Original Article

Fate of cadmium in coal-fired power plants in Guizhou, Southwest China: With emphasis on updated atmospheric emissions

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ABSTRACT

Coal-fired power plants (CFPPs) are important source of anthropogenic atmospheric releases of various pollutants, including cadmium (Cd). In this research, the distribution of Cd in seven CFPPs in Guizhou province, southwest China and the atmospheric Cd emissions from this source category in this province was studied. Among the boilers, one was a circulating fluidized bed boiler (CFB) and the others were pulverized coal-fired boilers (PC). All CFPPs are equipped with De-NOx, De-dust, and De-SO$_2$ devices. Solid samples including feed fuel (coal, gangue, and coal slime), limestone, bottom ash, fly ash, gypsum, as well as stack flue gas samples were simultaneously collected and analyzed. Cd in feed coal, bottom ash, fly ash, limestone, gypsum, and stack flue gas were in the range of 0.15–0.68, 0.08–0.42, 0.43–2.03, 0.01–0.67, 0.02–0.41 mg kg^{-1}, and 0.005–0.03 µg·Nm^{-3}, respectively. Cd release ratio during the coal combustion in the boiler was in the range of 95.91–98.77% for PC, but only 76.94% for CFB. Cd atmospheric emission factors were in the range of 0.03–0.2 mg Cd·t^{-1} coal, 0.02–0.1 µg·(kW·h)$^{-1}$ or 0.002–0.01 g Cd·TJ^{-1} for the seven CFPPs, lower values were found for CFB boiler than that of PC boilers. In 2017, the amount of Cd emitted from CFPPs in Guizhou province was estimated to be 51.4 kg y^{-1} (CFB: 2.4 kg y^{-1} and PC: 49 ± 32 kg y^{-1}), significantly lower than previous reports.

1. Introduction

Coal-fired power plants (CFPPs) are the main electricity provider and the largest coal consumer in China for the past several decades (Hao et al., 2017; Chang et al., 2019). In 2016, CFPPs in China consumed of 1827 Mt coal (Bai et al., 2018; National Bureau of Statistic of China, 2018) and produced 72.2% the national total electricity (National Bureau of Statistic of China, 2018). As a kind of non-clean fuel, coal consists of various components, including trace harmful elements (Zhao et al., 2010a, 2012). During the coal combustion and pollution control processes, these elements in coal would ended up in different coal combustion by-products, such as bottom ash, fly ash and flue gas desulfurization (FGD) gypsum, or been released into the ambient atmosphere with the stack flue gases (Tang et al., 2013). Atmospheric emissions of these trace harmful elements will exert dangerous effects on the environment and public health (Tian et al., 2013). Cadmium (Cd) is one of the main pollutants emitted from coal combustion

(Deng et al., 2014; Schröder et al., 2013). In 2010, the amount of Cd emitted from all coal combustion source in China were estimated to be 303 tons, accounting for 14% of the total anthropogenic emissions from the country (Shao et al., 2013). It has been reported that Cd exposure, even at low concentrations, can cause certain diseases such as cancer, reproductive system problems, cardiovascular diseases, brain malfunctions and neurological illness (Zhang et al., 2017). Excessive exposure to cadmium can also cause the itai-itai disease, kidney damage, etc. (Ueno et al., 2010; Chandra et al., 2001).

In China, only a few studies focused on Cd emissions from coal-fired power plants based on the actual field measurements (Deng et al., 2014; Zhang et al., 2017; Zhao et al., 2018), others are based on the emission factor method (Tian et al., 2012, 2014; Shao et al., 2013) that may face large uncertainties. Moreover, in the past two decades, China's coal-fired power plants have underwent tremendous changes, not only the boiler capacity, but also the air pollution control facilities (Ancora et al., 2015). Larger boilers (such as 600–1000 MW) are continuously

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installed with small boilers with capacity less than 100 MW or even 200 MW being phased out. Retrofit of venturi dust removal or mechanical dust removal to electrostatic precipitator (ESP) or ESP combined with fabric filter (FF), installation of desulfurization and denitration facilities were accomplished successively in the past two decades (Wu et al., 2016). These improvements have significantly reduced the emission of conventional pollutants, leading the emission of SO$_2$, NOx, and PM reduced by 80–91% in the period of 2006–2015 (Pan et al., 2010; Sheng et al., 2018). The emission of other trace harmful elements would also been impacted by the co-benefit effect of difference advanced APCDs. Therefore, there is an urgent need to update the emission inventory of such trace harmful elements to reduce the uncertainty in the assessment of anthropogenic emissions based on more on-site field studies.

Cd typically exist at a trace level in coal (such as 0.1–3 mg/kg, Swaine et al., 1995). According to the classification of Meij (1994), Cd is a moderate volatile element during the coal combustion process. Large amount of coal combustions in CFPPs would lead to a great many of Cd atmospheric emissions each year, for example, 64 tons of Cd was emitted from CFPPs in Europe in 1979 (Pacyna, 1987) and 59 tons from Chinese CFPPs in 2010 (Shao et al., 2013). Guizhou province, located in Southwest China, is the fifth largest coal reserve province after Inner Mongolia Autonomous Region, Shanxi, Shaanxi and Xinjiang Uygur Autonomous Region (Mao and Xu, 1999), and the largest in South China, most coal resource in this province is distributed in the central-west province. In 2017, 66 Mt of coal was used in Guizhou's CFPPs, this figure has expanded for more than 15 times compared to 1990 (Bureau of Statistics of Guizhou Province, 2018). The average Cd concentration in coal of western Guizhou (0.40 mg kg^{-1}, Dai et al., 2005) or the whole Guizhou (0.506 mg kg^{-1}, unpublished internal data), is much higher than the Chinese average (0.25 mg kg^{-1}) (Dai et al., 2012) and the world average (0.22 mg kg^{-1}) (Ketris and Yudovich, 2009; Table S1).

