Field pilot study on emissions, formations and distributions of PCDD/Fs from cement kiln co-processing fly ash from municipal solid waste incinerations

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HIGHLIGHTS
• Dioxin distributions in cement kiln co-processing MSWI fly ash was studied.
• Stack emissions of PCDD/Fs were below the European Union limit for cement kilns.
• Tetra- and penta-chlorinated furans are the major homologs formed in cement kilns.
• PCDD/F concentration in particulates was correlated with chloride content.
• Mass balance indicated 94% reduction in PCDD/F TEQ input from the feed materials.

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ABSTRACT
A pilot study was performed to evaluate formation, distribution and emission of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) from cement kilns that co-process fly ash from municipal solid waste incineration (MSWI). Stack gas and particulate samples from multiple stages in the process were collected and analyzed for PCDD/Fs. Stack emissions of PCDD/Fs were below the European Union limit for cement kilns (0.1 ng TEQ m⁻³). PCDD/F concentrations in particulates from the cyclone preheater outlet, suspension preheater boiler, humidifier tower, and back-end bag filter were much higher than in other samples, which suggests that these areas are the major sites of PCDD/F formation. Comparison of PCDD/F homolog and congener profiles from different stages suggested that tetra- and penta-chlorinated furans were mainly formed during cement kiln co-processing of MSWI fly ash. Three lower chlorinated furan congeners, including 2,3,7,8-tetrachlorodibenzo-p-dioxin and 2,3,4,7,8-pentachlorodibenzofuran, were identified as dominant contributors to the toxic

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1. Introduction

Waste incineration produces polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in stack gas and fly ash, which is of concern as these compounds are toxic, persistent, and can bioaccumulate [1–3]. Filters and activated carbon have been used to reduce emissions of PCDD/Fs into the atmosphere from industrial thermal facilities, including waste incinerators [4–9]. These techniques are very effective, for example, the stack gas concentrations of PCDD/Fs were reduced from 194 ng International Toxic Equivalents (I-TEQ) m⁻³ to below 1.0 ng I-TEQ m⁻³ by injection of activated carbon and addition of a dual baghouse filter system in a kiln using the Waels process [4]. However, at the same facility, the concentrations of PCDD/Fs in fly ash were still as high as (10–100) ng I-TEQ g⁻¹. Similarly, at a municipal solid waste incinerator (MSWI) in Spain, the stack gas emissions of PCDD/Fs were reduced to below 0.01 ng TEQ m⁻³ from 3.26 ng TEQ m⁻³ after installation of a new air pollution control system combined with injection of activated carbon [9]. However, in this case, the PCDD/F concentrations in fly ash samples remained around 0.5 ng TEQ g⁻¹ or higher. These case studies show that physical removal and adsorption techniques transfer unintentionally formed persistent organic pollutants into the fly ash phase. Therefore, the treatment of fly ash remains a serious problem for thermal related industries, including waste incineration operations.

Fly ash produced during waste incineration has been classified as hazardous waste in China [10]. It is considered to contain relatively high concentrations of PCDD/Fs because of it contains compounds that catalyze the heterogeneous formation reactions of PCDD/Fs [11,12]. Between 2007 and 2013, the number of MSWIs in China increased from 66 to 166, and the mass of incinerated solid waste increased from 14,351 to 46,337 thousand tons [13]. This increase in solid waste incineration will greatly increase in MSWI fly ash for disposal [13]. On incineration of solid waste, fly ash is produced at a mass fraction of 3–5% of the original waste mass [14–16]. Therefore, it is estimated that the mass of MSWI fly ash produced in China will have increased from 431–718 thousand tons in 2007 to 1390–2317 thousand tons in 2013. Disposal of this hazardous fly ash remains a challenge.

