



# Concentrations and congener profiles of chlorinated paraffins in domestic polymeric products in China<sup>☆</sup>

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## ABSTRACT

Chlorinated paraffins (CPs) are widely used in domestic polymeric products as plasticizers and fire retardants. In this study, concentrations and congener profiles of short-chain and medium-chain chlorinated paraffins (SCCPs and MCCPs) were investigated in domestic polymeric products, including plastics, rubber and food packaging in China. The average concentrations of SCCPs in polyethylene terephthalate (PET), polypropylene (PP), polyethylene (PE) and food packaging were 234, 3968, 150 and 188 ng/g, respectively and the corresponding average concentrations of MCCPs in these samples were 37.4, 2537, 208 and 644 ng/g, respectively. The concentrations of CPs in rubber and polyvinylchloride (PVC) were significantly higher than in other matrices. The highest concentrations of SCCPs and MCCPs were found in a PVC cable sheath with 191 mg/g and 145 mg/g, respectively. Congener group profiles analysis indicated C<sub>11</sub>- and C<sub>13</sub>-congener groups were predominant in carbon homologues of SCCPs, and C<sub>14</sub>-congener groups were predominant in MCCPs. High levels of SCCPs and MCCPs in domestic polymeric products implied that they might be a significant source to the environment and human exposure.

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## 1. Introduction

Chlorinated paraffins (CPs), which are also called polychlorinated n-alkenes, are semi-volatile and hydrophobic organic chemicals. CPs are divided into the following three subgroups based on the different carbon chain lengths: short-chain chlorinated paraffins (SCCPs, C<sub>10</sub>–C<sub>13</sub>), middle-chain chlorinated paraffins (MCCPs, C<sub>14</sub>–C<sub>17</sub>) and long-chain chlorinated paraffins (LCCPs, C<sub>>18</sub>) (Reth and Oehme, 2004). Among them, SCCPs have aroused widespread concern due to their persistence in the environment, long-range atmospheric transportation, bioaccumulation and toxicity to organisms (Tomy et al., 1997). Owing to those physico-chemical properties, the addition of SCCPs into the products in some regions have been banned or restricted (ECB, 2011; POPRC, 2015). SCCPs and MCCPs are ubiquitous in the different

environmental matrices (Wong et al., 2017; Yuan et al., 2017; Gao et al., 2016a), even in polar regions and alpine areas, for example, Tibet (Braune et al., 2005; Li et al., 2016; Wu et al., 2017). In May 2017, SCCPs were officially listed in Annex A under the Stockholm Convention at its Eighth Conference of Parties (UNEP, 2017).

CPs are used in many fields, such as flame retardants, plasticizers, lubricants and additives of polymeric materials (van Mourik et al., 2016). China is the biggest CP producer and consumer in the world. Annual production of CPs in China reached 1.05 million tonnes in 2013. CP-52 was the main technical product, which accounted for approximately 80% of total CP production (van Mourik et al., 2016). The mass fraction of the SCCPs in CP-52 was comparatively high, with content up to 24.9% (Gao et al., 2012). In 2011–2014, the largest consumer of SCCPs was plasticizer production (6258 tonnes) and flame retardant production (3693 tonnes) in China (Zhang et al., 2017). Burning and disposal of CP-containing wastes may release CPs into the environment (Tomy et al., 1998). CPs could also be discharged from the recycling of plastics, which may occur in chopping, grinding and washing. It was assumed that 0.05% of the CPs could be emitted into the environment during the lifetime of rubber products (U.K. Environment Agency, 2013). In the e-waste dismantling area, high

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levels of SCCPs were found in dust, soil and biota, and workers may have risk of exposure when recycling CP-containing products (Yuan et al., 2017; Zeng et al., 2016). Therefore, CP-containing products could be a significant source to the environment. However, the distribution and congener profiles of CPs in consumer products were scarce, and only a few studies reported concentrations of SCCPs in limited samples of leather and PVC (Xing et al., 2015).

In the present study, a total of 108 domestic polymeric products were collected in Beijing, China. The purposes of this work were to investigate the concentrations and congener profiles of SCCPs and MCCPs in domestic polymeric products using gas chromatography quadrupole time-of-flight mass spectrometry (GC-q-TOF-MS). The correlation among the CP products and CPs in domestic polymeric products was also assessed. The results of this study could help us to better understand the potential sources of SCCPs and MCCPs in the environment and provide scientific data for the possible emission inventory investigation and determining restrictions to governmental managers.

## 2. Material and methods

### 2.1. Chemicals and reagents

All reagents (*n*-hexane, dichloromethane, cyclohexane) were pesticide analytical grade and purchased from J. T. Baker (Phillipsburg, NJ, USA), DIKMA (LAKE FOREST, CA, USA) and TEDIA (Fairfield, OH, USA), respectively. Florisil was obtained from SUPELCO (St. Louis, MO, USA), and silica gel was obtained from Merck (Whitehouse Station, NJ). Commercial standards of SCCP mixtures (C<sub>10</sub>–C<sub>13</sub>, 51.5%, 55.5% and 63.0% chlorine content, 100 ng/μL in cyclohexane), MCCP mixtures (C<sub>14</sub>–C<sub>17</sub>, 42%, 52% and 57% chlorine content, 100 ng/μL in cyclohexane) and ε-hexachlorocyclohexane (ε-HCH, 100 ng/μL in cyclohexane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The 1,5,5,6,6,10-hexachlorodecane (<sup>13</sup>C<sub>10</sub>-labeled, 100 ng/μL in cyclohexane) was purchased from Cambridge Isotope Laboratories (Andover, USA).

