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Sources identification of PCDD/Fs in soil and atmospheric deposition in Taiwan

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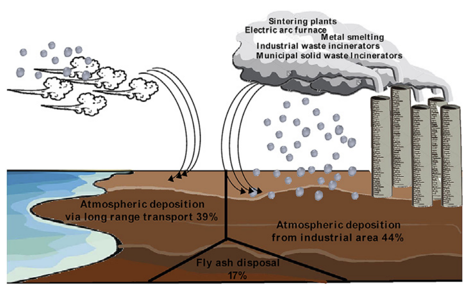
HIGHLIGHTS

- Taiwan systematic PCDD/F investigation of deposition (n = 57) and in-soil (n = 84).
- 10.4 pg WHO-TEQ/g (soil) and 7.39 pg WHO-TEQ/m^2/day (deposition) was found.
- Connection between atmospheric deposition and soil PCDD/Fs.
- 83% of soil PCDD/Fs correlate with atmospheric deposition process.
- Industrial activities and LRT are two main sources of deposited PCDD/Fs.

GRAPHICAL ABSTRACT



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ABSTRACT

PCDD/Fs are among pollutants, which gain major concern from Taiwan government and citizens during industrialization. PCDD/Fs can be emitted into the atmosphere, soil, and water environment in either vapor or solid forms. Atmospheric deposition is the main pathways for atmospheric PCDD/Fs to precipitate on surface soil. In this study, a simultaneous analysis of both soil and deposition PCDD/Fs was done to investigate the relationship between in-soil and deposited PCDD/Fs in Taiwan. Soil samples (n = 84) and atmospheric deposition samples (n = 57) were collected within overlapped periods of time. Geometric mean of 10.4 pg WHO-TEQ/g was found in the soil samples when the geometric mean of atmospheric deposited PCDD/F concentrations was found to be 7.39 pg WHO-TEQ/m^2/day. Concentration of PCDD/Fs in samples collected in industrial location were higher than those collected in other locations in all sampling areas. OCDD, OCDF, HpCDD, HpCDF, were the predominant congeners in PCDD/F profile in both soil and atmospheric deposited samples, when 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF were major contributors for PCDD/F fingerprint with WHO-TEQ transformation. Positive Matrix Factorization (PMF) analysis showed that 83% of soil PCDD/Fs correlate with atmospheric deposition process originated from industrial activities (44%) and long range transport activities (39%). Furthermore, the PMF analysis found long range transport, municipal solid water incinerators (MSWIs), industrial waste incinerators (IWIs), electric arc furnace, recycling process of aluminum, sintering plants to be the main sources contributing to atmospheric deposited PCDD/Fs.

1. Introduction

PCDDs (polychlorinated dibenzo-p-dioxins) and PCDFs

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(polychlorinated dibenzofurans) are commonly known as dioxins, which have been listed as persistent organic pollutants (POPs) according to Stockholm Convention in 2001 (Stockholm Convention on Persistent Organic Pollutants, 2001). Among 210 PCDD/F compounds, seventeen PCDD/F congeners with chlorine substitution in 2,3,7,8 positions are most toxic to humans. PCDD/Fs are byproducts formed during thermal industrial and nonindustrial activities (Schecter et al., 2006; Martínez et al., 2010; Chang et al., 2014; Minh et al., 2014; Ngo et al., 2017). Annual emission of PCDD/Fs in Taiwan observed a decreasing trend from 67.25 g I-TEQ/year in 2004 (Chen, 2004) to 57.8 g I-TEQ of PCDD/Fs in 2010 (Environmental Protection Bureau Kaohsiung City Government, 2010). This rate of emission was much lower than historical emission of PCDD/Fs found in 1980s in Japan (Weber et al., 2008) and in Taiwan itself (Chi et al., 2009). The decrease of this rate was mostly due to the issue of toxic chemical regulation, especially the prohibition of Pentachlorophenol in 1989 (Lee et al., 2006).

Studies about the emission of PCDD/F in various industrial facilities were carried out in Taiwan. Most of the studies were done in the west of the country, where large numbers of industrial parks were located (Environmental Protection Bureau Kaohsiung City Government, 2010). Estimation from the government pointed out major PCDD/F emission activities, namely secondary copper smelting industries (39.0%), waste incinerators (23.7%), cement kilns (>10%), and electric arc furnaces for steels (>10.0%) (Environmental Protection Bureau Kaohsiung City Government, 2010). At the same time, studies also found that winter monsoons and dust storm events during spring time can transport PCDD/Fs from the continent to Taiwan (Chi et al., 2008, 2013).

The PCDD/Fs emitted directly into the soil can hardly be transported, therefore, the sources of these PCDD/Fs can be easily zoned. However, atmospheric emitted PCDD/Fs might first undergo long range transport (AMAP, 2004) before being removed. Degradation process (through photolysis) is just a minor removal pathway when most of the undecomposed PCDD/Fs are removed through wet and dry deposition (Horstmann and McLachlan, 1997; Schröder et al., 1997; Lohmann and Jones, 1998; Vassura et al., 2011), which was also approved in one Taiwan study (Chi et al., 2011).

