



Fate of thallium during precalciner cement production and the atmospheric emissions



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ABSTRACT

The cement industry is considered to be an important anthropogenic thallium (Tl) emission source, and yet few reports have been released concerning the fate of Tl during cement production and the emissions of Tl from cement plants (CPs). In this study, three precalciner CPs in the Guizhou province in southwest China were systematically investigated, with all input/output solid materials collected and analyzed. Despite using different raw materials, strong Tl enrichment during the clinker production was observed in all three CPs, with enrichment factors ranging from 85 to 148. Tl concentrations in limestone and most other raw materials were low (0.032–4.163 mg kg⁻¹), but they were 100–700 times higher in the raw meal and kiln tail dust due to circulation and enrichment inside the system. Only a low percentage (3–8 %) of Tl exited the system via the clinker and stack emissions. Atmospheric emission factors of Tl from the three CPs ranged from 0.168 to 0.980 mg Tl tonne⁻¹ clinker, with an average of 0.674 mg Tl tonne⁻¹ clinker. Annual atmospheric Tl emissions from all the CPs were estimated to be 54 kg.yr⁻¹ in Guizhou province and 964 kg.yr⁻¹ over all of China in 2018. Shuttling kiln tail dust may reduce the Tl enrichment during clinker production, and Tl recycled from this material may have commercial value.

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1. Introduction

Thallium (Tl) is a rare earth element that is widely dispersed in the natural environment but is persistent in air, water, and soil (Liu et al., 2019; Belzile and Chen, 2017). It is more acutely toxic to mammals than lead, cadmium, or mercury (John and Viraraghavan, 2005; Maluszynski, 2009; López-Antón et al., 2013), and the acute toxicity of Tl to humans manifests as vomiting, diarrhea, temporary hair loss. Chronic intoxication could affect the nervous system, lungs, heart, liver, kidneys, and eventually results in death (Liu et al., 2019; Viraraghavan and Srinivasan, 2011). Therefore, Tl pollution in the environment is a serious problem due to transfer to terrestrial food web and risk to mammalian health when consuming contaminated food products (Wang et al., 2018). Tl and its compounds are

treated as top hazardous substances by the World Health Organization (World Health Organization (WHO), 2008), and they are listed as priority pollutants by the United States Environmental Protection Agency (USEPA) and the European Water Directive.

The influx of thallium from agricultural pesticides into the environment has steadily decreased in recent decades (Liu et al., 2016; Li et al., 2019a). Occupational Tl intoxication is also rare (Peter and Viraraghavan, 2005). However, Tl pollution from ferrous and non-ferrous smelting, sulfide mining, and coal combustion has been frequently observed (Liu et al., 2016). Therefore, industrial facilities, such as coal-fired power plants, lead and zinc smelters, and cement plants (CPs), where Tl is an impurity in the raw materials, are thought to be the major sources of Tl in the environment (Clarke and Sloss, 1992; Saha, 2005; López-Antón et al., 2013). During cement production, the high-temperature calcination (1450 °C) process of raw materials will volatilize heavy metals with medium to low boiling points, releasing them into the atmospheric environment (Hua et al., 2016). As an example, atmospheric deposition of thallium has been measured up to 400 µg m⁻² day⁻¹ near a cement plant in Germany resulting in elevated thallium levels in

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soil and crops and negative impact on local human and animal health (Kersten et al., 2014; Raffetti et al., 2019).

China is the largest cement producer and consumer in the world with a total production of 2.2×10^9 tonnes in 2018 accounting for more than a half of the total production globally and involving more than 1700 production lines (National Bureau of Statistics of China, 2019; Cai et al., 2020). The dominant production technique for cement has changed from using a shaft kiln before 2000 to a precalciner kiln, or a suspension pre-heater kiln which is a more complicated process albeit more modern, since 2010 (Hua et al., 2016). Cement production is highly energy-intensive and emits several pollutants into the atmosphere (Hua et al., 2016). This industrial sector in China accounts for the largest emissions of particulate matter into the air, estimated at about 40 % of the total from anthropogenic activities (China Environment Yearbook Editorial Committee (CEYRC, 2013) and annually a total of 2542 tonnes of the metals Hg, Cd, Cr, Pb, Zn, As, Ni, and Cu in the airborne state (Hua et al., 2016). As a semi-volatile element in emissions from cement production, Tl possesses an ability to be adsorbed onto the surface of preexisting particles in air that may settle local or regional environment (Kersten et al., 2014). However, few studies have been carried out to trace the fate of Tl during concrete production within CPs and its atmospheric emissions from CP's, especially in China.

