

# STABILIZED MSWI FLY ASH CO-LANDFILLED WITH ORGANIC WASTE: EFFECT OF LEACHATE PROPERTIES ON THE LEACHING BEHAVIOR OF PCDD/Fs

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## ABSTRACT

The leaching behavior and related influence factors of PCDD/Fs from stabilized fly ash were investigated during co-landfill of stabilized fly ash and municipal solid waste (MSW) with different co-landfill ways (layered co-landfill and mixed co-landfill). High leaching concentration of PCDD/Fs was observed at 14 – 56 d, and the fraction of high chlorinated PCDD/Fs exceed 80% in mass concentration of PCDD/Fs. However, the fraction of H<sub>6</sub>CDF attained 43% – 73% of the I-TEQ concentration of PCDD/Fs in the period of high leaching concentration of PCDD/Fs. In addition to the various octanol/water partitioning coefficients of PCDD/Fs, characteristics of leachate as well as DOM composition and the content of PCDD/Fs in stabilized fly ash were crucial factor to affect leaching behavior of high chlorinated PCDD/Fs and low chlorinated PCDD/Fs, respectively. This study contributes to the understanding of leaching pattern of PCDD/Fs and environmental risk assessment for MSW landfills.

## KEYWORDS

Municipal solid waste (MSW), Stabilized fly ash, Co-landfill, Dioxin (PCDD/Fs)

## 1. INTRODUCTION

Incineration is preferred as harmless municipal solid waste (MSW) treatment in China, due to advantage of volume reduction and energy recovery. As by-product of MSW incineration, many heavy metals and polychlorinated dibenzo-p-dioxins and dibenzofurans

(PCDD/Fs) were enriched in fly ash (FA) and it is classified as hazardous waste. Thus, stabilized FA was landfilled in designated area of MSW landfill after stabilized pretreatment in China. However, the conflict between the rapidly increase of the FA production and practical problems such as shortage of land resources and difficulties in landfill management may causes stabilized FA was co-landfilled with raw MSW. The co-landfill may destroy the stability of toxic components in stabilized FA and cause them to enter the surrounding environment. Numerous studies have been conducted regarding the leaching risk of heavy metals, while little attention has been given to PCDD/Fs in stabilized FA (Li et al., 2022). After MSW incineration, PCDD/Fs content in FA exceeds 80% of the total PCDD/Fs production (Hsu et al., 2021). Ren et al. (2020) found that above 92% of highly toxic chlorinated aromatics in flue gas was enriched in FA with the improvement of flue gas control device. The existence of PCDD/Fs was observed in the leachate from different landfill site, which was considered as the result of the co-landfill of MSW and FA (Choi et al., 2006; Ham et al., 2008; Osako et al., 2002). The leaching behavior for PCDD/Fs in FA was proved to significantly relevant for the variation of the concentration and composition of dissolved organic matter (DOM), as well as leachate characteristics (Hsi et al., 2007; Yasuhara et al., 2007). In this study, two co-landfill columns were designed to simulate different co-landfill ways, and the leaching behavior of PCDD/Fs for co-landfill of MSW and stabilized FA in different co-landfill ways was examined during the hydrolysis and

acidogenesis phase. The results can help us better understand the leaching behavior of PCDD/Fs for co-landfill of MSW and stabilized FA, and provide theoretical references for evaluating potential risk during the operation of the landfill.

## 2. MATERIALS AND METHODS

### 2.1 Materials

FA was taken from reciprocating grate furnace of the MSW incineration power plant with incineration technology of mechanical grate-type incinerator, semi-dry purification, activated carbon, and bag filter in Qingdao City, China. The chelating agent (sodium diethyldithiocarbamate, industrial grade) derived from incineration power plant was used to prepare of stabilized FA. The stabilization treatment of FA was carried out by blending FA, chelating agent, and water in the proportion of 100:30:4 (mass ratio) via JJ-5 planetary type motor mixer in laboratory.

Raw MSW was collected from the canteen and dormitory on campus from Qingdao University of Technology, and MSW used in this study was synthesized based on the typical MSW composition in Qingdao City. The composition of the synthesized MSW by wet weight was as follows: kitchen waste (69.37%), paper (7.31%), plastics (11.08%), construction waste (6.18%), textile (2.76%), glass (2.94%), and metal (0.30%). Different components of MSW were broken into pieces less than 4 mm and were uniformly mixed. The water content of MSW was 63.2%, and the organic matter content was 28.4%.

