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Abstract:

Thallium (Tl) is a toxic element that exists at trace level in coal. Coal-fired power plants (CFPPs) consume large amounts of coal and can potentially release this element into surrounding environment. However, knowledge of fates of Tl inside CFPPs and associated atmospheric emissions is still very limited. In this study, five CFPPs with pulverized coal boilers (PC) in Guizhou province, southwest China were selected for investigation. All input and output solid materials and the stack flue gas samples were collected simultaneously. Tl concentrations in feed coal (0.10-0.34 mg·kg^{-1}) of the five

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CFPPS were only a third to one half of the national average value. Tl concentrations were obviously higher in fly ash (0.39-1.13 mg·kg^{-1}) than bottom ash (0.09-0.25 mg·kg^{-1}), indicating notable redistribution of Tl during coal combustion. Tl concentrations were low in limestone (0.01-0.02 mg·kg^{-1}), flue gas desulfurization gypsum (0.01-0.03 mg·kg^{-1}), and the stack flue gas (0.006-0.011 μg·Nm^{-3}). Most Tl inside these CFPPs was captured by electrostatic precipitator or electrostatic precipitator-fabric filter fly ash (88.66 - 97.44%), followed by bottom ash (2.13-10.73%), gypsum (<3.89%), and stack emissions (0.01-0.05%). Atmospheric emission factors of Tl from different CFPPs are in the range of 0.04-0.09 mg Tl·t^{-1} coal, 0.02-0.04 μg·(kW·h)$^{-1}$ or 0.002-0.004 g Tl·TJ^{-1}. Using these emission factors, a total of 3.96 ± 1.32 kg (range: 2.64-5.94 kg) Tl is estimated to be released into the atmosphere annually from CFPPs in Guizhou in 2017. To avoid the cross-media contamination from the combustion products, careful treatment of the captured fly ash, bottom ash, and gypsum is needed, considering that a large amount of Tl (average: 728 kg·yr^{-1}; range: 664-792 kg·yr^{-1}) is retained in these solid combustion products and the possibility of formation of more toxic Tl^{3+} during the combustion process.

Graphical abstract:
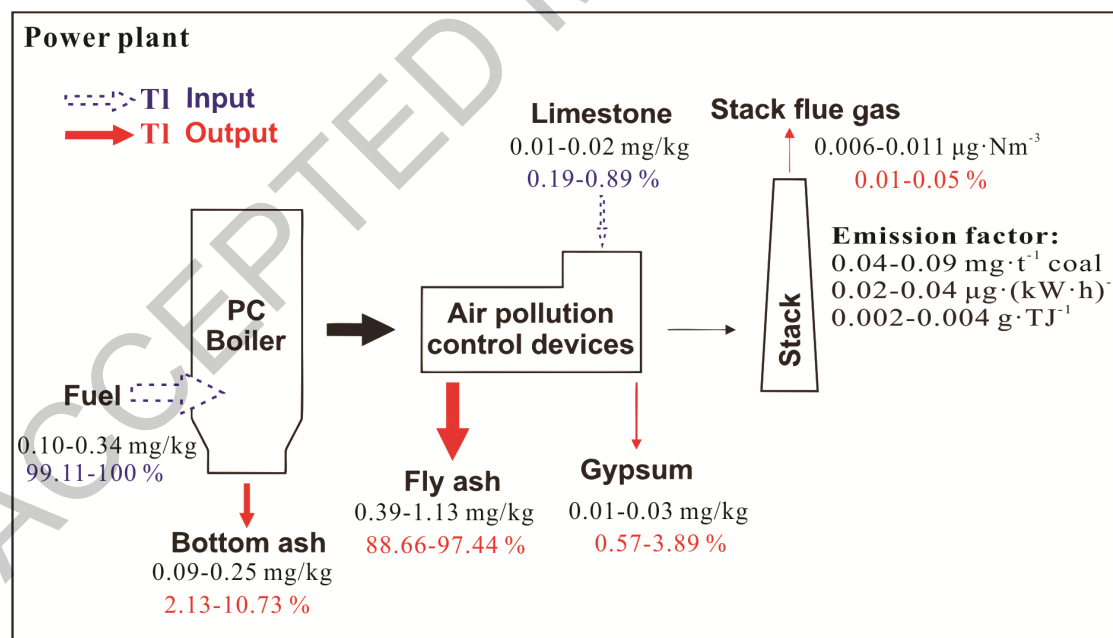
Key words: Thallium; Coal-fired power plants; Emission factors; PC boilers; APCDs

1. **Introduction**

Thallium (Tl) is a typical rare element distributed in natural environment (Liu et al. 2019a; Fang and Liu. 2019), but is persistent in air, water and soil (Belzile and Chen 2017). Tl is considered to be a more toxic element than lead, mercury and cadmium (Peter and Viraraghavan 2005; Maluszynski 2009), with its toxic effects being frequently recognized in animals and humans (Viraraghavan and Srinivasan 2011). Exposure to high level of Tl can result in serious health issues to human beings, including hair loss, mild progressive gastrointestinal disturbances, encephalopathy, tachycardia, degenerative changes in heart, liver and kidneys, changes in central nervous system and cardiovascular system, and ultimately death (Prick et al. 1995; Meggs et al. 1995; Hoffman 2000; Saha et al. 2004; U.S. EPA 2009a). Thus, Tl has been listed as a priority pollutant by many agencies, such as the United States (U.S.) Environmental Protection Agency (EPA) and the European Union (Directive 67/548/EEC).

Beside the geological sources, such as rock weathering and soil erosion (Xiao et al. 2012; Li et al. 2019a), industrial facilities, including coal-fired power plant, lead and zinc smelter, and cement plant where Tl exists as impurity in raw materials, are the major sources releasing Tl into natural environment (López-Antón et al. 2013; Saha 2005; Clarke and Sloss 1992). For example, available data indicate that coal-fired power plants (CFPPs) are among the main sources of Tl emissions to the atmosphere, with global atmospheric emissions from this source totally 600 tons/year (Peter and Viraraghavan 2005; Kazantzis 2000; Ewers 1988). In CFPPs, Tl levels in flue gas of CFPPs with as high as 700 μg·m^{-3} (López-Antón et al. 2013, 2015), and Tl contents in fly ash with 2 – 10 times higher than those in the coal before combustion were observed (López-Antón et al. 2013; Affolter et al. 2011).