Guizhou province, located in southwest China, has vigorously developed a cement industry in recent years due to its rich limestone and coal deposits. The cement output increased seven times during 2005–2018, reaching 1.1×10^8 tonnes in 2018 (Bureau of Statistics of Guizhou Province, 2006, 2019). All cement was produced using precalciner kilns after the mid-2010s. This study was therefore done to provide an updated estimate of Tl emissions from this industry that have changed in both technology and production volume by investigating three CPs with a precalciner process in Guizhou province, where many Tl-contaminated zones have been discovered (Liu et al., 2018; Xiao et al., 2012). The aims of the current study are to (1) understand the Tl distribution inside the CPs, (2) obtain the atmospheric emission factors and the mass balance of Tl from the CPs, (3) explore the degree of Tl enrichment in the CPs and analyze the relevant mechanisms of enrichment, and (4) estimate the total amount of atmospheric Tl emissions from the CPs in the Guizhou province as well as the entire country of China. Results from this study will provide relevant data to quantify Tl atmospheric emissions of the cement industry and to reveal the factors that control Tl emissions in China, information which is essential to assess the possible impacts of Tl pollution caused by CPs.

2. Materials and methods

2.1. Cement plants and sample collection

Three precalciner cement plants in Guizhou province were selected to study the Tl distribution over and during the entire production process. The CP labeled #1 is located in the eastern area, CP #2 is central, and CP #3 is in the western area of the province. Additionally, CP #1 is located only 22 km away from the defunct Wanshan mercury mine, China's historically largest mercury mine, while CP #2 and CP #3 have no obvious metal mining activity nearby. The main coal-producing areas in the Guizhou province are in the central and western areas of the province, and most coal is bituminous or anthracitic formed in the Late Permian. Also, no Tl-containing minerals were identified near any of the CPs.

At the time of sampling, the cement production lines had been operating for 1.5, 0.5, and 4 years for the CP #1, #2, and #3, respectively. In these three CPs, locally excavated limestone was used

mainly as the raw material. Coals used in CP #1 was produced from the Henan and Shaanxi provinces, which are located in central China. The coal used in CP #2 was produced from the central part of Guizhou, and in CP #3 local coal was utilized. The three plants differ slightly in terms of air pollution control devices (APCDs) when it comes to separators at the kiln tail, but otherwise the same type of electrostatic precipitator (ESP) at kiln head is used at the kiln head. The devices used at the kiln tail consisted of a selective non-catalytic reduction (SNCR) unit combined with an ESP for CP #1, a SNCR plus ESP combined fabric filter (FF) in CP #2, and an SNCR plus FF in CP #3. More detailed information is summarized in Table S1.

In general, the production process of the investigated CPs can be divided into two parts. The first part is clinker production, which involves heating and calcination of the raw materials and is the key process of each CP. The second part is the production of cement from the clinker material, which involves mixing a clinker with coal fly ash and gypsum retarder. The latter two ingredients are obtained from local coal power plants. In this study, solid samples from the two processes from each of the three CPs have been collected for evaluation, with the sampling points from each CP shown in Fig. S1.

Specifically, different raw materials (limestone, shale, etc.), intermediate products (raw meal and dust from APCDs at the kiln tail), coal, and clinker were collected from the clinker production stage, while additives, dust from APCDs at the kiln heads, and cement production from the second stages of each CP were also collected. Solid samples were collected simultaneously (about 1 kg per sample), 3–6 times over a 2–3-day sampling period for each plant. Stack flue gas were not explicitly sampled in this study, but data including mass content of particulate matter were provided through the companies' own measurements. Since the temperature in the stack was relatively low (70–100 °C), any elemental or ionic Tl vapor present would readily aggregate to particulates in the flue gas. It is therefore assumed justified to calculate the Tl emissions to air based on the Tl content of particles (kiln dust) and the particle content in the flue gas from the stack. At the same time, information about various input and output material quantities and flue gas flow were collected during cement production process through the CP company, which can be found in the Tables S2–S7 of the Supporting Information.

2.2. Sample preparation and determination

All solid samples were air-dried and ground to sizes smaller than 0.15 mm. The sample digestion method utilized is from Qi and Grégoire (2000) involving the following procedures: 50 mg powder was weighed into Teflon digestion bottles, then 1 mL HF and 1 mL HNO₃ were added and the sample was placed in a pre-heated oven at 190 °C for 24 h. After cooling, the solutions were heated on a plate at 120 °C to dryness. Subsequently, 0.5 mL HNO₃ was added and again the solution was evaporated to dryness at 120 °C. Then 200 ng Rhodium as an internal standard, 2 mL HNO₃, and 2 mL of deionized water were added sequentially and placed in an oven pre-heated to 150 °C for 5 h. Finally, 0.4 mL of the digestion solution was transferred into a 15 mL centrifuge tube, and Milli-Q water was added to obtain a volume of 10 mL. The Tl in this solution was measured by inductively coupled plasma mass spectrometry (ICP-MS, Analytik Jena, Germany). In the following, data for solid samples are communicated consistently based on dry weight.

2.3. Quality assurance and quality control

Precautions were taken during sampling and analysis to reduce possible contamination. All Teflon bottles used for digestion were prewashed with 20 % nitric acid (HNO₃) and rinsed thoroughly

Table 1
Tl concentrations in different input and output materials for clinker production at each CP.

