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Concentrations and patterns of polychlorinated biphenyls at different process stages of cement kilns co-processing waste incinerator fly ash

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ABSTRACT

Cement kilns can be used to co-process fly ash from municipal solid waste incinerators. However, this might increase emission of organic pollutants like polychlorinated biphenyls (PCBs). Knowledge of PCB concentrations and homolog and congener patterns at different stages in this process could be used to assess the possibility of simultaneously controlling emissions of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and "dioxin-like" compounds. To date, emissions from cement kilns co-processing fly ash from municipal solid waste incinerators have not been analyzed for PCBs. In this study, stack gas and particulate samples from two cement kilns co-processing waste incinerator fly ash were analyzed for PCBs. The average total tri- to deca-chlorinated biphenyl ($\sum_{3-10}$PCB) concentration in the stack gas samples was 10.15 ng m^{-3}. The $\sum_{3-10}$PCB concentration ranges in particulate samples from different stages were 0.83–41.79 ng g^{-1} for cement kiln 1 and 0.13–1.69 ng g^{-1} for cement kiln 2. The $\sum_{3-10}$PCB concentrations were much higher in particulate samples from the suspension pre-heater boiler, humidifier tower, and kiln back-end bag filters than in particulate samples from other stages. For these three stages, PCBs contributed to 15–18% of the total PCB, PCDD/F, and polychlorinated naphthalene toxic equivalents in stack gases and particulate matter. The PCB distributions were similar to those found in other studies for PCDD/Fs and polychlorinated naphthalenes, which suggest that it may be possible to simultaneously control emissions of multiple organic pollutants from cement kilns. Homolog patterns in the particulate samples were dominated by the pentachlorobiphenyls. CB-105, CB-118, and CB-123 were the dominant dioxin-like PCB congeners that formed at the back-end of the cement kiln. A mass balance of PCBs in the cement kilns indicated that the total mass of PCBs in the stack gases and clinker was about half the mass of PCBs in the raw materials.

1. Introduction

Polychlorinated biphenyls (PCBs) have adverse effects on the environment and human health, which resulted in their inclusion in the initial list of chemicals in the Stockholm Convention on Persistent Organic Pollutants (POPs). The production of technical PCB mixtures for use in capacitors, transformers, and other applications has been banned internationally (Breivik et al., 2007; Diamond et al., 2010; Hornbuckle and Robertson, 2010; Hu and Hornbuckle, 2010). However, PCBs can be unintentionally produced and released to the environment during many industrial thermal activities (Liu et al., 2013b).

Since the banning of production and use of technical PCB mixtures, the unintentional release of PCBs during industrial thermal processes has increased in relative importance as a source of PCBs to the environment. Waste incineration is an important source of unintentionally produced PCBs because solid waste is often incompletely combusted in waste incinerators (Abad et al., 1999; Sakai et al., 2006; Jansson et al., 2008; Jansson and Andersson, 2012; Khumsaeng et al., 2013). A large proportion of the PCBs that are unintentionally produced during waste incineration are released in fly ash. In earlier research, the total concentration range for twelve dioxin-like PCB (dl-PCB) congeners in fly ash from waste incinerators was of 1.10–60 ng g^{-1}, and the associated toxic equivalency (TEQ) range was 0.039–1.2 ng g^{-1} (Tabata et al., 2013). Therefore, fly ash from municipal solid waste incinerators (MSWIs) can contain high concentrations of PCBs, and appropriate methods are required for safe disposal of this ash.

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In China, huge quantities of MSWI fly ash are produced by waste incinerators (Liu et al., 2015), and disposal of this ash is challenging. Cement kilns have been used to destroy waste containing organic chemicals because these pollutants effectively decompose at kiln temperatures above 1000 °C. Emission of contaminants from cement plants and the risks posed to the surrounding environment and human health have attracted increasing attention (Schuhmacher et al., 2002, 2004; Garcia-Perez et al., 2015). The risk of increased emission of organic pollutants to the environment needs to be investigated before cement kilns are used to co-process solid wastes. Several studies have reported on the use of cement kilns for destruction of sewage sludge and soil contaminated with pesticides or polybrominated diphenyl ethers (Conesa et al., 2011; Yang et al., 2012). Other studies have investigated the emission of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) from cement kilns used to co-process solid waste (Wurst and Prey, 2003; Conesa et al., 2011; Yang et al., 2012). Unintentional formation and emission of PCBs and PCDD/Fs have been confirmed for many industrial thermal processes (Liu et al., 2009, 2013a; Lv et al., 2011; Nie et al., 2011, 2012). These earlier results suggest that PCBs will form in and be emitted from cement kilns co-processing solid waste. However, few studies have evaluated stack gas emissions of PCBs from cement kilns co-processing solid waste. To the best of our knowledge, only one study has investigated the long-term emissions of PCBs from a clinker kiln using alternative fuels, and analyses were performed for only twelve dl-PCB congeners (Rivera-Austrui et al., 2014). To date, no studies have investigated the emission, distribution within the kiln system, and homolog and congener patterns of PCBs for cement kilns co-processing MSWI fly ash.

