Characterization of short- and medium-chain chlorinated paraffins in outdoor/indoor PM₁₀/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 PM₁₀ 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 PM₁₀/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 ≤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.

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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 widely 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 m³). 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 PM₁₀/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 PM₁₀, PM_{2.5} and PM_{1.0} samples simultaneously in outdoor and indoor. The sampling machine had an air flow of 2.3 m³ 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 ¹³C₁₀-trans-chlordane). Extractions were performed by three cycles at 100 °C and 1.03 × 10⁴ kPa, 5 min of heating, a 12 min static extraction, a flush volume of 70% and a N₂ 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 Na₂SO₄ 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 N₂ 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 PM₁₀ 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 Na₂SO₄ 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% H₂SO₄. 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

(shown in detail in SI: Fig. S2, Table S2, and Table S3). An internal standard of $^{13}\text{C}_{10}$ -trans-chlordane ($100\text{ }\mu\text{g mL}^{-1}$ in nonane, 99% purity) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). A recovery standard of ϵ -Hexachlorocyclohexane (ϵ -HCH, 10 mg L^{-1} in cyclohexane, 99% purity) was obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany).

2.4. Identification and quantification method

According to the two most abundant $[\text{M}-\text{Cl}]^{-}$ ions in full scan mode, quantitative and qualitative ions were identified. A quantification procedure, described by Reth et al. (Reth et al., 2005), was on account of a linear correlation between the total response factors of CP standard mixtures and their chlorine content and makes up for the differences in the response factors between the reference SCCP mixtures and the SCCP pattern present in environmental samples. The detailed quantification method was reported in previous studies (Xia et al., 2016). In this study, twenty-four SCCP formula groups ($\text{C}_{10-13}\text{ Cl}_{5-10}$) and twenty-four MCCP formula groups ($\text{C}_{14-17}\text{ Cl}_{5-10}$) were analyzed in all PM samples.

2.5. Quality assurance and quality control

To eliminate background contamination, all glassware was thoroughly rinsed with methanol, acetone, and dichloromethane in succession before equipment. Each batch of five samples included a procedural blank to monitor the background levels. Field blanks were prepared by mounting QFFs to the sampler, left for five minutes and then recovered, wrapped in alumina foil and stored together with the other samples until analysis. Procedural and field blanks were spiked with the same amount of internal standard as the field samples. No difference was found between the concentrations in the field and laboratory blanks. In total, the concentrations of both SCCPs and MCCPs in the procedural and field blanks were less than 5% of those found in the PM samples. Therefore, the final reported data in this study were not blank corrected. The method detection limits were about 0.5 ng m^{-3} for the SCCPs and 0.2 ng m^{-3} for the MCCPs based on mean blank values plus three times the standard deviation. The method limit of quantification was three times the method limit of detection. Two of thirty samples were randomly selected for parallel experiments. The relative standard deviation obtained after repeating the analysis of each sample seven times was less than 15%. The recovery was calculated by dividing the ratio of the surrogate standard ($^{13}\text{C}_{10}$ -trans-chlordane) and injection internal standard (ϵ -HCH) in each sample by the ratio of $^{13}\text{C}_{10}$ -trans-chlordane and ϵ -HCH in the appropriate standard solution. The internal standard ($^{13}\text{C}_{10}$ -trans-chlordane) recoveries were generally between 69 and 105%. Data analysis was performed with Origin Pro 8.0 software packages.

3. Results and discussion

3.1. PM mass concentrations and size distributions

Outdoor and indoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ mass concentrations measured in Beijing, China, are shown in Fig. 1. The mass concentrations of PM_{10} , $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ in the outdoor ranged from 110.8 to 227.4 (mean: 174.9), 63.0 to 164.7 (mean: 114.9), and 50.9 to 111.7 (mean: 84.1) $\mu\text{g m}^{-3}$, respectively (Fig. 1). The PM_{10} and $\text{PM}_{2.5}$ mass concentrations in this study were three times higher than the standards of $50\text{ }\mu\text{g m}^{-3}$ and $35\text{ }\mu\text{g m}^{-3}$ set by China's National Ambient Air Quality Standard (GB/T 3095-2012) (Chang, 2012). The mass concentrations of PM_{10} , $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ in the indoor were in the range of 31.9–98.7 (average: 66.0), 20.2–50.8 (average: 37.6), and 14.7–32.6 (average: 24.2) $\mu\text{g m}^{-3}$, respectively. The PM_{10} mass

Fig. 1. $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ mass concentrations in the outdoor and indoor samples.