China has become the largest coal consumer in the world and consumed 3.86 billion tons in 2017, in which 47% is by the power plants sector (National Bureau of Statistic of China, 2019). However, little is known about the fates of Tl in CFPPs and its atmospheric emissions from this source in China. Guizhou province in Southwest China is the fifth largest coal reserve in China and the largest coal mining in southern China (Bai et al. 2018), but coal produced here is with higher ash yields and sulfur contents than those in other place in China (Li and Zhai 1994). Because coal property is a key factor controlling the behaviors of trace metals in combustion and air pollution control processes (Xu et al. 2003), the distributions of Tl inside the CFPPs might be different between Guizhou and other provinces in China. In this study, we selected five pulverized coal-fired boiler (PC) power plants in Guizhou province for investigating fates of T1 in CFPPs. The installation capacity of these five CFPPs

represents about a quarter of the provincial total. Feed fuel, limestone, bottom ash, fly ash, gypsum, as well as stack flue gas were collected simultaneously and analyzed for T1 contents. The main objectives are to: (1) understand the distribution behavior of Tl in these CFPPs with different APCDs; (2) obtain the release ratio of Tl during the combustion process; (3) gain the up-to-date atmospheric emission factors and the mass balance of Tl in these CFPPs; and (4) estimate the total amount of atmospheric Tl emissions from CFPPs in this province. Results from this study provide scientific knowledge and database for compiling Tl atmospheric emissions from this source category in China, which are needed for assessing possible impacts of Tl pollution caused by CFPPs.

2. Materials and methods

2.1. Plant description and sample collection

Five CFPPs in Guizhou province of southwest China were selected for sample collection in this study (Fig. 1). CFPPs #1 and #4 are situated in the central areas and #2, #3 and #5 in the western areas of the province. The central to western areas of the province are the main coal production areas, with most coal formed in Late Permian and in bituminous or anthracitic. All utility boilers are pulverized coal (PC) boilers, with capacity ranging from 200 to 660 MW. APCDs of these CFPPs are slightly different, namely, with selective catalytic reduction (SCR) for all CFPPs, cold-side electrostatic precipitator (C-ESP) for #1 and #2, cold-side electrostatic precipitator combined fabric filter (C-ESP-FF) for #3-5, organic amine desulfurization (OAD) for CFPPs #1, and limestone-gypsum wet flue gas desulfurization (WFGD) for #2-5. The detailed information about the boiler type, installed capacity, and APCDs are summarized in Table 1.

The sampling points for the solid and flue gas samples in each CFPP are shown in Fig. 2. Only one utility boiler system in each CFPP was sampled to represent the whole CFPP because the feed coal and APCDs are the same for different units. In addition, other units might not be accessible for sampling. Feed fuel (bituminous and anthracite), coal combustion products (CCPs, referred to as bottom ash and ESP/ESP-FF fly ash), limestone and desulfurized gypsum were collected simultaneously (about 1 kg per sample) for 3-6 samples during a 2-3 days period for each CFPP with half day sampling interval. Organic amines and sulphuric acid samples in CFPPs #1 were not collected. The fly ash was collected from the fly ash silo for truck transportation and the sample was a mixture of fly ash from different hoppers of ESP/ESP+FF. The temperature of the stack flue gas is 40 - 50 for

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the tested CFPPs, and thus only particulate matter (PM) was collected considering the much higher melting point (303.5) and boiling point (1457) of Tl, since volatile elements like Tl would condense onto the fly ash surfaces at such low temperatures in stack flue gas (Meij 1994). PM in the stack flue gas was collected on a teflon filter (Whatman®, 0.45 μm pore size) with the U.S. EPA Method 5 for particulate matter sampling in the stack flue gas (Fig. S1 in supporting information). PM in fly ash in CFPPs is dominantly larger than 1 μm, and thus will be mostly collected by the above method (Chen et al. 2018; Liu et al. 2019b). The sampling train for flue gas is maintained at a temperature of 120 ± 10 to avoid water condensation (U.S. EPA 1996). Each flue gas sample was collected for approximately 3 hours and 3 flue gas samples were obtained for one CFPP. At the same time, information about the boiler (Table S1) was recorded during the sampling period, including the daily feed fuel/limestone consumption ($t \cdot d^{-1}$), the daily output of different solid combustion materials ($t \cdot d^{-1}$), daily flue gas emissions ($Nm^3 \cdot d^{-1}$), and the actual operating power (MW).

In total, 108 solid samples were collected in this study, of which, 84 were subjected to Tl analysis with 3 set of different type samples for each CFPP, in addition, all fueled coals (No.=21) were analyzed for the proximate and ultimate analysis.

2.2. Analysis methods

All solid samples were air-dried and ground into sizes smaller than 0.150 mm. The results of solid samples are given based on air-dried masses.

The proximate analysis method of feed coal was referenced to the Chinese National Standard Method (GB/T 212-2008). Carbon (C), hydrogen (H), and nitrogen (N) were determined by an elemental analyzer (Vario MACRO Cube, Elementar, Germany), and total sulfur (S) was measured based on the Eschka method with Chinese standard method of GB/T 214-2007. The calorific value (Q) was determined by GB/T 213-2008.

Tl in solid samples was measured by inductively coupled plasma mass spectrometry (ICP-MS, Analytik Jena, Germany) after digestion with a method developed by Qi and Grégoire (2000). Briefly, around 50 mg of a sample was digested with 1 mL of concentrated HF and 1 mL of concentrated HNO_3 in 190 °C for 24 hours, and then heated to 140 °C for 5 hours with 6 mL of 40% v/v HNO_3 to dissolve the possible insoluble residues. Tl concentration in stack flue gas was calculated from the total amount

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of Tl on the filter relative to the sampled volume of flue gas.

To reveal the possible sources of Tl in feed coal, Hg and Zn in coal samples were also measured, with Hg being determined by cold-vapor atomic absorption spectrometry with a RA915+ Hg analyzer that equipped with PYRO 915+ pyrolysis attachment, and Zn being digested and analyzed with the same procedure as that of Tl.

2.3. Quality assurance and quality control

Precautions were employed for the sampling and analysis to reduce possible contamination. All glass/Teflon tubing and bottles used for flue gas sampling and digestion were washed with 20% nitric (HNO_3) acid and rinsed with deionized water. HF and HNO_3 were distilled twice to remove the impurities. Quality assurance and quality control were checked with blanks, duplicated samples, and certified reference materials (CRMs). Several CRMs of coal (GSB 06-2114-2007, GSB 06-2105-2007) were used for the proximate and ultimate analysis, and the recovery rate is 95-105% for different parameters. Standard materials of fly ash (BCR 176R), soil (GBW07404) and limestone (JLS-1; JDO-1) are also digested and analyzed along with solid samples, and the recovery of Tl was in the range of 97-113%. In addition, the detection limit of Tl of this study was less than 0.001 mg·kg^{-1} based on the procedure blanks.

2.4. Calculation of thallium behavior parameters

2.4.1. Relative enrichment factor

The parameter of relative enrichment factor (REF) is used to reveal the enrichment or partitioning of a target element in coal combustion products of fly ash or bottom ash during the combustion process in boilers (Meij 1994). REF is calculated using equation (1):

$$REF = \frac{C_{ash}^{Tl} \times A_{ad}}{C_{fuel}^{Tl} \times 100} \tag{1}$$

Where C_{ash}^{Tl} is Tl concentration in bottom ash or fly ash (mg·kg^{-1}), A_{ad} is ash yield of feed fuel on air-dried basis (%), and C_{fuel}^{Tl} is Tl concentration in feed fuel (mg·kg^{-1}). A higher REF indicates Tl is prone to be contained in the ash, while a lower one suggests a depletion of Tl in the ash. Meij (1994) classified elements into three groups according to their emission features, with Group I being hardly

volatile, Group II partially volatile, and Group III very volatile. Group I elements are those that do not volatilize during combustion, so their concentrations in all types of ash are almost the same; thus REFs for these elements are around 1 with an uncertainty of ± 0.3 (Meij 1994). Group II elements are those redistributed in both bottom and fly ashes because they volatilize during combustion in the boiler, and then condense (when temperature drops from 1300 to 120) on the particulate matter and emit to the stack, and hence, have higher REFs for fly ash (≈1) than bottom ash (usually < 0.7). Group III elements consist of volatile elements with very low REF (<<1 for bottom ash and < 1 for fly ash) in solid combustion products and are almost entirely emitted from the power plant.