Tl input/output		Material CP #1	Tl concentration (Mean ± SD, mg kg ⁻¹)		
			CP #2	CP #3	
Tl input	Raw material	Limestone	0.038 ± 0.029 (n = 3) ^a	0.046 ± 0.011 (n = 3)	0.067 ± 0.026 (n = 3)
		Sandstone	0.100 ± 0.007 (n = 3)	/ ^b	/
		Shale	0.803 ± 0.008 (n = 3)	0.279 ± 0.059 (n = 3)	0.407
		Coal gangue	4.163 ± 0.250 (n = 2)	/	/
		Iron-rich materials	0.128 ± 0.008 (n = 3)	0.512 ± 0.012 (n = 3)	/
		Beneficiation waste	/	/	0.313 ± 0.029 (n = 2)
		Yellow phosphorus slag	/	/	0.255 ± 0.022 (n = 3)
		Carbide slag	/	/	0.152 ± 0.058 (n = 2)
		Coal slag	/	/	0.120 ± 0.003 (n = 3)
		Fuel	Coal	0.089 ± 0.052 (n = 2)	0.215 ± 0.026 (n = 3)
Intermediate products	Raw meal	24.3 ± 1.9 (n = 3)	6.95 ± 1.15 (n = 3)	8.69 ± 0.19 (n = 3)	
	Kiln tail dust	176 ± 61 (n = 6)	10.35 ± 0.82 (n = 6)	56.2 ± 3.9 (n = 3)	
	Kiln head dust	0.32 ± 0.15 (n = 3)	0.028 ± 0.007 (n = 3)	0.039	
Tl output	Stack flue gas at the kiln tail	0.28 ^c	0.057 ^c	0.491 ^c	
	Stack flue gas at the kiln head	0.0003 ^c	0.0001 ^c	0.001 ^c	
	Clinker	0.003 ± 0.0004 (n = 3)	0.009 ± 0.004 (n = 3)	0.003 ± 0.002 (n = 3)	

^a n is the sample numbers.

^b not applicable.

^c Unit of Tl concentration in flue gas: μg m⁻³.

with deionized water. Concentrated HF and HNO₃ were distilled twice to remove impurities. Quality assurance and quality control were exercised by using blanks, duplicate samples, and certified reference materials (CRMs). Certified reference materials (CRM's) of limestone (JLS-1; JDO-1), coal (NIST 1632d), fly ash (NIST 1633c), and soil (GSS-5) were digested and analyzed along with solid samples from the CPs, and the resulting recovery of Tl from the various CRMs was in the range of 97–107 %.

2.4. Calculation of atmospheric emission factor

To quantify the atmospheric emissions of Tl from the three CPs, an emission factor (EMF) was estimated based on emissions from the kiln tail and head, respectively. The EMF was calculated either relative to the clinker production (EMF₁ in Eq. (1) in the unit of mg Tl tonne⁻¹ clinker) or relative to the cement production (EMF₂ in Eq. (2) using the unit of mg Tl tonne⁻¹ cement), as follows:

$$EMF_1 = \frac{M_{Tl} \times 1000}{M_{clinker}} \quad (1)$$

$$EMF_2 = \frac{M_{Tl} \times 1000}{M_{cement}} \quad (2)$$

where M_{Tl} is the amount of Tl emitted into the atmosphere per day (gram·day⁻¹), $M_{clinker}$ is the daily output of clinkers (tonnes·day⁻¹), and M_{cement} is the daily output of cement products (tonnes·day⁻¹).

2.5. Calculation of enrichment factor

To characterize the enrichment and cycling capacity of Tl in the rotary kiln, as well as the pre-calcining with preheating cyclones and raw mill system, the Tl enrichment factor was calculated according to the Hg enrichment factor method of CPs given by Wang et al. (2016):

$$\begin{aligned} \text{Tl Enrichment Factor} &= \frac{\text{total Tl in the kiln system}}{\text{input Tl per day}} \\ &= \frac{\text{Tl in raw meal}}{\text{Tl in raw materials} + \text{Tl in coal}} \quad (3) \end{aligned}$$

When the Tl enrichment factor is approximately unity, no enrichment of Tl occurs in the system. When the Tl enrichment factor is greater than 1, it represents Tl enrichment during the process, and the enrichment of Tl correlates with an increase of the Tl enrichment factor value.

3. Results and discussion

3.1. Tl contents in different solid materials

Among different raw materials and fuels, limestone was the main reactant material for the clinker production and accounted for 75–83 % of the raw material mass of the three CPs (Supporting Information Tables S2–S4). Coal was used as a fuel and accounted for 7–10 % of the total raw material mass (Tables S2–S4). The Tl content in various samples from the clinker production process is given in Table 1. From this tabulation, it was evident that the Tl contents were fairly low in the raw materials (with the exception of coal gangue) and clinkers (<0.8 mg kg⁻¹), but considerably higher in the intermediate products (up to 170 mg kg⁻¹) (Table 1). Specifically, Tl concentrations were 0.038–0.067 mg kg⁻¹ in limestone, 4.163 ± 0.250 mg kg⁻¹ in coal gangue, 0.100–0.803 mg kg⁻¹ in the other raw materials, 0.032–0.215 mg kg⁻¹ in coal fuel, and at extremely low level (0.003–0.009 mg kg⁻¹) in the clinkers from all three CPs (Table 1).

