Short- and medium-chain chlorinated paraffins in sediments from the middle reaches of the Yangtze River: Spatial distributions, source apportionment and risk assessment

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HIGHLIGHTS

- SCCPs and MCCPs in sediments from the Yangtze River were measured by GC × GC–TOFMS.
- CP concentrations in the sediments tended to decrease from urban to rural areas.
- Correspondence analysis indicated SCCPs in the sediments were from CP-42 and CP-52.
- CPs with nine carbon atoms in sediment samples were quantitated for the first time.
- Ecological risks posed by SCCPs in the sediments were assessed.

GRAPHICAL ABSTRACT

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ABSTRACT

Chlorinated paraffins (CPs) are easily adsorbed into sediments where they pose potential risks to the ecosystem and human health. Few studies have investigated short- and medium-chain CPs (SCCPs and MCCPs) in sediments. The aim of the present study was to comprehensively investigate contamination levels, spatial distributions, sources and risks posed by CPs in sediments from the middle reaches of the Yangtze River. The sediment samples were analyzed by two-dimensional gas chromatography coupled with time-of-flight mass spectrometry (GC × GC–TOFMS). The concentrations of SCCPs and MCCPs ranged from 4.19 to 41.6 ng/g dry weight (dw) and not detected to 14.6 ng/g dw, respectively. No significant correlation was found between the total organic carbon contents and CP concentrations ($P > 0.05$). The spatial distributions showed that CP contamination levels in the sediments were related to local human activities. The dominant congener groups were $C_{10-11}Cl_{6-7}$ for SCCPs, and $C_{14}Cl_{7-8}$ for MCCPs. Correspondence analysis revealed that likely sources of SCCPs were the production and use of CP-42 and CP-52. Principal component analysis indicated that SCCPs and MCCPs in the sediments may come from different sources. Moreover, CPs with nine carbon atoms were quantitated for the first time in sediment samples, and the results indicated they should not be neglected in future analyses. Risk assessments indicated that CPs in the sediments did not pose a great ecological risk currently.

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1. Introduction

Chlorinated paraffins (CPs), or named polychlorinated *n*-alkanes, are a class of complex mixtures containing thousands of different isomers, enantiomers, and diastereomers (Bayen et al., 2006). They generally have the form $C_xH_{(2x+2-y)}Cl_y$ with a degree of chlorination between 30% and 70%. According to the carbon chain length, CPs can be subdivided 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_{21}). Because of their high chemical and thermal stabilities, CPs are used as flame retardants, plasticizers, and used as additives in paints, sealants and metal working fluids (Tomy et al., 1998). They can enter into the environment during the production, transportation, use and disposal of CPs and CP-containing materials. Considering the potential for long-range transport (Tomy et al., 1999), persistence (Iozza et al., 2008), bioaccumulation (Fisk et al., 2000) and toxicity (Warnasuriya et al., 2010), SCCPs have been listed as candidate persistent organic pollutants (POPs) in the Stockholm Convention. The use of SCCPs in metal- and leather-working has been restricted in the European Union since 2004 because of their high toxicities (European Commission, 2002). However, CPs have been detected in a wide range of samples of air (Wang et al., 2013), water (Coelhan, 2010), soil (Wang et al., 2014), biota (Reth et al., 2006), and even human breast milk (Thomas et al., 2006) to date. In depth investigation of the occurrence and environmental fate of CPs would allow for control measures to be developed to reduce CP contamination.

