RESEARCH

Mass flows and characteristic of mercury emitted from coal-fired power plant equipped with seawater flue gas desulphurization

Mao Hung Huang, Wei Huan Chen, Minh Man Trinh and Moo Been Chang[*]

Abstract

This study investigated the characteristics of mercury emitted from a large-scale coal-fired power plant in Taiwan via intensive sampling campaigns. The air pollution control devices equipped in this coal-fired power plant include selective catalytic reduction, fabric filter and seawater flue gas desulfurization. During three sampling campaigns, mercury concentrations emitted from this large-scale coal fired power plant ranged from 0.04 to 0.35 µg Nm^{-3}. In addition, solid and liquid samples including coal, bottom ash, fly ash and inlet/outlet seawater were collected and analyzed for mercury content to provide the mass flows of mercury in this plant. The results indicate that mercury emitted from this coal-fired power plant is dominated by Hg^0, and the emission factor of mercury ranges from 0.37 to 3.37 mg Hg t^{-1} coal, which is relatively lower than those reported in other studies. The relative enrichment factor of mercury in fly ash (0.23–1.22) is significantly higher than that of bottom ash (0.10 × 10^{-3}–0.89 × 10^{-3}). Although this coal-fired power plant has a relatively low mercury atmospheric emission which accounts for 6.4% of the total mercury output, it is essential to further control mercury released from fly ash (62.6% of the total mercury output) and discharged seawater (33.7% of the total mercury output) to reduce environmental damage and human health effects.

Keywords Mercury, Hg, Coal-fired power plants, US EPA Method 30B, Mercury speciation, Seawater flue gas desulfurization, Mass balance

1 Introduction

Mercury (Hg) is one of the most important environmental contaminants that rouses a global concern due to its high toxicity to human health, long-range transport, persistence and bioaccumulation in the environment [1, 2]. In the ecological environment, methylmercury is considered as the most toxic form of mercury since it poses serious impact on the central nervous system of human [3–5]. According to the United Nation Environment Program (UNEP), coal combustion is predominant anthropogenic mercury emission source in the world, and coal-fired power plants are considered as one of the largest emission sources. In response to serious mercury pollution, UNEP enacted an international legally-binding treaty "the Minamata Convention" to reduce mercury emission in 2013 [6, 7] and many countries have taken strict measures to control mercury emission from coal-fired power plants. In December 2011, the US Environmental Protection Agency (EPA) issued the final Mercury and Air Toxics Standards (MATS), which set the standards for all hazardous air pollutants emitted from coal- and oil-fired electric utility steam generating units with a capacity of 25 MW or greater (US EPA, 2002). The MATS set the emission limits of mercury in existing units (not low rank virgin coal: 0.013 lb GWh^{-1}; low rank virgin coal: 0.040 lb GWh^{-1}) and new or reconstructed units

*Correspondence:
Moo Been Chang
mbchang@ncuen.ncu.edu.tw
Graduate Institute of Environmental Engineering, National Central University, Taoyuan 320317, Taiwan

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(not low rank virgin coal: 0.003 lb GWh^{-1}; low rank virgin coal: 0.040 lb GWh^{-1}) [3, 8]. As the largest coal producer and consumer in the world, China issued the latest Emission Standard of Air Pollutants for Thermal Power Plants (GB13223-2011) which effectively started on January 1, 2015 to limit the Hg emission below 30 μg Nm^{-3} [9–11]. In Taiwan, the EPA also issued the regulations for mercury emissions from coal-fired power plants, which limits steam power units for existing units to 5 μg Nm^{-3} and for new or reconstructed units to 2 μg Nm^{-3}.

Mercury in the flue gas emitted from coal-fired power plants is generally divided into three forms including elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate mercury (Hg^P) [12–14]. Each mercury species has its unique physical and chemical properties; therefore, coal-fired power plants would carry out mercury emission control based on speciation. In recent years, various strategies for the reduction of mercury emission have been adopted, and they can be generally divided into two categories, i.e., specific mercury removal technologies (sorbent or additives injection) and co-beneficial control via existing air pollution control devices (APCDs) [9, 15]. Currently, most coal-fired power plants apply co-beneficial control to reduce Hg emission via existing APCDs because no additional equipment and extra cost are needed [16]. To meet the stringent emission standards promulgated for various pollutants, coal-fired power plants have commonly installed conventional APCDs such as selective catalytic reduction (SCR), electrostatic precipitator (ESP)/fabric filter (FF) and wet flue gas desulfurization (WFGD) to reduce NO$_X$, particulate matter (PM), and SO$_X$ emissions, respectively. In addition, previous studies have shown that these APCDs also significantly affect mercury speciation and emission. Specifically, Hg^P is associated with the fly ash particles and can be removed by the PM control devices, i.e., ESP or FF while Hg^{2+} can be captured by WFGD due to its high water solubility. On the other hand, Hg^0 is extremely volatile and water-insoluble. Clever et al. [17] reported that the water solubilities of elemental and oxidized mercury at 298 K are 3.03×10^{-7} mol kg^{-1} and 0.269 mol kg^{-1}, respectively, so it is challenging to capture Hg^0 via WFGD process. Fortunately, newly built coal-fired power plants are commonly equipped with SCR system to reduce NO$_x$ emission, and commercial SCR catalyst (V$_2$O$_5$-WO$_3$(MoO$_3$)/TiO$_2$) can also promote the conversion of Hg^0 into Hg^{2+}, thereby improving mercury removal efficiency and achieving the objective of multiple pollutant control [15, 18].