The Tl concentrations are much higher in the intermediate products such as raw meal (6.95–24.3 mg kg⁻¹) and kiln tail dust (10.35–176 mg kg⁻¹), especially in the kiln tail dust of CP #1 (176 mg kg⁻¹) (Table 1). The average Tl content of kiln tail dust from the three CPs (70 mg kg⁻¹) was about 700 times higher than the weighted average Tl content (0.1 mg kg⁻¹) in the raw material mix, while that of the raw meal (12.7 mg kg⁻¹) was 127 times higher than that of the raw material mix. Since nearly no Tl was found in the clinker, and the atmospheric Tl emissions were very low (as discussed in the following part), this data suggests that Tl is highly circulated and consequently enriched during the clinker production.

Tl concentrations in the kiln tail dust and raw meal were much higher than the average Tl concentrations in the upper crust, soil, coal deposits, and various rocks (such as igneous rocks, metamorphic rocks, and sedimentary rocks) (see Table 2) and were roughly equivalent to that in the host rocks in some Tl mineralized areas and sulfide minerals (Table 2). Moreover, the Portland Cement Association of USA analyzed 97 cement kiln dust samples and yielding an average Tl content of 43 mg kg⁻¹ (Portland cement association, 1992), which is slightly lower than that in the present study (70 mg kg⁻¹). Therefore, the cement kiln tail dust from the three CPs in this study would be assessed as a promising source of thallium recycling.

Table 2
Tl contents in various minerals/rocks in the natural environment.

Minerals/rocks	Tl content (mg kg ⁻¹)	References
Upper crust	0.75	Taylor and McLennan (1985)
Soil	0.1–1	Fergusson (1990)
Coal deposits	0.01–2	
Igneous rocks	0.06–1.2	De Albuquerque and Shaw (1972); Heinrichs et al. (1980)
Metamorphic rocks	0.65	
Sedimentary rocks	0.27–0.48	
As-Tl ore (Lanmuchang Hg-As-Tl deposit, Guizhou Province)	300–42500	Tu et al. (2004)
Lead-zinc ore (Lanping Jinding lead-zinc ore, Yunnan, South China)	110	Jiang et al. (2014)
Tl mineralized rock (Nanhua As-Tl deposits, Yunnan, South China)	25–90	Zhang et al. (2005)
Tl mineralized rock (Lanmuchang Hg-As-Tl deposit, Guizhou Province)	65–84	Zhang et al. (1997)
Kuroko-type pyrite deposit (Japan)	23–55	Murao and Itoh (1992)

Table 3
Tl concentrations in different input and output materials during the clinker-to-cement production process of CPs.

Tl input/output	Material	Tl concentration (Mean ± SD, mg kg ⁻¹)		
		CP #1	CP #2	CP #3
Tl input	Clinker	0.003 ± 0.0004 (n = 3) ^a	0.009 ± 0.004 (n = 3)	0.003 ± 0.002 (n = 3)
	Kiln head dust	0.322 ± 0.154 (n = 3)	0.028 ± 0.007 (n = 3)	0.039
	Fly ash from coal-fired power plants	0.607 ± 0.013 (n = 2)	0.433 ± 0.038 (n = 3)	1.097 ± 0.224 (n = 3)
	Desulfurization gypsum	0.018 ± 0.002 (n = 3)	0.028 ± 0.002 (n = 3)	0.024 ± 0.002 (n = 3)
	Limestone	0.038 ± 0.029 (n = 3)	0.046 ± 0.011 (n = 3)	^b
	Bottom ash from coal-fired power plants	/	/	0.120 ± 0.003 (n = 3)
	Basalt	/	/	0.073 ± 0.002 (n = 3)
Tl output	Black stone	/	/	0.478 ± 0.065 (n = 3)
	Cement products	0.090 ± 0.009 (n = 6)	0.055 ± 0.010 (n = 5)	0.084 ± 0.024 (n = 6)

^a n is the sample numbers.

^b not applicable.

The Tl contents of samples collected in the process of clinker-to-cement production are shown in Table 3. The Tl contents were relatively low in clinker samples (0.003–0.009 mg kg⁻¹), kiln head dust (0.028–0.322 mg kg⁻¹), cement products (0.09–0.084 mg kg⁻¹), and in some additives (limestone, bottom ash from coal-fired power plants and basalt) and gypsum (0.018–0.120 mg kg⁻¹), but somewhat higher in other additive materials including coal fly ash (0.433–1.097 mg kg⁻¹) and black stone in CP #3 (0.478 mg kg⁻¹) (Table 3). In this process, both the clinker and the dust captured by ESP at the kiln head (kiln head dust) are used in the cement mill and are mixed with additives to produce cement.