Due to their high organic–carbon partition coefficients (Fisk et al., 1998), CPs are prone to be adsorbed into sediments when they enter the aquatic environment. They can be accumulated by benthic organisms, and then pose risks to human health through the food chain (Houde et al., 2008; Ma et al., 2014b). Meanwhile, CPs in sediments are likely to be re-released to the water under certain conditions, which would result in secondary pollution. Therefore, it is important to investigate CP contamination levels in sediments so as to reveal their sources and assess the potential risks. Several studies have reported the levels of CPs in sediments from lakes, rivers and coastal regions. For lakes, extremely high SCCP concentrations (1100–8700 ng/g) have been observed in sediments located downstream of a sewage treatment plant (STP) (Zeng et al., 2011b), suggesting that STP effluents might be a major source of SCCPs in lake sediments. For sediments from the Pearl River Delta, the highest levels of SCCPs (320–6600 ng/g) were found in pond sediments from electronic waste (e-waste) recycling areas (Chen et al., 2011), which indicated that e-waste recycling activities were a major source of sedimentary CPs in this area. Marine sediments from the East China Sea showed a decreasing gradient of SCCP levels and increasing proportions of lighter SCCPs for samples collected from the inner shelf to the open sea (Zeng et al., 2012b; Zhao et al., 2013), indicating the influence of river input and higher transport abilities of lighter congeners. The sedimentary records of CPs closely followed the historical production and use of CPs (Chen et al., 2011), and the vertical distributions of congener profiles reflected the potential degradation of CPs (Zeng et al., 2011b). However, there are still some gaps in the research for CPs in sediments. For example, data for MCCPs are scarcer than SCCPs because of the difficulties in analysis techniques. Although the toxicities of MCCPs are relatively lower compared with that of SCCPs (Wyatt et al., 1993), they have been widely used (Chen et al., 2011) and also shown bioaccumulation (Houde et al., 2008). Therefore, more attention should be given to MCCPs. Additionally, the source apportionment and risk assessment for CPs in sediments have not been specific or comprehensive. So it's of great importance to conduct a thorough study of SCCPs and MCCPs in sediments.

China began to produce CPs in the late 1950s, and has become the largest producer and user of CPs in the world. Three main commercial CP mixtures (CP-42, CP-52 and CP-70), named basing on the chlorine contents, are produced and utilized on a large scale. The annual production reached 600,000 tons in 2007 (De Boer et al., 2010) and 1000,000 tons in 2009 (Chen et al., 2011). So far, CPs have been found in a variety

of environmental matrices in China (Ma et al., 2014a; Wang et al., 2012; Zeng et al., 2015). The Yangtze River is the longest river in Asia, and the middle reaches of the river run through 13 towns in the province of Hubei. Dozens of electronics factories, petrochemical plants and CP manufacturers located there have been regarded as potential emission sources of CPs. CPs could be released into the environment and then contaminate the river. Considering that the Yangtze River is an important water resource for local industrial and agricultural production, it is very important to investigate CP pollution status in the sediment and assess the risks to ecological and human health.

In this study, two-dimensional gas chromatography coupled with time-of-flight mass spectrometer (GC × GC–TOFMS) was applied to quantify SCCPs and MCCPs in sediments collected from the middle reaches of the Yangtze River. The primary aims were to investigate the contamination levels, spatial distributions and congener group profiles of SCCPs and MCCPs in the sediment. This information could also be used to identify the contamination sources. Furthermore, CPs with nine carbon atoms in sediment samples were quantitated for the first time. Finally, ecological risks posed by SCCPs were assessed. The results will be helpful to increase the understanding of current pollution status and environmental fate of CPs, as well as develop strategies for future reduction of them in the environment.

2. Materials and methods

2.1. Sample collection

The sediment samples (0–5 cm) were collected from 13 locations in the middle reaches of the Yangtze River using a stainless steel grabber. The sampling points were comparatively evenly distributed over 200 km along the Yangtze River, from Yichang to Jingzhou in Hubei province (Fig. S1, Supporting information). Detailed geographical information of the sampling sites was recorded using the Global Positioning System (Table S1). All samples were stored in amber glass bottles and transported to the laboratory on ice. Then they were freeze-dried, homogenized, and kept at -20°C until analysis.