2.4.2. Release ratio

Release ratio (*R)* is derived to evaluate the volatility of Tl during the coal combustion in boiler at high temperatures (Deng et al. 2014; Zhou et al. 2020), or as an indicator to reflect the proportion of Tl entering into flue gas during the coal combustion. It is determined using equation (2):

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

where $C_{Tl,BA}$ is the concentration of Tl in bottom ash (mg·kg^{-1}), $C_{Tl,coal}$ is the concentration of Tl in feed coal (mg·kg^{-1}), C_{ash} represents ash yield in feed coal (%), and R_{BA} stands for the percentage of bottom ash with respect to the ash yield in coal.

2.4.3. Atmospheric emission factors

Emission factors (EMFs) of Tl are calculated based on different benchmarks (Zhao et al. 2008, 2017; Wang et al. 2010), such as coal consumption (*EMF$_1$*), power generation (*EMF$_2$*), and heat values (*EMF$_3$*), as shown in equations (3)-(5), respectively:

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

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

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

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Where M_{Tl} is the amount of Tl emitted into the atmosphere per day (g·d⁻¹), M_{coal} is the consumption of feed coal (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 mass (MJ·kg⁻¹).

3. Results and discussion

3.1. Coal properties

Slightly lower fixed carbon content was observed in bituminous (range 37.1-50.2%; average 44.6 ±5.6) used in CFPPs #1-3 and #5 than in anthracite (51.7%) used in CFPP #4 (Table 2), similar to what was found by Mokhtar et al. (2014). Ash yields of feed coal samples are in the range of 30.7 - 45.7%, most of which fall into the median range (30.0-40.0%), except those from CFPP #5 (45.7%), which is in the high range, according to the classification in the National Coal Classification Standard of China (GB 15224.1-2010). The sulfur contents in feed coals fall into high-sulfur category (>3.00 %) for CFPPs #1 and #4, low-sulfur category (0.51-1.00 %) for CFPPs #2 and #3, and medium sulfur category (1.01-2.00 %) for CFPP #5 according to Chinese standard of GB15224.2-2010 for sulfur content classification in coal. A previous study by Cao (2006) showed that the higher sulfur content observed in coal of eastern to central Guizhou than western Guizhou was a result of seawater intrusion. The calorific values of feed coals fall into medium category (21.3-24.3 MJ·kg⁻¹) for CFPPs #1 and #4, medium to high category (24.3-27.2 MJ·kg⁻¹) for CFPPs #2 and #3, and medium to low category (16.7-21.3 MJ·kg⁻¹) for CFPPs #5 based on GB 15224.3-2010 for calorific value classification. The above information indicates that the coal qualities used in different CFPPs are quite different. In general, feed coals used in Guizhou's CFPPs are featured with high ash yield, some with high sulfur content and low calorific values.

Tl concentrations in feed coals are in the range of 0.10 - 0.34 mg·kg⁻¹, with the highest value (0.34 mg·kg⁻¹) in CFPP #1 located in central Guizhou, which is 1.5 - 3.4 times of those in the other CFPPs (0.10 - 0.23 mg·kg⁻¹) located in western and northern Guizhou (Table 2). This distribution pattern of Tl in feed coal among the different CFPPs is similar to the spatial distribution pattern of Tl in mined coal in Guizhou (Fig. 1b). Note that coal mines in Guizhou are mainly distributed in the central to west

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areas of the province (Fig. 1a, Dai and Finkelman 2018), and all the CFPPs surveyed in the present study are located in these areas and only use the locally mined coals, which explains the similar spatial patterns of Tl in feed coal and mined coal. The average Tl concentration in feed coal of all the five CFPPs is 0.20 ± 0.10 mg·kg^{-1}, which is higher than that (0.09 mg·kg^{-1}) used in Bijie thermal power plant in western Guizhou (Li and Sun 2016). Nevertheless, these values are lower than the global average of 0.63 mg·kg^{-1} (Ketris and Yudovich 2009) and the average of Chinese coal (0.47 mg·kg^{-1}, Dai et al. 2012), but are higher than the average of western Guizhou coal (0.11 mg·kg^{-1}, Dai et al. 2005, Table S2).

The status of Tl in coal has not been studied in great details (Dai et al. 2012), but is generally considered to be mainly present in sulphides (Dai et al. 2006; Finkelman 1995). Tl is concentrated in pyrite in coal along with other environmentally sensitive elements, notably Hg (López-Antón et al. 2013; Dziok et al. 2018). Therefore, correlation analysis was conducted between Tl and ash yield, sulfur, mercury and zinc in feed coal, respectively (Fig. 3). It was found that Tl concentration in feed coal is not significantly correlated with ash yield of feed coal ($R^2 = 0.06$, $p = 0.68$, Fig. 3(a)), but significantly correlated with sulfur concentration ($R^2 = 0.81$, $p < 0.05$, Fig. 3(b)), Hg concentration ($R^2 = 0.86$, $p < 0.05$, Fig. 3(c)), and Zn concentration ($R^2 = 0.78$, $p < 0.05$, Fig. 3(d)) in feed coal. This suggests that Tl is a sulfophilic element, which is primarily associated with other sulfophilic elements that exist as pyrite (FeS), cinnabar (HgS) and sphalerite (ZnS) in feed coal, but not co-exist in the ash forming materials. This is consistent with other studies that indicated thallium is mainly associated with pyrite in hard coal (Smolka-Danielowska and Fiedor. 2018). Pyrite contains nearly all of the Hg, As, Se, Tl, and Pb and is also the major source of Mo, Ni, Cd and Sb (Spears and Tewalt 2009). The analyses of pyrite by Diehl et al. (2004) indicated the occurrence of high concentrations of Hg, As, Mo, Se, Cu and Tl. Hence, by coal washing, the input of Tl might be potentially reduced since this process removed a lot of pyrite (Pavlish et al. 2003).

