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Polychlorinated naphthalene concentrations and distribution in feed raw materials

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HIGHLIGHTS

- Concentrations of 75 PCN congeners were determined in feed raw materials.
- Relatively high PCN concentrations were found in fish meal.
- PCN TEQs were lower than those of PCDDs, PCDFs or PCBs in the same samples.
- Potential sources for PCNs in feed raw materials were discussed.

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ABSTRACT

Concentrations and patterns of 75 PCN congeners in feed raw materials of animal and plant origin were investigated. Six types of feed raw materials of animal origin and three types of feed raw materials of plant origin from China were collected in 2016. The total concentrations of PCNs in the collected materials ranged from 147 to 1009 ng kg-1, with the highest occurring in fish meal. The mean PCNs concentration in feed raw materials of animal origin (551 ng kg-1) was higher than in those of plant origin (294 ng kg-1). Additionally, lower chlorinated PCNs were the main homologues in raw feed materials, while Di-CNs were the predominant homologues in all samples (mean: 53%), followed by tri-CNs (mean: 28%). The most abundant congeners were CN5/7 and 24/14. Additionally, the toxicity equivalencies (TEQs) of PCNs in the feed raw materials ranged from 0.010 to 0.046 ng TEQ kg-1, with the highest TEQ concentrations of PCNs detected in gluten meal. Together, CN5/7, 66/67, 65/70, and 73 contributed approximately 64% of the total PCN TEQs in raw feed materials. Concentrations of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in the feed raw materials were detected to compare the TEQ distribution of those dioxin-like compounds. The mass concentrations of PCNs were 1–3 orders of magnitude higher than those of PCDD, PCDFs and PCBs, while the TEQ concentrations of PCNs contributed 2.0%–6.5% of the total TEQs of PCNs, PCDDs, PCDFs and PCBs in the feed raw materials.

1. Introduction

Polychlorinated naphthalenes (PCNs) are a group of compounds, consisting of 75 congeners. The chemical structure and toxicity mechanism of PCNs is similar to that of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Like 2,3,7,8-TCDD, some PCN congeners can bind to the aryl hydrocarbon receptor (AhR) and induce dioxin-like toxicity. The relative potency factors (RPFs) of individual PCN congeners have been reported based on *in vivo*, *in vitro*, and *in silico* tests (Puzyn et al., 2007; Falandysz et al., 2014). Because of the similarity in structure and toxicity among PCNs, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), they are all categorized as dioxin-like compounds. Although the toxicity of PCN congeners is lower than those of PCDD/F and PCB congeners, the contribution of PCNs to the total toxic equivalents (TEQs) of PCDD/Fs, PCBs and PCNs should not be ignored. In human serum samples collected from workers and residents living near municipal solid waste incinerators in Korea, PCNs contributed 26.8% of the total TEQs of PCDD/Fs, PCBs and PCNs (Park et al., 2010).

PCNs have been shown to have characteristics of persistent organic pollutants (POPs), such as high toxicity, persistence, bioaccumulation, and long-range transportation (Falandysz, 2003;

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Domingo, 2004; Bidleman et al., 2010). In 2015, PCNs were listed as new POPs under Annex A and C in the Stockholm Convention (POPRC, 2017). PCNs have been produced since the 1910s for use as additives in capacitors, lubricants, rubber and plastics (Fernandes et al., 2017). PCNs were sporadically used until recently. Some stockpiles of technical PCN formulation were hold for many years by some producers/companies and used illegally or ignorantly around the year 2000 (Yamashita et al., 2003; Falandysz et al., 2008). Although the production of PCNs has stopped, they are still released from disposed electrical equipment and may be produced unintentionally along with PCDD/Fs and PCBs during high-temperature industrial processes (Liu et al., 2014).

PCNs can be found in the environment, food and humans worldwide (Bidleman et al., 2010; Fernandes et al., 2017). Similar to PCDD/Fs and PCBs, human exposure to PCNs mainly occurs through dietary intake, especially from the consumption of animal-derived food products (Domingo et al., 2003; Fernandes et al., 2010, 2011). PCNs are lipophilic compounds that can bioaccumulate in the food chain (Lundgren et al., 2002; Hanari et al., 2004); therefore, contamination of animal-derived foodstuffs with PCNs has been of increasing concern. The PCN concentrations in aquatic foodstuffs were found to be relatively higher than those in other animal-derived foodstuffs (Domingo, 2004; Fernandes et al., 2017; Kim et al., 2018). Moreover, PCNs present in animal-derived food products might originate from industrial sources in the environment and/or dietary exposure of domestic animals through feedstuffs (Fernandes et al., 2017; Cui et al., 2018). Nevertheless, few studies have focused on the presence of PCNs in feedstuff. Guruge et al. reported tri-to octa-CN concentrations in feed ingredients, mixed feed and animal fat collected in Japan (Guruge et al., 2004). They found that the total concentrations of PCNs in the investigated feed ingredients ranged from 500 to 1500 pg g^{-1} lipid, which were higher than those in mixed feed and animal fat. Relatively high levels of PCNs were observed in fish meal. However, data describing the concentrations of mono-CNs and di-CNs in feedstuffs are unavailable, and information regarding the PCN concentrations and congener patterns in feedstuffs from China is scarce.