Cement kilns have increasingly been used for destroying hazardous waste because they operate at the high temperatures (normally >1200 °C) that are required for decomposition of organic chemicals [17]. Cement kilns have been used for the disposal of polybrominated diphenyl ether contaminated soils [17]. Formation and emission of PCDD/Fs from a cement kiln processing a solid fuel recovered from municipal solid waste has been studied [18,19]. Dioxins form in cement kilns, and their release and impact on surrounding environment has been demonstrated [20–24]. However, to date, incineration of MSWI fly ash in a cement kiln has not been performed on an industrial scale or in any pilot studies. To the best of our knowledge, the formation and distribution of PCDD/Fs in cement kilns that co-process MSWI fly ash have not been reported. There are hundreds of cement kilns in operation in China, and cement manufacture in China accounts for about 60% of global production. Therefore, application of cement kilns to destruction of MSWI fly ash is an attractive proposition. Research on the formation, emission and distribution of PCDD/Fs in cement kilns that co-combust MSWI fly ash will provide essential knowledge for assessing the suitability of cement kilns for incinerating this material.

In the present study, a pilot study was carried out on a MSWI fly ash pretreatment line and two cement kiln lines to gain insight into the formation, emission and distribution of PCDD/Fs in cement kilns that co-process MSWI fly ash. Stack gas and particulate samples from various stages in the process were collected and analyzed by isotope dilution high resolution gas chromatography combined with high resolution mass spectrometry (HRGC/HRMS). The aims of this study were as follows: (1) to measure emission of PCDD/Fs to the atmosphere during cement manufacturing with co-combustion of MSWI fly ash, which could be used to evaluate the effectiveness of cement kilns for MSWI fly ash destruction; (2) to identify the sites of PCDD/Fs formation in a cement manufacturing line, which could provide specific knowledge for controlling PCDD/F formation from these stages in the process; and (3) to evaluate variations in the distributions and profiles of PCDF/Fs from different stages in the process of cement manufacturing, which might aid understanding of the PCDD/F formation mechanisms in cement kilns that co-process MSWI fly ash.

2. Experimental

2.1. MSWI fly ash pretreatment line, cement kilns, and sample collection

MSWI fly ash was pretreated before co-combustions in the cement kilns in a pilot cement plant. A schematic of the pretreatment line is shown in Fig. 1(A). The capacity of the pretreatment line was about 30 tons per day. The primary aim of pretreatment was to remove compounds, such as chloride and metal ions, contained in the MSWI fly ash that might damage the cement kiln equipment. Removal of these ions would improve the quality of the cement clinker, and also potentially reduce PCDD/F formation in the cement kiln as these ions can act as catalysts for this process. Pretreatment involved washing the fly ash three times with water containing a small quantity of organic surfactant.

Two cement kilns suitable for high-temperature treatment of MSWI fly ash were investigated in the pilot study. The daily outputs for cement kiln lines 1 and 2 were about 2000 and 2500 tons of clinker, respectively. The kilns were both operated at around 1300 °C in a counter-current configuration, in which gases and solids flowed in opposite directions through the kiln to provide efficient heat transfer. Fabric filters were used as air pollution control devices (APCD). A schematic view of the cement kilns is shown in Fig. 1(B). Cement kiln line 1 had been used to co-process MSWI fly ash continuously for about 300 days, at a typical rate of 20 tons of fly ash per day, and produced cement clinker at a mass fraction of about 1% of the original fly ash mass. To evaluate the potential for a memory effect from long-term thermal treatment of MSWI fly ash on PCDD/F formation and distribution, cement kiln line 2 was also used. This cement kiln had not been used for the destruction of MSWI fly ash before this study. Operating parameters (temperature and pressure) for the pretreatment line and cement kiln lines 1 and 2 are provided along with sample labels for samples.
collected from these processes in Tables S1–S4 (Supplementary material).