3.2. Distribution of Tl in the combustion products

Tl concentrations in various solid combustion products and stack flue gas are presented in Table 3. Tl concentrations are in the range of 0.09 - 0.25 mg·kg^{-1} for bottom ash and 0.39 - 1.13 mg·kg^{-1} for fly ash, with much higher Tl concentration in fly ash than bottom ash in every CFPP. The highest Tl

concentrations among the five CFPPs occurred in CFPP #1, e.g., in coal (0.34 ± 0.05 mg·kg^{-1}), bottom ash (0.25 ± 0.07 mg·kg^{-1}) and fly ash (1.13 ± 0.25 mg·kg^{-1}) (Tables 2 and 3), suggesting that Tl in bottom ash and fly ash are dominantly inherited from the feed coals. Tl concentrations in both ESP/ESP-FF fly ash and bottom ash positively correlated with those in feed coal (Fig. 4). The larger regression slope of fly ash than bottom ash against feed coal suggests more Tl was detained in fly ash than bottom ash.

The mean Tl concentration in ESP/ESP-FF fly ash (0.59 ± 0.31 mg·kg^{-1}) is significantly higher than that in bottom ash (0.14 ± 0.06 mg·kg^{-1}), e.g., by 1.5 - 12 times. In literature, Tl in fly ash was 13 times of that in bottom ash in a Netherlands PC power plants (Meij 1994), and as high as 10.7 mg·kg^{-1} was found for fly ash of grate furnace (Smolka-Danielowska and Fiedor. 2018), while, similar Tl concentration were observed between fly ash (1.3 mg·kg^{-1}) and bottom ash (1.1 mg·kg^{-1}) in a Spanish circulating fluidized bed boiler (CFB) boiler (Table S3), which might be due to the weak redistribution effect of low combustion temperatures (800-950) (López-Antón et al. 2015). A study of Bijie CFB in the west of Guizhou province found very low Tl concentrations in fly ash (0.2 mg·kg^{-1}) and bottom ash (0.17 mg·kg^{-1}) (Li and Sun 2016; Table S3).

The re-distribution of Tl between bottom ash and fly ash depends not only on the property of fuel coal, but also on the combustion conditions, especially the combustion temperature (López-Antón et al. 2015; Smolka-Danielowska and Fiedor. 2018), since a higher combustion temperature might induce a more notable discrepancy of Tl between fly ash and bottom ash (Meij 1994). Tl could be easily melted and/or evaporated in the PC boilers since the temperature range of PC can reach 1200 -1500   (Chen et al. 2019). Therefore, Tl belongs to Group II elements with moderate volatility (Meij 1994), and is melted or evaporated inside the boilers and adsorbed onto the fly ash after flue gas temperature drops. Based on Eq (1), REF values of Tl in bottom ash and fly ash of the five CFPPs were estimated to be in the range of 0.23 - 0.30 (average 0.27) and 0.76 - 1.25 (average 1.08), respectively (Fig. 5), indicating that Tl is segregated more on fly ash than bottom ash (Chen et al. 2019).

Compared with those in feed fuels and fly/bottom ashes, Tl concentrations in limestone and FGD gypsum are extremely low, e.g., in the range of 0.01 - 0.02 mg·kg^{-1} and 0.01 - 0.03 mg·kg^{-1}, respectively. Tl concentrations are similar between those in limestone and gypsum in all CFPPs (Table 3); this indicates that negligible Tl was brought into gypsum from the flue gas downstream the ESP/ESP-FF. Tl concentrations in stack flue gas are 0.011 μg·Nm^{-3} in CFPP #1 and 0.006 - 0.008

μg·Nm^{-3} in CFPPs #2-5 (Table 3), which are lower than that observed from a PC CFPP equipped with ESP+WFGD in Netherland (0.18 μg·Nm^{-3}, Meij and te Winkel. 2007; Table S3). Emission standards for Tl from CFPPs do not exist in China, however, there is an emission limit for Tl (0.05 mg·m^{-3}) set for inorganic chemical industry in China (GB 31573-2015) enacted by the Ministry of Environment of China in 2015. Tl emission intensities from the CFPPs investigated in the present study were far less than the limit set by this regulation.

PM emitted from the stack flue gas of the five CFPPs are in the range of 10.03 - 18.28 mg·Nm^{-3} (average: 13.19 mg·Nm^{-3}), which are higher than those from eight PC CFPPs (2.35 - 13.70 mg·Nm^{-3}) that equipped with ultra-low emission device of SCR+ESP/FF/ESP&FF+WFGD+wet ESP (Wu et al.2020), and comparable to those from a 1000 MW PC CFPP with a SCR, low-low temperature electrostatic precipitator, WFGD and wet ESP (<15 mg·Nm^{-3}, Li et al. 2019b). Both these emitted PM values are lower than the national emission standard for CFPPs (30 mg·m^{-3}, GB 13223-2011), with PM emissions being significantly reduced after the additional installation of wet ESP (Wu et al. 2020).

It appears that there are two solid (TlCl$_3$(s) and (TlAsO$_4$(s)) and two condensed (TlCl (cr, l) and Tl$_2$SO$_4$(cr, l)) Tl species as the major species under oxidation condition when the temperature is lower than 277 (Yan et al. 2001a, 2001b), with cr here stands for the amorphous solid. The Tl species would be TlI (cr, l) (27), Tl$_2$S (cr, l) (77), Tl$_2$Se(s) (127), and TlBr (cr, l) (177) under reducing condition. Several gaseous Tl halides and free atom (Tl (g)) become dominant, e.g., TlBr (g) (227-1127), TlCl (g) (227-1227), Tl (g) (above 827), and TlI (g) (127-927), at higher temperature oxidation conditions. This makes the possibility of evaporation and redistribution of Tl in the PC utility boilers where the combustion temperature is higher than 1200 .

Thompson and Argent (2002) found the volatilization of Tl during coal combustion increases with increasing chlorine content because they react with each other, and this process intensifies under gasification condition. A portion of gaseous Tl is condensed into fly ash, and is released into the atmosphere as a hazardous waste（López-Antón et al. 2013). Querol et al. (1995) found the adsorption of Tl on calcium oxide is similar to the way of sulfur fixation in flue gas desulfurization (CaO+SO$_3$=CaSO$_4$). Therefore, the toxicity of fly ash is potentially increased when the volatile toxic element Tl is adsorbed into inhalable particles, and Tl compounds are easier than the other heavy metals to be leached out (Karbowska 2016).

3.3. Release ratio, mass balance and atmospheric emissions of Tl

The release ratio of a trace element from coal combustion depends on coal content and volatility of the trace element, coal property, boiler type, and operation condition (Ratafia-Brown 1994). As shown in Table 4, Tl has a high release ratio of 89.28-97.88% into flue gas during coal combustion process of the five CFPPs, despite its only moderate volatility, which is likely due to the high combustion temperatures (1200-1500°C) and that the vast majority of ash (80-90%) entering the flue gas in the form of fly ash.

Mass balance of Tl in every CFPP is assessed by incorporating the input/output material flows (Table S1) and Tl concentrations in solid and stack gas samples (Tables 2 and 3). Tl input and output are basically balanced in every CFPP, with output/input ratio being in the range of 73.41 - 127.84% (Fig. 6 and Table S4), which is considered to be an acceptable range (70-130%) when taking into account the inhomogeneity of the chemical composition of the combusted fuel and the much smaller sample quantities than the actually consumed feed coal quantities (Quick and Irons. 2002). Tl input into the installation is mostly from feed coal (> 99.11%) and little from limestone (0.19 - 0.89%) (Fig. 6 and Table S5), due to the relatively higher Tl concentration and much larger amount of consumption of feed coal than limestone (Table 3 and Table S1).

