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Short- and medium-chain chlorinated paraffins in urban soils of Shanghai: Spatial distribution, homologue group patterns and ecological risk assessment

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HIGHLIGHTS

- The levels of SCCPs and MCCPs in urban soil of Shanghai were relatively lower.
- Sewage sludge application and wastewater irrigation were the main sources of CPs.
- CP concentration in soils from Pudong area was higher than that in Puxi area.
- $C_{11,13}Cl_{5-7}$ for SCCPs and $C_{14-15}Cl_{7-8}$ for MCCPs were dominated in most soils.
- Soil CPs pose no significant ecological risk for soil organisms.

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ABSTRACT

Chlorinated paraffins (CPs) are toxic, bioaccumulative, persistent, and ubiquitously present in the environment. Data on the presence of short- and medium-chain chlorinated paraffins (SCCPs and MCCPs) in urban areas with dense population are still scarce to date. SCCPs and MCCPs were measured in urban soils from Shanghai to comprehensively investigate their levels, spatial distribution, homologue group patterns and ecological risk. The concentrations of CPs in soils varied from ND to 615 ng g^{-1} with a median value of 15.7 ng g^{-1} for SCCPs and from 1.95 to 188 ng g^{-1} with a median value of 7.98 ng g^{-1} for MCCPs, respectively. The concentrations of SCCPs in most soils were higher than those of MCCPs. The total CP concentrations in soil samples were between 4.10 and 625 ng g^{-1} with a median value of 26.4 ng g^{-1}. For different functional zones, the median concentrations of soil CPs were found higher in green land including park, greenbelt and campus than those in roadside. The highest concentrations of CPs in soils could be derived from sewage sludge application and wastewater irrigation for green land. Three types of soils were classified by hierarchical cluster analysis (HCA) for SCCPs and MCCPs, the most abundant homologue groups in the bulk of the soil samples were $C_{11}Cl_{5-7}$ and $C_{13}Cl_{5-7}$ for SCCPs, and $C_{14}Cl_{7-8}$ and $C_{15}Cl_{7-8}$ for MCCPs. Correlation analysis and PCA suggested that SCCPs and MCCPs in soils in the studied area derived from different sources. The preliminary ecological risk assessment indicates that soil CPs at present levels poses no significant ecological risk for soil-dwelling organisms.

1. Introduction

Chlorinated paraffins (CPs) are complex mixtures of polychlorinated n-alkanes containing thousands of different congeners, isomers, enantiomers and diastereomers. The commercial formulations are subdivided according to their carbon chain length into short-chain CPs (SCCPs, C_{10-13}), medium-chain CPs (MCCPs, C_{14-17}) and long-chain CPs (LCCPs, C_{18-30}). Since CPs were produced in the 1930s, the worldwide production was estimated to be 300 ktons in 1985 (WHO, 1996) and this increased by 1% per year between 1989 and 1998 (Lahaniatis et al., 2000). The production of SCCPs in the United Nations Economic Commission for Europe (UNECE) region in 2007 was estimated to range from 7.5 to 11.3 ktons $year^{-1}$ (UNECE, 2007). China began its CP production at the end of 1950s. The production capacity of CPs was less than 10 ktons $year^{-1}$ in the early 1980s, the capacity increased to nearly 800 ktons $year^{-1}$ in 2008 in China. China is currently the largest producer and consumer in the world and the number of CP factories in China is more than 150 (Xu et al., 2014).

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Due to their high chemical stability and viscosity, flame resistance and low vapor pressure, they were used for a wide range of industrial applications, such as flame retardants in paints, rubber and plastics, plasticizer in paints, coatings, sealants and adhesives, and extreme pressure additives in metal working fluids and fat liquors in leather processing (EU, 2011). As a result of their mass production, extensive uses, persistence, and tendency to bioaccumulate (Fisk et al., 2000; Muir et al., 2003), CPs have been found in natural environmental compartments (Takasuga et al., 2003; Barber et al., 2005; Houde et al., 2008; Chen et al., 2011; Y. Wang et al., 2013), human living environment (Fridén et al., 2011), aquatic and terrestrial food webs (Tomy et al., 1998), as well as in human breast milk (Reth et al., 2005a; Thomas et al., 2006).

The release of CPs into the environment can occur during production, storage, transportation, industrial usage of manufactured products and use of products containing CPs. Release can also occur from leaching, runoff, or volatilization from landfills, sewage sludge-amended soils (WHO, 1996; Tomy et al., 1998; Muir et al., 2000) and disposal and burning of waste (Feo et al., 2009). Some of the released SCCPs are collected in sewer systems and ultimately accumulate into sewage treatment plants (STPs) (Zeng et al., 2012). When released to the environment, CPs tend to partition primarily to sediment or soil. Level III fugacity modeling of SCCPs and MCCPs has shown that they would reach their highest concentrations in sediment and soil (UK environment Agency, 2007). Agricultural soils may also be a potentially major reservoir of CPs due to sewage sludge application (Nicholls et al., 2001; Stevens et al., 2003).

SCCPs showed chronic toxicity in aquatic organisms and carcinogenicity in rats and mice (IARC, 1990; WHO, 1996), and was categorized in group 2B as possibly carcinogenic to humans by IARC (IARC, 1990). A global ban on SCCPs is being considered under the Stockholm Convention on POPs. SCCPs and MCCPs are structurally similar, and have generally similar physicochemical and toxicological properties where comparative data are available (EU, 2011). There are increasing concerns about the toxic effects of the longer chain paraffins, as they have also been shown to bioaccumulate and biomagnify in the food chain (EU, 2011). Although toxicity of MCCPs is lower compared to SCCPs, they are widely used and show higher concentration levels than SCCPs (Stern and Tomy, 2000; Bayen et al., 2006). Environmental contamination by MCCPs has raised more and more public concern in recent years (EU, 2011).