The efficacy of seawater flue gas desulfurization (SWFGD) to remove SO$_2$, condensable particulate matter (CPM), filterable particulate matter (FPM) and polycyclic aromatic hydrocarbons (PAHs) have been reported

but the studies on the effectiveness of SWFGD in mercury removal are scarce. Darake et al. [19] conducted a lab-scale SWFGD experiment and found that more than 90% of SO$_2$ removal efficiency is achieved. Che et al. [20] investigated the efficiency of SWFGD in coal-fired thermal power units and the results showed that the SO$_2$ concentration reduced from 1450 to 98 mg m^{-3} via SWFGD (93.2% removal efficiency). Lu et al. [21] evaluated removal efficiencies of CPM, FPM and PAHs achieved with SWFGD of a coal-fired power plant (plant A), and a coal-fired boiler (plant B). The results indicate that high removal efficiency of total 16 PAHs congeners is achieved with BH + SWFGD (90%), however, a relatively lower removal efficiency (38%) is obtained for CPM with BH + SWFGD.

Accurate measurement of mercury concentration in the flue gas is important and Ontario Hydro Method is considered as the standard method for mercury sampling in flue gas of power plants [16], but it still has some disadvantages including complexity in operation and the potential contamination in solution preparation and analysis. On the other hand, US EPA Method 30B utilizes the sorbent traps to capture gaseous mercury in flue gas, and this method has been gradually accepted worldwide thanks to its convenient operation and high precision. In application, the sorbent traps of the US EPA Method 30B should be used under low PM concentration and low temperature conditions, and it is often used to measure gaseous mercury emitted from power plants [22]. So far, the emission characteristics and migration of mercury in the flue gas of Taiwan's coal-fired power plants and the effectiveness of mercury abatement are not fully understood. In this study, a large-scale pulverized coal fired power plant located in northern Taiwan was selected for systematic investigation of its mercury emissions. The US EPA Method 30B was applied in Taiwan for the first time to provide the data of high quality for Hg emission testing. The mercury concentrations measured in this study could validate the application of US EPA Method 30B as inexpensive and reliable approach for Hg emission management for the governments.

The purposes of this study are to (1) identify Hg emission from a typical large-scale coal-fired power plant via US EPA Method 30B, (2) report the emission factor of Hg into the atmosphere on different bases, (3) calculate the enrichment factor of Hg in fly ash and bottom ash and (4) understand the behavior of mercury and it speciation in a typical combustion process via the mercury mass flow.

2 Experimental

2.1 The coal fired power plant

This study investigated the characteristics and distribution of mercury emitted from three pulverized coal

boilers in a large-scale coal-fired power plant (total capacity 2,400 MW) located in northern Taiwan. The coal consumption rate of this plant is 275 t h^{-1} and the data from approximate and ultimate analysis of coal are presented in Table 1 and will be discussed in Sect. 3.1. The APCDs adopted in this plant include SCR, FF and SWFGD to control NO$_x$, PM and SO$_x$, respectively. Specifically, the SCR catalyst used in this plant is honeycomb-type V$_2$O$_5$-WO$_3$/TiO$_2$ while pulse-jet fabric filters are used for PM removal. The SWFGD system used in this power plant utilizes the abundant and slightly alkaline of seawater instead of limestone slurry to absorb SO$_x$ generated from coal combustion process.

The Hg contents in coal and emission in stack gas were collected from all three boilers and analyzed during three campaigns which were conducted in spring, summer and autumn of 2020 (denoted as A, B and C, respectively).

Figure 1 shows the schematic of the APCDs and the sampling locations in this coal-fired power plant. To further understand the mass flow of mercury, one more campaign (denoted as campaign D) was conducted in spring of 2021 to analyze Hg concentration in stack gas, coal, bottom ash, fly ash and inlet and outlet seawater of the boiler III.

