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Concentrations and congener group profiles of short- and medium-chain chlorinated paraffins in animal feed materials

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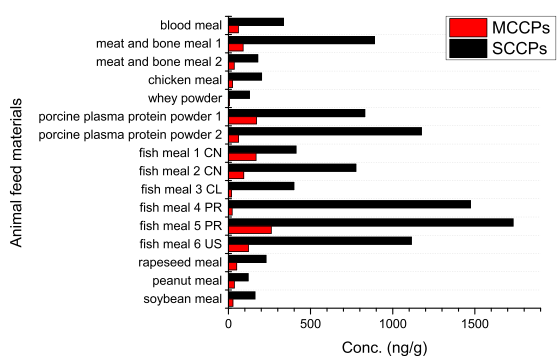
HIGHLIGHTS

- CP concentrations were determined in animal feed materials.
- SCCP concentrations were higher than those of MCCPs in each animal feed material.
- CP levels in animal-based feed material were higher than in plant-based material.
- Estimated concentrations of SCCPs and MCCPs in farmed fish were calculated.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorinated paraffins (CPs) are ubiquitous environmental pollutants that are lipophilic and can accumulate in the food chain. Animal-derived products are predominant contributors to human CP exposure. CPs in animal feed might accumulate in domestic animals through dietary exposure, leading to potential contamination of animal-derived food products and human health risks. However, information on the presence of CPs in animal feed materials is scarce. In this study, 16 animal feed material samples were collected in China in 2016. Thirteen of the samples were of animal origin and three were of plant origin. The concentrations and carbon and chlorine congener group profiles of shortchain chlorinated paraffins (SCCPs) and medium-chain chlorinated paraffins (MCCPs) in these animal feed materials were investigated. The concentrations of SCCPs were higher than those of MCCPs in all of the samples. The SCCP concentration range was 120 to 1700 ng/g (mean 640 ng/g), and the MCCP concentration range was 6.4 to 260 ng/g (mean 78 ng/g). Fish meal had the highest SCCP and MCCP concentrations. The lowest SCCP and MCCP concentrations were detected in peanut meal and whey powder, respectively. The concentrations of SCCPs and MCCPs varied among the types of animal feed materials. SCCP and MCCP concentrations also varied among samples of the same type of animal feed material. Relatively high concentrations of SCCPs and MCCPs were detected in feed materials of animal origin. The predominant congener groups in the animal feed materials were C10-11Cl6-7 for SCCPs and C14Cl7 for MCCPs. The carbon and chlorine congener group profiles of SCCPs indicated that SCCP contamination in the animal feed materials might arise from commercial CP mixtures.

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1. Introduction

Chlorinated paraffins (CPs) are industrial chemicals with the molecular formula $C_nH_{2n+2-m}Cl_m$, which is commonly shortened to C_nCl_m. They can be used as extreme pressure additives in metalworking fluids, flame retardants in plastics, and plasticizers in rubber(van Mourik et al., 2015). CPs have been produced since the 1930s and are now used in large volumes globally, with total production exceeding 1 million tonnes per year (van Mourik et al., 2015; Glüge et al., 2016). There are three types of CPs: short-chain CPs (SCCPs, C_{10-13}), medium-chain CPs (MCCPs, C_{14-17}), and long-chain CPs (LCCPs, C_{18-30}). The SCCPs have persistent organic pollutant (POP) characteristics, such as persistence and long-range transport (Diefenbacher et al., 2015; Li et al., 2016). Several SCCP congeners can accumulate in organisms (Ma et al., 2014; Zhou et al., 2018). SCCPs are likely to have adverse effects on the environment and human health (Zhang et al., 2016; Ren et al., 2018). In May 2017, SCCPs were listed as new POPs under Annex A in the Stockholm Convention (POPRC, 2017). Although several nations/regions have restricted the production and use of SCCPs, MCCPs and LCCPs are produced as alternatives and used in large amounts (van Mourik et al., 2015; Glüge et al., 2016). Therefore, the total production of CPs remains high.

CPs are ubiquitous environmental pollutants. They have the ability to accumulate in fat at increasing concentrations up the food chain (Huang et al., 2017). CPs have been detected in many environmental matrices, such as air (Diefenbacher et al., 2015; Liu et al., 2017), water (Zeng et al., 2011a), soil (Zeng et al., 2011b; Gao et al., 2012), and sediment (Přibylová et al., 2006; Yuan et al., 2017). Furthermore, CPs have been detected in biota (Iino et al., 2005; Harada et al., 2011; Gao et al., 2018) and human breast milk (Thomas et al., 2006; Xia et al., 2017), blood(Li et al., 2017), and placental tissue(Wang et al., 2018a). Adult exposure to CPs occurs mainly through dietary intake, with animal-derived products being major contributors (Harada et al., 2011; Gao et al., 2018), and followed by indoor dust (Gao et al., 2018). For toddlers, dust ingestion is the primary route for CP exposure (Gao et al., 2018). When SCCP levels in 11 food categories were investigated in Japan the highest SCCP concentration was found in fats (140 ng/g), and the SCCP concentrations in fish (16 ng/g), shellfish (18 ng/g), and meat (7 ng/g) were higher than those in other food categories (Iino et al., 2005). Milk had the lowest SCCP concentrations (0.75 ng/g) among the food categories tested. Krogseth et al. estimated that fish consumption contributed between 80% and 100% of human SCCP intake (Krogseth et al., 2013).