In this paper, we investigated seven coal-field power plants (CFPPs) in Guizhou during 2014–2016, with feed fuel, limestone, bottom ash, fly ash, gypsum, as well as stack flue gas collected and analyzed simultaneously. The main research objectives are: (1) to understand the distribution behavior of Cd in these CFPPs with different type of boiler and APCDs; (2) to obtain the release ratio of Cd in the combustion process; (3) to secure the up-to-date atmospheric emission factors and the mass balance of Cd in these CFPPs; (4) and finally, to estimate the total amount of atmospheric Cd emissions from CFPPs in this province. The research provide the necessary scientific knowledge and database for the assessment of Cd pollution impact and the countermeasures of pollution control in this source in China.

2. Material and methods

2.1. Plant description and sample collection

The locations of the seven CFPPs selected for the present study are illustrated in Fig. 1a and b. CFPPs #1, #3, #4, #6 and #7 are located in the western province, #2 and #5 are situated in the central province. The information about the boiler type, installed capacity, APCDs, and the sampling locations are given in Table 1 and Fig. 2. Briefly, CFPPs #1 is equipped with a circulating fluidized bed boiler (CFB, Fig. 2a) and CFPPs # 2–7 with pulverized coal-fired boilers (PC, Fig. 2b and c). APCDs for the seven CFPPs consisted of denitrification unit (selective non-catalytic reduction (SNCR) for #1, selective catalytic reduction (SCR) for #3–7, dust removal device (cold-side electrostatic precipitator (C-ESP) or cold-side electrostatic precipitator combined fabric filter (C-ESP-FF)), desulfurization system (limestone-gypsum wet flue gas desulfurization (WFGD) for #1, #3–7 and organic amine desulfurization (OAD) for CFPPs #2). Gangue and coal slime were used as feed fuel in CFPPs #1, bituminous was used in CFPPs #2–4, #6–7, and anthracite was used in CFPPs #5 (Table 2).

The sampling points for the solid and flue gas samples in the two types of CFPP are shown in Fig. 2. In each CFPP, only one utility boiler system was tested to represent the whole CFPP because all boilers in each CFPP were feed with the same type of coal and equipped with the same APCDs. Feed fuel (coal, gangue and coal slime), coal combustion products (CCPs, referred to as bottom ash and fly ash), limestone and desulfurized gypsum were collected simultaneously (about 1 kg per sample) for 3–6 times in a 2–3 sampling day for each CFPP. Noting that fly ash is a mixture of different fly ash hoppers for ESP/ESP + FF. And organic amines and sulphuric acid samples were not collected and analyzed for CFPPs #2. The temperature of the stack flue gas from the tested CFPPs is in the range of 40–50 °C, so only particulate matter (PM) was collected due to volatile elements such as Cd would condense onto the fly ash surfaces, due to the melting point (321 °C) and boiling point (765 °C) of cadmium are much higher than this temperature (Fotios el al., 2018). PM was withdrawn isokinetically from the flue gas and collected on a Teflon filter (Whatman®, 0.45 μm pore size) using equipment of APEX Model XC-572 (APEX Instruments, USA, Fig. S1). According to US EPA Method 5 (US EPA, US Environmental Protection Agency, US EPA, 1996). Since the PM size of fly ash is dominantly greater than 1 μm, this method will collect most of the PM in the flue gas (Chen et al., 2018; Liu et al., 2019). The flue gas sampling system is maintained at a temperature of 120 ± 10 °C to avoid water condensation (US EPA, 1996). Each flue gas sample was collected for approximately 3 h and 2–4 flue gas samples were obtained as well as other types of solid samples for a CFPP. At the same time, some operating parameters of the boiler (Table S2) were recorded during the sampling period, including the daily consumption of feed fuel (t·d^{-1}), the daily output of different solid materials (t·d^{-1}), daily flue gas emissions (Nm^3·d^{-1}) and the actual operating power (MW) of the boiler.

2.2. Analysis methods

Solid materials including feed fuel (coal, gangue and coal slime), limestone, CCPs (bottom ash and fly ash), and gypsum were air-dried and then ground into small pieces (< 0.150 mm). All the results of solid samples were given based on the air-dried basis. The proximate analysis method for feed fuel samples was referenced from the Chinese National Standard Method (GB/T 212-2008). Carbon (C), hydrogen (H), and nitrogen (N) contents in feed fuel samples were determined by an elemental analyzer (Vario MACRO Cube, Elementar, Germany) and the total sulfur (S) in feed fuel samples was measured based on the Eschka method (GB/T 214-2007). The calorific value (Q) was determined by GB/T 213-2008. Before measuring trace elements, the solid samples and Teflon filters were digested according to a method developed by Qi and Grégoire (2000). Briefly, 50 mg sample was digested using 1 mL of concentrated HF and 1 mL of concentrated HNO$_3$ in the PTFE-lined stainless-steel bombs and was heated to 190 °C for 24 h. The insoluble residues, if present, were dissolved using 6 mL of 40% v/v HNO$_3$ and were then heated to 140 °C for 5 h. After cooling down, 200 ng rhodium (Rh) was added into the liquid solution and full mixed together, then about 0.4 mL of the digest was transferred to a centrifuge tube with approximate 10 mL of Milli-Q water (18.2 MΩ cm, Millipore Inc.). Rh was used as an internal standard for correcting matrix effects and instrumental drift. Cd concentration in the digestion solution was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Analytik Jena, Germany) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. Cd concentration in the stack flue gas was determined by the total amount of Cd on the filter relative to the volume of sampled flue gas.