Stack gas samples from the pretreatment line and the cement kiln were collected by automatic isokinetic sampling. The sampling train was composed of a heated probe liner, a glass fiber filter and a water-cooled XAD-2 adsorbent trap. The glass fiber filter was used to collect particle-bound pollutants, and the XAD-2 adsorbent resin was used to trap vapor-phase contaminants. Surrogate \(^{13}\text{C}_{12}\)-PCDD/F and \(^{37}\text{Cl}_{4}\)-PCDD/F target compounds (Wellington Laboratories, Guelph, Canada) were added to the XAD-2 resin in the adsorbent sampling cartridge before stack gas sampling, and used to evaluate the sample recovery. The collection of stack gas samples is detailed in previous publications [25–27]. Particulate samples were digested with 1 mol L\(^{-1}\) hydrochloric acid, rinsed with deionized water, and dried before Soxhlet extraction with 250 mL of toluene for approximately 24 h. The extracts were concentrated in a rotary evaporator, then subjected to column cleanup. The volume of each final extract was about 20 \(\mu\)L. Before analysis, \(^{13}\text{C}_{12}\)-labeled PCDD/F standards were added to the corresponding fractions for calculation of the recoveries. PCDD/F congeners were identified and quantified by HRGC/HRMS. The sample extraction, preparation and instrumental analysis are detailed elsewhere [26,28,30].

![Fig. 1. Schematics and sampling points of pretreatment line (A) and cement kiln co-processing MSWI fly ash (B).](image)

PCDD/Fs in the stack gas and particulate samples were analyzed by isotope dilution HRGC/HRMS [27–29]. Briefly, the samples were spiked with known amounts of \(^{13}\text{C}_{12}\)-PCDD/F internal standards (Wellington Laboratories, Guelph, Canada). Particulate samples were digested with 1 mol L\(^{-1}\) hydrochloric acid, rinsed with deionized water, and dried before Soxhlet extraction with 250 mL of toluene for approximately 24 h. The extracts were concentrated in a rotary evaporator, then subjected to column cleanup. The volume of each final extract was about 20 \(\mu\)L. Before analysis, \(^{13}\text{C}_{12}\)-labeled PCDD/F standards were added to the corresponding fractions for calculation of the recoveries. PCDD/F congeners were identified and quantified by HRGC/HRMS. The sample extraction, preparation and instrumental analysis are detailed elsewhere [26,28,30].
2.3. Quality control and quality assurance

Congener peaks were identified based on their retention times compared with available individual standards and ion ratios, and by considering their elution order from the DB-5 column. Peaks were quantified if the target/qualifier ion ratios were within 15% of theoretical values. The limits of detection (LODs) of the PCDD/F congeners in the stack gas samples ranged from 0.07 to 3.17 pg m\(^{-3}\). The LODs of the PCDD/F congeners in the particulate samples ranged from 0.04 to 5.70 pg g\(^{-1}\). The sampling recoveries of five \(^{13}\)C\(_{12}\)-PCDD/F surrogate standards were measured relative to the \(^{13}\)C\(_{12}\)-PCDD/F internal standards to obtain a measure of the collection efficiency. The recoveries for the surrogate labeled PCDD/F sampling standards were between 70% and 130%. For the particulate samples, the recoveries of the \(^{13}\)C\(_{12}\)-labeled PCDD/F internal standards were between 38% and 125%. Laboratory blank experiments were carried out for each batch of samples. A few congeners, including octachlorodibenzo-p-dioxin (OCDD) and 1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin, were detected at concentrations higher than their LODs, but were present at mass fractions of less than 10% in the samples. Thus, the concentrations of PCDD/F congeners in the samples were not blank corrected. The analytical laboratory had participated in international intercalibration studies on PCDD/F analysis for several years. The z-scores for the laboratory in the 13th round of the international intercalibration study organized by the United Nations Environment Program (Intercal AB, Sweden), and the Norwegian Institute of Public Health were within the acceptable range \(-1 < z\text{-scores} < +1\) for the PCDD/F toxic equivalents (TEQs) in fly ash samples from waste incinerators.

