the boiler (Fig. 9). Shape of the correlation curve
7 was determined by the chlorine content, bromine content, and M/A ratio of the coal. The
8 combination of SCR+ESP+WFGD has relatively higher mercury removal efficiency than
9 ESP+WFGD due to the oxidizing effect of SCR. Combination of ESP+CFB-FGD+FF has a
10 relatively lower efficiency than ESP+WFGD, which indicates stronger co-benefit of mercury
11 abatement from wet FGD than from dry FGD system.

12 **3.4 Mercury mass balance in coal-fired power plants**

13 Table 4 shows the Hg concentrations of solid and liquid samples collected in the field.
14 The Hg concentration in bottom ash ranged from 1 to 16 $\mu\text{g}/\text{kg}$. The concentration of Hg in
15 fly ash from the ESP hopper varied from 10 to 295 $\mu\text{g}/\text{kg}$. The Hg content of gypsum
16 (by-product from wet FGD) ranged from 38 to 561 $\mu\text{g}/\text{kg}$. In addition, the Hg in fine ash from
17 FF was 2945 $\mu\text{g}/\text{kg}$. All of the collected data have been used for the calculation of mercury
18 mass balance in the coal-fired power plants.

19 The mercury balance was estimated based on the results of Hg analysis in above
20 sessions. Table 5 gives the details of the daily average mass balance calculations for all the six
21 plants. For all the six power plants, the mercury balances recovery rates ranged from 87 to
22 116% of the mercury in feed-coals. All the results were within the acceptable error range of
23 $\pm 20\%$.

24 The mass balance results indicate the fate of mercury across APCDs in power plants.
25 Figure 10 is the summarized diagram with mass distribution of mercury in the coal-fired
26 power plants. Only a very small part ($<1\%$) of Hg in coal was retained in bottom ash. About
27 5–43% of Hg is collected in the ESP fly ash hopper. About 13–63% of the Hg in coal is
28 captured in gypsum of wet FGD and 19–72% of Hg is emitted to the atmosphere.

29 **3.5 Mercury emission factors**

30 The atmospheric mercury emission factors of each tested power plants are given in

1 Table 5. The emission factor for ESP+WFGD was in the range of 25 to 75 mg Hg/t coal. That
2 for SCR+ESP+WFGD was 11mgHg/t coal and for ESP+CFB-FGD+FF 131 mg Hg/t coal.
3 The wide distribution of the emission factors obtained in this study indicates that mercury
4 emissions in Chinese power plants are rather complicated. Therefore, great caution shall be
5 taken when apply the mercury emission characteristics measured in US or other countries to
6 estimate mercury emissions in China.

8 **4 Conclusions**

9 To investigate the Hg emission characteristics from coal-fired power plants in China, Hg
10 sampling was carried out at six typical power plants burning various types of coals. It was
11 found that the Hg emission was dependent on coal properties and APCDs configuration.

12 Type of coal was a major factor affecting the Hg emission and speciation in flue gas
13 right after the coal-fired boilers without controls. Anthracite coal with a higher concentration
14 of Hg emitted than bituminous coal. Mercury speciation was mainly influenced by the content
15 of chlorine and bromine in coal.

16 Mercury concentration and speciation was changed across APCDs. Some of the Hg⁰ in
17 flue gas was oxidized to Hg²⁺ in SCR. Large amounts of particulate-bound Hg were removed
18 through ESP and small amounts of Hg⁰ oxidized to Hg²⁺. Around 67–98% of Hg²⁺ in flue gas
19 was absorbed in the scrubber solution and retained in the FGD gypsum. CFB-FGD plus FF
20 system also removed 80% of Hg²⁺.

21 For the six power plants tested, the mercury mass balances varied from 87 to 116% of
22 the input coal mercury to the plants, which was enough to describe the distribution of mercury
23 in the plant. The distribution of mercury confirmed significant amount of Hg removal by ESP
24 and FGD systems. The average mercury removal efficiencies of the ESP, ESP+WFGD, and
25 ESP+CFB-FGD+FF systems were 24%, 73% and 66%, respectively. And 19–72% of Hg in
26 flue gas was emitted to the atmosphere through stack, which was dominated by Hg⁰.