2.3. Quality assurance and quality control

Careful pre-treatment was implemented for flue gas sampling and the laboratory testing to reduce possible contamination. All glassware and Teflon tubing were washed with 20% nitric (HNO$_3$) acid and rinsed
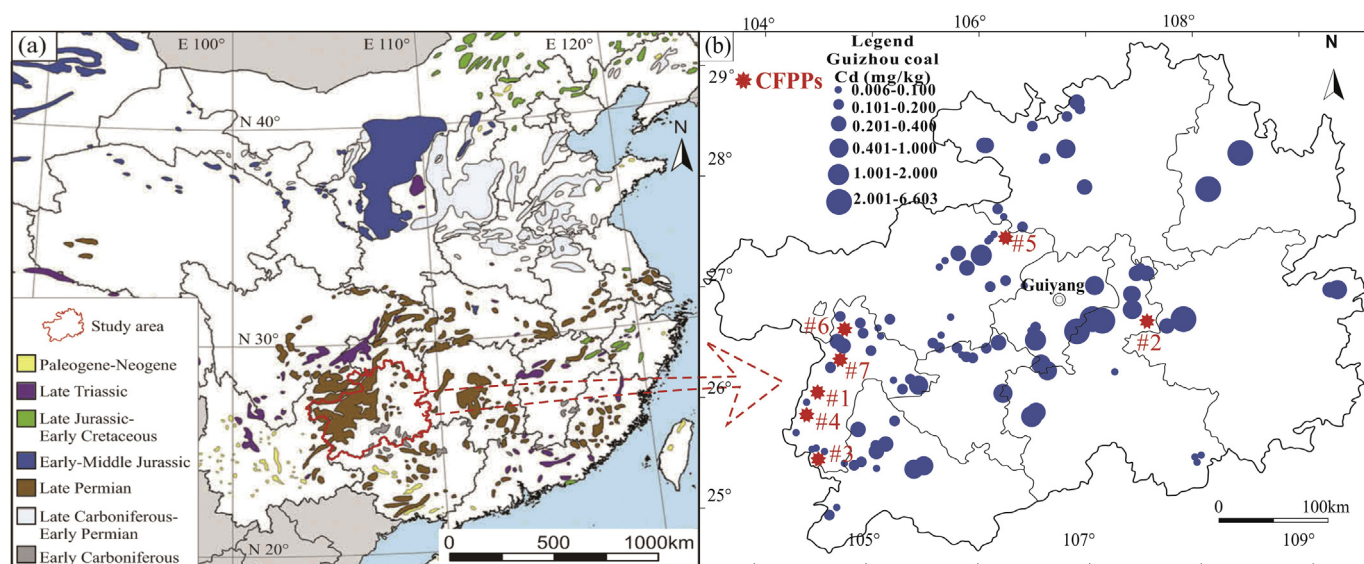
Fig. 1. (a) Distribution and formation ages of coal in China (modified from Dai and Finkelman, 2018), and (b) locations of the seven selected CFPPs in this study and Cd concentration in Guizhou's coal (unpublished internal data).

Table 1
Information of the seven CFPPs investigated in the present study.

Power plants	Boiler type	Installed capacity	APCDs
#1	CFB	2 × 300 MW	SNCR + C-ESP-FF + WFGD
#2	PC	2 × 600 MW	SCR + C-ESP + OAD
#3	PC	2 × 600 MW	SCR + C-ESP + WFGD
#4	PC	2 × 660 MW	SCR + C-ESP + WFGD
#5	PC	4 × 300 MW	SCR + C-ESP-FF + WFGD
#6	PC	4 × 200 MW	SCR + C-ESP + WFGD
#7	PC	4 × 600 MW	SCR + C-ESP + WFGD

Note: CFB, circulating fluidized bed boiler; PC, pulverized coal-fired boiler; SNCR, selective non-catalytic reduction; SCR, selective catalytic reduction; C-ESP, cold side electrostatic precipitator; C-ESP-FF, cold side electrostatic precipitator and fabric filter; WFGD, limestone-gypsum wet flue gas desulfurization; OAD, organic amine desulfurization.

with deionized water before use. The reagents used were all trace metal grade reagents, and hydrofluoric (HF) acid and nitric (HNO$_3$) acid were subjected to secondary distillation to remove possible impurities.

System blanks, duplicate samples, and certified reference materials (CRMs) are used for quality assurance and quality control purposes. For the proximate and ultimate analysis, CRMs of coal gangue (ZBM 110A, GSB 06-2182-2008-1), anthracite (ZBM 095, GSB 06-2105-2007) and bituminous coal (ZBM 113, GSB 06-2114-2007) were used. The recovery rate is between 95 and 105%. Coal standard materials (NIST SRM 1632d; NIST SRM 1635a), fly ash (NIST SRM 1633c), gypsum (NIST SRM 2429) and limestone (JLS-1; JDO-1) are simultaneously digested and analyzed with solid samples to ensure analytical quality of trace elements. The recovery of Cd in different CRMs is in the range of 90–110%, and the process blank is as low as 0.01 mg kg^{-1}.

2.4. Calculation of relative enrichment factor, release ratio and atmospheric emission factor

2.4.1. Relative enrichment factor

Relative enrichment factor (REF) is an important parameter to reveal the enrichment of target elements in CCPs during the combustion process in boilers (Meij, 1994). REF was calculated as follows:

$$REF = \frac{C_{ash}^{Cd} \times A_{ad}}{C_{fuel}^{Cd}} \tag{1}$$

where C_{ash}^{Cd} is Cd concentration in bottom ash or fly ash, A_{ad} is ash yield of feed fuel on air-dried basis, and C_{fuel}^{Cd} is Cd concentration in feed fuel.