3.2. Atmospheric Tl emissions

The concentration of particulate-bound Tl in the stack flue gas was much higher at the kiln tail (0.057–0.491 μg m⁻³) than at the kiln head (0.0001–0.001 μg m⁻³) (Table 1), however, both are far below a value of 2500 μg m⁻³ predicted by López-Antón et al. (2013) for CPs and an emission upper limit (0.05 mg m⁻³) set for the inorganic chemical industry in China (GB 31573, 2015). The average Tl flue gas emissions from two Portland cement kilns in Portugal ranged between 0.46 to 0.63 μg m⁻³ (Zemba et al., 2011), which was very similar to the levels reported in this study. To quantify atmospheric emissions of Tl from the three CPs, EMFs of Tl from pre-calcined CPs were estimated from the emission from the kiln tail and head, respectively (using Eqs. (1) and (2)). The EMFs of Tl of the studied CPs are detailed in Table 4 and show that the atmospheric Tl emissions from all three CPs occurred primarily from the kiln tail (>99 %).

The average daily production capacity of the three CPs was 4500–5000 tonne clinker·day⁻¹ line⁻¹ (Table S1), and the atmospheric Tl emission was estimated to be 1.21 kg·yr⁻¹ on average (range: 0.30–1.76 kg·yr⁻¹) per cement production line by using EMF₁ (range: 0.168–0.980 mg Tl tonne⁻¹ clinker; average: 0.674 mg Tl tonne⁻¹ clinker). This estimated value was similar to previously reported values (<10 kg·yr⁻¹) for 44 modern rotary and

precalciner kilns in Germany studied in 2008 (Kersten et al., 2014). The production of clinker in the Guizhou province in 2018 was 8.03 × 10⁷ tonnes (Liu., 2019), and the total provincial atmospheric Tl emissions in 2018 were estimated to be 54 kg·yr⁻¹ (range: 13–79 kg·yr⁻¹). These data are much higher than those estimated for coal-fired power plants (3.96 ± 1.32 kg·yr⁻¹, range: 2.64–5.94 kg·yr⁻¹) in the same province (Li et al., 2021). The total atmospheric Tl emissions attributed to the cement industry in China was estimated to be 964 kg·yr⁻¹ (range: 240–1401 kg·yr⁻¹) in 2018 based on the amount of clinker (1.43 × 10⁹ t) produced in that year (Li, 2020). The field measurement data on Tl emissions in China are scarce, and more studies are needed in the future so that the estimated emissions levels can be ascertained with more confidence.

3.3. Tl mass balance and enrichment

Detailed information of the material input/output and the Tl input/output during clinker and cement production are shown in Tables S2–S7, and in Fig. 1. Although the Tl concentration in limestone was low, the daily input of limestone (5405–7960 tonnes·day⁻¹) was generally more than 5 times that of other raw materials (1292–1833 tonnes·day⁻¹). This rendered the daily Tl input from limestone to be relatively higher (207–530 g·day⁻¹, or 45–66 %) than from the other raw materials in CPs #2 and #3. In CP#1, however, the contribution of limestone was lower (18 %) due to the high Tl concentration in coal gangue that contributed the largest portion of Tl input (39 %) (Fig. 1; Tables S2–S4). The output/input ratio of Tl was seriously imbalanced during clinker production, with ratios of 4.1 %, 7.9 %, and 2.9 % for CP #1, CP #2, and CP #3, respectively (Fig. 1; Tables S2–S4). The main output pathways of Tl are clinker for CPs #2 and #3 and kiln head dust for CP #1.

In contrast, the output/input ratio of Tl in the clinker to cement production ranged from 95.8 %–151.2 % in the three CPs (Tables S2–S7, Figs. 2, and S2, S3), suggesting that Tl was roughly balanced during this process. The Tl input for cement products was mainly

Table 4
EMFs of Tl for the three CPs studied.

Cement plant	EMF ₁ (mg Tl tonne ⁻¹ clinker)			EMF ₂ (mg Tl tonne ⁻¹ cement)		
	Kiln tail	Kiln head	Total	Kiln tail	Kiln head	Total
CP #1	0.870	0.001	0.871	0.704	0.0004	0.705
CP #2	0.168	0.001	0.169	0.161	0.0003	0.162
CP #3	0.980	0.001	0.981	0.822	0.0005	0.823
Mean	0.673	0.001	0.674	0.562	0.0004	0.563