27 For a better reliable understanding of the mercury behavior from a coal-fired power
28 plant and other combustion facilities, long-term experiment plan and continuously monitoring
29 of the flue gas are necessary.

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Tables

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Table 1. Information of the onsite tested utility boilers

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Power plant	Installed capacity (MW)	Location	Boiler type	Air pollution control devices (APCDs)	Coal type	Coal consumption (kt/yr)
Plant 1	200	Guizhou	PC boiler	ESP+WFGD	Bituminous	894
Plant 2	600	Guizhou	PC boiler	ESP+WFGD	Bituminous	1672
Plant 3	300	Guizhou	PC boiler	ESP+WFGD	Anthracite	836
Plant 4	600	Guangdong	PC boiler	ESP+WFGD	Lignite	1280
Plant 5	100	Shanxi	PC boiler	ESP+CFB-FGD+FF	Bituminous	363
Plant 6	165	Beijing	PC boiler	SCR+ESP+WFGD	Lignite	452

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Notes:

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PC boiler – pulverized-coal boiler

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ESP – electrostatic precipitator

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FF – fabric filter

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FGD – flue gas desulfurization

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WFGD – wet FGD

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CFB-FGD – circulating fluidized bed FGD

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SCR – selective catalytic reduction

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Table 2. Proximate and ultimate analysis of tested coals

Coal sample	Proximate analysis										Ultimate Analysis			
	M _{ad}	A _d	V _{daf}	FC _d	Q	C _d	H _d	N _d	O _d	S _d	Cl	F	Br	Hg
	%	%	%	%	MJ/kg	%	%	%	%	%	mg/kg	mg/kg	mg/kg	μg/kg
Plant 1	1.70	32.49	15.30	57.18	21.17	59.35	2.41	0.92	0.80	4.03	63±46 (4)	215±25	55±19	233±12 (6)
Plant 2	1.27	34.37	25.06	49.18	19.60	57.27	3.06	0.95	3.21	1.14	190±115 (4)	150±55	34±17	142±38 (3)
Plant 3	1.74	31.06	12.31	60.45	20.51	59.82	2.22	0.92	2.02	3.96	117±32 (3)	235±26	55±22	174±19 (6)
Plant 4	7.60	21.34	35.99	50.35	21.73	62.18	3.46	0.76	11.70	0.56	136±15 (5)	N.A.	N.A.	35±10 (5)
Plant 5	1.25	36.32	24.11	48.33	20.51	52.39	2.88	0.79	5.22	2.40	318±68 (4)	149±43	63±6	385±113 (5)
Plant 6	6.11	7.42	34.70	60.46	22.82	75.52	4.13	0.84	11.65	0.44	160±83 (4)	114±32	42±7	17±5 (7)

4 Note: the numbers in brackets are number of samples analyzed; the numbers of samples for analysis of F and Br
5 are same as that for analysis of Cl content.
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Table 3. Concentrations of different mercury species in flue gas at each sampling location

		Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Before SCR ($\mu\text{g}/\text{m}^3$)	Total Hg						1.92±0.05
	Hg ²⁺						0.15±0.04
	Hg ⁰						1.55±0.12
	Hg _p						0.22±0.02
Before ESP ($\mu\text{g}/\text{m}^3$)	Total Hg	20.77±2.17	15.06±1.99	27.15±0.46	3.13±0.13	26.93±2.33	1.89±0.13
	Hg ²⁺	11.42±0.74	4.64±0.83	22.22±0.35	0.42±0.11	23.73±1.83	0.40±0.10
	Hg ⁰	6.00±0.66	7.05±0.32	2.11±0.32	2.48±0.26	2.78±0.40	1.02±0.07
	Hg _p	3.36±0.17	3.37±0.53	2.82±0.36	0.23±0.04	0.42±0.10	0.47±0.02
After ESP ($\mu\text{g}/\text{m}^3$)	Total Hg	13.20±1.89	8.07±1.15	24.35±0.64	2.94±0.11	21.96±4.13	1.44±0.04
	Hg ²⁺	8.92±1.24	3.99±0.39	17.90±0.58	0.42±0.06	18.36±3.64	0.44±0.03
	Hg ⁰	4.27±0.74	4.08±0.63	6.44±0.55	2.50±0.14	3.58±0.57	1.00±0.03
	Hg _p	0.01±0.00	0.00±0.00	0.00±0.00	0.02±0.00	0.02±0.00	0.00±0.00
After FGD ($\mu\text{g}/\text{m}^3$)	Total Hg	6.69±1.24	4.53±0.68	5.06±0.43	2.27±0.19		1.22±0.12
	Hg ²⁺	1.66±0.64	0.84±0.20	0.45±0.09	0.14±0.03		0.13±0.02
	Hg ⁰	5.03±1.05	3.70±0.40	4.61±0.46	2.13±0.20		1.08±0.11
	Hg _p	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00		0.00±0.00
After FF ($\mu\text{g}/\text{m}^3$)	Total Hg					9.16±1.69	
	Hg ²⁺					3.04±0.64	
	Hg ⁰					6.11±1.09	
	Hg _p					0.01±0.00	

