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Levels, sources, and potential human health risks of PCNs, PCDD/Fs, and PCBs in an industrial area of Shandong Province, China

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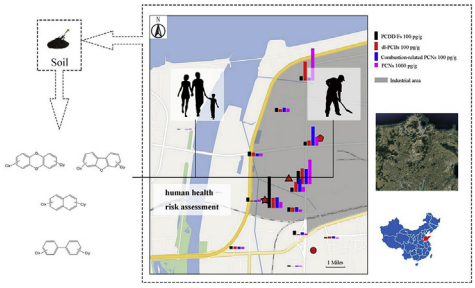
HIGHLIGHTS

- Extremely high concentrations of PCNs were observed in two soil sample.
- High level samples had similar PCN congener profiles with a PCN product.
- A sample obtained near the secondary copper smelter had a high carcinogenic risk.

GRAPHICAL ABSTRACT



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ABSTRACT

Polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated biphenyls (PCBs) are of public concern worldwide because of their persistence and toxicity. To address the human health risks of these pollutants and identify possible sources, soil samples were collected from an industrial area and surrounding residential area in Shandong Province, China. The PCN, PCDD/F, and PCB levels in these samples were determined. Extremely high concentrations of PCNs were detected in two soil samples, and their congener distributions were similar to those of a PCN industrial technical product. The levels of combustion-related PCNs and PCDD/Fs were high in samples collected near a secondary copper smelter. The distribution of total PCB concentrations was similar to that of PCNs. Both historical residues from industrial technical products and emissions from the secondary copper smelter were likely sources of PCNs and PCBs, whereas emissions from the smelter were the main source of PCDD/Fs. A soil sample from near the smelter had a high ΣTEQ concentration (PCDD/Fs + PCBs + PCNs = 18.33 pg TEQ/g) and carcinogenic risk (0.85×10^{-6}) to workers. For all the other samples, the levels of PCDD/Fs, PCBs and PCNs exhibited low carcinogenic and noncarcinogenic risks to workers and residents.

1. Introduction

The levels of persistent organic pollutants (POPs) in different environmental matrices are of global concern because of their

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persistence, bioaccumulation, and toxicity (Nieuwoudt et al., 2009). Polychlorinated naphthalenes (PCNs), polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), and polychlorinated biphenyls (PCBs) are three groups of structurally similar POPs (Liu et al., 2010; Moon et al., 2012). Among the PCDD/Fs and PCBs, seventeen 2,3,7,8-substituted PCDD/Fs and twelve dioxin-like PCBs (dl-PCBs) have been investigated more widely because of their high toxicity to biota and humans (Zheng et al., 2008). PCNs could have similar toxicity to 2,3,7,8-subsituted PCDD/Fs and dl-PCBs (Mahmood et al., 2014). Because of the potential adverse effects of PCNs on the environment and human health, these pollutants have attracted increasing attention (Park et al., 2010; Hu et al., 2013a).

PCDD/Fs are unintentionally generated as by-products of industrial or thermal processes in chemical and petrochemical plants, ferrous and non-ferrous metal smelting operations, paper and pulp production, cement production, and fuel combustion (Nadal et al., 2007; Nie et al., 2012; Nguyen et al., 2017). The only deliberate production of PCDD/Fs is for scientific research (Meng et al., 2016). PCBs and PCNs were manufactured for industrial purposes from the early 1930s to the 1980s, when their production and use were banned (Noma et al., 2006). Currently, these two compounds are formed unintentionally in the same way as PCDD/Fs (Nie et al., 2011; Liu et al., 2016).

The identification of contaminant sources is a critical step in POP risk assessment and management, especially in complex environments, such as industrial areas, which have several point and diffuse sources rather than a single source. Industrial areas usually produce large quantities of unintentional emissions of PCNs, PCDD/Fs, and PCBs. The pollutants from these sources are primarily emitted to the atmosphere, and after transport over short and long distances in both gaseous and particulate forms, they accumulate in soil after dry and wet atmospheric deposition (Cetin, 2016). The use of industrial products can also result in the accumulation of PCBs and PCNs in soils (Die et al., 2014). Historical residues of industrial technical products and unintentional emission make it difficult to identify sources in industrial areas.