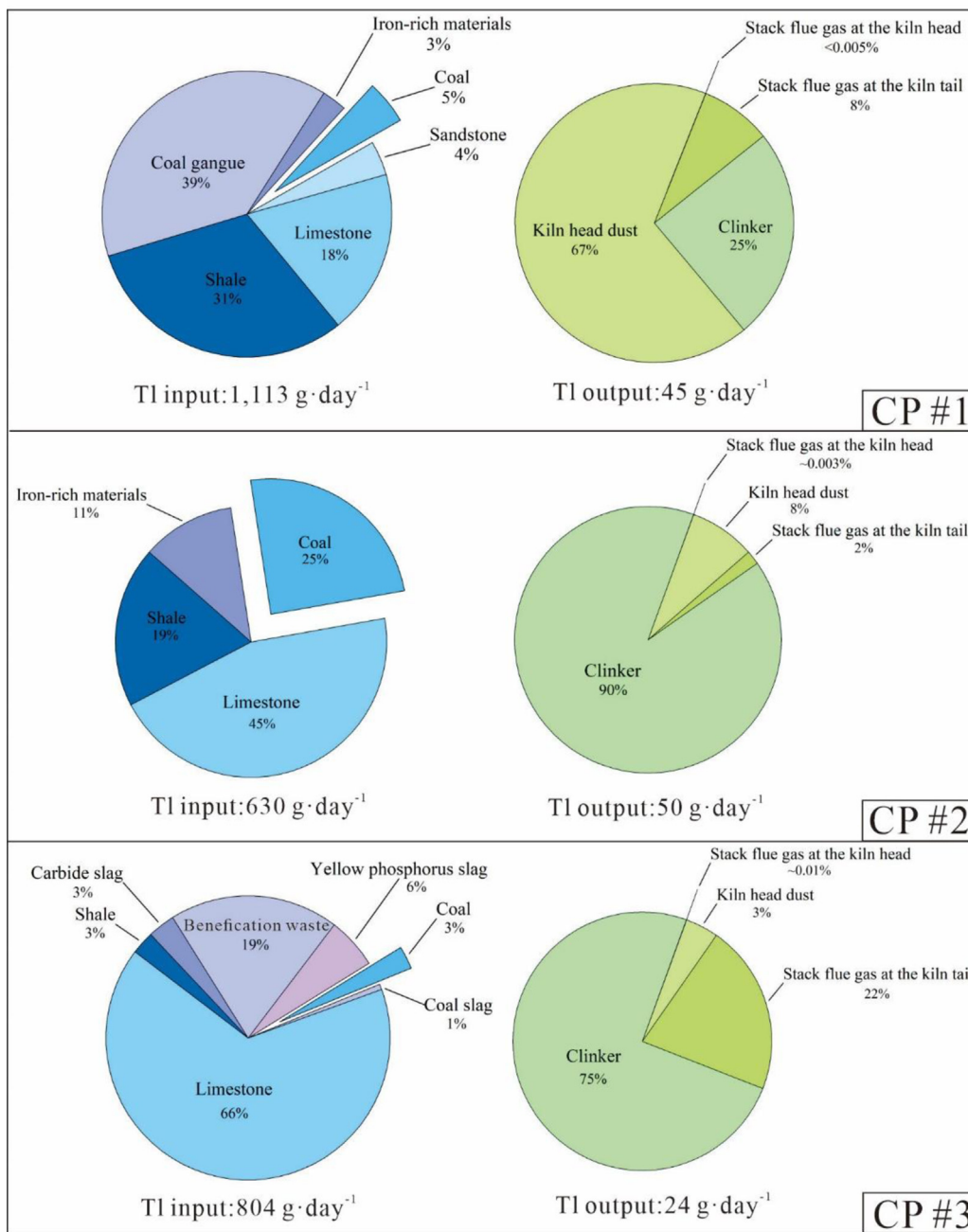


Fig. 1. Daily Tl input and output during the clinker production process of three CPs.

introduced by additives (83.17–97.36 %), especially fly ash from coal-fired power plants (76.14–87.74 %) (Tables S5–S7), with the overall contribution from gypsum being quite small (<3 %).

To explain the above phenomena and characterize the enrichment and cycling capacity of Tl in the raw mill systems, pre-calcining and preheating cyclones, and rotary kilns, the Tl

enrichment factor was calculated according to Eq. (3). Additionally, the enrichment factors of Tl and other toxic elements (Hg, Cd, Pb) in the studied CPs were compared and are shown in Fig. 3. The enrichment factors of Tl were 148, 85, and 93 for CP #1, CP #2, and CP #3, respectively. More variable enrichment factors (5.9–104) were found for Hg in the three CPs, which will correlate to the atmo-