### 2.2 Experimental device and operation

Two anaerobic bioreactor co-landfill columns were designed via thick acrylic pipe with height of 1800 mm and diameter of 300 mm. Details of the landfill columns were presented in Fig. 1. MSW and stabilized FA were landfilled in the landfill area of co-landfill columns at a ratio of 10:1 including 15 kg stabilized FA and 150 kg MSW. Different co-landfill ways including layered co-landfill way (column L) and mixed co-landfill way (column M) were simulated. For column L, 1600 mm

landfill area was divided into 750 mm MSW layer, 100 mm stabilized FA and 750 mm MSW layer. For column M, stabilized FA and MSW were landfilled in the landfill area after well-mixing.

Two co-landfill columns were operated at room temperature to simulate the actual landfill environment. Before the operation, 8 L of distilled water was added to each column to attain optimum moisture content, which enhanced the MSW biodegradation. 4 L distilled water was injected weekly into each column with a peristaltic pump at a flow rate of 40 mL/min to accelerate the biodegradation process and ensure adequate leachate. Before injecting distilled water into each column weekly, leachate in leachate storage space was collected and stored at 4 °C for physicochemical analysis. Due to the 10 L leachate requirement for instrumental analysis of PCDD/Fs, the stored leachate is fully mixed and the volume of collected leachate weekly was determined during different co-landfill phase including 0 – 14 d, 14 – 28 d, 28 – 56 d, 56 – 84 d and 84 – 112 d, then the mass concentrations of PCDD/Fs homologues of different co-landfill phase were measured.

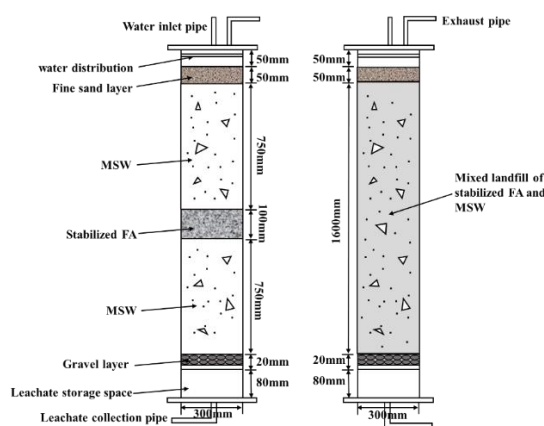


Fig. 1 Schematic diagram of the experimental device

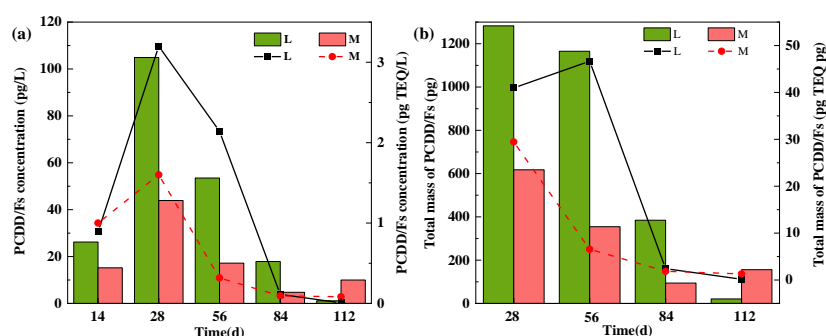
## 3. RESULTS AND DISCUSSION

### 3.1 Variation of PCDD/Fs concentration in leachate

Fig. 2 illustrates the mass concentrations and the I-TEQ concentration of PCDD/Fs in leachate for each column. For column L, the mass concentration of PCDD/Fs increased to 104.9 pg/L from 26.2 pg/L, and gradually decreased to 1.13pg/L. The similar trend was

observed in variation of the I-TEQ concentration of PCDD/Fs, which was evidently increased to 3.2 pg I-TEQ /L from 0.89 pg I-TEQ/L and gradually decreased to 0.0082 pg I-TEQ/L. The change trend of mass concentration and I-TEQ concentration of PCDD/Fs in the leachate for column M was approximately consistent with that of column L. The mass concentration of PCDD/Fs increased from 15.2 pg/L to 43.9 pg/L and decreased to 10 pg/L, while the I-TEQ concentration increased from 1 pg I-TEQ/L to 1.6 pg I-TEQ/L and subsequently decreased to 0.083 pg I-TEQ/L. The similar leaching tendency under different co-landfill ways may be responsible for properties of stabilized FA, which was also observed in pervious study (Hsi et al.,