The presence of PCNs in feedstuffs has the potential to accumulate in domestic animals through dietary intake, leading to the contamination of animal-derived food products with PCNs. Animal feed is composed of feed raw materials of both plant and animal origin. To determine which material is the predominant contributor of PCNs to animal feed, it is necessary to study and compare PCN concentrations in different categories of feed raw materials. The congener profiles of PCNs are helpful for identification of the source of PCNs in these raw materials. Considering the lipophilicity of PCNs, feed raw materials with relatively high lipid contents were investigated in this study. A total of 75 CN congeners in six types of animal-based feed raw materials and three types of plant-based feed raw materials were analyzed by isotope dilution high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). Concentrations as well as homologue and congener profiles of PCNs in feed raw materials were identified. Additionally, because PCNs usually produced unintentionally along with PCDD/Fs and PCBs, to compare the toxic equivalent (TEQ) contributions of PCNs to PCDDs, PCDFs and PCBs, seven PCDDs, 10 PCDFs and 12 dioxin-like PCB (dl-PCB) congeners in the feed raw materials were also measured using the HRGC/HRMS method.

2. Materials and methods

2.1. Feed material sampling

A total of 22 feed raw samples were collected in 2016 from major feed factories in China, including six types of animal-based and three types of plant-based materials. Samples were collected according to the standard procedure method of China (Feeding stuffs-Sampling GB 14699.1–2005) (Chinese Standards, 2005), and each sample was a composite of at least eight individual samples. Samples of animal origin included fish meal (n = 12), meat and bone meal (n = 2), chicken meal (n = 1), porcine plasma protein powder (n = 2), blood meal (n = 1), and whey powder (n = 1). Samples of plant origin consisted of rapeseed meal (n = 1), peanut meal (n = 1) and soybean meal (n = 1). Feed raw materials investigated in the present study were sampled at feed factory warehouses in China and kept at −18 °C until analysis. Nine of the 12 fish meal samples were imported to China from Peru (n = 5), Chile (n = 3), and the United States (n = 1), while the remaining samples were produced in China. Information on the fish meal samples were shown in Table S1.

2.2. Sample extraction and analysis

The procedures for PCNs analyses were conducted according to the established HRGC/HRMS method (Dong et al., 2013). Additionally, analyses of the 17 toxic PCDD/F and 12 dl-PCB congeners were conducted according to the USEPA Methods 1613B and 1668C, respectively. Approximately 2 g of feed raw material sample was used for extraction and analysis. ^{13}C-labeled PCNs, PCDD/Fs and PCBs were added to the samples as internal standards before extraction. The samples were then extracted with an accelerated solvent extraction instrument (ASE 350, Dionex, CA, USA), after which the lipid content was determined by gravimetric analysis. An acidic silica gel column, multilayer silica gel column and carbon column were used to clean up the samples. Corresponding ^{13}C-labeled injection standards of PCNs, PCDD/Fs and PCBs were added before instrument analysis. A detailed description of the extraction and cleanup procedures for PCN analysis of feed raw materials is shown in the Supplementary Material.

The HRGC-HRMS analyses of the 75 mono-to octa-CN congeners were conducted on a gas chromatograph coupled with a DFS mass spectrometer (Thermo Fisher Scientific, Hudson, NH, USA). A DB-5MS fused silica capillary column (60 m × 0.25 mm i.d. × 0.25 μm, J&W) was used for the separation of PCN congeners. Analyses of PCDD/Fs and PCBs were conducted using an Agilent 6890 gas chromatograph (Agilent Technologies, CA, USA) coupled with an Autospec Ultima mass spectrometer (Waters Micromass, Manchester, UK). The GC separation of PCDD/Fs and PCBs was also performed on a DB-5MS fused silica capillary column (60 m × 0.25 mm i.d. × 0.25 μm, J&W). The MS was operated in selected-ion monitoring mode (SIM) at a resolution of approximately 10,000 with an electron impact source. The HRGC/HRMS methods for PCN, PCDD/F and PCB analysis have been described in detail elsewhere (Dong et al., 2013; Li and Su, 2015).

2.3. Quality control and quality assurance

The recoveries of the ^{13}C-labled standards of the PCNs, PCDD/Fs and PCBs in the 22 feed raw material samples were 44%–87%, 53%–92% and 49%–106%, respectively. The limits of detection (LOD, equivalent to a signal-to-noise ratio of 3) of the PCNs, PCDD/Fs and PCBs in the present study were 0.13–2.30 ng kg^{-1}, 0.06–0.53 ng kg^{-1} and 0.08–1.91 ng kg^{-1}, respectively. The concentrations of the PCN, PCDD/F and PCB congeners in feed raw materials below their particular LOD were assigned the value of the LOD for that congener. Blank samples were analyzed in each batch. Concentrations of the target compounds in the blanks were lower than 5% of those in the feed raw material samples; thus, there was no blank correction in this study.