As the largest CP producer in the world, three commercial CP mixtures (CP-42, CP-52, and CP-70) are produced in large quantities and are widely used in China, with CP-42 and CP-52 accounting for over 80% of the total production of CPs (Tang and Yao, 2005). Only a few reports on CPs in soils are available to date (Zeng et al., 2011a; Gao et al., 2012; X.T. Wang et al., 2013; Y. Wang et al., 2013; Sun et al., 2013). The objectives of the present study were to investigate the contamination levels of SCCPs and MCCPs in urban soil from Shanghai, to obtain detailed information on the spatial distribution, homologue group patterns and the potential sources, and to assess their ecological risks to soil organisms.

2. Materials and methods

2.1. Sampling site and sample collection

A total of 75 surface soil samples from Shanghai main districts were collected in April, 2011. For each sampling site, 5 sub-samples were taken from the same area (at the depth of 0–20 cm in 100 m^2 area), and bulked together to form one composite sample. As shown in Fig. 1, all samples were classified into greenbelt ($n = 60$), roadside ($n = 5$), park ($n = 4$), and campus ($n = 6$) soils. Soil samples were air-dried for one week at room temperature in a storage room which was separated from the laboratory, and sieved into 60-mesh size particles after removing stones, residual roots and other unwanted materials, then sealed in glass bottles and conserved in refrigerator at -4 °C until analysis. The organic carbon content of the soil samples was determined by potassium dichromate titrimetric method (Lu, 2000).

2.2. Chemicals and materials

SCCP ($C_{10–13}$, 51.5%, 55.5%, and 63% chlorine content) and MCCP standards ($C_{14–17}$, 42%, 52% and 57% chlorine content) at 100 ng μL^{-1} in cyclohexane were purchased from Dr. Ehrenstorfer (Augsburg, Germany). The SCCP stock solutions with 53.5% and 59.2% chlorine content were obtained by 1:1 (v/v) mixing of the SCCP stock standard solutions with 51% and 55.5% chlorine content as well as with 55.5% and 63% chlorine content, respectively. The MCCP stock solutions with 47% and 54.5% chlorine content were obtained in the same way by mixing corresponding MCCP standards, respectively. $^{13}C_{10}$-trans-chlordane and $^{13}C_6$-hexachlorobenzene ($^{13}C_6$-HCB) (Cambridge Isotope Laboratories, Andover, MA, USA) were used as surrogate and internal standards, respectively. Silica gel (100–200 mesh) (Qingdao Haiyang Chemical Co. Shandong, China) and neutral alumina (100–200 mesh) (Sinopharm Chemical Reagent Co., Shanghai, China) were activated at 130 °C for a minimum of 16 h prior to use, then neutral alumina was deactivated by ultrapure water (6%, w/w), acid silica gel (30%, w/w) was prepared by thoroughly mixing 100 g of silica gel with 44 g of concentrated sulfuric acid (USEPA, 2010), and stored in a desiccator. Anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., Shanghai, China) was baked at 450 °C for 5 h before use. All solvents (Sinopharm Chemical Reagent Co., Shanghai, China) used were of analytical grade and redistilled in an all-glass system before use.

2.3. Sample extraction and cleanup

Detailed procedures are provided in our previous study (X.T. Wang et al., 2013). In brief, about 20 g of air-dried soil samples mixed with 20 g of anhydrous sodium sulfate, spiked with 6 ng of $^{13}C_{10}$-trans-chlordane as a surrogate standard and equilibrated for 24 h, and then Soxhlet extracted with 200 mL of n-hexane/acetone (1:1, v/v) for 24 h with activated copper to remove elemental sulfur. After being exchanged into hexane and reduced to approximately 1 mL, the extract was cleaned by a column containing 6 g of deactivated neutral alumina, 6 g of acid silica gel and anhydrous Na_2SO_4 from the bottom to top. The column was eluted with 30 mL of n-hexane and 60 mL of n-hexane/dichloromethane mixture (1:1, v/v), respectively. The second fraction containing CPs was concentrated, solvent-exchanged to n-hexane, and reduced to near dryness, and finally redissolved in 50 μL of isooctane containing 6 ng of $^{13}C_6$-HCB before GC/MS analysis.

2.4. Instrumental analysis, identification and quantification

The analyses of SCCPs and MCCPs were carried out according to CP carbon chain length and degree of chlorination as described previously (Reth and Oehme, 2004; Reth et al., 2005b). Briefly, analyses were performed with an Agilent 6890N gas chromatograph-5975 mass selective detector (GC/MS) system. Separation was performed with a DB-5HT (15 m, 0.25 mm I.D., 0.1 μm film) fused-silica capillary column (J&W Scientific, Folsom, USA). Helium was used as carrier gas at a constant flow of 0.9 mL min^{-1}. Sample volumes of 1 μL were injected in the pulse/splitless mode at an injector temperature of 260 °C. The oven temperature program was as follows: 80 °C (held for 1 min), to 270 °C at 10 °C min^{-1} (held for 10 min). The MS was employed in the electron capture negative ionization mode (ECNI) with methane (99.995%) as reagent gas. The electron collision energy was 100 eV. The ion source, quadruple and transfer line temperatures were held at 200, 100 and 280 °C, respectively. 24 SCCP homologue groups (C_{10}–C_{13} with 5–10 chlorines) and 24 MCCP homologue groups (C_{14}–C_{17} with 5–10 chlorines) were monitored in selected ion monitoring (SIM) mode; the