concentrations in this study were lower than the standard of $150\text{ }\mu\text{g m}^{-3}$ set by China's National Indoor Air Quality Standard (GB/T 18883-2002). The indoor and outdoor PM_{10} and $\text{PM}_{2.5}$ mass concentrations were much higher than the average concentrations of $20\text{ }\mu\text{g m}^{-3}$ (PM_{10}) and $10\text{ }\mu\text{g m}^{-3}$ ($\text{PM}_{2.5}$) recommended by the World Health Organization (WHO, 2005). The limits set by the Chinese government are much higher than the World Health Organization limits. At present, guidelines for $\text{PM}_{1.0}$ values have not been proposed. Comparison results showed that PM mass concentrations in outdoor and indoor were higher. Air-borne particulate pollution in Beijing, China was serious. In addition, PM_{10} mass concentrations from outdoor in this study were higher than those from indoor, which are in agreement with the literature (Hassanvand et al., 2015; Houyin, 2005). One road that experienced heavy traffic flows was near the sampling site, so high levels of PM in the outdoor may be related to the heavy vehicular traffic flow.

The fractions of the particles associated with particles $\leq 2.5\text{ }\mu\text{m}$ in diameter accounted for 66% of PM_{10} in outdoor (SI Fig. S3). This proportional distribution was consistent with those reported by Sánchez-Soberón et al. (Sánchez-Soberón et al., 2016) and Zhu et al. (Zhu et al., 2016). For indoor PM in the present study, the fractions of the particles associated with particles $\leq 2.5\text{ }\mu\text{m}$ in diameter accounted for 57% of PM_{10} , were slightly higher than those of coarse particles ($2.5\text{ }\mu\text{m} < d_{ae} \leq 10\text{ }\mu\text{m}$, 43%, Fig. S3). The above phenomenon was consistent with the contributions of coarse particles to PM_{10} in the indoor air of five districts of Beijing (Liu et al., 2004). The present study demonstrated that the majority of PM in outdoor and indoor was in the fine particle range ($d_{ae} \leq 2.5\text{ }\mu\text{m}$).

3.2. SCCP and MCCP levels in the outdoor and indoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ samples

The SCCP and MCCP concentrations in the outdoor and indoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ samples were seen in Fig. 2. To our best knowledge, this is the first report of CP concentrations among particles of different sizes. The SCCP concentration ranges in the outdoor PM_{10} , $\text{PM}_{2.5}$, and $\text{PM}_{1.0}$ samples were 16.9–28.8 (average: 23.9), 9.2–19.6 (average: 14.9), and 4.1–15.4 (average: 10.4) ng m^{-3} , respectively. MCCPs ranged from 2.2 to 5.0 (average: 3.6), 0.6–2.7 (average: 1.7), 0.3–1.3 (average: 1.0) ng m^{-3} , respectively. The mean chlorine contents of SCCPs in the outdoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ samples were 64%, 63%, 63%, respectively. For MCCPs, the mean chlorine contents were 58%, 58%, 58%, respectively. The SCCP and MCCP

Fig. 2. SCCP and MCCP concentrations in the outdoor and indoor PM₁₀/PM_{2.5}/PM_{1.0} samples.

concentrations in the outdoor samples (SI Table S4) were higher than the values reported in the literature (Table 1). The SCCP concentrations in the indoor PM₁₀/PM_{2.5}/PM_{1.0} ranged from 38.3 to 87.7 (mean: 61.1), 16.8 to 49.4 (mean: 31.4), 6.4 to 32.5 (mean: 20.7) ng m⁻³, respectively, while the MCCP levels were in the range of 3.2–9.6 (mean: 6.9), 1.6–7.5 (mean: 4.8), 1.0–6.4 (mean: 3.4) ng m⁻³, respectively. The average chlorine contents of SCCPs in the indoor PM₁₀/PM_{2.5}/PM_{1.0} samples were 64%, 64%, 63%, respectively. And the average chlorine contents of MCCPs were 58%, 57%, 57%, respectively. The mean SCCP and MCCP concentrations in the indoor samples (Table S4) were higher than the mean values reported in the literature (Table 1).