3. Results and discussion

3.1. Effect of pretreatment, concentrations and profiles of PCDD/Fs in stack gas emissions from the pretreatment line and cement kilns

The MSWI fly ash was treated in the pretreatment line before co-combustions in the cement kiln. The primary aim of pretreatment was to remove compounds in MSWI fly ash that might negatively affect the cement quality and cement kiln equipment. Pretreatment reduced the chlorine concentration in the MSWI fly ash to below 1% from a starting concentration of 9–26%, and the sodium and potassium concentrations were reduced from about 8% to below 3%. Because of the addition of a small quantity of surfactant to the washing water, the pretreatment also dissolved some PCDD/Fs from the MSWI fly ash. The concentrations of PCDD/Fs were 9.2 and 5.7 pg TEQ L\(^{-1}\) in water samples collected from the #1 and #3 water washing tanks, respectively. The PCDD/F concentration in the original MSWI fly ash was 790 pg TEQ g\(^{-1}\). The PCDD/F concentrations in the particulate samples collected from the #3 filter compressor and air blast dryer were 462 and 58 pg TEQ g\(^{-1}\), respectively. The concentrations of the PCDD/F congeners in the wash water and particulate samples collected from the pretreatment line are shown in Tables S5 and S6 in the Supplementary material. The wash water was recirculated and was not discharged to the environment. This pretreatment of MSWI fly ash could reduce PCDD/F emissions from cement kilns by removing chlorine and metals, which can catalyze PCDD/F formation.

The concentrations and TEQs of the PCDD/F congeners in the stack gas samples were converted to dry standard conditions and are shown in Fig. 2. International-toxic equivalency factors were used for the TEQ calculations of the PCDD/F congeners to allow for comparison to PCDD/F emission data from cement kilns in Europe [22], where PCDD/F emission levels were mostly below 0.1 ng TEQ m\(^{-3}\). An emission limit of 0.1 ng TEQ m\(^{-3}\) is mandatory for MSWIs and cement kilns co-processing hazardous waste in Beijing, China [31,32]. In this study, the average concentration and TEQ of PCDD/Fs in two stack gas samples collected from the end of the pretreatment line were lower than 0.1 ng TEQ m\(^{-3}\) at 166 pg m\(^{-3}\) and 0.04 ng TEQ m\(^{-3}\). Pretreatment of the MSWI fly ash was conducted at temperatures below 200 °C. It is widely considered that PCDD/F formation does not occur below this temperature, but thermal desorption of PCDD/Fs in the air blast dryer might contribute to the presence of PCDD/Fs in the stack gas emitted from the pretreatment line.

Three stack gas samples from the cement kiln were collected to evaluate atmospheric emission of PCDD/Fs from cement kilns co-processing MSWI fly ash. The average mass and TEQ concentrations of PCDD/Fs were 374 pg m\(^{-3}\) and 0.03 ng TEQ m\(^{-3}\), respectively. The mass concentrations were slightly higher than those in stack gas emissions from the pretreatment line. Rivera et al. and Abad et al. studied the stack gas emissions of PCDD/Fs from cement kilns using alternative fuels [33,34]. In one study, long-term monitoring of dioxins indicated that the PCDD/F emissions varied from 0.43 to 2.02 pg TEQ m\(^{-3}\) for a cement line using petroleum coke as fuel, and from 0.07 to 3.31 pg TEQ m\(^{-3}\) for a cement line using conventional fuel, recovered derived fuel and wastewater treatment plant sludge as alternative fuels [34]. In the other study, the stack gas emissions of PCDD/Fs from Spanish cement kilns using waste materials, such as tires or meat meal, as a secondary fuel during clinker production were reported to range from 1 to 42 pg TEQ m\(^{-3}\) [33]. The results obtained in the present study were higher than those in the
long-term study by Rivera-Austrui et al., and comparable to that in the Spanish cement kiln study by Abad et al. In our previous investigation, the average stack gas emissions of PCDD/Fs from this cement kiln without co-processing of MSWI fly ash were 23.7 pg m\(^{-3}\) and 0.95 pg TEQ m\(^{-3}\). By comparison, the values obtained in the present study with co-processing of MSWI fly ash were higher, which indicates that the co-combustion of MSWI fly ash in the cement kiln might lead to higher stack gas emission levels of PCDD/Fs. However, the TEQ for stack gas emissions of PCDD/F from the cement kilns when co-processing MSWI fly ash were still lower than both the Chinese limit (0.1 ng TEQ m\(^{-3}\), Standard for Pollution Control on Co-processing of Solid Waste in Cement Kiln in China, GB 30485-2013)\cite{32} and the European limit (Waste Incineration Directive 2000/76/CE)\cite{33}. Therefore, despite the addition of MSWI fly ash containing PCDD/Fs to the cement kiln, the atmospheric emissions of PCDD/Fs from the pilot plant met the required emission limit (0.1 ng TEQ m\(^{-3}\)).