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2 **Table 4.** Mercury contents in solid samples

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	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Feed coal ($\mu\text{g}/\text{kg}$)	233 \pm 12(6)	142 \pm 38(3)	174 \pm 19(6)	35 \pm 10(5)	385 \pm 113(5)	17 \pm 5(7)
Bottom ash ($\mu\text{g}/\text{kg}$)	3 \pm 1(6)	16 \pm 4(4)	7 \pm 3(3)	3 \pm 1(3)	3 \pm 1(6)	1 \pm 0(7)
Fly ash ($\mu\text{g}/\text{kg}$)	295 \pm 59(5)	245 \pm 34(5)	160 \pm 19(4)	10 \pm 2(6)	134 \pm 36(4)	24 \pm 3(6)
Gypsum ($\mu\text{g}/\text{kg}$)	368 \pm 108(3)	561 \pm 8(3)	309 \pm 12(6)	90 \pm 7(4)		38 \pm 4(5)
Fine ash ($\mu\text{g}/\text{kg}$)					2945 \pm 132(3)	

4 Note: the numbers in brackets are number of samples analyzed.

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2 **Table 5.** Mass balance and emission factors of the tested coal-fired power plants

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	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5	Plant 6
Hg in (g/d)	570.7	757.6	479.6	138.6	799.2	26.4
Feed coal	570.7	757.6	479.6	138.6	799.2	26.4
Hg out (g/d)	554.3	773.4	556.7	120.0	816.8	27.5
Bottom ash	0.2	7.3	0.1	0.1	0.2	0.0
Fly ash	194.9	332.5	101.0	5.4	88.6	6.5
Gypsum	200.9	237.1	351.8	27.5		3.5
Fine ash					464.3	
Stack gas	158.3	196.5	103.7	87.0	263.7	17.5
Hg out/in (%)	97.1	102.1	116.1	86.5	102.2	104.3
Emission factor (mg Hg/t coal)	75	43	32	25	131	11

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Figure Caption

Fig. 1. Sampling locations in tested power plants

Fig. 2. Ontario Hydro Method for measuring mercury speciation in flue gas

Fig. 3. Correlation between mercury content of coal and total mercury concentration in flue gas released from boilers

Fig. 4. Correlation between halogen content of coal and the Hg^{2+} percentage in flue gas released from boilers: (a) chlorine; (b) bromine

Fig. 5. Correlation between the M/A ratio of coal and the Hg_p percentage in flue gas released from boilers

Fig. 6. Influence of Hg^{2+} concentration in flue gas before ESP on the transformation from Hg^{2+} to Hg^0

Fig. 7. Influence of Hg^{2+} concentration before wet FGD on the removal rate of Hg^{2+} by wet FGD