2.4.2. Release ratio

In order to evaluate the volatility of Cd during coal combustion in the boiler at high temperature, a release ratio R was derived as (Deng et al., 2014):

$$R = (1 - \frac{C_{Cd,BA} \cdot C_{ash} \cdot A}{C_{Cd,coal}}) \times 100\% \tag{2}$$

where $C_{Cd,BA}$ is the concentration of Cd in bottom ash. $C_{Cd,coal}$ is the concentration of Cd in feed coal. C_{ash} represents ash yield in feed coal. A stands for the percentage of bottom ash with respect to the ash yield in coal. It is assumed that the proportion of bottom ash is 10% for PC boiler and 40% for CFB (Deng et al., 2014). Release ratios of trace metals during coal combustion depend on the boiler types, the boiler operation conditions and the metal volatility (Deng et al., 2014).

2.4.3. Cadmium emission factor

In order to estimate Cd atmospheric emissions more accurately, emission factors (EMFs) of Cd (Zhao et al., 2008b, 2017b; Wang et al., 2010) were calculated as follows:

$$EMF_1 = \frac{M_{Cd}}{M_{coal}} \tag{3}$$

$$EMF_2 = \frac{M_{Cd}}{P \times t} \tag{4}$$

$$EMF_3 = \frac{M_{Cd}}{M_{coal} \times Q_{net,ad}} \tag{5}$$

where EMF_1, EMF_2, and EMF_3 are Cd emission factors based on the fuel consumption, actual generation power, and heat value of fuel, respectively; M_{Cd} is the amount of Cd emitted into the atmosphere per day (g·d^{-1}); M_{coal} is the consumption of fuel (t·d^{-1}, based on CFPP statistics); P is the actual power of tested power plant (On-line monitoring data); t is the running time of a utility boiler (24 h d^{-1}); and $Q_{net,ad}$ is heat value of feed fuel based on air-dried (MJ·kg^{-1}) (Li et al., 2019).
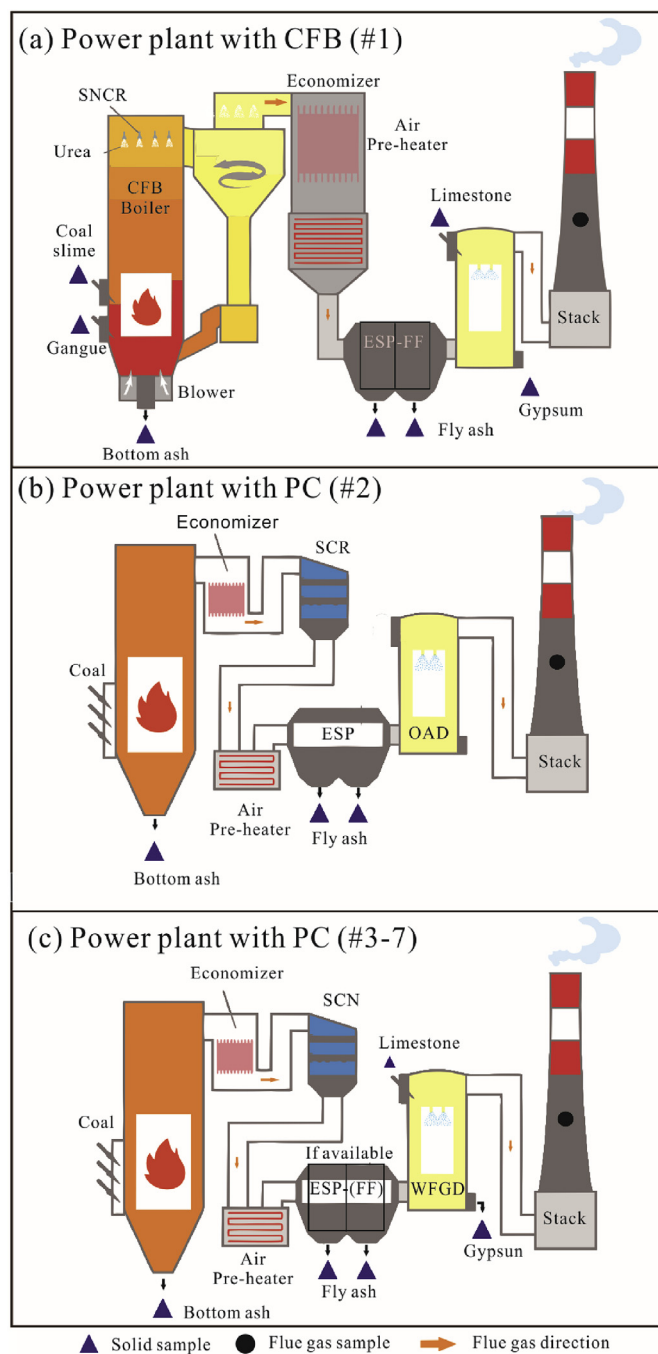
Fig. 2. Schematic diagram of sampling sites in the seven CFPPs with (a) CFB and (b, c) PC.

3. Results and discussion

3.1. Fuel analysis

Proximate and ultimate analysis of the feed fuels at the seven CFPPs are presented in Table 2. Moisture content of coal gangue (2.89%) and coal slime (9.06%), and ash yield based on air-dried basis (45.15% and 43.94% for coal gangue and slime, respectively) of CFPP #1 are significantly higher than that of other power plants (0.66–1.43% of moisture and ash yield of 30.68–39.56%), with the exception of CFPP #6 with high ash yield (45.73%); the content of sulfur in feed coal in western Guizhou (0.29–2.50%) is significantly lower than that in the central and eastern regions (3.41–3.82% for CFPPs #2 and #5). The

calorific value (17.03–25.10 MJ kg^{-1}) for all CFPPs is generally in a low to medium level. Compared with the national average of ash yield (16.85%, Li and Zhai, 1994) and sulfur content (1.15%, Li and Zhai, 1994), the coal used in Guizhou's power plants is nearly one more time higher, indicating that the feed coal quality is poor. In addition, the feed fuels of seven CFPPs are characterized by medium volatile matter (15.05–22.44%), with the exception of CFPP #5, which show a low volatile matter (8.77%) and high fixed carbon (51.73%) since anthracite was used.

