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Source identification of PCDD/Fs in agricultural soils near to a Chinese MSWI plant through isomer-specific data analysis

Meng-xia Xu [a], Jian-hua Yan [a,*], Sheng-yong Lu [a], Xiao-dong Li [a], Tong Chen [a], Ming-jiang Ni [a], Hui-fen Dai [b], Ke-fa Cen [a]

[a] *State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering of Zhejiang University, Hangzhou 310027, China*
[b] *Zhejiang University School of Medicine, Hangzhou 310058, China*

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Abstract

Isomer-specific data were investigated in order to identify the sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in agricultural soils, including Fluvo-aquic and paddy soils, in the vicinity of a Chinese municipal solid waste incineration (MSWI) plant. Homologue and isomer profiles of PCDD/Fs in soils were compared with those of potential sources, including combustion sources, i.e., MSWI flue gas and fly ash; and the impurities in agrochemicals, such as the pentachlorophenol (PCP), sodium pentachlorophenate (PCP–Na) and 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP). The results showed that the PCDD/F isomer profiles of combustion sources and agricultural soils were very similar, especially for PCDFs, although their homologue profiles varied, indicating that all the isomers within each homologue behave identically in the air and soil. Moreover, factor analysis of the isomer compositions among 33 soil samples revealed that the contamination of PCDD/Fs in agricultural soils near the MSWI plant were primarily influenced by the combustion sources, followed by the PCP/PCP–Na and CNP sources. This implication is consistent with our previous findings based on chemometric analysis of homologue profiles of soil and flue gas samples, and identifies PCP/PCP–Na as an additional important source of PCDD/Fs in the local area. This makes the similarities and differences of isomer profiles between Fluvo-aquic and paddy soils more explainable. It is, therefore, advisable to use isomer-specific data for PCDD/F source identifications where possible.

Keywords: Polychlorinated dibenzo-*p*-dioxins and dibenzofurans; Municipal solid waste incinerator; Pentachlorophenol (PCP); Sodium pentachlorophenate (PCP–Na); 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP); Factor analysis

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are two groups of persistent and toxicologically significant trace organic contaminants that are produced unintentionally (Lohmann and Jones, 1998). The proposed major sources of PCDD/Fs are combustion processes, the production and use of chlorinated organic compounds, and the bleaching of pulp and paper (Kiguchi et al., 2007).

In China, it is estimated that 200 million tons of municipal solid waste (MSW) is generated annually, accounting for 29% of the total world MSW production (Jun et al., 2004). The lack of landfill sites for the wastes has forced the local governments, especially for developed regions, to choose the incineration as a substitute option. Consequently, more than 20 large scale fluidized bed incinerators (FBIs) (unit capacity between 150 and 400 t MSW d^{-1}) have been commercially operated in China since 1998 (Yan et al., 2006). However, PCDD/F emissions from the municipal solid waste incineration (MSWI) plants have stirred public concerns for their potential adverse effects

* Corresponding author. Tel.: +86 571 87952629; fax: +86 571 87951614.
E-mail addresses: xumengxia@zju.edu.cn (M.-x. Xu), yanjh@cmee.zju.edu.cn (J.-h. Yan).

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on the surrounding environment. It was estimated that 3–924 g I-TEQ (International Toxic Equivalents) of PCDD/Fs in China was released into the atmosphere by the MSWI plants during the year of 2002 (Jun et al., 2004).

In addition to the MSWI plants, impurities in agrochemicals such as pentachlorophenol (PCP), sodium pentachlorophenate (PCP–Na), and 1,3,5-trichloro-2-(4-nitrophenoxy) benzene (CNP) might be important PCDD/F sources in China. PCP had been extensively used in agricultural activities as a pesticide since 1930s (Feng et al., 1995). In order to control the spread of snailborne schistosomiasis, an estimated 10 000 t yr^{-1} of PCP–Na had been applied in 11 provinces along the downstream portion of Yangtse River since 1950s, and the total environmental input of PCDD/Fs (sum of the concentrations of tetra- to octa-PCDD/F homologues) amounted to about 240 kg (Bao et al., 1995; Zhang et al., 2001). As one of the most effective pesticides, CNP has been applied in agricultural fields to remove weeds since 1970s in China (Zhao, 2002; Zhong, 2005).