China is the largest producer of CPs in the world (van Mourik et al., 2015), and CP pollution in China is higher than in other countries (Glüge et al., 2018). Harada et al. reported that people in Beijing in 2009 had dietary exposure to SCCPs that was one order of magnitude higher than the exposure experienced in Japan (Hokkaido, Okinawa, and Kyoto) or South Korea (Seoul) (Harada et al., 2011). In Beijing, SCCP concentrations increased two orders of magnitude from 1993 to 2009. The mean concentrations of SCCPs and MCCPs in meat and meat products collected during a recent national diet survey in China were 130 ng/g wet weight (w.w.) and 5.7 ng/g w.w., respectively (Huang et al., 2018). Another survey in China showed that the average concentrations of SCCPs and MCCPs in aquatic food samples were 1500 ng/g w.w. and 81 ng/g w.w., respectively (Wang et al., 2018b). Wang et al. recently reported concentrations of SCCPs and MCCPs in domestic polymeric products in China, and SCCP and MCCP concentrations in a polyvinylchloride cable sheath could reach to 190 mg/g and 150 mg/g, respectively (Wang et al., 2018c).

Although SCCPs and MCCPs are commonly identified in animal-derived products in China, the concentrations of SCCPs and MCCPs in animal feed are unclear. Animal-derived food products currently constitute a large portion of the Chinese diet, with animal feed comprising the major diet of farmed animals. In contrast to the health benefits provided by feed, the risk derived from exposure to potential pollutants contained in some feed materials should not be ignored (Adamse et al., 2015). Animal feed is a significant contributor to the occurrence of POPs, such as dioxins in food (Malisch and Kotz, 2014). Because CPs are lipophilic compounds that can bioaccumulate and biomagnify in food chains, CPs present in animal-derived food products might originate from contaminated feed materials through bioaccumulation.

Little information is available on SCCP and MCCP contamination in different feed materials. Lahaniatis et al. reported on SCCPs and MCCPs in fish, fish oil, and fish feed (Lahaniatis et al., 2000), but focused primarily on fish feed. In the current study, SCCP and MCCP concentrations and their carbon and chlorine congener group profiles were investigated in raw feed materials commonly used in China to produce animal feed. Considering the lipophilicity of CPs, feed materials of plant and animal origins wtih relatively high lipid contents were selected for this study. The concentrations of 24 SCCP and 24 MCCP formula groups in the animal feed materials were measured using two-dimensional gas chromatography coupled with time-of-fight mass spectrometry in electron capture negative ionization (ECNI) mode.

2. Materials and methods

2.1. Sample collection

Sixteen feed material samples, were collected in 2016. The samples included six types of feed materials of animal origin and three types of feed materials of plant origin All sample were stored at −18 °C until required for analysis. Samples were collected according to a standard procedure (Chinese Standards, 2005). Each sample was a composite of at least eight individual samples. The samples of animal origin were blood meal ($n = 1$), meat and bone meal ($n = 2$), chicken meal ($n = 1$), whey powder ($n = 1$), porcine plasma protein powder ($n = 2$), and fish meal ($n = 6$). The samples of plant origin were rapeseed meal ($n = 1$), peanut meal ($n = 1$), and soybean meal ($n = 1$). Feed materials investigated in the current study were sampled at feed factory warehouses in China. Four of the six fish meal samples were imported, with one from Chile, two from Peru, and one from the United States. All other samples were produced in China, but the geographical origins of the raw materials used in these products were uncertain. Information on the six fish meal samples was shown in Table S1.

2.2. Sample extraction and analysis

In the present study, extraction and clean-up procedures for the analysis of SCCPs and MCCPs in animal feed materials were conducted according to established methods (Huang et al., 2018; Qiao et al., 2017). Each feed material sample (approximately 2.0 g) was homogenized with anhydrous Na_2SO_4 and then spiked with $^{13}C_{10}$-*trans*-chlordane (2.5 ng) as an internal standard. The samples were extracted with an extraction apparatus (ASE 350, Dionex, CA, USA). After that, the extract was evaporated to dryness and the lipid content was determined using gravimetric analysis. Sulfuric acid–silica gel, gel permeation chromatography and multilayer silica gel columns were used for cleanup. Before analysis, ε-hexachlorocyclohexane (2.5 ng) was added as internal standard. The SCCPs ($C_{10-13}Cl_{5-10}$) and MCCPs ($C_{14-17}Cl_{5-10}$) were analyzed using a two-dimensional gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled with a time-of-flight mass spectrometer (Tofwerk, Thun, Switzerland). Analysis was performed in ECNI mode at a resolution of >3000, using the method established by Xia et al (Xia et al., 2016). The applied mass accuracy was <2 ppm with perfluoroperhydrophenanthrene as the mass calibrant. Interferences within and between different CP congener groups occur by using one dimensional gas chromatograph for CP analysis (Bo et al., 2016), which could be avoided or minimized by a combination of two-dimensional gas chromatograph and time-of-flight mass spectrometer (Xia et al., 2016). The individual SCCP and MCCP congener