3.2. Distribution of Cd in feed fuel and combustion products

Cd concentrations of solid samples and stack flue gas are illustrated in Table 3. Cd concentrations in feed fuel of CFPPs (#1,3–4,6-7) in western Guizhou were in the range of 0.15–0.26 mg kg^{-1}, much lower than Cd in feed coal of CFPP #5 (0.68 mg kg^{-1}) and CFPP #2 (0.4 mg kg^{-1}), that located in central and eastern Guizhou. This distribution pattern is similar to the spatial distribution pattern of Cd in Guizhou's coal (Fig. 1b, unpublished internal data), which means that coal Cd content in central and northeastern Guizhou is much higher than that in other areas of Guizhou.

Cd concentrations were much higher in coal fly ashes (range: 0.43–2.03 mg kg^{-1}, mean: 0.85 ± 0.54 mg kg^{-1}) than bottom ashes (range: 0.08–0.42 mg kg^{-1}, mean: 0.22 ± 0.12 mg kg^{-1}) for PC boilers (Table 3), and 2–6 times more Cd were found in fly ash than that in bottom ash for the same utility boiler, indicating that Cd is more easily enriched in fly ash. A higher fold, 17 times more Cd was found for fly ash than bottom ash in a Netherlands PC power plants (Meij, 1994). While, for the CFB boiler, this discrepancy was not too much, Cd content in fly ash (0.45 mg kg^{-1}) was slightly higher than that of bottom ash (0.39 mg kg^{-1}) in CFPP#1. The average Cd content in fly ash in the present study is 0.85 mg kg^{-1} (Table 3). Compared with feed fuels and the corresponding CCPs, Cd in limestone was very low, with range of 0.01–0.67 mg kg^{-1}, FGD gypsum was also low in Cd, with range of 0.02–0.41 mg kg^{-1}. There is no significant difference between the Cd content of limestone and the Cd content of desulfurized gypsum. The concentrations of Cd in limestone were slightly higher than that of gypsum for most case (Table 3), indicating the negligible impact of Cd in flue gas involved in the WFGD process and the dilution effect of the forming of WFGD gypsum (CaHSO$_4$·2H$_2$O, molecular weight 172) from limestone (CaCO$_3$, molecular weight 100) (Meawad el al., 2010). Cd in the stack flue gas was in the range of 0.005–0.03 μg·Nm^{-3} for the seven CFPPs (Table 3), with CFPPs #2, 4, 5, (0.012–0.030 μg·Nm^{-3}) much higher than others (0.005–0.010 μg·Nm^{-3}, Table 3). In addition, PM emitted from the stack flue gas was in the range of 10.03–18.28 mg·Nm^{-3} (Table S2), comparable to other PC boilers in North China (9.10–17.83 mg·Nm^{-3}, Liu et al., 2019), all these values were lower than the national emission standard of PM for CFPPs (30 mg m^{-3}, GB 13223-2011).

Cd could melt and/or evaporate in the CFB/PC boilers since the temperature range of CFB and PC can reach 800–950 °C and 1200–1500 °C (Chen et al., 2019), respectively. Based on Eq (1), REF values of Cd in bottom ash and fly ash were estimated to be in the range of 0.13–0.41 (average 0.24) and 0.88–1.24 (average 1.05) in PC CFPPs #2–7, respectively (Table 4). But REF values of Cd in bottom ash in CFPP with #1 is very high to 0.83 and in fly ash is 0.97, indicating more Cd were retained in the bottom ash for CFB than PC boilers. It was consistent with report showing that higher temperature will facilitated more Cd transferred into fly ash (Huang et al., 2004). Results of correlation analysis showed that there is a positive correlation between Cd concentration in fly ash and feed fuel (R^2 = 0.9656, p < 0.01), but a weak correlation between bottom ash and feed fuel (R^2 = 0.2672, p = 0.23) (Fig. 3), suggesting more Cd being transferred from the feed coal to fly ash than bottom ash for PC boilers.

Table 2
Proximate and ultimate analysis of feed fuels.