Fig. 2 shows that PCDFs were more abundant than PCDDs in both the mass and TEQ concentrations. The average ratios of PCDF to PCDD were 3.9 for the mass concentrations and 4.6 for the TEQ concentrations. The fractions of octachlorodibenzo-p-dioxin (OCDD), OCDD, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), 1,2,3,7,8-pentachlorodibenzo-p-dioxin (PeCDF), 2,3,4,7,8-PeCDF and 2,3,4,6,7,8-hexachlorodibenzo-p-dioxin in the mass concentrations were much higher than those of the other eleven congeners, and 2,3,4,7,8-PeCDF was the largest contributor to the total TEQ.

3.2. Distributions of PCDD/Fs in particulate samples from different stages in the cement kiln process

Particulate samples collected from different stages in the cement kiln process from the two cement kiln lines were analyzed to study the distributions of PCDD/Fs. The concentrations of PCDDs and PCDFs in the particulate samples are shown in Fig. 3. For cement kiln line 1, the mass concentrations of 2,3,7,8-PCDD/Fs from Ck-p2, Ck-p3, Ck-p5 were 227, 202 and 190 pg g\(^{-1}\), respectively. The mass concentration of 2,3,7,8-PCDD/Fs from Ck-p1 was 109 pg g\(^{-1}\). In particulate samples from the other stages in the process, the mass concentrations of 2,3,7,8-PCDD/Fs were well below 100 pg g\(^{-1}\). PCDF concentrations were much higher than those of PCDDs. For cement kiln line 2, the mass concentrations of 2,3,7,8-PCDD/Fs in particulate samples from Ck-p1, Ck-p2, and Ck-p3 were higher than those from the other stages in the process. The concentrations of PCDD/Fs in particulate samples from the cyclone preheater outlet, suspension preheater boiler, humidifier tower, and bag filter at the kiln back end were markedly higher than those in particulate samples from other stages (Fig. 3). This indicates that these processes might be important contributors to PCDD/F formation and emission in cement kilns. This knowledge of key stages in the cement kiln process will aid development of techniques to control PCDD/F formation and emission during co-processing of MSWI fly ash.

With the two cement kilns used in this study, cement kiln line 1 had been used for co-processing MSWI fly ash for an extended period, whereas cement kiln line 2 had not been used for co-processing MSWI fly ash before this research. The concentrations of PCDD/Fs in particulate samples from cement kiln line 2 were far lower than those from cement kiln line 1. Studies have indicated that memory effects can increase formation and emission of PCDD/Fs during industrial thermal processes\cite{36,37}. In this study, the mass and TEQ concentrations of PCDD/Fs from cement kiln line 1 were much higher than those from cement kiln line 2 (Fig. 4). Moreover, the variations in mass and TEQ concentrations of PCDD/F among different stages in cement kiln line 2 were lower than the variations in cement kiln line 1. These differences between cement kiln lines 1 and 2 suggest the existence of memory effects in cement kiln 1. Furthermore, the ratio of PCDFs to PCDDs was much higher for cement kiln line 1 than for line 2. This indicates that formation of PCDFs is more pronounced than that of PCDDs in the cement kiln during co-processing of MSWI fly ash. The dominance of PCDFs over PCDDs also suggests that most formation of PCDD/Fs occurs through de novo synthesis during cement kiln co-processing of MSWI fly ash, which is in agreement with theoretical assumptions\cite{38}.
The positive effect of chloride on PCDD/F formation during waste incineration has been demonstrated in earlier laboratory scale experiments [39–41]. In the present study, the content of chloride in the particulate samples was determined according to the Chinese standard method for chemical analysis of cement (GB/T 176-2008) [42]. Fig. 3 shows that the variations among PCDD and PCDF levels and chloride content were closely correlated. This indicates chloride promotes PCDD/F formation. Molar concentrations of PCDDs and PCDFs, and chloride were calculated and correlation analysis was performed. Significant positive correlations were observed between the chloride content and PCDD and PCDF levels in particulate samples collected from the cement kiln lines (Fig. S1). The correlation coefficient (R²) was 0.72 (n = 16) between chloride content and PCDF levels in particulate samples collected from the cement kiln lines, and 0.66 (n = 16) between chloride content and PCDD levels. These results imply that decreasing the chloride content could be important for reducing PCDD/F formation in cement kilns during co-processing of MSWI fly ash.