Table 1 Proximate and ultimate analyses, source and calorific value of coal samples during campaign A, B and C

	Boiler	Coal type	Hg (mg kg^{-1})	Cl (mg kg^{-1})	S (%)	Proximate analysis (W$_{ad}$%)				Lower heating value (MJ kg^{-1})
						M	A	V	FC	
A	I	Indonesian coal + Australian coal	0.046	95.7	0.50	4.08	11.4	33.7	50.8	28.3
	II	Indonesian coal + Australian coal	0.033	95.4	0.50	4.41	10.3	35.0	50.3	28.1
	III	Indonesian coal + Australian coal	0.041	101	0.51	6.73	8.76	35.4	49.1	27.4
	Average		0.040	97.4	0.5	5.07	10.1	34.7	50.1	28.0
B	I	Indonesian coal + Russian coal	0.055	45.2	0.60	4.07	10.8	28.2	56.9	28.7
	II	Indonesian coal + Australian coal	0.039	81.8	0.60	7.19	7.18	35.2	50.4	27.1
	III	Indonesian coal + Russian coal	0.057	42.2	0.59	6.71	8.44	33.2	51.7	27.4
	Average		0.050	56.4	0.6	5.99	8.8	32.2	53.0	27.7
C	I	Indonesian coal + Russian coal	0.043	41.3	0.52	3.82	10.9	33.5	51.7	28.9
	II	Australian coal	0.034	137	0.47	3.46	12.2	30.8	53.5	28.2
	III	Russian coal + Australian coal	0.031	51.6	0.51	4.66	12.4	32.2	50.7	27.6
	Average		0.036	76.6	0.50	3.98	11.8	32.2	52.0	28.2

M Moisture content, *A* Ash content, *V* Volatile content, *FC* Fixed carbon content, *W$_{ad}$%* air dried weight percentage
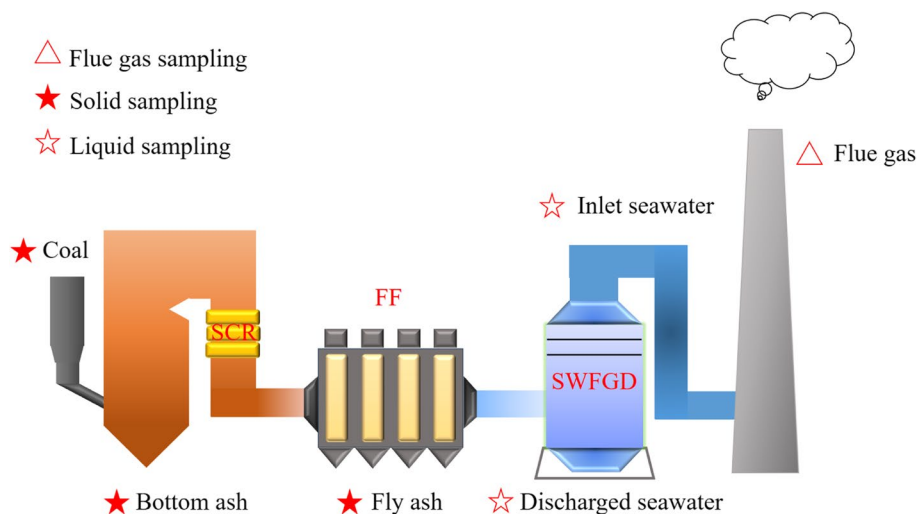

Fig. 1 Schematic of the APCDs and the sampling locations

2.2 Sampling and analysis

Mercury samples of flue gas were collected on halogen-impregnated carbon sorbent traps following the US EPA Method 30B. The sorbent traps can be divided into three components including unspiked trap (Φ 10 × 185 mm), spiked trap (Φ 10 × 185 mm) and speciated trap (Φ 10 × 300 mm) purchased from the Lumex Co. (Cleveland, Ohio, USA). Unspiked traps can be applied to determine the concentration of total gaseous mercury, spiked traps is applied for quality assurance and quality control, while speciated traps is used to determine the individual concentration of Hg^0 and Hg^{2+}. Flue gas sampling was conducted by XC-30B Automated MercSampler™ System (Apex Instruments, Fuquay-Varina. North Carolina, USA). Two parallel sorbent traps were installed in a stainless steel probe and heated to 120 °C. The mercury contents of flue gas samples and solid samples were analyzed by using the Lumex RA-915 M mercury analyzer and PYRO-915 pyrolysis furnace (Lumex), respectively, following the procedures of NIEA M318.01C (Taiwan EPA). The mercury contents of liquid samples were determined following the standard methods of NIEA W330.52A and NIEA W331.50B (Taiwan EPA). Due to the fact that EPA Method 30B does not measure Hg content in particle matter, Hg is collected from the flue gas of this plant following Ontario Hydro method. All the solid samples, i.e., coal, bottom ash and fly ash were stored in clean plastic bags or plastic bottle while liquid samples, i.e., inlet/outlet seawater were stored in clean glass bottles in accordance with the standard method (NIEA W331.50B). Samples collected were pretreated and analyzed within one week after sampling.
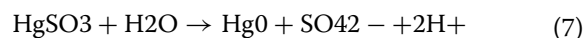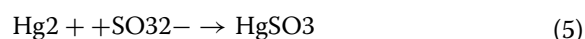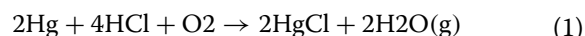
2.3 Quality assurance and quality control

