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Size-dependent distribution and inhalation exposure characteristics of particle-bound chlorinated paraffins in indoor air in Guangzhou, China

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ABSTRACT

Chlorinated paraffins (CPs) are now attracting special concerns worldwide as one type of new persistent toxic substances as classified by the Stockholm Convention. CPs are extensively applied in household goods and indoor decoration materials, but information on their occurrence and exposure risk in such environments is still very scarce. In this study, the current concentrations, particle size distributions, and inhalation exposure characteristics and risk of CPs were investigated in regard to indoor air particulate matter. Both short chain (SCCPs) and medium chain CPs (MCCPs) were determined in all size-fractioned particle samples with a range of 6.20–17.8 and 5.98–40.5 ng m^{-3}, respectively. MCCPs were more abundant than SCCPs. Size distributions revealed that individual homologs, SCCPs, and MCCPs exhibited a similar unimodal distribution peaking in the fine particles with a diameter of 0.56–1.0 μm. The relative abundance of longer-chain or more heavily chlorinated homologs tend to gradually increase with particle size shift from coarse to fine mode. Vapor pressure may be a critical factor governing the size-dependent distribution of CPs. Deposition of particulate CPs in the human respiratory tract is also size-dependent. The contributions of fine particles to the regional depositions of CPs in the human respiratory tract increase with increasing carbon chain length or chlorine content. Based on the size-dependent distributions of CPs, inhalation exposure assessment from the ICRP model indicated no significant health risk due to CPs in current indoor environments.

1. Introduction

Chlorinated paraffins (CPs) are complex industrial chemicals consisting of thousands of homologs and isomers with chlorine contents of 30–70%. The commercial CPs are generally classified based on the carbon chain length into short chain CPs (SCCPs, C_{10}-C_{13}), medium chain CPs (MCCPs, C_{14}-C_{17}), and long chain CPs (LCCPs, C_{18}-C_{30}). They are widely applied as plasticizers in polyvinyl chloride (PVC) and flame retardants in many commercial products (UNEP, 2016). Production and use amounts of CPs exceeded 1000 kt in 2013, and thus CPs are identified as having the highest production volume among current industrial chemicals (Glüge et al., 2018). China is still the globally largest producer, consumer and exporter of CPs at present, and the emission alone of SCCPs in China could be up to 2.56 kt in 2016 (Xu et al., 2014). In the last few years, CP research has focused mainly on SCCPs relative to MCCPs and LCCPs because of their higher environmental persistence, long-distance migration abilities, bioaccumulation and biomagnification, and greater toxicological and potential endocrine disruption effects (UNEP, 2016; van Mourik et al., 2016). SCCPs have been shown to affect the thyroid, liver and kidneys by causing hepatic enzyme induction and thyroid hyperactivity, which in the long-term can result in carcinogenicity in these organs (UNEP, 2016). Therefore, SCCPs are suspected to cause cancer in humans and disrupt endocrine function. In view of these severe adverse health effects, SCCPs have been added to the list of Persistent Organic Pollutants (POPs) by the Stockholm Convention as a kind of new POPs in May 2017 (UNEP, 2017). Compared to SCCPs, MCCPs have been less well studied (Glüge et al., 2018). The available data suggest that MCCPs are more bioaccumulative than SCCPs (Zeng et al., 2017a), and present similar ecological risks as SCCPs (Kobeticova and Cerny, 2018). The production amounts of MCCPs on a global scale are estimated to be much higher than those of SCCPs (Glüge et al., 2018; Glüge et al., 2016), and especially MCCPs are often frequently detected at higher levels in various matrices than SCCPs (Gallistl et al., 2018). With the phasing out and banning of SCCPs, MCCPs are suggested to be a suitable and a preferred alternative to SCCPs (Kobeticova and Cerny, 2018). Therefore, MCCPs are also of

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currently great concern in regard to the environment (Glüge et al., 2018; Wang et al., 2017).

Widespread use of CP-added products in houses, such as PVC flooring, increases the opportunities for fugitive emissions of CPs to enter the indoor environment including dust, air, and suspended particles (Zhan et al., 2017). Indoor concentrations of CPs have been sporadically reported in Europe and China (Friden et al., 2011; Gao et al., 2018; Hilger et al., 2013; Zhu et al., 2017), and in general, they are found to be higher than in outdoor settings although particulate matter (PM) mass concentrations in indoor environments are relatively lower (Huang et al., 2017). Thus, indoor CPs in highly urbanized areas can pose a higher health risk than outdoor CPs. This is because urban residents, especially the elderly and young children, tend to spend more time indoors. Secondly, CPs associated with indoor PM are expected to be more persistent due to their slow oxidative degradation under suppressed levels of hydroxyl radicals (Li et al., 2014; Zhang et al., 2012). In addition, depositing particles can form indoor dust. Thus, inhalation is believed to be an important exposure pathway of CPs to humans in indoor environments.