The sum of SCCP and MCCP concentrations in the outdoor and indoor were the same order of magnitude as PAHs (Hassanvand et al., 2015; Mandalakis et al., 2002) and even an order of magnitude higher than the PCBs, PCDD/Fs, PCNs, OCPs (Chrysikou et al., 2009; Mandalakis et al., 2002; Yeo, 2003; Zhu et al., 2016). Furthermore, SCCPs may disrupt endocrine function and even cause cancer in humans (POPRC, 2015). A recent study found that SCCPs exposure decreased viability of and caused significant metabolic disruption to human hepatoma HepG2 cells (Geng et al.,

2015). Because MCCPs have similar physico-chemical properties and toxicity to SCCPs, the concentrations of both SCCPs and MCCPs in atmospheric PM should be of concern. SCCP concentrations in the outdoor and indoor PM₁₀/PM_{2.5}/PM_{1.0} samples were also higher than the corresponding MCCP concentrations. SCCP and MCCP concentrations in the indoor PM₁₀/PM_{2.5}/PM_{1.0} samples were higher than the corresponding values in the outdoor PM₁₀/PM_{2.5}/PM_{1.0} samples, which was consistent with some previous reports that average concentrations of PCBs and PBDEs in indoor air were higher than those in outdoor air (Harrad et al., 2010; Harrad et al., 2006). One reason might be some commercial products containing CPs in the indoors, like paints and coatings, leather and rubber products.

The pathways for exposure of humans to CPs are dietary intake (Harada et al., 2011; Iino et al., 2005), inhalation (Fridén et al., 2011), dust intake (Fridén et al., 2011; Harrad et al., 2006), and dermal uptake (Cherrie and Semple, 2010). The evidence so far indicates that non-occupational exposure to SCCPs and MCCPs for adult humans occurs mainly through the diet (~85% of total exposure), with the relative contribution of exposure via inhalation much lower (~15% of total exposure), and that from dust is thought to be negligible (Fridén, 2010). Although it is much lower than dietary exposure, exposure via inhalation is an important exposure pathway for the general population. The method for assessment of inhalation exposure is detailed in the SI. SCCP concentrations in the inhalable PM fraction (PM₁₀) were used to roughly calculate the daily SCCPs inhalation exposure. The inhalation exposure risk of SCCPs to human health was estimated as a margin of exposure (MOE), and the MOEs were compared with uncertainty factors. In present study, the MOEs in outdoor and indoor air were 1.1×10^7 and 3.9×10^5 (Table S5), respectively, which were larger than the uncertainty factor (1,000). Consequently, SCCPs might present a low risk to human health. This is consistent with the results of an indoor inhalation exposure assessment conducted for an adult and a toddler from Stockholm, Sweden (Fridén et al., 2011).

3.3. Particle size dependent distributions of SCCPs and MCCPs in PM fractions

The PM masses and CP concentrations for particles with diameters of 2.5–10 μm, 1.0–2.5 μm, and <1.0 μm in outdoor and indoor air are given in Table S6. The PM₁₀ fraction contains all

Table 1
Concentrations of CPs in outdoor and indoor from different countries and areas.

	Countries/areas	CPs	Sampling time	Sampling method	Concentrations
Outdoor	Norway/Bear Island (Borgen et al., 2002)	SCCPs	2000	GFF + PUF	1.8–10.6 ng m ⁻³
	China/Beijing (Wang et al., 2012)	SCCPs	2011 in winter	GFF + PUF	1.9–33 (7.7 ± 6.7) ng m ⁻³
		SCCPs	2011 in summer	GFF + PUF	112–332 (200 ± 57) ng m ⁻³
	UK (Barber et al., 2005)	SCCPs	2003	PUF	<185–3430 pg m ⁻³
		MCCPs	2003	PUF	<811–14 500 pg m ⁻³
	India (Chaemfa et al., 2014)	SCCPs	2006	PUF	n.d.–47.4 (8.11) ng m ⁻³
		MCCPs	2006	PUF	n.d.–38.2 (4.83) ng m ⁻³
	Pakistan (Chaemfa et al., 2014)	SCCPs	2011	PUF	0.37–14.2 ng m ⁻³
		MCCPs	2011	PUF	0.29–9.45 ng m ⁻³
	China (Li et al., 2012)	SCCPs	2008	PUF	13.5–517 (137) ng m ⁻³
	South Korea (Li et al., 2012)	SCCPs	2008	PUF	0.60–8.96 (2.06) ng m ⁻³
	Japan (Li et al., 2012)	SCCPs	2008	PUF	0.28–14.2 (2.26) ng m ⁻³
	This study	SCCPs	2016	GFF (PM ₁₀)	16.9–28.8 ng m ⁻³
		MCCPs	2016	GFF (PM ₁₀)	2.2–5.0 ng m ⁻³
Indoor	UK (Barber et al., 2005)	SCCPs	2003	PUF	220–17 000 ng sample ⁻¹
		MCCPs	2003	PUF	450–19 000 ng sample ⁻¹
	Sweden/Stockholm (Fridén et al., 2011)	SCCPs + MCCPs	2007	PUF	<5–210 ng m ⁻³
	Beijing (Gao et al., 2016)	SCCPs	2014	PUF	0.06–1.35 μg m ⁻³
	This study	SCCPs	2016	GFF (PM ₁₀)	38.3–87.7 ng m ⁻³
		MCCPs	2016	GFF (PM ₁₀)	3.2–9.6 ng m ⁻³