2.2. Chemicals and materials

Commercial standards of SCCP with chlorine contents of 51.5%, 55.5% and 63%, and MCCP standards with chlorine contents of 42%, 52% and 57%, all at a concentration of 100 ng/ μL in cyclohexane, were purchased from Dr. Ehrenstorfer (Augsburg, Germany). SCCP solutions with chlorine contents of 53.5% and 59.2% were prepared by mixing equal volumes of the SCCP standards with chlorine contents of 51.5% + 55.5% and 55.5% + 63%, respectively. Similarly, MCCPs with chlorine contents of 47% and 54.5% were prepared by mixing equal volumes of the MCCP standards with chlorine contents of 42% + 52% and 52% + 57%, respectively. $^{13}\text{C}_{10}$ -*trans*-chlordane (Cambridge Isotope Laboratories, Tewksbury, MA) was used as a surrogate standard, and ϵ -hexachlorocyclohexane (ϵ -HCH; Dr. Ehrenstorfer) was used as the internal standard. Silica gel (63–100 μm) (Merck Company, Kenilworth, NJ) was activated at 550°C for 12 h, and Florisil (60–100 mesh) from the same manufacturer was baked at 140°C overnight prior to use. Anhydrous sodium sulfate (Sinopharm Chemical Reagent Company, Beijing, China) was baked at 660°C for 6 h before use. Acidified silica gel (30%, mass fraction) was gained by thoroughly mixing 100 g of activated silica gel and 23.3 mL of concentrated sulfuric acid.

2.3. Sample extraction and cleanup

The extraction and clean-up procedures were modifications of established methods (Gao et al., 2011; Zeng et al., 2011a). Each 5 g of homogenized sediment sample was spiked with 2.5 ng of $^{13}\text{C}_{10}$ -*trans*-chlordane, and then extracted with the mixed solvent of *n*-hexane and dichloromethane (1:1, v/v) in an Accelerated Solvent Extractor at

1.03×10^4 kPa and 150 °C. The extract was evaporated to about 1 mL, and passed through a gel permeation chromatography column, which was cleaned with 70 mL of dichloromethane/n-hexane (1:1 v/v) to remove sulfur-containing compounds firstly and then eluted with 130 mL of dichloromethane/n-hexane (1:1 v/v). The eluent was concentrated, and fractionated on a multi-layer silica gel column containing 3 g of Florisil, 2 g of neutral silica gel, 5 g of 30% acidified silica gel, and 4 g of anhydrous sodium sulfate from the bottom to top. The column was rinsed with 50 mL of *n*-hexane. Afterwards, the sample was added and eluted with 40 mL of *n*-hexane as well as 100 mL of *n*-hexane/dichloromethane (1:1, v/v). The second fraction was collected, concentrated to near dryness, and solvent-exchanged with 50 μ L of cyclohexane. Before analysis, 2.5 ng of ϵ -HCH was added as an injection internal standard.

2.4. Instrumental analysis

Analysis of SCCPs (C_{10} – C_{13} with 5–10 chlorine atoms) and MCCPs (C_{14} – C_{17} with 5–10 chlorine atoms) in the sediment samples were carried out by a GC $\times$ GC–TOFMS instrument. The detailed conditions were described in our previous study (Xia et al., 2016). Briefly, each 1- μ L sample was injected in splitless mode, and the injector was set at 280 °C. The GC oven temperature started at 140 °C for 1 min, then increased at 10 °C/min to 200 °C, increased at 1.5 °C/min to 310 °C, and finally maintained at 310 °C for 5 min. The modulation period was set to 8 s. The mass spectrometer was performed in ECNI mode with methane as the reagent gas.

Twelve groups of ordered structures were shown on the two-dimensional chromatogram, and those congeners with the same number of carbon plus chlorine atoms (e.g., $C_{10}H_{13}Cl_9$, $C_{11}H_{16}Cl_8$, and $C_{12}H_{19}Cl_7$, $C_{13}H_{22}Cl_6$) were divided into the same group. The two most abundant $[M - Cl]^-$ m/z were selected as the quantification and qualification ions. The detailed quantification method of SCCPs and MCCPs in the sediment samples followed an established procedure (Reth et al., 2005). The calibration curves between total response factors and chlorine contents of prepared CP solutions were established, so that differences of the chlorine contents between the experimental samples and referenced CP standards can be corrected. The GC $\times$ GC data were processed via GC Image® R2.5 Software (GC Image, Lincoln, NE).

In addition, the total organic carbon (TOC) contents of all sediment samples were determined with a TOC Analyzer (O.I. Analytical, College Station, TX) after being processed with 5% phosphoric acid.