The breakdown of Tl in different input and output materials of the five utility boilers is shown in Table S5. In terms of different output materials, ESP/ESP-FF fly ash is the leading output pathway (88.66 - 97.44%), followed by bottom ash (2.12-10.72%) (Fig. 6 and Table S5), and the WFGD gypsum (0.57-3.89%) (Fig. 6 and Table S5). It was noticed that the output percentage of Tl in bottom ash is much higher in CFPP #3 (10.73%) than in the other CFPPs (2.13 - 4.86%), likely due to the much higher production of bottom ash in CFPP #3 (597 t·d⁻¹) than in the other CFPPs (101-149 t·d⁻¹) (Table S1).

Gas-phase volatile elements produced under high temperatures will condense or adsorbed onto existing particles when temperature drops (Klein et al. 1975). Tl released from coal combustion condenses rapidly when flue gas cools down, causing Tl mostly accumulated in fly ash (Pavageau et al. 2004). Tl in fly ash is further captured by ESP or ESP-FF at a very high removal efficiency (over 99.9%), followed by an additional removal process by downstream WFGD for particulate matters at a removal efficiency of 30-56% (Yao et al. 2019; Liu et al. 2019b). Thus, most Tl in fly ash is captured by these devices and only 0.57 - 3.89% of Tl enters into the WFGD gypsum. Eventually, Tl in stack

flue gas only makes up of < 0.05% of the total Tl output (Fig. 6 and Table S5), which is equivalent of an atmospheric emission rate of 0.07-0.38 g Tl·d⁻¹ for the five CFPPs (Table S4).

The atmospheric emission factors of Tl from the five CFPPs are estimated to be 0.04 - 0.09 (mean: 0.06 ± 0.02) mg Tl·t⁻¹ coal, 0.02-0.04 (mean: 0.03 ± 0.01) μg Tl·(kW·h)⁻¹, or 0.002 - 0.004 (mean: 0.0024 ± 0.001) g Tl·TJ⁻¹ (Table 4), with the maximum values for CFPP #1 and the low-end values for all the other four CFPPs (Table 4). In 2017, the output of coal in Guizhou was 163 million tons, of these 66 million tons were consumed by the electricity generation sector for generating 121 billion kW·h power (Bureau of statistics of Guizhou Province, 2018). Tl atmospheric emissions from CFPPs in Guizhou are estimated to be 3.96 ± 1.32 kg·y⁻¹ (range: 2.64 - 5.94 kg·y⁻¹) and 3.63 ± 1.21 kg·yr⁻¹ (range: 2.42 - 4.84 kg·yr⁻¹) in 2017 based on the coal consumption and power generation, respectively. The emission factors (0.02 - 0.04 μg·(kW·h)⁻¹ and 0.002 - 0.004 g·TJ⁻¹) generated from the present study are significantly lower than previously reported values (0.58 μg·(kW·h)⁻¹ and 0.07 g·TJ⁻¹) from an on-site study in Netherlands (Meij and te Winkel, 2007). However, it should be noted that studies on Tl concentrations in stack flue gas are very limited, and further research are still needed to improve the accuracy of its emission inventory from this industrial source.

With upgrading APCDs technology and phasing out small and old boilers in the past two decades, China has made significant progress in reducing atmospheric pollutants emissions from CFPPs including nitrogen oxides, sulfur dioxide and PM (Wu et al. 2020；Yang et al. 2018). Tl in feed coals has also been significantly controlled from the flue gas due to the implementation of modern APCD in Guizhou. For example, data collected in the present study show very high removal efficiency of Tl by a combination of different APCDs (99.95 - 99.99%, Table 4). Consequently, the total amount of Tl entering into fly ash, bottom ash, and desulfurized gypsum are estimated to be 681.06 ± 27.37 kg·yr⁻¹, 35.43 ± 25.19 kg·yr⁻¹, and 11.69 ± 11.26 kg·yr⁻¹, respectively, from all CFPPs in Guizhou in 2017. Compared to the behaviors of Tl in CFPPs, Hg in Guizhou's 12 PC CFPPs has been captured more in the gypsum (54.4%) than in ESP/ESP-FF fly ash (40.4%), and a higher percentage of Hg (4.6%) than Tl has been discharged from the stack emissions (Internal unpublished data). Anyhow, over 90% of Tl ending up in fly ash raises the concern of Tl leaching out from these ashes since Tl (I) in coal could be oxidized to Tl (III) during the combustion process (López-Antón et al. 2013; Llorents et al. 2001; Zhang et al. 2019) and Tl and thallium-based compounds are more soluble compared to the other heavy metals and are thus more readily available for bioaccumulation in living organisms (Karbowska 2016).

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Although the environmental standard of Tl has been set at 2 $\mu g \cdot L^{-1}$ for drinking water (U.S. EPA 2009b) and 1 $mg \cdot kg^{-1}$ for arable soils (Xiao et al. 2004), little has been done for investigating the leach-ability of Tl in the coal combustion products.

4. Conclusions

Based on the field investigation of five PC utility boiler installations in Guizhou province, it was found that Tl in feed coals is associated with sulfur and sulfophilic elements (e.g., Hg, Zn), and the average Tl concentration of feed coals in Guizhou (0.20 $mg \cdot kg^{-1}$) is about 1/3 to 1/2 of those of national and global average. During the combustion process and the subsequent APCDs, over 99.9% of Tl in flue gas was captured by the combination of different pollution control devices. Among the Tl output pathways, the ESP/ESP-FF fly ash is the leading one that accounts for 88.7-97.4% of the total output, and the stack gas emissions only contribute a very small portion (<0.05%) of output. The total amount of Tl atmospheric emissions from CFPPs in Guizhou province was estimated to be 3.96 ± 1.32 $kg \cdot yr^{-1}$ in 2017. Tl in fly ash has the highest concentration among the different solid byproducts of bottom ash and gypsum, and a large amount of T1 (681 $kg \cdot yr^{-1}$ at provincial level) is retained in fly ash. Furthermore, conversion of Tl (I) in feed coal to more toxic Tl (III) in final products is also possible during the combustion process (Karbowska 2016; López-Antón et al. 2013). It is thus recommended to pay more attention on the subsequent treatment of fly ash since it might be piled or landfilled. In addition, the Tl speciation and stability in fly ash and its potential across-media contamination should be investigated in the future.