### 2.2. Sampling and sample preparation

A total of 108 samples were collected from markets and waste tire recycling stations in Beijing, China. The samples contained plastic bottles, oil tankers, lunch boxes, cable sheathes, PVC tubes, floorings, tires, and other products. According to the differences in the materials, samples were divided in six subgroups, including polyethylene terephthalate (PET, *n* = 19), polypropylene (PP, *n* = 18), polyethylene (PE, *n* = 5), rubber (*n* = 25) and polyvinylchloride (PVC, *n* = 21). The rest of the samples (*n* = 20) were food packaging (FP), and they mainly are made with biaxially oriented polypropylene (BOPP) and vacuum metalized PET (VMPET). The detailed information of the samples and the CPs industrial products were listed in Table S1 and Table S2 (Supporting Information).

All samples were washed by deionized water to remove dust on the surface and air dried in a fume hood and then cut into pieces (approximately 0.5 cm × 0.5 cm) before pretreatment. Sample pretreatment was based on our previous work with some modifications (Zeng et al., 2011). The pretreatment of PVC and rubber samples was minimally different from other samples because they may have high concentrations of CPs. The extract of PVC or rubber samples was diluted before pretreatment, the detailed description of dilution was shown in the Supporting Information. Briefly, 10 ng of 1,5,5,6,6,10-hexachlorodecane (<sup>13</sup>C<sub>10</sub>-labeled) were spiked in approximately 1 g of the sample as surrogate standards, except PVC and rubber samples, and then the sample was ultrasonically extracted with 10 mL of *n*-hexane/dichloromethane (1:1, *v/v*) 3 times (20 min for each run). The extracts of PVC and rubber were

diluted 300 and 30 times, respectively. Then, 50 ng surrogate standards (1,5,5,6,6,10-hexachlorodecane, <sup>13</sup>C<sub>10</sub>-labeled) were spiked in the PVC and rubber samples. Next, the extract was concentrated to approximately 1 mL via rotary evaporation, and the concentrate was then cleaned. Clean-up was performed by a composited column packed with Florisil (3 g), neutral silica gel (2 g), acidic silica gel (5 g, 30% mass fraction), and anhydrous sodium sulfate (4 g) from bottom to top. The column was conditioned with 50 mL of *n*-hexane, and the concentrate was added and then eluted by 35 mL of *n*-hexane (this fraction contained other organochlorine compounds, discarded), following eluted by 100 mL 1:1 *v/v* *n*-hexane/dichloromethane (this fraction contained target compound). The elution was concentrated to approximately 1 mL and further concentrated to near-dryness by nitrogen. Then, the sample was re-dissolved in cyclohexane (PVC and rubber samples in 1 mL, others in 200 μL). Before instrumental analysis, ε-HCH was spiked as instrumental standards (50 ng in PVC and rubber samples, 10 ng in other samples).

### 2.3. Instrumental analysis and quantification method

As described in our previous work (Gao et al., 2016b), SCCPs and MCCPs were analyzed with gas chromatography coupled with a quadrupole time-of-flight mass spectrometry (7200, Agilent Technologies, Santa Clara, USA). The mass spectrometer was operated with negative chemical ionization and at full-scan mode. The details on the parameters of GC-MS were showed in the Supporting Information.

The quantification method is based on the work of Reth et al. (2005) with some modifications. The LCCPs are not measured in this work, due to the low volatility of the LCCPs in the gas chromatography. A total of 96 accurate [M – Cl]<sup>–</sup> ions were used to quantify and qualify the SCCPs and MCCPs coupled with their retention times. The most abundant ion was used as the quantitative ion and the second most abundant ion was used as the qualitative ion for each CP congeners (C = 10–17, Cl = 5–10). The [M – Cl]<sup>–</sup> ions were extracted and autointegrated using MassHunter Quantitative Analysis B.07. The interference between the SCCPs and MCCPs could be reduced by extracting the accurate *m/z* using the high-resolution mass spectrometer. The resolution of mass spectrometer was at the range of 10,000–15,000. Although the separation of interferential ions generated in the ion source need a high resolution (usually >20,500) and used mathematical deconvolution method by the work of Yuan et al. (2016), the simplified reduction of mass interferences in this work could satisfy the quantification of SCCPs and MCCPs. The quantification of SCCPs and MCCPs were shown in the Supporting Information in detail.

### 2.4. Quality assurance and quality control

To avoid contamination, all glassware was soaked in Decon 90 water solutions over 6 h, then washed 2 times using deionized water followed by baking to dryness in an oven at 100 °C and then baking in a muffle furnace at 450 °C over 8 h. Before use, all glassware was rinsed two times with *n*-hexane and dichloromethane. Florisil was baked in a muffle furnace at 140 °C over 7 h, and silica gel and anhydrous sodium sulfate were baked in a muffle furnace at 550 °C over night before use. During the analysis, a procedural blank was added for each batch (8–10 samples). Since no SCCPs or MCCPs were found in procedural blanks, a small quantity of SCCPs (0.1 μg/mL) and MCCPs (0.5 μg/mL) standard mixtures were spiked in the procedural blanks to determine the method detection limits (MDLs). The MDLs of SCCPs and MCCPs were 7.2 and 19.4 ng/g, respectively in this study and the measurement of MDL was described in the Supporting Information. The

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