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Characterization of short- and medium-chain chlorinated paraffins in outdoor/indoor $PM_{10}/PM_{2.5}/PM_{1.0}$ in Beijing, China☆

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ABSTRACT

Persistent organic pollutants (POPs) were listed in the Stockholm Convention, because of their adverse health effects, persistence, bioaccumulation and ubiquitous presence in the environment. Short chain chlorinated paraffins (SCCPs), chlorinated derivatives of n-alkanes, have been listed as candidate POPs under Stockholm Convention. Inhalation uptake was an important exposure pathway for non-occupational adult human and the pollution of particle matter has caused great concern. There are some studies focused on POPs such as polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzofurans and polybrominated diphenyl ethers in different size particles. However, there were no studies that discussed CP concentrations in particulate matter (PM) with different sizes. In this study, a total of 30 PM samples were collected both outdoors and indoors at a sampling site in Beijing. These samples were used to investigate the concentrations and distributions of SCCPs and medium chain chlorinated paraffins (MCCPs) in PM fractions of different sizes, and to evaluate inhalation exposure risks. The results showed that the average SCCPs and MCCPs in the outdoor PM_{10} were 23.9 and 3.6 ng m^{-3}, while the mean values in indoor were 61.1 and 6.9 ng m^{-3}, respectively. The levels of SCCPs and MCCPs in indoor and outdoor were relatively high. SCCP and MCCP concentrations in the indoor $PM_{10}/PM_{2.5}/PM_{1.0}$ samples were higher than the corresponding values in the outdoor, because of the using of some products containing CPs in the indoors, like paints and coatings, leather and rubber products. In both outdoor and indoor air, CPs are mainly associated with particles $\leq$2.5 μm in diameter. The main homolog groups for both SCCPs and MCCPs were $C_{10-11}Cl_{7-8}$. It is assumed that SCCPs in the outdoor and indoor PM samples may mainly derive from the production and use of CP-42 and CP-52.

1. Introduction

Chlorinated paraffins (CPs), also called polychlorinated n-alkanes (PCAs), are highly complex technical mixtures that consist of a large number of homologues and isomers (Feo et al., 2009). CPs are divided into short- (SCCPs, C_{10-13}), medium- (MCCPs, C_{14-17}), and long-chain chlorinated paraffins (LCCPs, C_{18-30}), depending on their carbon chain length. Chlorine contents are in a range of 30%–70% on a weight. Because of their environmental persistence (van Mourik et al., 2016), higher toxicity to aquatic organisms (Cooley et al., 2001), long-range atmospheric transport (Ma et al., 2014c), and bioaccumulation potential (Li et al., 2016), SCCPs have been widespreadely concerned and have been reviewed as a candidate of persistent organic pollutants (POPs) by the Stockholm Convention on POPs (POPRC, 2015). Moreover, MCCPs were persistent in the environment, bioaccumulative in biota, and toxic to sensitive aquatic organisms (EPA, 2009), which is similar to SCCPs. Therefore, it is very necessary to concern the condition of SCCPs and MCCPs in the environment.

In 2009, annual production volumes of CPs in China were reported about 1000 ktons (Ma et al., 2014b). There are no regulations limiting the use of CPs in China, which has led to China becoming the largest producer and consumer of CPs in the world. CPs were

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widely used in commercial products, like plasticizers, flame retardants, lubricants and coolants, and additives in paints and coatings, leather, sealants and rubber applications (Qiao et al., 2016a). CPs might be released during production, transportation, storage, use, recycling and disposal of CPs, along with CP containing products (van Mourik et al., 2016). As a result, CPs have become ubiquitous in air, (Peters et al., 2000; De Boer, 2010; Wang et al., 2012), dust (Fridén et al., 2011; Hilger et al., 2013), soil (Wang et al., 2013), sediment (Gao et al., 2012), water (Zeng et al., 2013), food webs (Ma et al., 2014b), etc. CPs were found at high concentrations in the air (Chaemfa et al., 2014; Gao et al., 2016; Wang et al., 2013). It has been reported that SCCPs concentrations in the atmosphere were clearly greater in China than those in Japan and South Korea (Li et al., 2012). Although food was the main exposure pathway, inhalation was also an important exposure pathway of CPs to humans (POPRC, 2015). Thus CPs in air should be given enough attention.

Recent years, particulate matter (PM) in China caused the great concern, because the pollutants on the PM may cause respiratory tract infections and other diseases. Particle size could influence the amount of particle deposition in different positions of the respiratory system and the smaller particles are believed to be easily respired into the deep portions of the lungs, producing a greater danger to health (Hassanvand et al., 2015). Along with particulate matter (PM) size, chemical components (including organic carbons, elemental carbon and metals etc.) also influence the toxicity of PM (Hassanvand et al., 2015). At present, researches about classical POPs (such as OCPs (Chrysikou et al., 2009), PAHs (Hassanvand et al., 2015), PCBs (Chrysikou et al., 2009), PCDD/Fs (Oh et al., 2002) and PCNs (Zhu et al., 2016)) in different diameter airborne particle have been reported in the literature. However, investigation about SCCPs and MCCPs in different diameter airborne particle has been never reported.

Indoor air may represent an important exposure pathway of chlorinated paraffins to humans (Fridén et al., 2011). Thus, concern about CPs in the different diameter particulate matter from indoors and outdoors, China, is particularly important. This study sampled the different diameter PM samples at indoor and outdoor, aiming at: 1) investigating the concentrations of SCCPs and MCCPs in the indoor and outdoor PM samples; 2) studying the distribution of SCCPs and MCCPs in the different particle phases; 3) assessing the exposure risk of human body at indoor and outdoor.