The sampling and analysis of mercury were conducted following QA and QC procedures regulated in the above mentioned standard methods and no mercury was detected in the sorbent traps before sampling. During the sampling process, the paired sorbent traps were applied to sample the flue gas simultaneously to ensure the accuracy of the experiment. Specifically, they must comply with the paired sorbent trap agreement and sorbent trap section. 2 breakthrough regulations set by the US EPA Method 30B. Finally, the sampling system before and after sampling must comply with pre/post-test leak check ($\leq$ 4% of target/average sampling rate). In addition, spiked traps are also used for field recovery test, and they must comply with the US EPA Method 30B.

3 Results and discussion

3.1 Coal proximate and ultimate analysis

The results of proximate and ultimate analysis and lower heating value of the coal applied are listed in Table 1. Blended coal used in the power plant investigated is classified as bituminous coals or sub-bituminous coals with low sulfur, chloride and ash contents and high calorific value. To obtain stable power generation, calorific values of coal mixture were maintained at 27.4–28.9 MJ kg^{-1}. The average mercury contents in the coal burnt in campaigns A, B, and C are 0.040, 0.050 and 0.036 mg kg^{-1}, respectively. In addition, the average sulfur, chloride and ash contents of the combusted coal are 0.47–0.6%, 41.3–137 mg kg^{-1} and 7.18–12.4%, respectively, and the coal can be generally considered as low sulfur and chloride content compared with other studies [10, 23]. The contents of chloride and sulfur in coal significantly affect Hg behavior in flue gas, i.e., hydrogen chloride (HCl) and sulfur dioxide (SO_2) may react with Hg and affect its speciation. For example, HCl is able to enhance the oxidation of Hg^0 in the flue gas (Eq. (1)) [3, 24] while SO_2 can reduce or increase Hg^0 emission, depending on its concentration [8]. At a high concentration, SO_2 will dissolve in seawater to form HSO_3 or SO_3^{2-} (Eqs. (2) and (3)) which would later react with Hg^{2+} to form $HgSO_3$ (Eqs. (4) and (5)) and excess SO_3^{2-} may continue to react with $HgSO_3$ to form $Hg(SO_3)_2^{2-}$ complex which is considered as a highly stable compound (Eq. (6)). However, $HgSO_3$ is likely to hydrolyze and release Hg^0 when the concentration of SO_2 in flue gas and SO_3^{2-} in SWFGD solution decreased as described in Eq. (7) [25].

$$2Hg + 4HCl + O2 \rightarrow 2HgCl + 2H2O(g) \tag{1}$$

$$SO2 + H2O \rightarrow H + +HSO3- \tag{2}$$

$$SO2 + H2O \rightarrow 2H + +SO32- \tag{3}$$

$$Hg2 + +HSO3- \rightarrow HgSO3 + H+ \tag{4}$$

$$Hg2 + +SO32- \rightarrow HgSO3 \tag{5}$$

$$HgSO3 + SO32- \rightarrow Hg(SO3)22- \tag{6}$$

$$HgSO3 + H2O \rightarrow Hg0 + SO42- + +2H+ \tag{7}$$

The ash contents of coal range from 7.18 to 12.4%, which affects not only the concentration of particulate matter but also Hg^p concentration in flue gas [2]. Furthermore, the mercury contents of coal in this study range from 0.031 to 0.057 μg g^{-1}, which are relatively

low compared with the mercury content of coal in the world as listed in Table S1. Additionally, the calorific values of coal used in this plant range from 27.1 to 28.9 MJ kg^{-1}, which is considered as high calorific value coal.

3.2 Mercury emission from stack gas

Table 2 shows the operating parameters of the stack including temperature, gas velocity and concentrations of CO, CO_2 and O_2 during the sampling period. The stack temperatures range from 96 to 113 $^{\circ}$C while gas velocities range from 14.0 to 24.8 m s^{-1}. In addition, CO_2 and O_2 concentrations in flue gas range from 11.6 to 13.6% and from 4.8 to 6.5%, respectively, which indicate that operating conditions of the plant are stable and consistent during all three campaigns. It is notable that relatively higher O_2 content, lower temperature and gas velocity were measured in boiler II of the C sampling campaign due to lower power output (400 MW) compared with other boilers (800 MW) during the sampling period.

