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Source identification and quantification of chlorinated and brominated polycyclic aromatic hydrocarbons from cement kilns co-processing solid wastes☆

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ABSTRACT

Chlorinated and brominated polycyclic aromatic hydrocarbons (Cl/Br-PAHs) are widespread persistent organic pollutants (POPs) in environments. Identifying the new sources of Cl/Br-PAHs is important for implementing source control and reducing environmental risk. Although co-processing of solid wastes by cement kilns increased recently, the occurrences and characteristics of Cl/Br-PAHs as emerging POPs during cement kiln co-processing solid wastes have not been investigated. This study firstly investigated the occurrences, characteristics, and variations of Cl/Br-PAHs from four cement kilns co-processing different solid wastes. The concentration ranges of Cl-PAHs and Br-PAHs in stack gas samples from the investigated cement kilns were 15.6–94.1 ng m^{-3} and 1.04–4.28 ng m^{-3}, respectively. Emission factors of Cl-PAHs and Br-PAHs through stack gases were 29.9–275 μg t^{-1} and 3.0–8.3 μg t^{-1}, respectively. Variations of Cl/Br-PAHs in particle samples collected from different process stages within the cement kiln system indicated that the kiln end was the major formation zone for Cl/Br-PAHs. Congener profiles of Cl/Br-PAHs varied with the co-processed solid waste types, indicating the important influence of raw material compositions. Calculations of net emissions of Cl/Br-PAHs within the cement kiln systems suggested efficient destruction (87.6%–98.8%) of Cl/Br-PAHs by the cement kilns.

1. Introduction

Chlorinated or brominated polycyclic aromatic hydrocarbons (Cl/Br-PAHs, > 3 rings) have attracted increasing concerns and are considered as emerging environmental organic contaminants. Studies on the toxicities of Cl/Br-PAHs reported their inducing activities to the aryl hydrocarbon receptor (AhR), which are similar with the notorious polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs) (Horii et al., 2009; Ohura et al., 2007a,b). It was reported that Cl/Br-PAHs tend to be formed by thermochemical or photochemical reactions in the presence of PAHs and halogens (Fujima et al., 2006; Sankoda et al., 2013; Wang et al., 2016). PAHs and halogens are ubiquitous during anthropogenic activities or in the natural environments. Therefore, Cl/Br-PAHs are considered to be potentially ubiquitous organic compounds. Actually, Cl/Br-PAHs have been detected in many environmental matrices, such as the air, soil, sediment, water, and so on (Haglund et al., 1987; Ieda et al., 2011; Sun et al., 2011). Based on the toxicities of the Cl/Br-PAH congeners relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxins (2,3,7,8-TCDD), the toxic equivalent concentrations of Cl/Br-PAHs in some environmental matrices were also reported. Results revealed that toxic equivalent concentrations of Cl/Br-PAHs in some environmental matrices were even much higher than those of PCDD/Fs (Jin et al., 2017b; Ma et al., 2009; Ohura et al., 2007a,b). Therefore, considering their great contribution to the toxic equivalents aroused from dioxins and dioxin-like compounds in the environments, it is significant to clarify their environmental levels and potential sources.

Source identification is the primary step for proposing strategy on priority control of the emissions of pollutants. Formations and

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releases during industrial activities have been identified to be the major sources of unintentional produced persistent organic pollutants (POPs) (Li et al., 2015a; Li et al., 2014; Nie et al., 2012). Studies on their emission characteristics would also provide important information on the fingerprints and emission factors, which would be helpful for source tracing and environmental impact evaluation. As for Cl/Br-PAHs, however, study on their industrial emission sources is very lacking. Among numerous industrial activities, waste incinerations and metallurgical processes have been identified to be the sources of Cl/Br-PAHs through stack gas or solid residue emissions (Horii et al., 2008; Jin et al., 2017b; Ohura et al., 2007a,b). Detection of Cl/Br-PAHs in some environmental matrices also provided indirect information on the formation of Cl/Br-PAHs during some anthropogenic activities. For example, Cl/Br-PAHs have been detected in air, soil and dust samples around e-waste dismantling areas, suggesting that the e-waste dismantling was also one of sources of Cl/Br-PAHs into environments (Ma et al., 2009; Wang et al., 2012). The detection of Cl-PAHs in air collected from tunnels also indicated that automobiles are the potential sources of Cl-PAHs (Nilsson and Ostman, 1993). As for other industrial sources or anthropogenic activities, relevant study about the emission levels and characteristics of Cl/Br-PAHs is lacking.