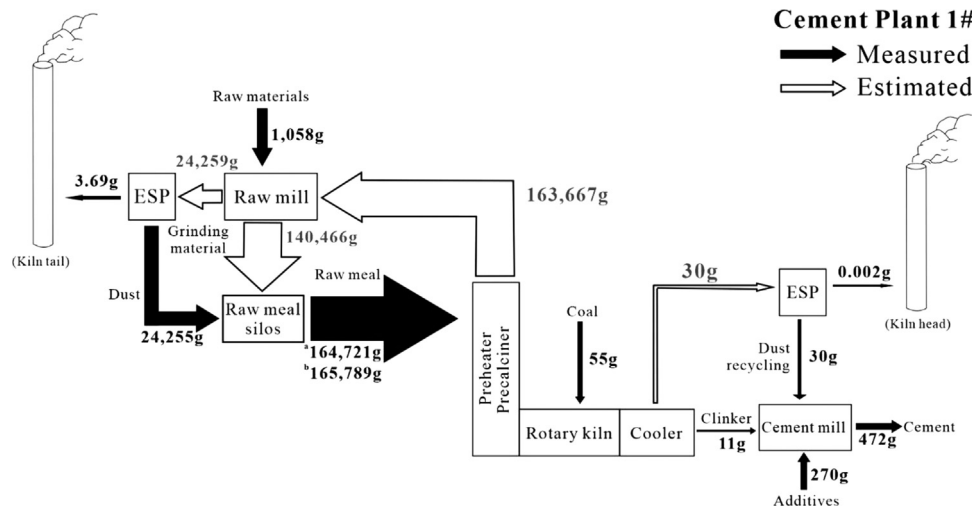


Fig. 2. The mass flow of Tl in CP #1 (Values are based on one day; ^a, Test value on the first day; ^b, Test value on the second day).

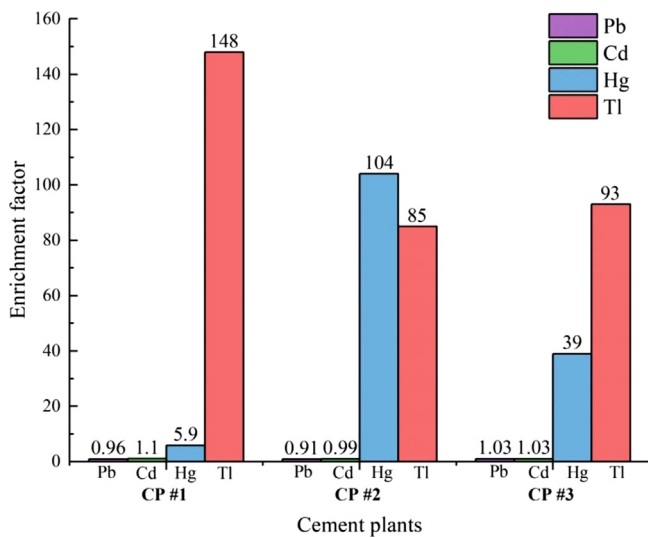


Fig. 3. Enrichment factors for Tl and other metals in the three CPs (Pb and Cd in the three CPs and Hg in CP #3 are internal unpublished data, and Hg in CPs #1 and #2 are quoted from, Li et al., 2019b).

spheric emission levels of Hg from these CPs. Considerable amount of Hg was emitted into the atmosphere from CP #1 (Li et al., 2019b), supporting the low enrichment factor of 5.9 obtained in this study (Fig. 3). The negligible release of Hg detected from CP #2 (Li et al., 2019b) corresponds to the high enrichment factor of 104 for Hg within this CP, which was similar in magnitude to the enrichment factor of Tl (85) for CP#2. The moderate enrichment factor of Hg (39) for CP #3 should correlate to moderate Hg emissions from CP #3. In contrast, the enrichment factors of Pb and Cd were both close to 1 at all three CPs, indicating that there is no enrichment of Pb and Cd during the clinker production (Fig. 3). Hence, the behavior of Tl inside precalciner CPs is much different from that of the other toxic heavy metals Hg, Pb, and Cd. Qiao (2002) proposed that Tl in CPs will display high enrichment during the initial phase of operation, then the enrichment become to a stable level after about a year of continuous production. The Tl enrichment factors of the three CPs did not show such a trend, even though they started operating at different times. This may be related to the staggered peak production policy for the Chinese cement industry in recent years (China Cement Association, 2014).

The behavior of Tl in the precalciner, preheater, and rotary kiln is the main reason for Tl enrichment during precalciner cement production. A large amount of Tl in the raw meal entered the multi-stage suspension preheater and rotary kiln, and volatilized in the high-temperature (1450–2000 °C) zone of the rotary kiln; hence, the clinker contained negligible amounts of Tl. Tl vapor in flue gas will be condensed on and adsorbed onto the particulate matter when the flue gas cools down (Tian et al., 2015), then a portion of the particulate matter in flue gas from the rotary kiln will react and enter into the raw mix in the raw mill at 110–130 °C, causing the internal circulation of Tl. After the raw mill, the remaining particles in the flue gas entered the ESP or ESP-FF, where most of the particulate matter in the flue gas (kiln tail dust) is captured and returned to the raw meal silo, leading to the external circulation of Tl. Only a small portion of the particles passed through the ESP or ESP-FF and reach the stack, where they are discharged as air pollutants.