2007). The maximum leaching concentration of PCDD/Fs in leachate was observed in 14 ~ 28 days, which indicated that the initial stage of co-landfill was accompanied by high PCDD/Fs leaching risk. Although the leaching trend of PCDD/Fs is similar, the mass concentration and the I-TEQ concentration of PCDD/Fs in different landfill ways are quite different. Generally, the mass concentration and the I-TEQ concentration of PCDD/Fs for column M was significantly lower than that of column L. The discrepancy in leaching concentration of PCDD/Fs may resulted from distinct variation of leachate characteristics and composition of DOM for each column (Osako et al., 2002).



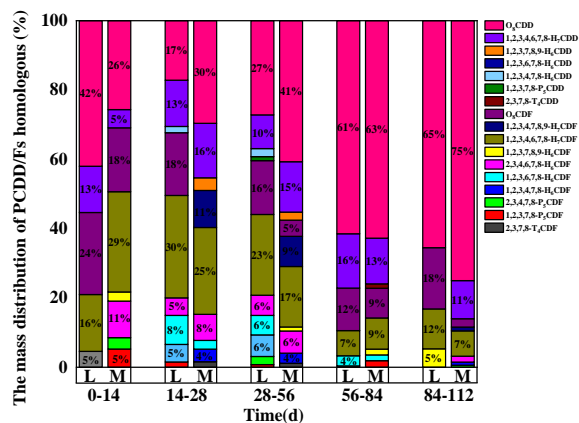
**Fig. 2** The variation of (a) the mass concentration and I-TEQ concentration of PCDD/Fs and (b) cumulative mass amount and cumulative I-TEQ amount of PCDD/Fs in different co-landfill phase for each column (L and M represented the columns that layered co-landfill and mixed co-landfill, histogram represents the mass change of PCDD/Fs, and the dotted line chart represents the I-TEQ change of PCDD/Fs).

### 3.2 The mass distribution of PCDD/Fs homologous

The mass distribution of PCDD/Fs homologous in each column during the co-landfill process were displayed in **Fig. 3**. The highly chlorinated homologues were dominant and the total mass proportion of O<sub>8</sub>CDD/Fs and H<sub>7</sub>CDD/Fs exceeded 80%. Despite the contents of O<sub>8</sub>CDD and H<sub>7</sub>CDD in stabilized FA were similar, the mass proportion of O<sub>8</sub>CDD was always higher than that of H<sub>7</sub>CDD for both column L and column M. In addition, the content of H<sub>7</sub>CDF in stabilized FA was 4.8 time higher than that of O<sub>8</sub>CDF, whereas the fraction of H<sub>7</sub>CDF in leachate was slightly higher than that of O<sub>8</sub>CDF. The strong leachability shown by O<sub>8</sub>CDD/Fs may be attributed to its high

affinity for organic matter due to the abundant DOM in leachate. In the presence of DOM, solubility enhancement in highly chlorinated PCDD/Fs is higher than that in low chlorinated PCDD/Fs (Kim et al., 2002). The high content of O<sub>8</sub>CDD and H<sub>7</sub>CDD in stabilized FA may also be another reason for the high mass concentration of leachate, while the high mass concentrations of O<sub>8</sub>CDF and H<sub>7</sub>CDF were still observed in leachate when total content of low chlorinated PCDFs exceed that of O<sub>8</sub>CDF and H<sub>7</sub>CDF. In addition to the characteristics of high chlorinated PCDD/Fs, DOM characteristic of leachate was considered as main factor for the high concentration of highly chlorinated homologues in leachate. Nevertheless, the content of

PCDD/Fs in stabilized FA has significant influence on the leaching behavior of low chlorinated homologues. In stabilized FA, the content of low chlorinated PCDFs is higher than that of low chlorinated PCDDs, which was also observed in previous paper (Yao et al., 2012). The fraction of low chlorinated PCDFs in leachate was significantly higher than that of low chlorinated PCDDs, which is consistent with the content in stabilized FA. Low octanol/water partitioning coefficients of low chlorinated homologues results in weak affinity for organic matter compared with highly chlorinated homologues (Chen et al., 2001). Leachability of low chlorinated homologues was not only controlled by DOM characteristics of leachate, but the availability of low chlorinated homologues in stabilized FA cannot be ignored. To sum up, the leaching behavior of PCDD/Fs during co-landfill process is related to the content of PCDD/Fs in stabilized FA and the physical-chemical parameters as well as DOM characteristics of leachate.