Fig. 8. Comparison of mercury removal efficiencies

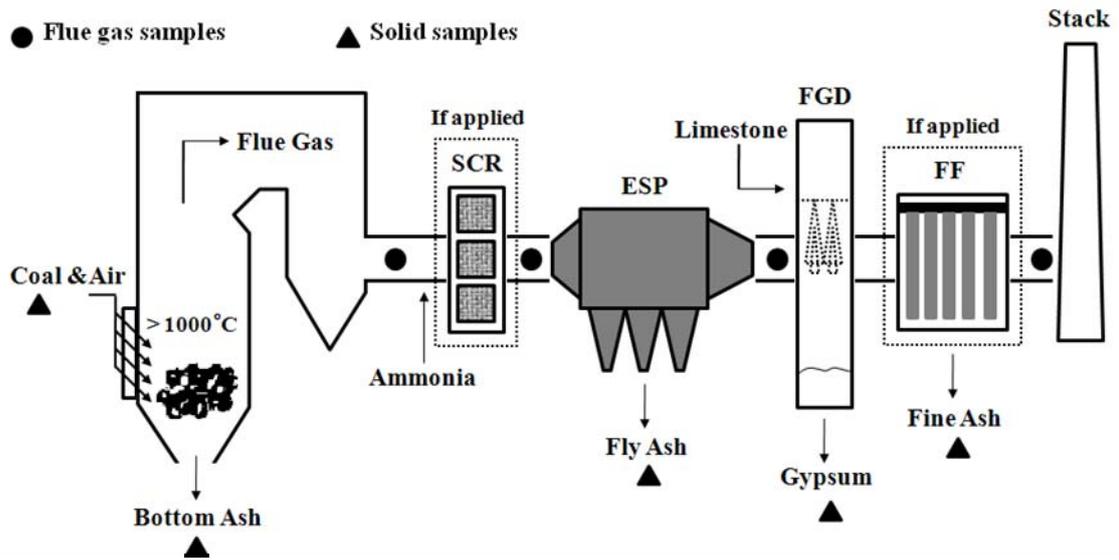
Fig. 9. Overall mercury removal efficiencies of tested power plants

Fig. 10. Mass distribution of mercury in the coal-fired power plants

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Figures

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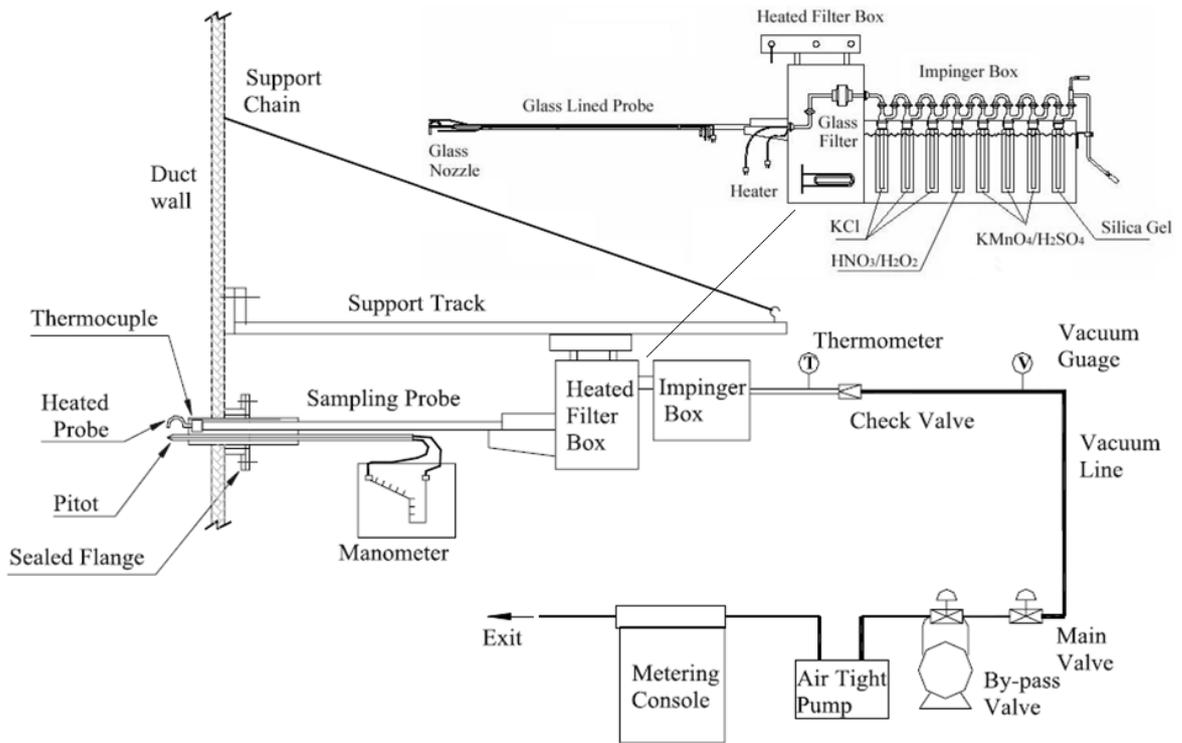