Power plants	Fuel type	Proximate analysis (%)				Ultimate analysis (%)				$Q_{net,ad}$
		M_{ad}	V_{ad}	A_{ad}	FC_{ad}	C_{ad}	H_{ad}	N_{ad}	S_{ad}	(MJ·kg-1)
#1(No. = 4)	Gangue	2.89 ± 0.42	18.77 ± 0.27	45.15 ± 2.83	33.19 ± 2.87	47.24 ± 3.43	3.21 ± 0.13	0.85 ± 0.05	0.45 ± 0.07	19.29 ± 1.28
#1(No. = 4)	Coal slime	9.06 ± 3.18	17.53 ± 0.63	43.94 ± 4.18	29.47 ± 1.69	41.86 ± 1.96	2.96 ± 0.15	0.82 ± 0.03	0.29 ± 0.04	17.03 ± 0.79
#2(No. = 6)	Bituminous	1.26 ± 0.13	22.44 ± 0.90	32.27 ± 1.96	44.03 ± 1.51	57.73 ± 1.65	4.18 ± 1.07	1.19 ± 0.44	3.82 ± 0.52	24.25 ± 1.29
#3(No. = 4)	Bituminous	1.08 ± 0.13	18.07 ± 1.70	30.68 ± 2.85	50.17 ± 4.50	62.38 ± 2.86	3.19 ± 0.32	1.07 ± 0.08	0.64 ± 0.06	24.47 ± 1.19
#4(No. = 4)	Bituminous	1.16 ± 0.08	19.93 ± 3.59	31.78 ± 1.27	47.13 ± 3.55	60.25 ± 1.91	4.51 ± 1.42	1.59 ± 0.58	0.63 ± 0.07	25.10 ± 1.90
#5(No. = 3)	Anthracite	1.43 ± 0.20	8.77 ± 1.21	38.08 ± 8.00	51.73 ± 9.01	52.56 ± 12.81	3.64 ± 0.70	1.18 ± 0.28	3.41 ± 0.86	21.89 ± 4.96
#6(No. = 4)	Bituminous	1.22 ± 0.11	15.96 ± 1.14	45.73 ± 1.94	37.09 ± 1.18	47.04 ± 3.34	3.04 ± 0.20	0.79 ± 0.06	1.37 ± 0.17	19.19 ± 1.32
#7(No. = 4)	Bituminous	0.66 ± 0.14	15.05 ± 0.72	39.56 ± 2.22	44.72 ± 1.76	51.21 ± 1.72	3.04 ± 0.07	0.85 ± 0.04	2.50 ± 0.27	20.74 ± 0.53
Min-Max		0.66–9.06	8.77–22.44	30.68–45.73	29.47–51.73	41.86–62.38	2.96–4.51	0.82–1.59	0.29–3.41	17.03–25.10
Mean ± SD		2.35 ± 2.79	17.07 ± 4.06	38.40 ± 6.24	42.19 ± 8.09	52.53 ± 7.15	3.47 ± 0.58	1.04 ± 0.27	1.64 ± 1.41	21.5 ± 2.93

Note: No., Number of samples collected; M, moisture; V, volatile; A, ash; FC, fixed carbon; C, carbon; H, hydrogen; N, nitrogen; S, sulfur; Qnet, net heat value; subscript "ad", air-dried basis.

Table 3
Cd concentration in the solid materials and stack flue gas of the seven CFPPs.

CFPPs	#1(No. = 6)	#2 (No. = 3)	#3 (No. = 4)	#4 (No. = 6)	#5 (No. = 4)	#6 (No. = 3)	#7 (No. = 3)
Feed fuel (mg·kg-1)	0.26 ± 0.11a 0.18 ± 0.01b	0.42 ± 0.08	0.15 ± 0.02	0.17 ± 0.00	0.68 ± 0.15	0.22 ± 0.01	0.26 ± 0.01
Bottom ash (mg·kg-1)	0.39 ± 0.06	0.16 ± 0.06	0.20 ± 0.08	0.18 ± 0.01	0.42 ± 0.09	0.08 ± 0.02	0.13 ± 0.01
Fly ash (mg·kg-1)	0.45c	1.17 ± 0.15	0.43 ± 0.15	0.65c	2.03 ± 0.15	0.50 ± 0.20	0.72 ± 0.38
Limestone (mg·kg-1)	0.31 ± 0.08		0.14 ± 0.01	0.20 ± 0.01	0.01 ± 0.001	0.46 ± 0.03	0.67 ± 0.02
Gypsum (mg·kg-1)	0.41 ± 0.27		0.18 ± 0.03	0.22 ± 0.003	0.02 ± 0.004	0.33 ± 0.00	0.29 ± 0.04
Flue gas (μg·Nm-3)	0.006 ± 0.001	0.012 ± 0.001	0.006 ± 0.002	0.016 ± 0.006	0.030 ± 0.003	0.005 ± 0.003	0.010 ± 0.006

Note: a, Gangue; b, Coal slime; c, Weight average based on fly ash from ESP and FF.

Table 4
Relative enrichment factors (REFs) of Cd in coal combustion productions (CCPs) of seven CFPPs in the present study.

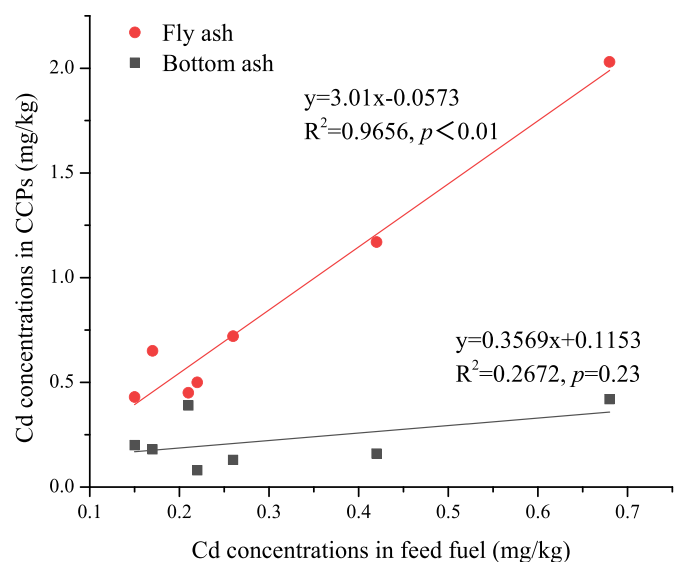| CCPs	#1	#2	#3	#4	#5	#6	#7
Bottom ash	0.83	0.13	0.41	0.34	0.24	0.16	0.19
Fly ash	0.97	0.91	0.88	1.24	1.13	1.06	1.10

Fig. 3. The Pearson correlations between Cd concentration in feed fuel and the corresponding CCPs of the seven CFPPs.