Gaseous mercury concentrations in flue gas measured by the US EPA Method 30B are shown in Table 2. Total gaseous mercury concentrations in the first, second and third campaigns are within the ranges of 0.20–0.27, 0.10–0.24, 0.04–0.34 µg Nm^{-3}, respectively, indicating that this coal-fired power plant meets the mercury emission standard (2 µg Nm^{-3}) regulated by the Taiwan EPA. The gaseous mercury concentrations measured at this large-scale coal-fired power plants are significantly lower than those reported in other studies, (0.55–6.72 µg Nm^{-3}) as reported by Cui et al. [6], Zhang et al. [9] and Liu et al. [10], indicating that mercury is effectively removed by the APCDs adopted in this plant. Mercury emission measured in this study was in the same range with those measured from power plants in Taiwan conducted by Chou et al. [26] (0.24–0.67 µg Nm^{-3}).

The mercury emission factor (MEF) is an important parameter for calculating mercury emissions from coal-fired power plants. Its calculation is based on the following three equations in this study:

a. Expressed in terms of coal consumption:

$$\text{MEF} = \frac{M_{Fluegas}}{M_{Coal}} \times 1000$$

where MEF is the emission factor (mg-Hg t^{-1} coal); $M_{Fluegas}$ is the mercury mass flow rate of flue gas (g h^{-1}); and M_{Coal} is the mass flow rate of coal (t h^{-1}).

b. Expressed in terms of actual power generation:

$$\text{MEF} = \frac{M_{Fluegas}}{P/1000}$$

where MEF is the emission factor (g-Hg GWh^{-1}); $M_{Fluegas}$ is the mercury mass flow rate of flue gas (g h^{-1}); P is the actual power generation (MW).

iii. Expressed by the calorific value of coal:

$$\text{MEF} = \frac{M_{Fluegas}}{M_{Coal} \times Q}$$

where MEF is the emission factor (g-Hg TJ^{-1}); $M_{Fluegas}$ is the mercury mass flow rate of flue gas (g h^{-1}); M_{Coal} is the mass flow rate of coal (t h^{-1}), Q is the calorific value of coal (TJ t^{-1}).

The emission factors of mercury in this coal-fired power plant are presented in Table 3. The MEF in terms of coal production, actual power generation and calorific value of coal are within the ranges of 0.37–3.37 mg-Hg t^{-1} coal, 0.13–1.07 g-Hg GWh^{-1} and 0.013–0.122 g-Hg TJ^{-1}, respectively. Generally speaking, the MEF of this coal-fired power plant is significantly lower than those reported for other large-scale coal-fired power plants

Table 2 Important parameters of stack gas in coal-fired power plant investigated

Campaign	Boiler	Temperature ($^{\circ}$C)	Gas velocity (m s^{-1})	CO (ppm)	CO_2 (%)	O_2 (%)	Gaseous Hg (µg Nm^{-3})
A	I	105	23.3	18.1	13.4	5.2	0.20
	II	108	24.1	25.3	12.7	5.3	0.27
	III	106	23.9	24.3	13.2	5.3	0.27
B	I	112	24.8	16.8	13.5	5.2	0.13
	II	111	24.6	29.6	13.4	4.9	0.24
	III	113	24.7	11.9	13.6	4.7	0.10
C	I	111	24.3	21.0	13.3	4.7	0.18
	II	96.1	14.0	60.5	11.6	6.5	0.04
	III	111	24.9	21.1	13.2	5.0	0.35

Table 3 The mercury emission factor for campaign A, B and C in the coal-fired power plant investigated

Campaign	Boiler	Mercury emission factor		
		mg-Hg t^{-1} coal	g-Hg GWh^{-1}	g-Hg TJ^{-1}
A	I	1.70	0.58	0.060
	II	2.27	0.80	0.081
	III	2.44	0.80	0.089
B	I	1.07	0.40	0.037
	II	2.10	0.74	0.077
	III	0.95	0.31	0.035
C	I	2.13	0.72	0.074
	II	0.37	0.13	0.013
	III	3.37	1.07	0.122

Table 4 The relative enrichment factors of mercury in bottom ash and fly ash

Campaign	Boiler	Mercury relative enrichment factor	
		Bottom ash	Fly ash
A	I	0.89×10^{-3}	0.67
	II	0.34×10^{-3}	0.23
	III	0.46×10^{-3}	0.27
B	I	0.28×10^{-3}	1.22
	II	0.28×10^{-3}	0.80
	III	0.31×10^{-3}	1.05
C	I	0.20×10^{-3}	0.51
	II	0.50×10^{-3}	0.72
	III	0.10×10^{-3}	0.51

Hg in bottom ash is below the MDL and calculated as 1/2 of the MDL

[8, 9, 27]. The MEF can be influenced by the fuel types, boiler types, and the operation conditions of APCDs. Therefore, with the increasing global attention of mercury and the technological development of APCDs, it is essential to further reduce the MEF of power plants to reduce the burden to the environment.

4 Enrichment factor

The mercury relative enrichment factor (MREF) which describes the enrichment of trace elements in fly ash or bottom ash relative to the feeding coal is calculated as [9, 27]:

$$\text{MREF} = \frac{C_x}{C_{Coal}} \times \frac{A_{Coal}}{100}$$

where MREF is mercury relative enrichment factor; C_x is mercury concentration in fly ash or bottom ash (mg

kg^{-1}); A_{coal} is the ash content of coal on air-dried basis (%); C_{coal} is the mercury concentration in coal (mg kg^{-1}).