Since the first detection of PCDD/Fs in the flue gas of MSWIs, the emission of PCDD/Fs has become one of the most controversial issues worldwide (Olie et al., 1977). Given their semi-volatile and hydrophobic characters, they can be easily accumulated in organic-rich environmental sinks, such as soil and sediment (Schuhmacher et al., 1997). Therefore, comprehensive research has been conducted to investigate the levels and sources of PCDD/Fs in soils in the vicinity of MSWIs in the last three decades (Berlincloni and Domenico, 1987; Schuhmacher et al., 1997, 1998, 1999, 2000; Lorber et al., 1998; Coutinho et al., 1998; Ohta et al., 2000; Domingo et al., 2000, 2001a,b, 2002; Cheng et al., 2003; Caserini et al., 2004; Oh et al., 2006; Schuhmacher and Domingo, 2006).

It is believed that isomer-specific data could well reflect the mixture of PCDD/F input from various origins, and are far more effective in elucidating the relationships between sources and environmental sinks than those based only on homologues and/or the seventeen toxic 2,3,7,8-substituted ones (hereafter called congeners) (Sakurai et al., 2000; Masunaga et al., 2003). As a result, isomer-specific data has been successfully applied in source identification of PCDD/Fs in environmental sinks, mostly for sediments and paddy soils in Japan (Yasuhara et al., 1987; Sakurai et al., 1996, 1998, 2000; Sakurai, 2003; Masunaga et al., 2001a, 2003; Kiguchi et al., 2007), and sediments in the UK (Green et al., 2001), Australia (Gaus et al., 2001, 2002), US (Czuczwa and Hites, 1984), Norway (Oehme et al., 1989) and Sweden (Kjeller and Rappe, 1995).

However, until now, in China there have been limited studies focusing on the occurrence of PCDD/Fs in the neighbourhood of the MSWI plants. Moreover, previous investigations of PCDD/Fs conducted in soils near the MSWIs mentioned above were only focused on the homologues and/or the congeners. In September, 2006, we investigated PCDD/F levels of agricultural soils in the vicinity of FBIs of co-firing MSW with coal in Hangzhou, China (Yan et al., 2007). The comparisons of homologue and congener patterns as well as multivariate analysis of soil and flue gas samples strongly indicated that most soil samples were influenced by the MSWI plant. Besides, the study revealed that historical PCDD/F emissions of hazardous waste incinerator (HWI) and motor vehicles, as well as the application of CNP, seemed to play an important role in soil samples adjacent to these potential sources. Accordingly, the objectives of this study are to: (1) present the isomer-specific data of PCDD/Fs in agricultural soils, including Fluvo-aquic and paddy soils, in the vicinity of the MSWI plant; (2) identify possible PCDD/F sources of agricultural soils through the isomer-specific data analysis of soils and their potential sources; (3) compare the results of this study with previous ones based on the homologue and congener patterns.

2. Materials and methods

2.1. Description of the study area

The detailed descriptions of the study area as well as the MSWI plant were presented elsewhere (Yan et al., 2007). Briefly, the study area belongs to a satellite town, where industrial and residential areas coexist. Approximately 57% of the study area is covered by agricultural fields, which are made up of two soil types, with the prevailing Fluvo-aquic type and paddy soil found 2 km or more to the east of the stack. The MSWI plant referred to in this study is located in an industrial zone in the center of the town, adjacent to two motorways with heavy traffic on the west and north sides (Fig. 1). It is equipped with three FBIs and has been in full operation with a total daily capacity of 800 t since 2003. The PCDD/F emission level measured during its full operation in 2003 was between 0.0054 and 0.1961 ng I-TEQ Nm^{-3}, which was quite below the national legal limit of 1 ng I-TEQ Nm^{-3} (Yan et al., 2006). In addition, a small-scale HWI plant, about 800 m northward of the MSWI plant, operated intermittently between 2002 and 2004 for a total operation time of approximately half a year. Moreover, agricultural activities with a possible use of agrochemicals including PCP/PCP–Na and CNP can be suspected.

2.2. Agricultural soil samples

A total of 33 soil samples were collected from agricultural fields in the vicinity of the MSWI plant. Sampling was performed with the aid of a handheld GPS device (*Meridian Color*, Thales Navigation, US) in September 2006 within a period of two days. Twenty-nine Fluvo-aquic soil samples were collected within a radius of 3 km from the stack, mainly in the historical prevailing downwind directions, while the remaining four paddy soils were collected in the upwind direction, east, 2–7 km from the stack. Sampling sites within a radius of 2 km from the MSWI plant