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4 **Fig. 1.** Sampling locations in tested power plants

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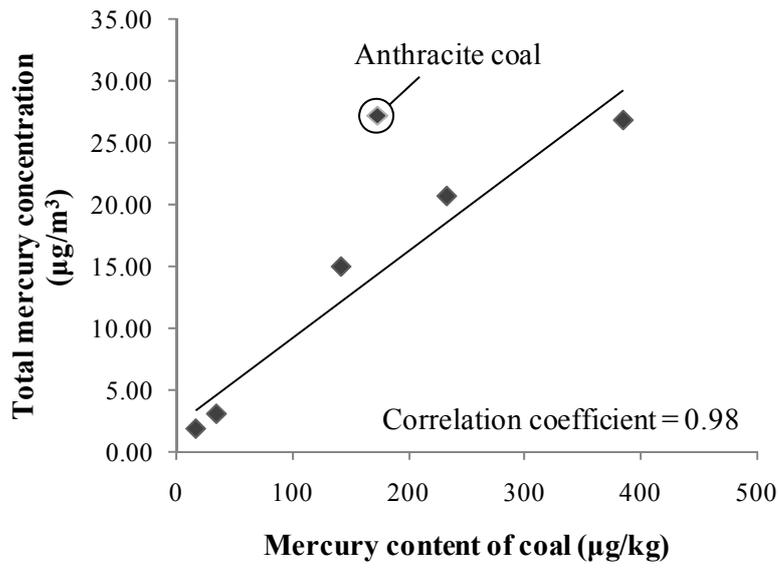
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Fig. 2. Ontario Hydro Method for measuring mercury speciation in flue gas

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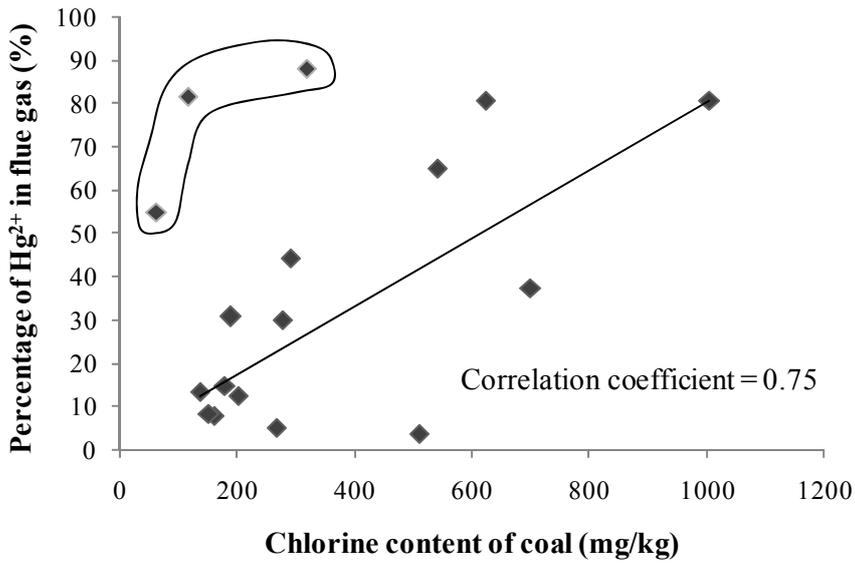
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3 **Fig. 3.** Correlation between mercury content of coal and total mercury concentration in flue gas
4 released from boilers