Table 4 shows the relative enrichment factors of mercury in bottom ash and fly ash, respectively. The MREFs of the bottom ash collected in this study are within the range of 0.10×10^{-3}–0.89×10^{-3} while those of fly ash range from 0.23 to 1.22, the trend is consistent with that reported in previous studies [9, 11, 27]. The MREF of fly ash is much higher than that of bottom ash, indicating that fly ash has a stronger mercury enrichment capacity.

4.1 Speciation and mass flows of mercury

To better understand the effect of SWFGD on the behavior of Hg, the speciation of mercury in stack gas, seawater and solid samples are collected ($n=3$) in boiler III (denoted as campaign D). The concentrations of Hg^T in stack gas are 0.097, 0.141 and 0.011 µg Nm^{-3} (Table 5) and are consistent with those reported in Sect. 3.2. The concentrations of Hg^P in stack gas of samples #1, #2 and #3 are 0.003, 0.005 and 0.003 µg Nm^{-3}, respectively, and contribute 3.1, 3.5 and 27.3%, respectively, to the Hg^T concentrations. Oxidized mercury concentrations in stack gas of samples #1, #2 and #3 are 0.032, 0.009 and 0.002 µg Nm^{-3}, respectively, and contribute 33.0, 6.4 and 18.2%, respectively, to the Hg^T concentrations. On the other hand, elemental mercury concentrations in stack gas of samples #1, #2 and #3 are 0.062, 0.127 and 0.006 µg Nm^{-3}, respectively, and contribute 63.9, 90.1 and 54.5%, respectively, to the Hg^T concentrations.

Significantly lower Hg concentration in sample #3 could be attributed to the relatively high contents of chloride and sulfur in the feeding coal during this sampling period. Specifically, the mean chloride contents of coal combusted in #3 sampling is 638 mg kg^{-1} while that in #1 and #2 sampling period are 150 and 158 mg kg^{-1}, respectively. As mentioned earlier, the chloride in coal consequently transform into HCl during combustion, which affects Hg speciation [3, 8, 24]. In this study, high concentration of HCl in flue gas during the combustion process leading to the high conversion of Hg^0 to Hg^{2+}, and Hg^{2+} is later adsorbed on fly ash and removed from the gas stream via fabric filter, resulting in higher concentration of Hg in fly ash during #3 sampling period.

In addition, the distribution of elemental mercury in stack gas during #2 sampling period (90.1%) is significantly higher than that of #1 sampling period (63.9%) as illustrated in Fig. 2. Since the coal burned in #2 sampling period is of lower heating value (27.1 MJ kg^{-1}) compared with #1 sampling period (29.0 MJ kg^{-1}), higher coal feeding rate is required in #2 sampling period (271 t h^{-1}) compared with #1 sampling period (257 t h^{-1}). As a result, besides higher mercury emission measured in stack gas of #2 sampling period, more fly ash is generated

Table 5 Mercury content in solid and liquid samples and important parameters of the coal-fired power plant investigated during campaign D

| Sample		#1	#2	#3
Stack gas (μg Nm^{-3})	Hg^p	0.003	0.005	0.003
	Hg^{2+}	0.032	0.009	0.002
	Hg^0	0.062	0.127	0.006
	Hg^T	0.097	0.141	0.011
Coal (mg Hg kg^{-1})		0.033	0.030	0.021
Bottom ash (mg Hg kg^{-1})		<0.005^a	<0.005^a	<0.005^a
Fly ash (mg Hg kg^{-1})		0.131	0.153	0.362
Inlet seawater (μg Hg L^{-1})		0.016	0.015	0.010
Discharged seawater (μg Hg L^{-1})		0.783	0.201	0.020
Particulate matter (mg Nm^{-3})		0.567	0.384	0.114
Feeding coal	Chloride content (mg kg^{-1})	150	158	668
	Heating value (MJ kg^{-1})	29.0	27.1	26.7
	Combustion rate (t h^{-1})	257	271	298
	Ash content (%)	12.9	10.8	9.7
Fly ash generation (t h^{-1})		28.7	34.2	21.8