3.3. Homolog and congener profiles of PCDD/Fs in particulate samples from different stages of the cement kiln process

The homolog and congener profiles of PCDD/Fs in particulate samples from various stages in the pretreatment line and cement kiln line are shown in Fig. 5. For the pretreatment line, the homolog profiles of PCDD/Fs in particulate samples from different stages were very similar. Hexachlorobenzene (PCDF 176-2008) was the most abundant and accounted for about 40% (mass fraction) of the total PCDD/Fs in the pretreatment line. The temperature at all stages of the pretreatment process was relatively low (<200 °C), and the similarity between PCDD/F profiles in particulate samples collected during the pretreatment process confirmed the absence of chemical transformation of PCDD/Fs during pretreatment.

The homolog profiles of PCDD/Fs from the cement kiln line differed from those from the pretreatment line. The TCDF homolog was the most abundant and contributed about 70% (mass fraction) of the total PCDD/Fs in the particulate samples collected from Ck-p1, Ck-p2, Ck-p3 and Ck-p5 of the cement kiln line. PCDF was the dominant homolog in the particulate samples collected from Ck-p6, Ck-p7 and Ck-p8, accounting for 50–70% (mass fraction) of PCDD/Fs. In the particulate sample collected from Ck-p4, the mass fractions of TCDF and PCDF were similar, with each contributing about 40% of the total PCDD/Fs.

The congener profiles of 2,3,7,8-PCDD/Fs in particulate samples collected from different stages of the pretreatment process and cement kiln process are shown in Fig. 5(B). The congener profiles of PCDD/Fs in three particulate samples from the pretreatment line were very similar, with 1,2,3,4,6,7,8-heptachlorobenzene-p-dioxin and OCDD being the dominant congeners. These similar congener profiles indicated the absence of chemical transformation of PCDD/Fs in the pretreatment line because the low temperature (<200 °C). However, the congener profiles of PCDD/Fs in particulate samples from different stages of the cement kiln process were clearly different. For the samples from Ck-p1, Ck-p2, Ck-p3 and Ck-p5, 2,3,7,8-TCDF, 1,2,3,7,8-PCDF, and 2,3,4,7,8-PCDF were dominant, whereas for the samples from Ck-p4, Ck-p6, Ck-p7 and Ck-p8, OCDD and OCDF were the dominant congeners. The mass fractions of OCDD and OCDF were very similar for Ck-p4, and were about 60% of the total 2,3,7,8-PCDD/Fs. The mass fraction of OCDF (<20%) was lower than that of OCDD (>45%) for Ck-p6, whereas for Ck-p7 and Ck-p8, the mass fraction of OCDF was higher than that of OCDD. Comparison of the dominant congeners from different stages suggested that lower chlorinated furans, such as 2,3,7,8-TCDF, 1,2,3,7,8-PCDF, and 2,3,4,7,8-PCDF, were mainly formed at four sites, including at the cyclone preheater outlet (Ck-p1), suspension preheater boiler (Ck-p2), humidifier tower (Ck-p3) and bag filter at kiln back end (Ck-p5). This implies that the formation mechanisms of PCDD/Fs in cement kilns could be understood by studying the formation pathways of the dominant congeners, including 2,3,7,8-TCDF, 1,2,3,7,8-PCDF, and 2,3,4,7,8-PCDF.