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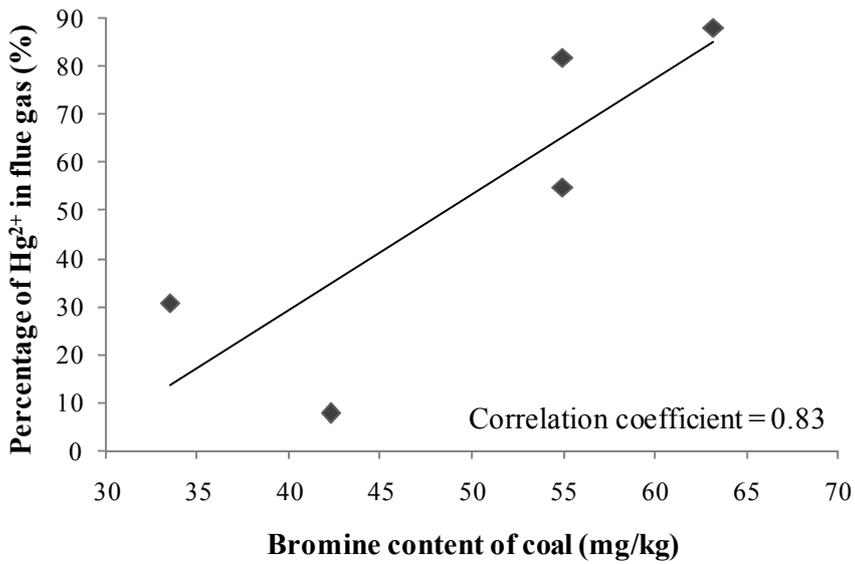
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3 (a) Chlorine



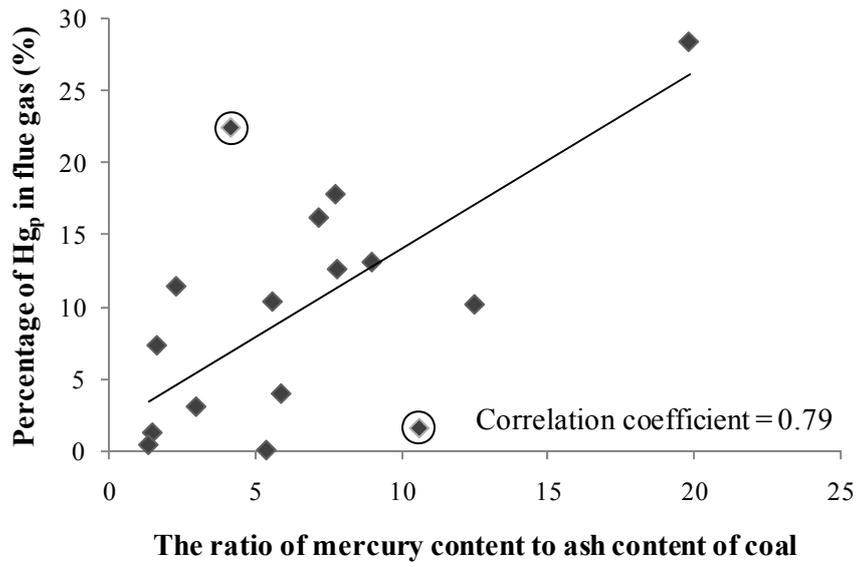
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5 (b) Bromine

6 **Fig. 4.** Correlation between halogen content of coal and the Hg^{2+} percentage in flue gas released
7 from boilers: (a) chlorine; (b) bromine

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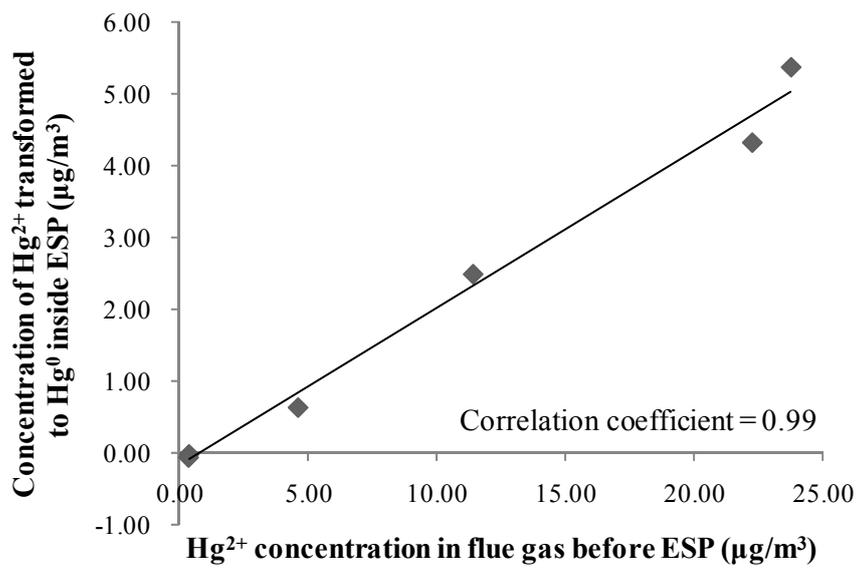
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Fig. 5. Correlation between the M/A ratio of coal and the Hg_p percentage in flue gas released from boilers