We have previously studied the formation and distribution of PCDD/Fs and polychlorinated naphthalenes (PCNs) in two cement kilns co-processing MSWI fly ash, and the emissions of PCDD/Fs and PCNs from these kilns (Liu et al., 2015, 2016). However, the distributions within the kiln and homolog and congener patterns of PCBs have not been described. An understanding of the distributions within the kiln and homolog and congener patterns of PCBs, and comparison of the behaviors of PCBs with those of PCDD/Fs and PCNs, could be used to develop techniques for simultaneously controlling multiple pollutants. In this study, PCB concentrations were determined in stack gas samples and particulate samples from different process stages of the same two cement kilns as in our earlier research. The aim of this study was to clarify the distributions within the kiln and homolog and congener patterns of PCBs, and to evaluate the possibility of simultaneous control of PCB, PCDD/F, and PCN emissions.

2. Materials and methods

2.1. The cement kilns and sample collection

The pilot cement kilns the samples were collected from are described in detail in our earlier research (Liu et al., 2015, 2016). Cement kilns 1 and 2 had daily clinker outputs of about 2000 and 2500 t, respectively. Kiln 1 had been used to continuously co-process MSWI fly ash at a rate of 20 t d^{-1} for about 300 d. Kiln 2 had not previously been used to co-process MSWI fly ash, and was studied to evaluate the effect of long-term treatment of MSWI fly ash on the formation of PCBs in kiln 1 (Liu et al., 2015, 2016). The chemical composition of MSWI fly ash added into the cement kilns was determined by X-ray fluorescence (Table S1).

Stack gases released from the back end of kiln 1 were collected using an automatic isokinetic sampling method described in detail elsewhere (Ba et al., 2010; Liu et al., 2010; Lv et al., 2011). Particulate samples were collected from different process stages of the kiln systems. A diagram showing the processes that occur in a cement kiln, and further information on the locations for sample collection is included in our earlier research (Liu et al., 2015, 2016). Kiln back-end particulate samples from the cyclone preheater outlet, suspension pre-heater boilers, humidifier towers, raw mill, bag filters were labeled as Ck-p1, Ck-p2, Ck-p3, Ck-p4 and Ck-p5, respectively. Kiln head particulate samples from the boiler, clinker area, and bag filter were labeled Ck-p6, Ck-p7, and Ck-p8, respectively.

2.2. Sample pretreatment and instrumental analysis for PCBs in stack gas and particulate samples

PCB congeners in the samples were identified and quantified by isotope dilution high-resolution gas chromatography combined with high resolution mass spectrometry. The extraction, purification, and instrumental analysis of PCBs in samples are described in our previous studies (Liu et al., 2009, 2013a,b). Briefly, each sample was spiked with known amounts of $^{13}C_{12}$-labeled PCB internal standards (1668B-LCS), and then digested with 1 mol L^{-1} HCl. Each sample was Soxhlet extracted using toluene for 24 h, then the extract was concentrated under reduced pressure. Each extract was purified first with silica gel treated with 44% (mass fraction) sulfuric acid, a multilayer silica gel column, and then a basic alumina column. The extract was finally concentrated to about 20 μL under a gentle stream of nitrogen gas. Then, $^{13}C_{12}$-labeled PCB injection standards (1668B-IS) were added to evaluate the recoveries of the $^{13}C_{12}$-labeled internal standards.

The high-resolution gas chromatography combined with high resolution mass spectrometry used a DB-5 ms fused-silica column (60 m × 0.25 mm i.d., 0.25 μm film thickness). The mass spectrometer was operated in selected ion monitoring mode with a resolution of around 10,000, and the most abundant ions in the molecular ion cluster were monitored (Liu et al., 2009, 2013a,b).

2.3. Quality assurance and quality control of PCB analysis

Each selected PCB congener was identified by comparing the retention time of a selected chromatographic peak with the retention time of the same peak for the appropriate $^{13}C_{12}$-labeled standard. For quantification, the ratio of the target ion to qualification ion should be within 15% of the theoretical value. The range for recovery of the $^{13}C_{12}$-labeled PCB internal standard was 43–136%. Laboratory blanks were analyzed with each batch of samples. The CB-28 and CB-101 concentrations in the blanks were slightly higher than the limits of detection but much lower than 5% of the concentrations in the samples. Therefore, the PCB concentrations in the samples were not blank corrected.

3. Results and discussion

3.1. Emissions of PCBs in stack gases produced by cement kilns co-processing MSWI fly ash

The PCB concentration range in the stack gas samples collected from the cement kilns was 61.2–110.4 ng m^{-3} (average 87.2 ng m^{-3}, relative standard deviation (RSD) 28.4%). The dl-PCB concentration range in the stack gas samples was 0.39–0.91 ng m^{-3} (average 0.66 ng m^{-3}, RSD 40%), and the indicator PCB concentration range was 1.20–1.56 ng m^{-3} (average 1.38 ng m^{-3}, RSD 13.0%). The PCB TEQs were calculated using published toxic equivalency factors (TEFs) for PCBs (Van den Berg et al., 1998). The PCB TEQ range in the stack gas samples was 5.33–14.3 pg TEQ m^{-3} (average 9.84 pg TEQ m^{-3}, RSD 45.4%). There have been few studies of stack gas emissions of PCBs from cement kiln