^{a} Detection limit = 0.005
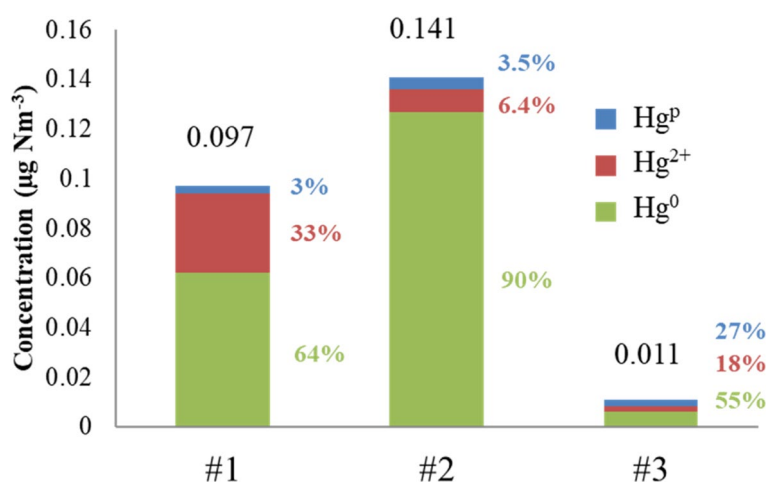
Fig. 2 Concentrations and speciation of mercury in stack gas in campaign D

during this period (34.2 t h^{-1}) compared with the #1 sampling period (28.7 t h^{-1}). This result indicates that higher concentration of PM exists in the gas stream during #2 sampling period, which provides more active sites to adsorb Hg^{2+} and consequently reduces the proportion of Hg^{2+} in stack gas. This phenomenon is supported by the high correlation between Hg in FA and chloride content in FA and coal, as well as those between Hg in FA and sulfur in FA as illustrated in Fig. 3.

Regarding the mercury contents in liquid samples, total Hg concentrations of the inlet seawater range from 0.010 to 0.016 μg L^{-1}, which is in line with the results reported by Su et al. [8]. On the other hand, mercury concentrations of the discharged seawater are within the range of 0.020–0.783 μg L^{-1}. Due to high vaporization characteristic, most of the mercury in the coal is released into the flue gas under high-temperature combustion, and only a small portion of mercury remains in the bottom ash [11, 27]. As a result, mercury concentrations in the bottom ash in this study are all lower than the detection limit and are calculated as 1/2 of the MDL. In contrast, Hg concentrations in fly ash range from 0.131 to 0.362 mg kg^{-1}. High mercury concentration in fly ash is attributed to the fact that Hg is likely to adsorb on fly ash particles and is removed from the gas stream by the baghouse [8, 12].
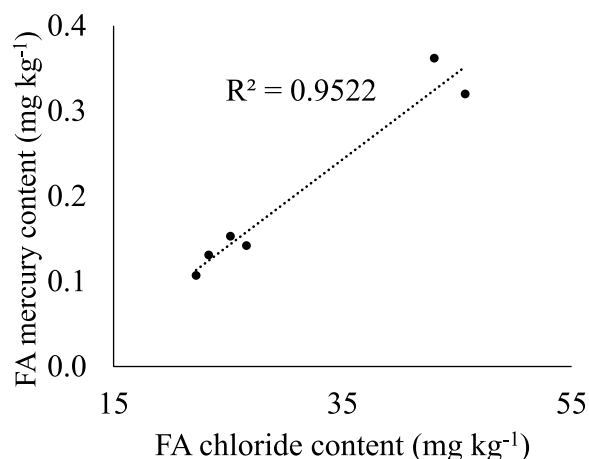
Fig. 3 Correlation of Hg in fly ash with chloride content in FA

Figure 4 shows the mass balance of mercury distribution in campaign D and calculation equation was present in Table S2 (Supplementary Materials). Mercury concentrations in coal, bottom ash, fly ash and discharged seawater measured in this study were in the same range with those measured from power plants in Taiwan conducted by Chou et al. [26] (0.021–0.04, 0.001–0.003, 0.060–0.305 mg kg^{-1} and 0.269–0.523 µg L^{-1}). For the inlet, coal is the main mercury input, accounting for 98.6% (7.65 g h^{-1}) while inlet seawater only accounting for 1.40% (0.11 g h^{-1}) of the total inlet mercury. For the outlet, mercury output is dominated by fly ash and output seawater, accounting for 62.6% (4.98 g h^{-1}) and 33.7%

(2.68 g h^{-1}) of the total output, respectively, while bottom ash only accounts for 0.01% (0.001 g h^{-1}) of the total output. This could be explained by the fact that as flue gas passed through the SCR, a majority of the Hg^0 was oxidized to Hg^{2+} which is of higher adsorption capacity and water solubility compared with Hg^0, and is effectively removed by FF and SWFGD. Overall, mercury emissions to the atmosphere accounted for 3.8% (0.30 g h^{-1}) of the total output in this coal-fired power plant. The overall mass balance of mercury in inlet and outlet is 103%, indicating that mercury speciation measurements in this study are carefully controlled. Notably, there is a reverse trend between Hg content in FA and discharged seawater. This can be explained by the increasing Hg content in FA (3.09, 4.90 and 6.96 g h^{-1} during #1, #2 and #3 sampling period, respectively) with the increasing chloride content in FA (22.2, 26.6 and 45.7 mg kg^{-1} during #1, #2 and #3 sampling period, respectively) as explained earlier. Higher amount of Hg^{2+} adsorbed by FA results in the lower Hg^{2+} measured in discharged seawater.