3.3. Release ratio of Cd

As shown in Table 5, Cd has the highest release ratio of 95.91–98.77% for PC CFPPs #2-7, but lower (76.94%) in CFB CFPP #1,

indicating CFB boiler have lower release rate of Cd compared to PC boilers, which can be attributed to the lower combustion temperature in CFB boiler than the PC boiler, and the coarse feed coal and the cycling process of CFB boiler, both facilitate more Cd retained in the bottom ash than PC boilers. Release ratios (88.21–94.93%) of PC boilers reported by Deng et al. (2014) and Tian et al. (2012) were slightly lower than this study (95.91–98.77%), and reported 78.31% for CFB boiler (Deng et al., 2014) was close to this study (76.94%), but reported value (91.50%) for CFB by Tian et al. (2012) was significantly higher than this study.

3.4. Cd mass balance and atmospheric emissions

Cd mass balance between the input and output was calculated based on the operating parameters of boilers, including the daily consumption/production materials, the daily stack flue gas volume, and the actual operating power of boilers (Table S2), as well as Cd concentrations in solid samples and stack flue gas (Table 3). The results from the seven CFPPs revealed that Cd input and output were basically balanced, for example, the ratio of Cd in output to input of the seven CFPPs were in the range of 79.28–125.98% (Fig. 4 and Table S3). Nevertheless, it is acceptable when this value falls in the range of 70%–130% (Quick and Irons, 2002). The input of Cd was predominantly contributed by the feed fuel, which accounts for more than 90.04% of total input (Fig. 4 and Table S4), because both the concentration of Cd in feed fuel and the consumption rate of feed fuel were much higher than those of the limestone, and the input of Cd by limestone was 1.55% in CFPPs #1 with CFB, and 0.21–9.96% in CFPPs #3–6 with PC. But Cd output through FGD gypsum in CFPPs #7 is as high as 13.63%, might because this CFPP has a larger amount of FGD gypsum production rate and the relative higher Cd in it than other CFPPs (Table S2; Table 3).

For the output materials, 78.90–95.85% Cd occurred in fly ash and 1.00–10.85% in bottom ash in CFPPs with PC boilers; 67.62% Cd occurred in fly ash and 29.17% in bottom ash in CFPPs with CFB boiler (Fig. 4 and Table S4). Indicating that CFB system increased the yield of

Table 5
Release rate, removal efficiency and emission factors of Cd in the seven CFPPs.

CFPPs	#1	#2	#3	#4	#5	#6	#7	Mean $\pm$ SD
Release ratio (%)	76.94	98.77	95.91	96.64	97.65	98.34	98.02	94.61 $\pm$ 7.85
Removal efficiency (%)	99.98	99.97	99.95	99.95	99.97	99.99	99.98	99.97 $\pm$ 0.01
EMF_1 (mg·t^{-1} coal)	0.03	0.09	0.05	0.09	0.20	0.03	0.08	0.08 $\pm$ 0.06
EMF_2 (μg·(kW·h)$^{-1}$)	0.02	0.04	0.02	0.05	0.10	0.02	0.04	0.04 $\pm$ 0.03
EMF_3 (g·TJ^{-1})	0.002	0.004	0.002	0.004	0.01	0.002	0.004	0.004 $\pm$ 0.003

Note: Release ratio, release ratio of Cd in the combustion process; Removal efficiency, overall removal efficiency of Cd by APCDs; EMF, emission factor.
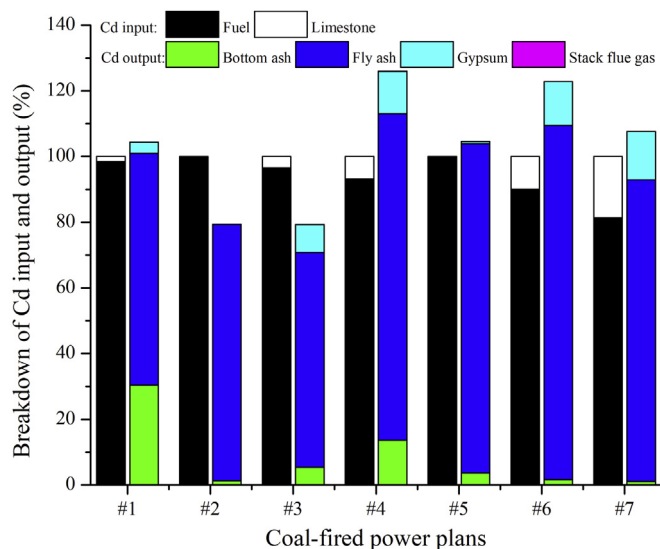

Fig. 4. Proportion of Cd in input and output materials of the seven CFPPs (the output ratio is based on the total input of Cd). Note: Organic amines and sulphuric acid are not collected and analyzed in CFPP #2.

bottom ash and decreased the Cd output ratio in fly ash. The mass ratio of bottom ash to fly ash was 0.43 in CFPPs #1 and about 0.01–0.14 in CFPPs #3–7, high Cd ratio in CFB bottom ash is related to the combustion of gangue and coal slime, and the addition of limestone that increased the yield of bottom ash, as well as due to the different operation mode between CFB (800–950 °C with cyclic process, Fig. 2a and b) and PC (1200–1500 °C, Chen et al., 2019). Briefly, the mass ratio of bottom ash to fly ash was positively correlated with the proportion of the total amount of Cd in bottom ash to total Cd output, but inversely correlated to the proportion of Cd in fly ash to total Cd output (Fig. S2). Cd in WFGD gypsum contributed 3.20% of total Cd output in CFPPs #1 with CFB and 0.62–13.63% CFPPs #3–7 with PC (Fig. 4, Table S4).

Cd condenses rapidly during the flue gas cooling, resulting in the accumulation of most Cd in fly ash (Pavageau et al., 2004). With the high removal efficiency of particulate matter by ESP or ESP-FF (over 99.9%), and the further removal (30–56%) by WFGD (Yao et al., 2019; Liu et al., 2019), Cd in stack flue gas accounted for less than 0.05% of the total Cd output (Fig. 4, Table S4). There was only 0.07–0.47 g d^{-1} Cd emitted into the atmosphere from the seven tested utility boiler (Table S3).