particles with diameters smaller than 10 μm , and includes the $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ fractions. Consequently, the CP concentrations for the $\text{PM}_{2.5}$ and $\text{PM}_{1.0}$ fractions are included in the CP concentration for the PM_{10} fraction. Particle size dependent distributions of SCCPs and MCCPs in PM fractions were seen in Fig. S4.

For outdoor air, the SCCP concentrations associated with particles ≤ 2.5 μm in diameter accounted for 62% of the SCCP concentration in the PM_{10} fraction (Fig. S4). MCCPs associated with particles ≤ 2.5 μm in diameter accounted for 46% of the MCCP concentration in the PM_{10} fraction. The sum of SCCP and MCCP concentrations associated with particles ≤ 2.5 μm in diameter accounted for 60% of the total SCCP and MCCP concentrations in the PM_{10} fraction. For indoor air, the SCCP concentrations associated with particles ≤ 2.5 μm in diameter accounted for 51% of the SCCP concentration in the PM_{10} fraction (Fig. S4). For MCCPs in indoor air, the contributions of the concentrations in different PM fractions to the MCCP concentration in the PM_{10} fraction were 50% ($d_{\text{ae}} \leq 1$), 20% ($1 < d_{\text{ae}} \leq 2.5$), and 30% ($2.5 < d_{\text{ae}} \leq 10$). The contribution from the MCCP concentration in PM with particles ≤ 2.5 μm in diameter was high. The sum of SCCP and MCCP concentrations for particles ≤ 2.5 μm in diameter accounted for 53% of the total SCCP and MCCP concentrations in the PM_{10} fraction. The different size distributions observed for SCCPs and MCCPs in outdoor and indoor air could be caused by their differences in molecular weight and volatility, or by differences at the sampling site and with emissions. In both outdoor and indoor air, CPs are mainly associated with particles ≤ 2.5 μm in diameter. These small particles have long atmospheric residence times, and can be inhaled. Inhalation would introduce these particles to the human body, and could cause health issues.

The mean SCCP and MCCP concentrations based on the PM masses and the ratios of SCCPs/MCCPs are given in Table 2. The ratios of SCCPs/MCCPs in outdoor and indoor air samples were different. In the present study, the temperature indoors was much higher than that outdoors (Table S1). There was sometimes wind in outdoor sampling, while there was never wind in indoor. According to Wang et al. the partitioning between gas and particle phases depends largely on the temperature (Wang et al., 2012). Therefore, the indoor and outdoor ratios in the present study could have been affected by differences in temperature, wind and humidity conditions.

To date, no studies have reported on the partitioning of CPs between PM fractions. However, many studies have reported on particle size dependent distributions of POPs. For example, Degrendele et al. (2014) discovered that 71% of PAHs and 60% of dl-PCBs on average were associated with fine particles ($d_{\text{ae}} < 0.95$ μm) (Degrendele et al., 2014). Oh et al. (2002) found that more than 60% of PCDD/Fs were associated with particles of diameters $d_{\text{ae}} < 0.41$ μm (Oh et al., 2002). In another study, most PCNs (mean 68.4%) were found to adsorb onto finer PM ($d_{\text{ae}} \leq 1.0$ μm) (Zhu et al., 2016). Overall, POPs were mainly associated with fine particles ($d_{\text{ae}} < 1$ μm), whereas the majority of CPs were associated with slightly larger particles ($d_{\text{ae}} < 2.5$ μm). The distribution of CPs among PM fractions could be affected by the physico-chemical characteristics of the CPs, season, emissions or sources, sampling

method, and site characteristics. However, the reasons for this need to be studied further.

3.4. Formula group abundance profiles in the PM samples

As can be seen in Fig. 3, the average formula group abundance profiles are quite similar for outdoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ samples. Take the case of outdoor PM_{10} samples, C_{10} congeners were up to about 45.90% of the total abundance of $\sum\text{SCCPs}$ and $\sum\text{MCCPs}$, followed by C_{11} congeners (27.96%). Cl_7 and Cl_8 congeners were the dominant chlorine congener groups, which contributed 59.06% and 28.30% of the total abundance of $\sum\text{SCCPs}$ and $\sum\text{MCCPs}$, respectively. The total SCCP concentrations accounted for 86.83% of the sum of $\sum\text{SCCPs}$ and $\sum\text{MCCPs}$. As for outdoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ samples, the SCCP and MCCP homolog patterns are also similar to indoors (Fig. 3).