Inhalation exposure is the most difficult to regulate and thus can be used as an excellent indicator of human health hazards among the four main exposure pathways, i.e., inhalation, food intake, dermal adsorption, and dust ingestion (Luo et al., 2014a). Previous studies indicated that the size distribution of particulate contaminants is a key factor controlling their behavior and fate in the atmosphere, and the contributions of particle-bound toxic chemicals to inhalation exposure risk is strongly particle size-dependent (Luo et al., 2014a; Luo et al., 2016; Yang et al., 2014). For example, particles with different sizes can accumulate in different regions with size-specific deposition efficiencies in the human respiratory system. In general, smaller size particles can carry more contaminants and enter into the deeper respiratory system, and pose a higher risk than coarse particles (Zhang et al., 2012). Although a few published concentrations of indoor particulate CPs in urban regions can be used to evaluate inhalation exposure levels, not all of these CPs can deposit in the respiratory tract or go deep into the lungs. Thus, the size distribution of particle-bound CPs must be considered when inhalation exposure is evaluated, which is crucial for accurate evaluation of the risk of exposure to inhaled CPs. Among the published studies, only one study focused on the levels and compositions of CPs in airborne $PM_{10}/PM_{2.5}/PM_{1.0}$ (Huang et al., 2017). To date, no size-dependent distribution of particle-bound CPs has been systematically investigated, and also no size effect has been taken into account in the assessment of inhalation exposure to particle-bound CPs in indoor air.

To fill this knowledge gap, we carried out the first systematic study on the particle size distribution of CP homologs in indoor air. Suspended particles with different diameters were collected from 10 offices and 5 residential homes at urban sites in Guangzhou, and were simultaneously analyzed for SCCPs and MCCPs on the particles. The current study therefore aimed to (1) reveal the current level and detailed size distribution of atmospheric particle-bound CPs; (2) explore the potential mechanism for the size distribution of CPs in size-fractionated particles; (3) evaluate the size-dependent respiratory deposition of particle-bound CPs; and (4) characterize the inhalation exposure to particulate CPs based on their size distribution in indoor air. The results of this study are expected to provide a deeper cognition of the behavior, fate and human health risk of CPs in indoor environments.

2. Materials and method

2.1. Field sampling

Size-segregated PM samples were collected in 10 office rooms and 5 residential homes during October to December 2017 in the city center locations of Guangzhou (23°7′ N and 113°20′ E), China. Ten offices were selected in separate areas located in three office buildings of the city center. These offices were far away from industrial activity and approximately 100 m away from a main road, which were furnished with common desks, filing cabinets and office electronic products including computers and printers but differed in the type and number of these items. Five residential houses were randomly selected in two populated areas which were about 500 m away from a main road. These houses were built in the 2000s and have not been redecorated in recent years. They were equipped with essential furniture and household electrical appliances with no upgrading or replacement in the last few years. The selected 15 sampling sites can represent the typical urban offices and homes in the megacities of South China according to our survey. The sampling was conducted on a desk near the central area of the room and placed at 1 m above the ground by an 11-stage Micro-Orifice Uniform Deposit Impactor (MOUDI) (MSP Corporation, Shoreview, MN). All doors were closed in the rooms with the windows slightly open to simulate common indoor environments. The weather was sunny with the temperature ranging from 16 to 25 °C and the humidity ranging from 35 to 50% during the sampling time. Each size segregated PM sample was collected on prebaked glass microfiber filters (GFF, 47 mm i.d., Whatman) at a constant flow rate of 30 L min^{-1}. Particle samples were separated by cutoff aerodynamic diameters (*D*p) into 11 fractions as > 18, 10–18, 5.6–10, 3.2–5.6, 1.8–3.2, 1.0–1.8, 0.56–1.0, 0.32–0.56, 0.18–0.32, 0.10–0.18, and 0.056–0.10 μm, respectively. Size segregated particles were subdivided into coarse (D_p > 1.8 μm), fine (0.10 < D_p < 1.8 μm), and ultrafine (D_p < 0.10 μm). In order to collect sufficient particle mass and minimize the interday variations, each sampling was conducted for a continuous 48 h. The total air volume for each sampled room was 86.4 m^3. Overall, a total of 165 field particle samples (15 suits of samples containing 11 size-segregated fractions) were collected. Field blanks were prepared during the period of sampling by mounting GFFs to the MOUDI sampler. After sampling, the GFF filters were placed into clean glass boxes, wrapped in aluminum foil and then stored at −20 °C.

2.2. Sample preparation, instrumental analysis, identification and quantification

Sample preparation was performed according to the previously developed procedures with minor modifications (Zeng et al., 2012, 2013; Zeng et al., 2017b). Detailed information is presented in the Supplementary Information (SI). SCCPs and MCCPs were simultaneously analyzed by high-resolution gas chromatography equipped with a low-resolution mass spectrometer (Agilent 7890B-7000D, USA) using an electron capture negative ion (ECNI) mode based on our previously developed method (Zeng et al., 2011; Zeng et al., 2015; Zeng et al., 2017b). Detailed information with regard to the instrumental analysis, identification and quantification is also given in the SI.

2.3. Quality assurance and quality control (QA/QC)

All glassware was carefully solvent-rinsed and then heated for 5 h at 450 °C prior to use to eliminate potential background contamination. Every batch consisting of five samples was followed by a procedural blank. SCCPs or MCCPs in the procedure blanks and field blanks were below the limits of detection, and thus the reported concentrations of SCCPs or MCCPs were not blank-corrected. The recoveries of SCCP standards (chlorine content: 51.5%, 55.5% and 63.0%) and MCCP standards (chorine content: 42.0%, 52.0% and 57.0%) in spiked samples were 72–102% and 75–103%, respectively, and the relative standard deviations (RSDs) were < 10% (n = 7). The surrogate recoveries of $^{13}C_{10}$–1,5,5,6,6,10-hexachlorodecane (Fig. S1) in all of the samples were between 70% and 105%, and the final concentrations were corrected by the surrogate. The method detection limits (MDLs) were estimated to be 0.4 ng m^{-3} for the total SCCPs (ΣSCCPs) and 0.6 ng m^{-3} for total MCCPs (ΣMCCPs) based on three times the standard deviation of blank values.