In the current study, EMFs were estimated to be as low as 0.03–0.2 (0.08 $\pm$ 0.06) mg Cd·t^{-1} coal, 0.02–0.1 (0.04 $\pm$ 0.03) μg Cd·(kW·h)$^{-1}$, and 0.002–0.01 (0.004 $\pm$ 0.003) g Cd·TJ^{-1} (Table 5). EMFs of CFB boilers (0.03 mg t^{-1} coal, 0.02 μg·(kW·h)$^{-1}$, 0.002 g TJ^{-1}) are lower than PC boilers (0.03–0.2 (0.09 $\pm$ 0.05) mg·t^{-1} coal, 0.02–0.1 (0.045 $\pm$ 0.03) μg·(kW·h)$^{-1}$, 0.002–0.01 (0.004 $\pm$ 0.003) g·TJ^{-1}) (Table 5). In 2017, the coal consumption and power generation of CFPPs in Guizhou were 66 million tons and 121 billion kW·h, respectively (Bureau of statistics of Guizhou Province, 2018), with 10% and 90% contributed by CFB and PC boilers, respectively (Wu et al., 2016). Therefore, the Cd emissions of CFPPs in Guizhou were estimated

to be 51.4 kg y^{-1} (the Cd emissions of CFB were estimated to be 2.4 kg y^{-1} and PC were estimated to be 49 $\pm$ 32 kg y^{-1} with range of 22–109 kg y^{-1})) based on the power generation, Cd concentration in coal and the associated emission factors for each type of boiler obtained from this study. This estimation is significantly lower than previous result (430 kg y^{-1}) reported by Tian et al. (2014) for the year 2010 from the same province. That might due to the higher Cd content (0.79 mg kg^{-1}) in Guizhou's coal and the higher emission factor (10 mg Cd·t^{-1} coal) adopt by these researchers through the literature review. Some field studies on solid materials and stack flue gas of Cd in CFPPs were shown in Table S5. Cd concentrations in stack flue gas of a Chinese CFPP (0.009 μg·Nm^{-3}, Chang et al., 2019) and a Japanese CFPP (0.0145 μg·Nm^{-3}, Ito et al., 2006) (Table S5) was comparable to this study (0.006–0.03 μg·Nm^{-3}). The emission factor (0.03 mg Cd·t^{-1} coal) of CFB boiler of this study is significantly lower than that (4.2 mg Cd·t^{-1} coal) reported by Deng et al. (2014). The emission factors of PC boilers in this study (0.09 mg Cd·t^{-1} coal) are close to those of Chang et al. (2019) (0.09 mg Cd·t^{-1} coal) and Goodarzi et al. (2008) (0.08 mg Cd·t^{-1} coal), which are significantly lower than those of other studies (1.3–13.1 mg Cd·t^{-1} coal). There are relatively few studies on the concentration of Cd in stack flue gas, which requires further research.

The overall removal efficiency of Cd by the current APCDs is 99.95–99.99% (Table 5). With the development of APCDs technology and the elimination of small boilers and old boilers, China has made significant progress in atmospheric pollutants such as nitrogen oxides, sulfur dioxide and PM in the past decade. According to the data collected in this study, Cd emissions from CFPPs have also been significantly reduced due to the implementation of modern APCD, and Cd emissions are much lower than earlier reports.

4. Conclusions

Based on the onsite study, the following conclusions could be achieved:

(1) Most Cd input was from the feed coal (81.40–90.04%) of the seven investigated CFPPs and the majority Cd output was the captured fly ash (CFB: 67.62%, PC: 78.90–95.85%), followed by bottom ash (CFB: 29.17%, PC: 1.00–10.85%).

(2) The concentration of Cd is significantly higher in the fly ash (range:0.43–2.03 mg kg^{-1}, mean:0.85 $\pm$ 0.54 mg kg^{-1}) than the bottom ash (range:0.08–0.42 mg kg^{-1}, mean:0.22 $\pm$ 0.12 mg kg^{-1}). Cd has the highest release ratio of 95.91–98.77% in CFPPs, but lower in CFB (76.94%), indicating that CFB has lower release ratio of Cd.

(3) Atmospheric Cd emissions were low under the control of the current APCDs. With Cd concentration of 0.06-0.03 μg·Nm^{-3} in the stack flue gas, MEFs were estimated to be as low as 0.03–0.2 mg Cd·t^{-1} coal, 0.02–0.1 μg Cd·(kW·h)$^{-1}$, and 0.002–0.01 g Cd·TJ^{-1}. In 2017, the amount of Cd emitted from CFPPs in Guizhou province was estimated to be 51.4 kg y^{-1} (CFB: 2.4 kg y^{-1} and PC: 49 $\pm$ 32 kg y^{-1} (range: 22–109 kg y^{-1})), significantly lower than previous estimates. In addition, considering the high concentration of Cd in fly ashes, more attention should be paid to the secondary discharge of Cd from this solid waste (Zhao et al., 2006).

CRediT authorship contribution statement

Xian Zhou: Formal analysis, Software, Visualization, Writing - original draft, Writing - review & editing. **Xiangyang Bi:** Investigation, Writing - review & editing. **Xinyu Li:** Methodology, Formal analysis, Software. **Shan Li:** Methodology. **Ji Chen:** Investigation, Methodology. **Tianrong He:** Methodology. **Zhonggen Li:** Conceptualization, Data curation, Investigation, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper "**Fate of cadmium in coal-fired power plants in Guizhou, Southwest China: with emphasis on updated atmospheric emissions**".

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Appendix A. Supplementary data

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