5 Conclusions

The emission and distribution of mercury from a large coal-fired power plant in Taiwan is investigated. The results indicate that the main mercury species emitted into the atmosphere is Hg^0, which accounts for 86–98% of the total gaseous mercury emission. The mercury relative enrichment factor of fly ash is much higher than that of bottom ash. Coal is the main input of mercury, which accounts for 94.5%, and the rest is inlet seawater. The main mercury output is fly ash and outlet seawater,
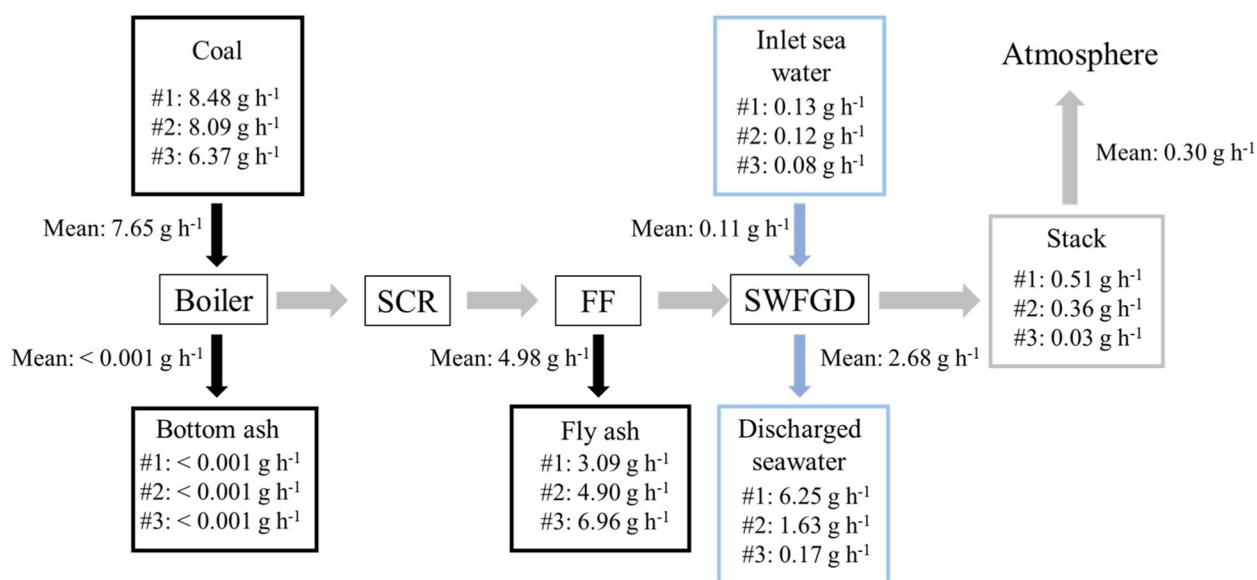

Fig. 4 The mass flow of mercury in coal-fired power plant

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which account for 62.6 and 33.7% of the total mercury output, respectively. Overall, approximately 3.77% of the total mercury output is emitted into the atmosphere. In addition, the MEF of this coal-fired power plant are 0.37–3.37 mg-Hg t^{-1}coal, 0.13–1.07 g-Hg GWh^{-1} and 0.013–0.122 g-Hg TJ^{-1}). Although the MEF of this coal-fired power plant are relatively low, it is deemed necessary to further reduce mercury emissions to alleviate its damage to the environment and human health, considering 33.7% of the mercury released is discharged into the sea.

So far, the validity of Method 30B is merely conducted during normal operation period. To ensure the accuracy of this method, a long term study should be conducted in future to measure Hg concentration in various scenarios including startup and shutdown periods. The successful application of US EPA Method 30B in this study indicate that this method could be applied as a reference method for relative accuracy test audits of vapor phase mercury Continuous Emission Monitoring systems. Due to the accurately and cost-effective, US EPA Method 30B could be widely deployed as on-site determination of total and speciated mercury emissions in various regions and conditions and is considered by UN Environment Programme as one of the best available techniques/best environmental practices of monitoring of mercury emissions.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s42834-023-00168-9.

> **Additional file 1: Table S1.** Mercury contents in coals from various studies. **Table S2.** Calculating equation of mass flow.

Authors' contributions
Mao Hung Huang and Wei Huan Chen developed and designed the methodology of this experiment and prepared the original draft. Minh Man conducted a research and investigation process, specifically performing the experiments, or data/evidence collection. Moo Been Chang supervised the project and had the oversight and leadership responsibility for the research activity planning and execution, including mentorship external to the core team. All authors read and approved the final manuscript.

Declarations

Availability of data and materials
All data generated or analyzed during this study are included in this published article.

Competing interests
The authors have no relevant financial or non-financial interests to disclose.

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