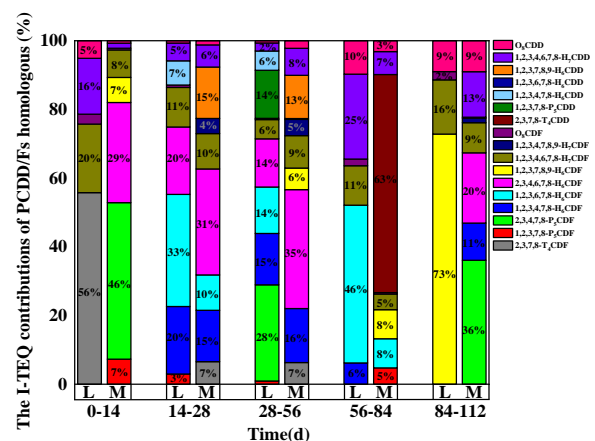


**Fig. 3** The variation of mass distribution of PCDD/Fs homologous in different co-landfill phase for each column (L and M represented the columns that layered co-landfill and mixed co-landfill).

### 3.3 The I-TEQ contributions of PCDD/Fs homologous

The I-TEQ contributions of PCDD/Fs homologous during the co-landfill process were presented in Fig. 4. Although the highly chlorinated PCDD/Fs were the most abundant homologues detected in leachate, the low international toxicity equivalence factors of them

resulted in low I-TEQ contributions for the total I-TEQ value. H<sub>7</sub>CDD and H<sub>7</sub>CDF were crucial proportions in total I-TEQ values, accounting for 5 – 25% and 4 – 20% of the total I-TEQ value, respectively. For low chlorinated PCDD/Fs, low chlorinated PCDFs were the dominant homologous for I-TEQ contributions due to the low mass concentration of low chlorinated PCDDs. H<sub>6</sub>CDF represented a great fraction of the total I-TEQ value during the period of high I-TEQ concentration, and the proportion of H<sub>6</sub>CDF was attained 43% – 73% at 14 – 56 d. However, the I-TEQ contribution of P<sub>3</sub>DF in stabilized FA was largest, accounting for 41% of the total I-TEQ value. It is now acknowledged that bioavailability is a more significant key parameter than the total concentration to evaluate the environment risk. Obviously, it is difficult to determine the environmental risk of PCDD/Fs via calculating the I-TEQ contribution of PCDD/Fs homologues in stabilized FA. In addition, although the high chlorinated PCDD/Fs in the leachate showed low contribution to the total I-TEQ value, in the long-term landfill process, the microbial transformation of high chlorinated PCDD/Fs is an important hidden danger to aggravate the environmental risk of PCDD/Fs, and reductive dechlorination of microorganism has been found in sediment and compost (Chen et al., 2016; Xu et al., 2016). High chlorinated PCDD/Fs may become the source of continuously exporting chlorinated PCDD/Fs to surrounding environment.



**Fig. 4** The variation of I-TEQ contribution of PCDD/Fs homologous in different co-landfill phase for each column (L and M represented the columns that layered

co-landfill and mixed co-landfill).

#### 4. CONCLUSION

Co-landfill of stabilized FA and MSW increased the leaching of PCDD/Fs during the hydrolysis and acidogenesis phase, and high leaching concentration of PCDD/Fs was observed at 14–56 d. Co-landfill ways had a significant impact on release of PCDD/Fs from stabilized FA, and layered co-landfill has higher leaching concentration of PCDD/Fs than mixed co-landfill. High chlorinated PCDD/Fs were dominant fraction of mass concentration of PCDD/Fs, and H6CDF represented a great fraction of the TEQ concentration of PCDD/Fs. However, P5CDF was the main contribution to the TEQ concentration of PCDD/Fs in stabilized FA, which indicated the content of different PCDD/Fs homologues in stabilized FA cannot effectively assess the environmental risk of PCDD/Fs. The leaching behavior of high chlorinated PCDD/Fs was controlled by DOM characteristic, and the content of PCDD/Fs homologues in stabilized FA was the crucial factor for leaching behavior of low chlorinated PCDD/Fs.

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