Cement production is an important industry in the world. According to the "Development plan of building material industry (2016–2020) in China" (Ministry of Industry and Information Technology of the People's Republic of China, 2016). 1.33 billion tons of the clinker was produced in 2015 in China. In 2020, the requirement of the clinker was estimated to be 1.2 billion tons. In addition, cement kilns co-processing solid wastes took about 7% of the total industry in 2015, and the percent was estimated to be 15% in 2020. That is, in 2015, about 93.1 million tons of clinkers would be produced together with dealing solid wastes, and in 2020, this value would increase to 180 million tons. The co-processing of solid wastes including the municipal solid waste (MSW) and sewage sludge by cement kilns have been intensively applied in many countries including Germany, Netherland, Spain, Japan, USA and so on (Conesa et al., 2011; Li et al., 2015b; Schuhmacher et al., 2009; Valderrama et al., 2013; Yang et al., 2012). However, there are still many problems needed to be comprehensively addressed (Chen et al., 2014; Karstensen, 2008; Rovira et al., 2011). Emissions of several unintentional produced POPs, such as PCDD/Fs, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), and polybrominated biphenyl ethers (PBDEs) during cement kilns co-processing solid wastes have been investigated (Jin et al., 2017c; Jin et al., 2016; Liu et al., 2015; Yang et al., 2012; Zhao et al., 2017). Based on these studies, cement kiln co-processing solid waste has been identified as one of important sources for the atmospheric POPs. Releases of PAHs as the potential precursors for the formation of Cl/Br-PAHs during cement kiln co-processing solid wastes have also been reported (Conesa et al., 2011). Therefore, we consider that Cl/Br-PAHs have the potential to be formed during cement kilns co-processing solid wastes. Considering the fast promotion of cement kiln technique co-processing solid wastes and the potential of Cl/Br-PAHs formation and releases, it is essential to clarify the levels, characteristics and variations of Cl/Br-PAHs during cement kilns co-processing solid wastes. This is significant for compiling their global emission inventories and evaluating their environmental risks.

In this study, four cement kilns co-processing multiple solid wastes including MSW, sewage sludge, MSWI fly ash and carbide slag were firstly investigated for clarifying the occurrences, characteristics and variations of Cl/Br-PAHs. Stack gas samples and particle samples from different stages during cement kilns co-processing solid wastes were collected and analyzed for 18 Cl-PAH and 17 Br-PAH congeners by isotopic dilution gas chromatography coupled with high resolution mass spectrum (HRGC-HRMS) method. The primary aims of this study are (1) to investigate the levels and characteristics of Cl/Br-PAHs during cement kilns co-processing solid wastes, which could provide the fingerprints of Cl/Br-PAHs during cement kilns co-processing solid wastes as source tracers of Cl/Br-PAHs in environments; (2) to clarify the variations of Cl/Br-PAHs in different process stages, which could provide useful information for controlling their emissions; (3) to derive the emission factors and destruction efficiency of Cl/Br-PAHs during cement kilns co-processing solid wastes, which is significant for compiling their global emission inventories and evaluating their environmental risks.

2. Material and methods

2.1. Basic information of the investigated four cement kilns co-processing solid wastes

Four cement kilns that co-processed different types of solid wastes were investigated in this study. Basic information on the investigated cement kilns were listed in Table 1. In cement kiln (Ck) 1, the MSW was sorted to remove the non-combustible materials, and then added into the pyrolyzer. Then the pyrolysis gas of MSW was directly conducted into the bottom of the pre-calciner. In Ck 2, the dried sewage sludge was added into the pre-calciner with the raw meals. In Ck 3, the MSWI fly ash was co-processed. MSWI fly ash was classified to be hazardous materials in China, and thus needed to be disposed properly. MSWI fly ashes were pretreated to remove the chloride and metal ions by water washing before being added into the rotary kilns.

In Ck 4, carbide slag produced from chlor-alkali industries was co-processed. Carbide slag was produced in the generation of acetylene from the reaction of carbide (CaC_2) with water. With the rapid industrial development of polyvinyl chloride (PVC) with acetylene involved, an increasing amount of carbide slag as solid wastes has been produced. Using the carbide slag as a raw material substitute of the cement kilns has been explored considering that the main content of carbide slag is calcium oxide, which is similar with the raw meals of cement production. In this study, the carbide slag was mixed with the raw meals, and constituted about 76% of the total raw materials of cement production.

The diagram of the processes of cement kilns co-processing solid wastes in Ck 1 to 3 was shown in Fig. 1. There are several stages within a cement kiln co-processing solid wastes process. There are chimney, bag filter at kiln end, back end boiler (SP boiler) and humidifier tower, cyclone preheaters, pre-calciner, rotary kilns, coolers, boiler at kiln head and bag filter at kiln head from the kiln end to kiln head. Particle samples from different process stages were collected in Ck 1 to 3. In Ck 4, there was a by-pass system connected with the kiln, through which the chloride salts would be reduced. Specific information of the by-pass system in Ck 4 has been clarified in our previous study (Zhao et al., 2017). The particle samples collected in Ck 4 included the particles from bag filter at kiln end, coals, raw materials and clinkers.

There are 18 Cl-PAH and 17 Br-PAH congeners analyzed in this study. The Cl-PAHs include: 3-chlorophenanthrene (3-ClPhe), 9-ClPhe/2-ClPhe, 1-chloroanthracene (1-ClAnt), 2-ClAnt, 9-ClAnt, 2,7-dichlorofluorene (2,7-Cl_2Fle), 1,4-dichloroanthracene (1,4-Cl_2Ant), 1,5-Cl_2Ant/9,10-Cl_2Ant, 9,10-dichlorophenanthrene (9,10-Cl_2Phe), 3-chlorofuloranthene (3-ClFlu), 1-chloropyrene (1-ClPyr), 3,8-dichlorofluoranthene (3,8-Cl_2Flu), 7-chlorobenz[a]anthracene (7-ClBaA), 1,5,9,10-tetrachloroanthracene (1,5,9,10-Cl_4Ant), 7,12-dichlorobenz[a]anthracene (7,12-Cl_2BaA), 6-chlorobenzo[a]pyrene(6-ClBaP). The Br-PAHs include: 1,2-dibromoacenaphthylene