In summary, for SCCPs and MCCPs in the outdoor and indoor PM samples, the C_{10} homologue was the predominant carbon chain group, and was thereafter followed by C_{11} homologues. The Cl_7 group was the most abundant chlorine congener groups, and then came Cl_8 group. In addition, it is obvious that C_{10} and C_{11} groups for SCCPs were the main congeners. For MCCPs, C_{14} group was the dominant. Proportion of SCCPs in the sum of $\sum(\text{SCCPs} + \text{MCCPs})$ was much higher than that of MCCPs. The SCCP composition profiles in this study were similar to those previously reported in the particle phase during the wintertime in the Beijing which was mainly dominated by C_{10} and C_{11} carbon chains with six or seven chlorine atoms (Wang et al., 2012), but significantly different from those reported for Fildes Peninsula of Antarctica (C_{12} predominated in particle-phase) (Ma et al., 2014c). It is speculated that different distributions might be due to the partitioning in the process of long-range atmospheric transport or the use of different commercial SCCP products.

As is known to all, commercial CP-42, 52 and 70 mixtures at present were mainly produced in China. Among them, CP-70 had the relatively low production amount. According to the previous report by Gao et al. the C_{10} -CPs and C_{11} -CPs are the dominant congener groups in the SCCP congener group profiles in CP-42 and CP-52 and the dominant congener groups in commercial CP-70 are C_{10} -CPs and C_{12} -CPs (Gao et al., 2012). In this study, congener distributions in the PM samples were consistent with the above results of CP-42 and CP-52. In addition, the SCCP mass fractions in CP-42, CP-52, and CP-70 were detected to be 3.7%, 24.9%, and 0.5%, respectively (Gao et al., 2012). That is to say, the content and production amount of CP-70 were low. Therefore, SCCPs in the outdoor and indoor PM could mainly derive from the production and use of CP-42 and CP-52, which was the same with the other reports (Gao et al., 2012; Ma et al., 2014a; Qiao et al., 2016b).

4. Conclusion

In this study, SCCPs and MCCPs in the indoor and outdoor $\text{PM}_{10}/\text{PM}_{2.5}/\text{PM}_{1.0}$ were first investigated in Beijing, China, with a GC $\times$ GC-TOFMS instrument and used to conduct a preliminary inhalation

Table 2
The mean SCCP and MCCP concentrations based on the PM masses and the ratios of SCCPs/MCCPs.

	Outdoor			Indoor		
	PM (μm) ≥ 2.5 – ≤ 10	PM (μm) ≥ 1.0 – ≤ 2.5	PM (μm) ≤ 1.0	PM (μm) ≥ 2.5 – ≤ 10	PM (μm) ≥ 1.0 – ≤ 2.5	PM (μm) ≤ 1.0
SCCPs ($\text{ng } \mu\text{g}^{-1}$, PM)	0.150	0.0146	0.124	1.046	0.799	0.855
MCCPs ($\text{ng } \mu\text{g}^{-1}$, PM)	0.032	0.023	0.012	0.074	0.104	0.140
SCCPs/MCCPs	4.7	6.4	10.4	14.1	7.6	6.1

Fig. 3. Average congener group abundance profiles of SCCPs and MCCPs in the outdoor and indoor PM₁₀/PM_{2.5}/PM_{1.0} samples.

exposure assessment. Compared to the reported values in the references, the SCCP and MCCP levels in this study were relatively high. Moreover, SCCP and MCCP concentrations in the indoor PM₁₀/PM_{2.5}/PM_{1.0} samples were higher than the corresponding values in the outdoor. One reason might be some commercial products containing CPs in the indoors, like paints and coatings, leather and rubber products. The main homolog groups for both SCCPs and MCCPs were C_{10–11}/C_{7–8}. Based on the congener distributions and the production amount of commercial products, SCCPs in the indoor and outdoor PM samples may mainly derive from the production and use of CP-42 and CP-52. In both outdoor and indoor air, CPs are mainly associated with particles $\leq 2.5 \mu\text{m}$ in diameter. Adsorption mechanism of SCCPs and MCCPs in different size particles required further researched.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.03.054>.

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