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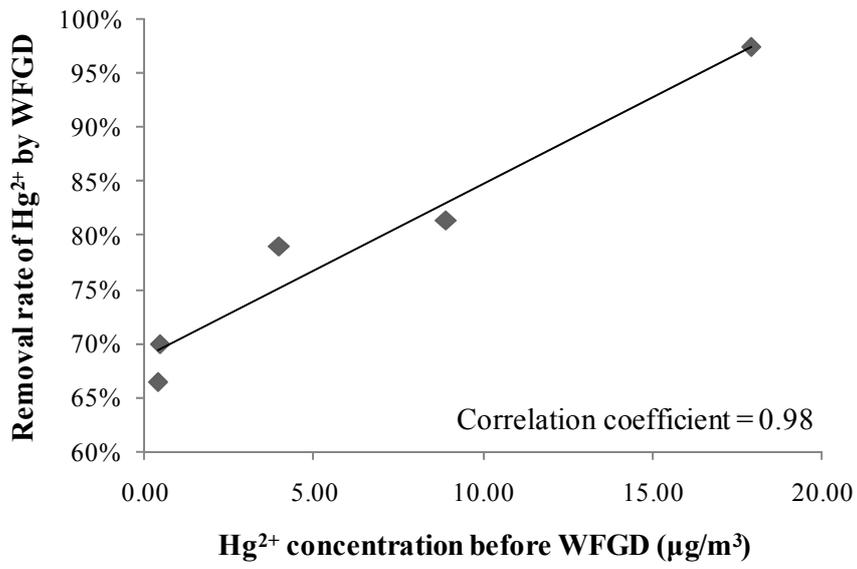


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3 **Fig. 6.** Influence of Hg²⁺ concentration in flue gas before ESP on the transformation from Hg²⁺ to
4 Hg⁰

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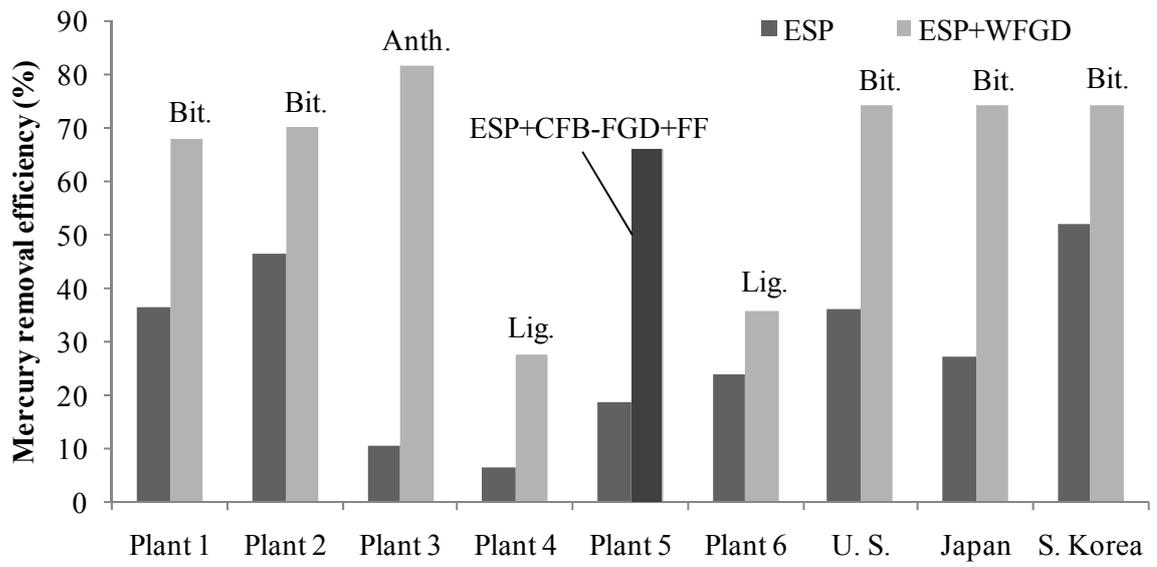