Human body can be exposed to soil by three different pathways: incidental ingestion of soil, dermal contact with soil, inhalation of volatiles and fugitive dust. Once in the body, these pollutants have adverse effects on human health (USEPA, 2017). The potential health risks to people who live or work in industrial areas and on the periphery of these areas should be evaluated because of the relatively high population densities and levels of pollution (Colombo et al., 2011; Demond et al., 2012). Furthermore, the potential risks that PCNs, PCDD/Fs, and PCBs pose to human health for workers, children, and adults can be assessed by using the Risk Assessment Guidance for Superfund methodology from the US Environmental Protection Agency (USEPA, 1991, 2017). The carcinogenic and noncarcinogenic risks for these pollutants resulting from exposure to soils during daily work and activities were calculated. Despite several limitations (e.g. variation between theoretical and experimental results, data fluctuations), this approach provides an indication of any potential hazard.

This research presents a comprehensive study on PCNs, PCDD/Fs, and PCBs in an industrial region and the surrounding residential area in Shandong Province, China. We identified sources of these contaminants, evaluated their behavior, and assessed the levels and their potential risks to human health. The results will be helpful for developing and implementing control strategies for PCNs, PCDD/Fs, and PCBs in soil in industrial areas and surrounding residential areas in China.

2. Materials and methods

2.1. Sampling

The area investigated was located in Shandong Province, China. Nine samples were collected from the industrial area and six samples from the surrounding residential area in May 2015. One soil sample was collected at a forest located more than 45 km away from this area, and this sample was used as a background sample (Fig. 1).

Factories from different sectors are located in the sampling area, including a secondary copper smelter, chlor-alkali plant, polyester production plant, and power plant. The presence of a highway and several roads with high traffic densities, and the prevailing wind direction (southerly) influence the environment in the sampling zone. Considering the multiple possible sources of PCNs, PCDD/Fs, and PCBs, some sampling points were located in proximity to industrial activities. For example, samples S8, S11, and S14 were collected near the secondary copper smelter (<500 m away), and samples S1 and S13 were collected close to the power plant (<500 m away).

2.2. Chemicals

Pesticide grade *n*-hexane and methylene chloride were obtained from J.T. Baker (Phillipsburg, USA). High purity nitrogen was obtained from Cheng Wei Xin (Beijing, China). Analytical grade anhydrous sodium sulfate was baked at 600 °C for over 6 h before use. Silica gel (100–200 mesh; Merck, Darmstadt, Germany) was washed with methylene chloride and baked at 180 °C for a minimum of 1 h, then cooled in a desiccator. A PCDD/Fs standard (1613 STOCK) and PCDD/Fs internal standard (DF-LCS-C) were purchased from Wellington Laboratories (Guelph, Canada). A PCBs standard (World Health Organization Congener Mix) and PCBs internal standard were purchased from Cambridge Isotope Laboratories (Andover, MA). A PCNs standard (ECN-5497) and PCNs internal standard (ECN-5102) were purchased from Cambridge Isotope Laboratories. Halowax 1013 was purchased from Dr. Ehrenstorfer GmbH (Germany). Details about compounds of standard and internal standard mix solution can be found in Table S1.

2.3. Sample preparation

We have previously reported the details for methods used to analyze the samples for PCDD/Fs, PCBs, and PCNs in soils (Wu et al., 2017). First, each soil sample was freeze-dried, and then the samples (20.0 g of soil) were spiked with known amounts of internal standards ($^{13}C_{12}$-labeled PCDD/Fs, PCBs and PCNs) and extracted by accelerated solvent extraction with hexane: methylene chloride (50:50, v/v) at 120 °C and 1500 psi. Subsequently, the sample extracts were concentrated and subjected to a series of cleanup steps using an acidic silica gel column, a multilayer silica gel column (from top to bottom, anhydrous sodium sulfate, 1 g of activated silica gel, 8 g of silica/H_2SO_4 44% (w/w) gel, 1 g of activated silica gel, 5 g of silica/NaOH (1 M) 33% (w/w) gel, 1 g of activated silica gel, 2 g of silica/$AgNO_3$ 10% (w/w) gel, and 1 g of activated silica gel), and a basic alumina column. The extracts were eluted with hexane: methylene chloride (95:5, v/v) to obtain the PCBs and PCNs, and then hexane: methylene chloride (50:50, v/v) to obtain the PCDD/Fs. The purified extracts were concentrated to approximately 20 μL using a rotary evaporator and then under a gentle stream of nitrogen gas.