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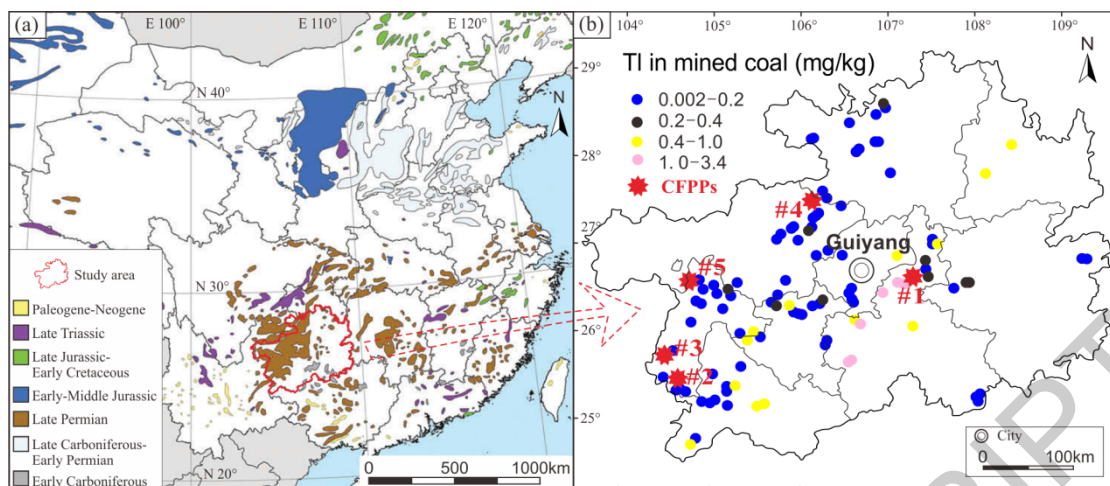
Figure legends

Fig. 1. (a) Distribution and formation ages of coal in China (modified from Dai and Finkelman 2018), and (b) locations of the five coal-fired power plants in this study and Tl concentration in Guizhou's coal (unpublished internal data)
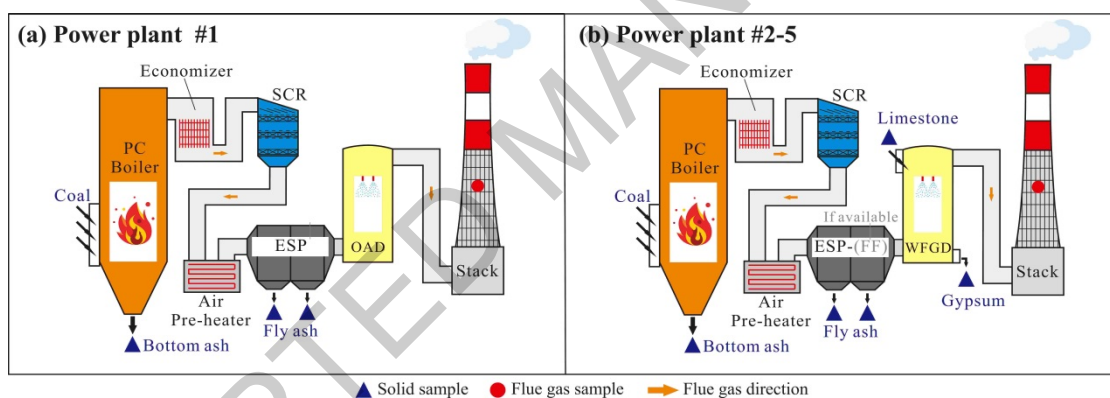
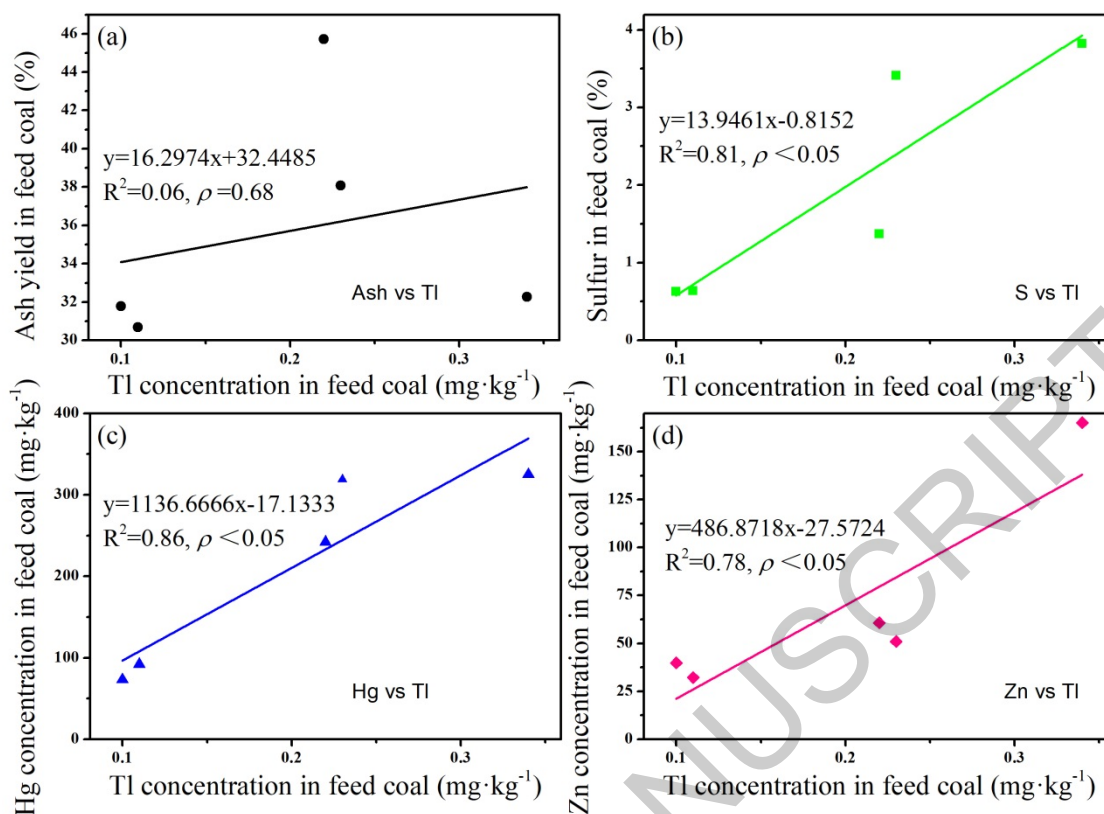**Fig. 2.** Sampling sites inside the five coal-fired power plants