3.4. Mass balance and emission factors of PCDD/Fs from cement kilns co-processing MSWI fly ash

Mass balance is useful for understanding the input, output and net emissions of PCDD/Fs from cement kilns co-processing MSWI fly ash. In this study, the mass balances of seventeen 2,3,7,8-chlorine substituted PCDD/F congeners and PCDF/F TEQs for the cement kiln co-processing MSWI fly ash were calculated. These mass balances were calculated based on the PCDD/F concentrations in the feedstock, stack gas and clinker, and using the parameters associated with production in cement kiln system. The feed rates of raw meal and coal powder were 176.9 t h⁻¹ and 15.6 t h⁻¹, respectively. The output rate of clinker was about 120.3 t h⁻¹. The average flow rate of stack gas was 233,599 m³ h⁻¹. The TEQ concentrations of PCDD/Fs in raw meal and coal powder were 0.55 and 34 pg TEQ g⁻¹, respectively. The detailed congener concentrations of PCDF/Fs in raw meal and coal powder are listed in the Table S7 of the Supplementary material. The particulates from the APCD at the kiln back end are normally recycled into the raw materials. In the present study, because these particulates were collected as a sample for analysis, there was no PCDF/F release in particulates from the APCD at the back end of the cement kiln. The hot air produced from cyclone preheater outlet was cooled to about 200 °C and introduced into the coal mill for drying the coal.
powder. The cyclone preheater outlet was identified as an important site of PCDD/F formation in the cement kilns. Thus, the introduction of air produced from cyclone preheater outlet into the coal mill might increase the PCDD/F content of the coal powder used for the fuel. The calculated mass balances of PCDD/F congeners and TEQ are shown in Table 1. The mass balance indicated that the net release of $\sum_{2,3,7,8}$-PCDD/Fs from the cement kiln system was $-9295 \mu g \cdot h^{-1}$ or $-640 \mu g \cdot TEQ \cdot h^{-1}$. The reductions in PCDD/F content from input to output in the cement kiln were more than 84% for the tetra- to heptachlorinated congeners. For OCDF and OCDD, the reductions in PCDD/Fs from input to output in the cement kiln were 50% and 71%, respectively.

The emission factor is useful for estimating PCDD/F emission from cement kilns co-processing MSWI fly ash. Usually, the particularates captured by the cement kiln APCDs are recycled back into the raw materials. Therefore, it was considered that there is no PCDD/F released as residues from this cement plant. The emission factors of $\sum_{2,3,7,8}$-PCDD/Fs to the atmosphere were calculated to be 1.05 $\mu g \cdot TEQ \cdot t^{-1}$ and 0.084 $\mu g \cdot TEQ \cdot t^{-1}$. The emission factor of PCDD/Fs to air adopted in the Stockholm Convention “Toolkit for Identification and Quantification of Releases of Dioxins, Furans and Other Unintentional Persistent Organic Pollutants” was 0.05 $\mu g \cdot TEQ \cdot t^{-1}$ for a state-of-the-art dry kiln with a preheater/precalciner [43]. The emission factor of 0.084 $\mu g \cdot TEQ \cdot t^{-1}$ from the present study was very similar to the adopted emission factor in the Stockholm Convention toolkit. Mass balance data and emission factors of PCDD/Fs suggest that cement kilns are promising for destruction of MSWI fly ash.

4. Conclusions

This pilot study investigated the formation, distribution and emission of PCDD/Fs from cement kilns used to co-process hazardous MSWI fly ash. Stack emissions of PCDD/Fs were below the European Union limit for cement kilns (0.1 ng TEQ·m$^{-3}$). The cyclone preheater outlet, suspension preheater boiler, humidifier tower, and back-end bag filter were identified as major sites of PCDD/F formation in the cement kilns during co-processing of MSWI fly ash. Among the congeners, tetra- and pentachlorinated furan homologs were the most likely to form at these sites in the cement kiln. The chloride content in particle samples was correlated with PCDD/F concentrations. Mass balance indicated that cement kilns eliminated about 94% of the PCDD/F TEQ input from the feed materials, which indicates that the use of cement kilns to destroy MSWI fly ash is a promising approach.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.07.052

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