Several gaseous elemental Tl atoms and Tl-halide molecules (Tl (g)), such as TlBr (g) (227–1127 °C), TlCl (g) (227–1227 °C), Tl (g) (> 827 °C), and TlI (g) (127–927 °C), are the dominant species of Tl at higher temperatures (Yan et al., 2001a, b). The boiling point temperatures of these compounds fall within the temperature range of the outlet of the five-stage preheater and rotary kiln (~300–1450 °C), hence these compounds would exist in the gaseous state between the preheater and rotary kiln. Halides are also enriched in the clinker production stage, where they will facilitate the evaporation of Tl (Renzone et al., 2010). Hence, gaseous Tl halides will penetrate the pre-heater and enter the raw mill, where they react with raw materials and are captured by the dust collector, resulting in an additional mechanism of both internal and external Tl circulation. Finally, Tl is gradually accumulated inside the clinker production process. Therefore, Tl circulation occurred between the rotary kiln, the preheaters for raw-mix drying, and the APCDs, from where the cement kiln tail dust was fed back into the raw mix. Some reports assumed that Tl mainly circulates between the first and the second stage of preheaters (Anonymous, 2020), but our data showed that Tl penetrated the first stage preheater and entered the raw mill and the kiln tail dust. The enrichment of halogens in the precalciner CPs is another factor involved in the recycling of Tl within the CPs; therefore, future research must consider the behaviors of Tl within the five-stage preheaters and precalciner.

During the clinker production process, cement kiln tail dust can be regularly shuttled to break up the Tl enrichment, making the Tl in the kiln tail dust available to be recovered for commercial use. Considering the Tl input from different raw materials and feed coal, the material ratio of raw materials plus coal to clinker ratio

reported as (1.677:1) in this study, the overall clinker production in the Guizhou province (8.03×10^7 tonnes) (Liu, 2019) and China (1.43×10^9 tonnes) (Li, 2020) in 2018, then the annual TI input into the CPs is estimated to be 22.5 tonnes.yr⁻¹ in the Guizhou province and 401.4 tonnes.yr⁻¹ in total throughout China. If this element was all recovered from the kiln tail dust, it would become an efficient and lucrative TI resource, especially considering the high price of TI due to its inherent scarcity (USGS, 2009, 2017).

3.4. Potential environmental risks

The main direction of TI in precalciner CPs during cement production process is enrichment in intermediate products (kiln tail dust and raw meal), and the atmospheric emissions through flue gas at kiln tail/head and solidification in cement products are relatively small as discussed above. It is difficult for heavy metals, including TI, in cement products to diffuse into the environment (Hillier et al., 1999), the low concentration of TI in cement products in this study make it is hard to cause potential risks to the environment and the human body. Due to the development of APCDs, especially the highly efficient dust removal devices like fabric filter (bag house) which has high dust removals (>99.9 %), only a small part of TI was emitted into the atmosphere, but its potential environmental impact cannot be ignored. The adsorbed TI compounds in flue gas are predominantly present in the exchangeable/acid-extractable fraction, which is the most readily bioavailable (Liu et al., 2016), and once deposited on the ground surface, it can be easily transferred into the water or soil systems and ultimately accumulate in organisms, thus, leading to TI entry into the food chain and causing serious damage to human health (Schedlbauer and Heumann, 2000; Vaněk et al., 2012, 2015). However, some previous studies have explored the concentration of heavy metals in the soil and plants near CPs and assessed the related human health risks, and found that the concentration of hazardous trace elements in the surrounding environment of CPs were indeed higher than in other areas, but the risk to human health was generally low, especially TI (Mari et al., 2018; Halim et al., 2018). As for the intermediate products that were rich in TI, the cement plant was regularly cleaned the kiln tail dust according to its management plan, but in some cases, the cleaned dust was disposed of in piles, quarries and landfills (Kersten et al., 2014). This approach may cause the diffusion and transfer of TI, resulting in huge environmental risks. Thus, in order to control cement-related thallium pollution and reduce the risk of its emissions, the kiln tail dust is proposed not to be open dumped or landfilled, but to reused in the cement plants or recovery TI resource from this kind of high TI laden material.

4. Conclusions

Based on the field investigations of three precalciner CPs in the Guizhou province, it was found that TI was significantly enriched in the clinker production process of the CPs, and the TI enrichment factors were reported as 148, 86, and 93 for CPs #1, #2, and #3, respectively. Aside from the main input material of limestone, the remaining raw materials of the three studied CPs had varying amounts of TI. The TI content of limestone was found to be relatively low (0.038–0.067 mg kg⁻¹), while the levels were slightly higher in the other raw materials (0.100–4.163 mg kg⁻¹) and in the coal fuel (0.032–0.215 mg kg⁻¹). Much elevated levels of TI were detected in the raw meal (6.95–24.3 mg kg⁻¹) and kiln tail dust (10.35–176 mg kg⁻¹) while only traces of TI were detected in the clinker (0.003–0.009 mg kg⁻¹). The TI detected in cement products was mainly introduced by coal fly ash from power plants used as an additive. The atmospheric emission factors for TI ranged from 0.168 to 0.980 mg TI tonne⁻¹ clinker, with an average factor of 0.674 mg TI

tonne⁻¹ clinker. In 2018, total TI emissions from CP industrial sector were estimated at 54 kg.yr⁻¹ for Guizhou province and at 964 kg.yr⁻¹ for mainland China. This study indicates that the controls for TI enrichment and emissions to air from cement plants are complex and to elucidate these more detailed experiments are required. In addition to this, cement kiln tail dust is potentially interesting from the TI recycling point of view due to its high content of the industrially valuable metal.

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.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.psep.2021.05.013>.

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