Fig. 3. The correlation analysis of Tl with (a) ash yield, (b) sulfur, (c) mercury, and (d) zinc in feed coal
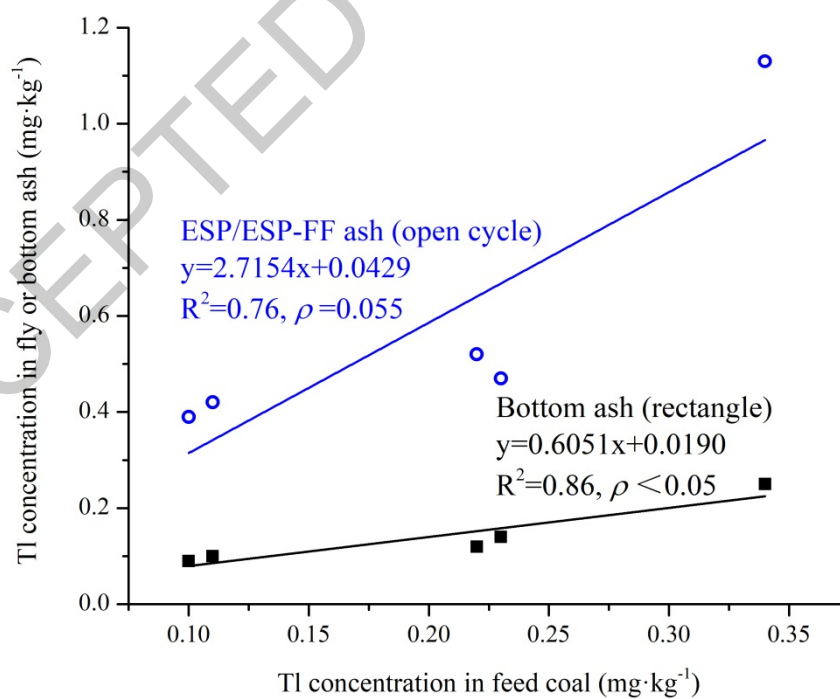
Fig. 4. The Pearson correlations between Tl concentration in feed fuel and fly (open cycle)/bottom (rectangle) ashes of the five coal-fired power plants

Fig. 5. Relative enrichment factors of Tl in coal combustion productions of five coal-fired power plants

Fig. 6. Proportion of Tl in input and output materials of the five coal-fired power plants (the output ratio is based on the total input of Tl)

Note: Organic amines and sulfuric acid are not collected and analyzed in coal-fired power plants #1

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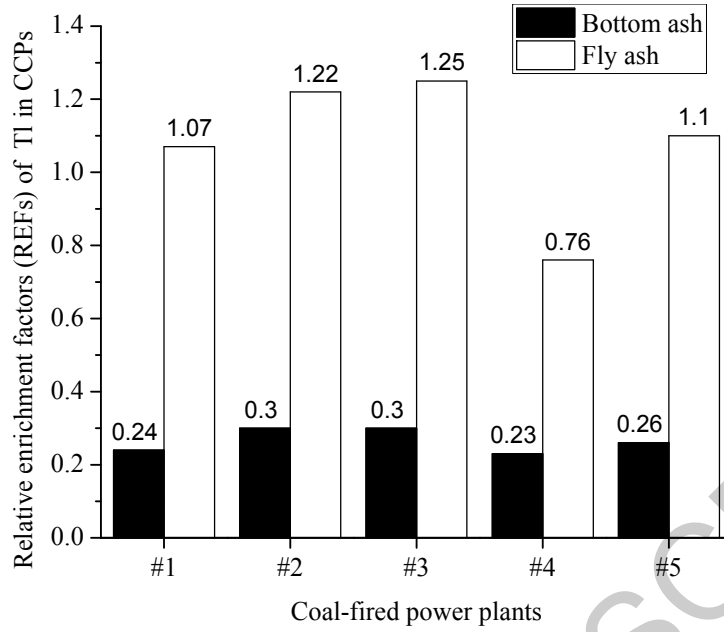
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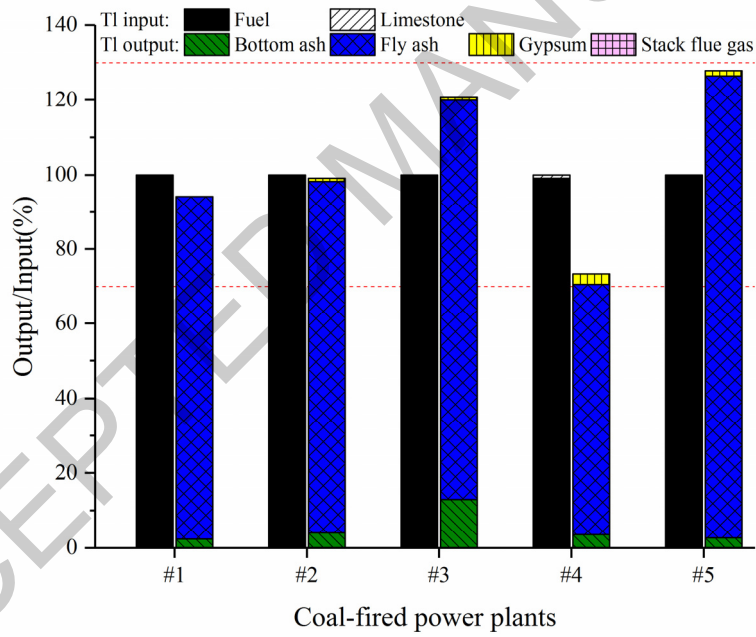

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Note: Organic amines and sulfuric acid are not collected and analyzed in coal-fired power plants #1

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

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

Note: PC, pulverized coal-fired boiler; 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.

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} (%)	Tl (mg·kg^{-1})*	(MJ·kg^{-1})
#1(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	0.34±0.05	24.25±1.29
#2(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	0.11±0.03	24.47±1.19
#3(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	0.10±0.004	25.10±1.90
#4(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	0.23±0.07	21.89±4.96
#5(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	0.22±0.03	19.19±1.32
Min-Max		1.08-1.43	8.77-22.44	30.68-45.73	37.09-51.73	47.04-62.38	3.04-4.51	0.79-1.59	0.63-3.82	0.10-0.34	19.19-25.10
Mean±SD		1.23±0.13	17.03±5.2	35.71±6.3	46.03±5.8	55.99±6.2	3.71±0.63	1.16±0.29	1.97±1.53	0.20±0.10	22.98±2.44

Note: No., Number of samples collected; M, moisture; V, volatile; A, ash; FC, fixed carbon; C, carbon; H, hydrogen; N, nitrogen; S, sulfur; Tl, thallium; Qnet, net heat value; subscript "ad", air-dried basis. *, the data number for Tl of each CFPPs is three.

Table 3. Tl concentration in the solid materials and stack flue gas of the five CFPPs

(the analyzed sample number is three for each sample of a CFPP)

CFPPs	#1	#2	#3	#4	#5
Bottom ash (mg·kg^{-1})	0.25±0.07	0.1±0.02	0.09±0.004	0.14±0.01	0.12±0.001
Fly ash (mg·kg^{-1})	1.13±0.25	0.42±0.17	0.39[a]	0.47±0.03	0.52±0.10
Limestone (mg·kg^{-1})	NA	0.01±0.001	0.01±0.001	0.02±0.001	0.01±0.001
Gypsum (mg·kg^{-1})	NA	0.01±0.003	0.01±0.001	0.03±0.003	0.03±0.02
Flue gas (µg·Nm^{-3})	0.011±0.003	0.006±0.003	0.008±0.002	0.007±0.001	0.007±0.002

Note: a, Weight average of fly ash from ESP and FF; NA, not applicable.