2. Materials and methods

2.1. Sampling

A total of 30 samples in outdoor and indoor were collected from February 2016 to May 2016. The sampling site is located in the North of Beijing (40° 0′ 26.88″ N and 116° 20′ 13.89″ E). There was only one heavy road near the sampling site. The outdoor sampling site was on a building rooftop and approximately 20 m above ground level. The indoor sampling site was on a desk in a large office (room size 150 m^3). Over the 24 h sampling period, the windows and door of the office were kept closed. After the sampling period was complete, the office was ventilated by opening the door for 3 h. The outdoor and indoor sampling sites were located in the same building. Outdoor and indoor PM_{10}/$PM_{2.5}$/$PM_{1.0}$ samples were collected on quartz fiber filters (QFFs, 47 mm diameter, Whatman) using low volume samplers (LVS3, Sven Leckel Ingenieurbüro GmbH, Berlin/Germany). There were three instruments collecting the PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ samples simultaneously in outdoor and indoor. The sampling machine had an air flow of 2.3 m^3 h^{-1}. Samples were taken at intervals of almost 24 h. Each outdoor sample was combined with approximately 6 d, in order to ensure that the target objects in each sample could be detected. Similarly, each indoor sample was combined with approximately 8 d. Sampling details are provided in Table S1 of the Supporting Information (SI). Before sampling, the QFFs were baked at 450 °C for 12 h to remove organic contaminants. After sampling, QFFs were wrapped in aluminum foil, sealed in a sealed bag and kept at −18 °C until analysis.

2.2. Sample pretreatment

Sample extractions were carried out in an accelerated solvent extraction device (ASE350; Dionex, Sunnyvale, CA, USA) with the dichloromethane (DCM)/n-hexane (1:1, *v*/*v*) as the extraction solvent. The collected QFF samples were placed in an ASE cell (cell size of 66 mL) and spiked with the recovery standard (2.5 ng of $^{13}C_{10}$-*trans*-chlordane). Extractions were performed by three cycles at 100 °C and 1.03 × 10^4 kPa, 5 min of heating, a 12 min static extraction, a flush volume of 70% and a N_2 purge time of 60 s. Extracts were solvent-reduced (~2 mL) and cleaned on a multi-layer silica gel column consisting of: 4 g of Florisil, 3 g of activated silica gel, 6 g of acid silica gel (44%, w/w) and 6 g of anhydrous Na_2SO_4 from bottom to top. Firstly, the extract was eluted with 40 mL of n-hexane, which was discarded. Then, the extract was eluted with 100 mL hexane/DCM (1:1 *v*/*v*), which was collected and concentrated to about 2 mL by rotary evaporation. The solution was further concentrated to near dryness under a gentle N_2 stream and solvent was exchanged into 50 μL of cyclohexane, containing 2.5 ng of internal standard (ε-hexachlorocyclohexane, ε-HCH).

2.3. Instrumental analysis and chemical standards

The target CPs were analyzed by an Agilent 7890A GC (Agilent Technologies, Santa Clara, CA, USA) coupled with a high resolution time-of-flight mass spectrometry (Tofwerk, Thun, Switzerland) fitted with a ZX2004 loop cryogenic modulator (Zoex corporation, Houston, TX, USA) using an electron capture negative ion (ECNI) mode, according to our previous study (Xia et al., 2016). GC×GC−ECNI-HRTOF-MS TIC chromatogram in the outdoor PM_{10} were seen in Fig. S1. The first-dimension and second-dimension column were an Agilent DB-5MS (30 m × 0.25 mm inner diameter (i.d.) × 0.25 μm film thickness, Agilent Technologies, Santa Clara, USA) and a BPX-50 (1 m × 0.10 mm i.d. × 0.10 μm film thickness, SGE, Melbourne, Australia), respectively. The GC oven program was as follows: held at 140 °C for 1 min, increased at 20 °C min^{-1} to 200 °C, and increased at 1.5 °C min^{-1} to 310 °C (held 5 min). 1 μL of extract was injected into the instrument in splitless mode at an injector temperature of 280 °C. Helium (99.999% purity) was used as carrier gas at a constant of 1 mL min^{-1} and methane (99.9998% purity) was used as reagent gas at a constant of 2 mL min^{-1}. The ion source and transfer line temperature were 200 °C and 280 °C, respectively. The electron energy was set to 120 eV. The modulation period was 8 s with the hot gas duration time of 300 ms.

Pesticide grade acetone, n-hexane, and dichloromethane (DCM) were purchased from J.T. Baker (Phillipsburg, NJ, USA). Anhydrous Na_2SO_4 was baked at 660 °C for 6.5 h before use. Florisil was activated at 550 °C for 12 h. The silica gel was activated at 550 °C for 6.5 h. Acidified silica gel (44% *w*/*w*) was prepared by mixing 100 g of activated silica gel with 43 mL of 98% H_2SO_4. Reference SCCP technical mixtures (100 ng μL^{-1} in cyclohexane) with chlorine contents of 51.0%, 55.5% and 63.0%, and three MCCPs mixtures (100 ng μL^{-1} in cyclohexane) with chlorine contents of 42.0%, 52.0%, and 57.0%, were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Ten SCCP and MCCP mixtures with different chlorine contents were used to establish linear calibration curves