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3 **Fig. 7.** Influence of Hg²⁺ concentration before wet FGD on the removal rate of Hg²⁺ by wet FGD

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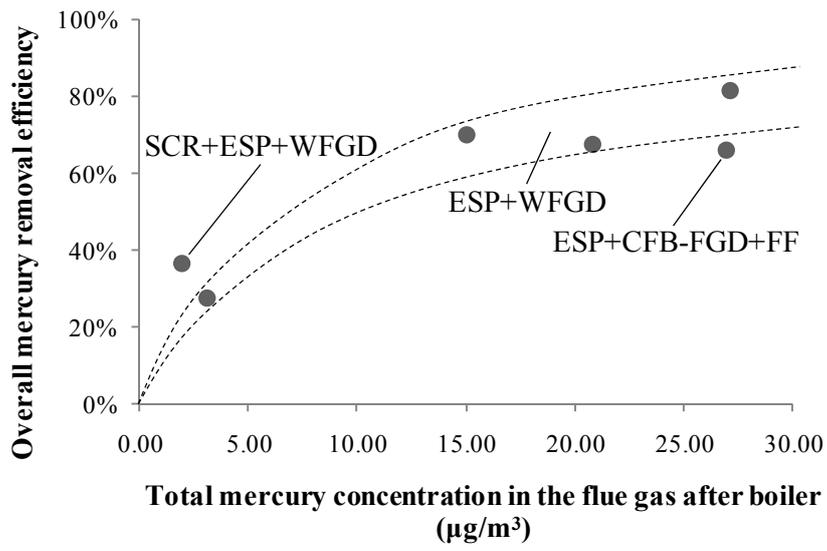


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3 **Fig. 8.** Comparison of mercury removal efficiencies

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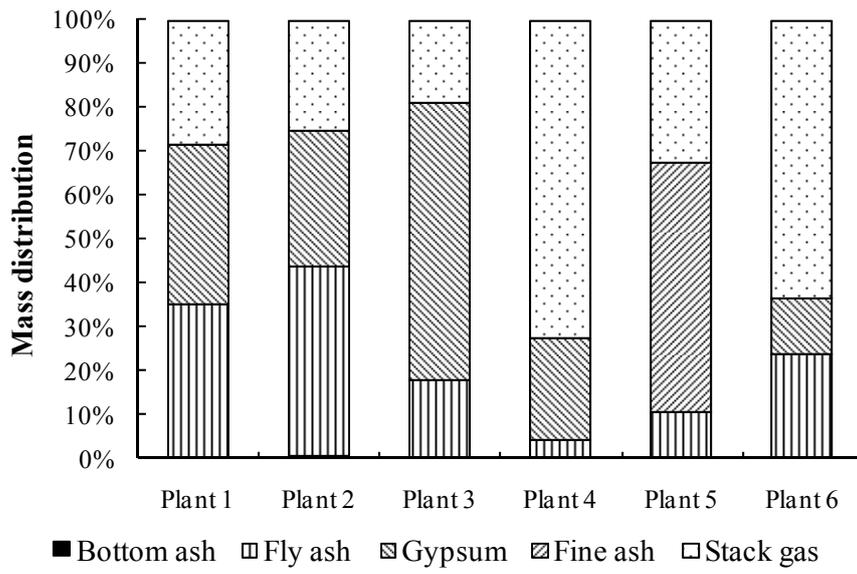


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3 **Fig. 9.** Overall mercury removal efficiencies of tested power plants

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Fig. 10. Mass distribution of mercury in the coal-fired power plants

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