However, studies reporting soil PCDD/F concentrations in Taiwan are still limited and scattered. One study found these concentrations to be 0.524 to 5.02 pg-TEQ/g in the vicinity of a municipal solid waste incinerator (Cheng et al., 2003) which was comparable with other researches in Turkey (Bakoglu et al., 2005) or Korea (Park et al., 2004). However, a severe PCDD/F contamination incident was reported in a petrochemical company land where the recorded concentrations of 20,000 to 5,000,000 pg-TEQ/g was found in the soil (Taiwan, 2009). Therefore, most of the studies on soil PCDD/Fs were carried out in this hot spot area.

From another point of view, the deposition concentrations of PCDD/Fs also varied at different locations. At northern background area, a concentration of 5.48 pg I-TEQ/m^2/d was found (Chi et al., 2011). Whereas, research in the south industrial areas of Taiwan found depositions fluxes of PCDD/Fs of 13.1–26.1 pg I-TEQ/m^2/day in fall and 8.30–14.3 pg I-TEQ/m^2/day in spring (Mi et al., 2012). Multiple solid waste incinerators (MSWIs) have always been concerned as a major source of PCDD/Fs in developed countries. In Taiwan, high deposition fluxes of 18.0 and 23.5 pg I-TEQ/m^2/d were also found at two different MSWIs (Wu et al., 2009).

In order to evaluate the soil PCDD/F concentration and their possible sources, in this study, a national monitoring of PCDD/F-contaminated soil throughout the country was carried out. At the same time, dioxin deposition samples were also collected in urban and some industrial areas of Taiwan. This research is expected to provide a general knowledge of PCDD/F inventories and their sources in Taiwan. In addition, the highly overlapping rate between the sampling time of soil and deposited PCDD/Fs might help to elucidate the relationship of PCDD/Fs in the two matrixes. Moreover, the assessment of possible sources will also have a policy implication during the effort to reduce PCDD/F inventory of Taiwan government.

2. Materials and method

Soil samples of PCDD/F were collected in four regions of Taiwan (northern, central, southern, and eastern areas) (Fig. 1A) from September 2011 to March 2013. Most of the samples were collected in November–December of 2011 and April–May of 2012 (71/84 samples). Since the data on dioxin contamination in Taiwanese soil was yet available, the inventory of dioxin emissions from stationary sources in Taiwan (Environmental Protection Bureau Kaohsiung City Government, 2010) was used for the selection of sampling sites. The soil samples were collected in the northern ($n = 28$), central ($n = 7$), southern ($n = 46$), and eastern ($n = 3$) areas of Taiwan. In the four sampling areas, 35 samples were collected in industrial locations, 20 samples were collected in resident locations, 21 samples were collected at agricultural locations (none was collected at eastern area), and 8 samples were collected at wasteland locations. In total, eighty-four samples were collected using grid sampling method (one sample per 5 ha). In the laboratory, soil samples were dried before being grinded into 100-200 mesh-sized powder using an agate mortar and pestle before analysis.

To measure atmospheric PCDD/F depositions in Taiwan, the sampling regions included urban area (National Yang Ming University - NYMU, Taipei) and three industrial parks selected in northern (N), central (C) and southern (S) Taiwan (Fig. 1B). The atmospheric PCDD/F depositions were collected at eleven locations from July 2011 to Oct 2012 ($n = 57$). For sample collection, stainless steel cylindrical vessels, which were made from mirror-polished stainless steel (D: 500 mm, H: 600 mm), were used. Before sampling, about 10 L of deionized water was added to the vessel to cover the bottom surface. When sampling was complete, the water and dust remaining in the cylindrical vessel were collected by the portable sampling system using the glass fiber filter, PUF and gear pump. Sampling information and meteorological parameters are summarized in Table S1. The PCDD/F industrial deposition samples were collected at urban area (NYMU, $n = 13$), three sites in the North of Taiwan (N1, N2, and N3 with $n = 4$ at each sampling station), at three sites in the Centre (C1, C2, C3 with $n = 4$ at each sampling station), and at four sites in the South (S1, S2, S3, S4 with $n = 5$ at each sampling station).

The analysis of PCDD/F was carried out in Environmental Analysis laboratory EPA, Taiwan. The samples were spiked using known amounts of internal quantification standards according to US. EPA methods 1613. Detailed information regarding the extracted and clean-up procedure of the PCDD/F samples was provided elsewhere (Chi et al., 2007, 2011). Finally, the PCDD/F samples were analyzed using high-resolution gas chromatography (HRGC)/high-resolution mass spectrometer (HRMS) equipped with a fused silica capillary column (60 m × 0.25 mm x 0.25 μm, J&W). The concentrations of PCDD/Fs were analyzed two times to confirm the constancy of the measurements. The variations between the two analyses of PCDD/F concentrations were less than 10% (2.6–8.9%). In addition, a laboratory blank and a matrix spiked sample (2.0–20 pg/μl PCDD/Fs) were used in the analytical procedure for every eight to ten samples for quality control purpose. Method detection limits were around 0.04–1.30 pg/g and calculated based on the measurements of the blanks and quantified as three times the standard deviation of the concentration in the blanks. In this study, the concentrations of all laboratory blank samples were less