Table 4. Release ratio, removal efficiency and emission factors of Tl in the five CFPPs

CFPPs	#1	#2	#3	#4	#5	Mean±SD
Release ratio (%)	97.47	95.97	89.28	95.14	97.88	95.15±3.46
Removal efficiency (%)	99.97	99.95	99.95	99.97	99.99	99.97±0.02
EMF1 (mg·t^{-1} coal)	0.09	0.05	0.05	0.05	0.04	0.06±0.02
EMF2 (µg·(kW·h)$^{-1}$)	0.04	0.02	0.03	0.02	0.02	0.03±0.01
EMF3 (g·TJ^{-1})	0.004	0.002	0.002	0.002	0.002	0.002±0.001

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

Implication statement

Thallium is rare but toxic element. Identification and quantification its source are a high priority for control its contamination. Coal-fired power plants were thought an important source of Tl, but few field studies had been conducted for this area. In this paper, we investigated the fate of Tl in five pulverized coal utility power plants in Guizhou province, Southwest China, and found the Tl concentration in stack gas is in low levels of 0.006-0.011 $\mu g \cdot Nm^{-3}$, and less than 0.05% of total input of Tl is escaped into the ambient atmosphere. The majority of Tl (88.7-97.4% of the total output) is detained by the ESP/ESP-FF fly ashes. Compared to the little amount (~4 $kg \cdot yr^{-1}$) of Tl that discharged into atmosphere from Guizhuo's coal-fired power plants in 2017, more Tl (over 700 kg) is end up in the solid coal combustion products each year, makes the need of careful disposal of these solid combustion waste to prevent the mobilization of Tl into the environment.
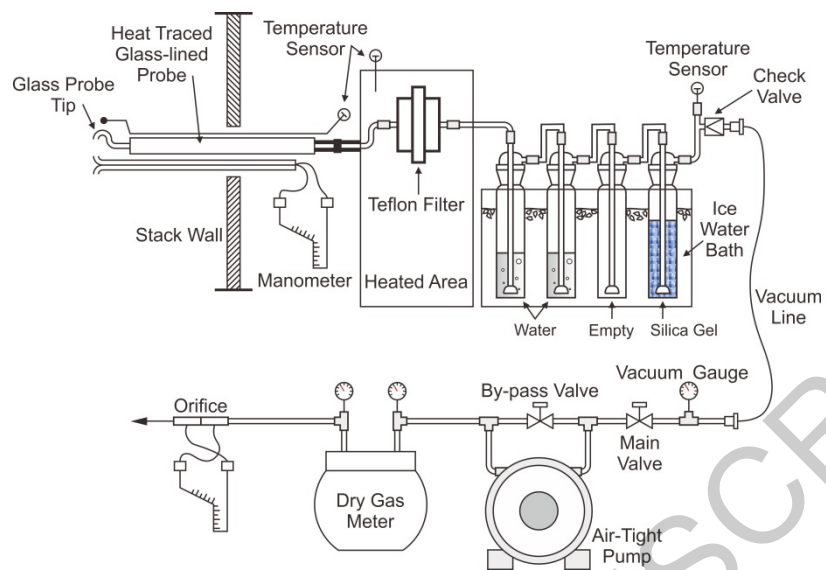
Supporting Information

Fig. S1. The U.S. EPA test method 5 for particulate matter sampling in the stack flue gas (U.S. EPA 1996)

Table S1. The material consumption and production rates and PM content in the stack flue gas of the five utility boiler systems

CFPPs	#1	#2	#3	#4	#5
Feed fuel (t/d)	4293	3551	4376	2366	2032
Limestone (t/d)	/	140	269	265	108
Bottom ash (t/d)	137	149	597	141	101
Fly ash (t/d)	1192	841	1195	800	1054
Gypsum (t/d)	/	252	462	495	202
Stack flue gas (10^4 Nm³/d）	3390	3367	3279	1571	1420
Boiler load (MW)	450	368	360	190	153

Table S2. Regional information of Tl concentrations in coal and coal ash

Regions	Types	Coal (mg/kg)	Coal ash (mg/kg)	References
World	Brown coal	0.68±0.07	5.1±0.5	Ketris and Yudovich 2009
World	Hard coal	0.58±0.04	4.6±0.4	Ketris and Yudovich 2009
World	Coal (Average)	0.63	4.9	Ketris and Yudovich 2009
China	Coal	0.47	/	Dai et al. 2012
Western Guizhou	Coal	0.11	/	Dai et al. 2005
Guizhou	Bituminous and Anthracite	0.20	0.59	This study

Table S3. Comparison of Tl concentrations in solid materials and Tl emissions data from coal-fired power plants (CFPPs)

Region	Boiler type	APCDs	Installed capacity	Coal (mg/kg)	Bottom ash (mg/kg)	Fly ash (mg/kg)	Gypsum (mg/kg)	Stack flue gas ($\mu g/Nm^3$)	Emission factors	References
Guizhou, China (No.=5)	PC	SCR+C-ESP(-FF)+WFGD	200-600 MW	0.2	0.14	0.59	0.02	0.01	0.06 mg/t coal	This study
									0.03 μg/(kW·h)	This study
									0.0024 g/TJ	This study
Spain	PC	ESP	3×350 MW	0.4	0.5	1.4				Llorens et al. 2001
Netherland	PC	ESP+WFGD	Unknown					0.18	0.58 μg/(kW·h)	Meij and te Winkel 2007
									0.07 g/TJ	Meij and te Winkel 2007
				0.63		4.9				Ketris and Yudovich 2009
La Pereda, Spain	CFB	ESP	50 MW	0.76	1.1	1.3				López-Antón et al. 2015
Inner Mongolia, China	PC	Unknown	200 MW	0.22	0.19	0.45				Dai et al. 2010
Brazil	Unknown	ESP	446 MW	0.8	0.4	2.1				Pires and Querol 2004
Bijie, China	CFB	ESP	150 MW	0.09	0.17	0.2				Li and Sun 2016

Table S4. Tl flow and mass balance of five tested utility boilers

CFPPs	#1	#2	#3	#4	#5
Input (g/d)	1469	375.73	432.66	560	442
Feed fuel	1469	375	431	555	441
Limestone	/	0.73	1.66	5	1
Output (g/d)	1384.38	372.57	522.03	411.11	565.07
Bottom ash	35	15	56	20	12
Fly ash	1349	354	463	375	547
Gypsum	/	3.39	3	16	6
Flue gas	0.38	0.18	0.23	0.11	0.07
Output/Input (%)	94.24	99.24	120.66	73.41	127.84

Table S5. Tl contribution (%) from different input and output materials in the five tested utility boilers

Direction	Samples	CFPP #1	CFPP #2	CFPP #3	CFPP #4	CFPP #5
Input	Feed fuel	100	99.81	99.62	99.11	99.77
	Limestone	*	0.19	0.38	0.89	0.23
Output	Bottom ash	2.53	4.03	10.73	4.86	2.13
	Fly ash	97.44	95.01	88.66	91.22	96.80
	Gypsum	**	0.91	0.57	3.89	1.06
	Flue gas	0.03	0.05	0.04	0.03	0.01

Note: Organic amine (*) and sulfuric acid (**) are not analyzed in CFPP #1

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