2.5. Quality control and quality assurance

To eliminate the possible background contamination, all glassware was rinsed with methanol, acetone, and dichloromethane three times before the experiment. For each batch of four samples, a procedural blank was processed to monitor the background levels. Three of the 13 sediment samples were randomly selected for parallel analysis. The

relative standard deviations ($n = 7$) were all <15%. The recoveries of the surrogate standard ($^{13}C_{10}$ -*trans*-chlordane) in all samples ranged from 70.8–89.5%. The method detection limits (MDLs) were calculated to be 2.21 ng/g for Σ SCCPs and 1.86 ng/g for Σ MCCPs.

2.6. Statistical analysis

Correlation analysis was applied to determine the relationships between CP concentrations and TOC contents in the sediments. All samples collected were hierarchically clustered using the relative contents of CP congeners by Ward's method and Euclidean distance. Correspondence analysis was conducted to explore the potential source of SCCPs according to the congener group profiles. And principal component analysis was performed to reveal the relationships between SCCPs and MCCPs with an eigenvalue > 1 after varimax rotation. All analyses were performed using SPSS 20.0 software.

3. Results and discussion

3.1. Contamination levels and spatial distributions of SCCPs and MCCPs in the sediments

SCCP and MCCP concentrations in sediments from the middle reaches of the Yangtze River were all reported basing on the dry weight (dw). As shown in Table 1, the concentrations of SCCPs in the sediment samples ranged from 4.19 to 41.6 ng/g dw, and the range for the chlorine contents was 61.8–63.8%. The MCCP concentrations ranged from not detected (n.d.) to 14.6 ng/g dw, and the chlorine contents of MCCPs were 55.2–59.9%. The concentrations of MCCPs were lower than those of SCCPs in all of the investigated sediment samples in this study. By contrast, MCCP concentrations have been found to be higher than those of SCCPs in some other regions (Chen et al., 2011; Pribylova et al., 2006). CPs are generally produced by chlorination of paraffins, which means their chain length depends on the number of carbon atoms in the raw material. The numerical relationship of SCCPs and MCCPs in the manufacturing process may be different in different places. Besides, different physicochemical properties of SCCPs and MCCPs affect their migration and accumulation capabilities. Therefore, the ratio of MCCPs/SCCPs in sediments may be influenced by both the discharge situation and environmental behavior.

Compared with previous studies of SCCPs in sediments, the concentrations in the present samples were similar to those found in the East China Sea (5.8–64.8 ng/g dw) (Zeng et al., 2012b) and Chinese Bohai and Yellow Seas (14.5–85.2 ng/g dw) (Zeng et al., 2013), but lower than those found in the Liaohe River Basin (39.8–480.3 ng/g dw) (Gao et al., 2012) and Liaodong Bay (65–541 ng/g dw) (Ma et al., 2014b). In addition, they were much lower than those found in typical industrial regions, such as the Pearl River Delta (320–6600 ng/g dw) (Chen et al., 2011) and a lake which receives effluents from a STP (1.1–8.7 μ g/g dw) (Zeng et al., 2011b). The MCCP concentrations in the present study were also much lower than those found in the Pearl River Delta (880–38,000 ng/g dw)

Table 1

Concentrations of SCCPs and MCCPs and relative abundances of their homologs in sediments from the middle reaches of the Yangtze River, China.

No.	Cl%- SCCPs	C_{10} (%)	C_{11} (%)	C_{12} (%)	C_{13} (%)	Σ SCCPs (ng/g dw)	Cl%- MCCPs	C_{14} (%)	C_{15} (%)	C_{16} (%)	C_{17} (%)	Σ MCCPs (ng/g dw)
Y1	62.6	66.1	14.3	9.75	9.89	19.2	59.4	87.7	9.60	1.52	1.17	10.3
Y2	63.6	72.4	17.5	4.55	5.54	41.6	59.3	83.7	10.1	3.69	2.51	4.43
Y3	63.8	85.2	11.4	1.68	1.72	11.6	56.5	62.4	19.1	10.9	7.70	3.07
Y4	63.3	77.9	16.9	3.33	1.89	34.8	59.4	59.4	18.5	11.6	10.5	2.40
Y5	63.1	59.3	22.4	9.78	8.46	5.94	59.9	–	–	–	–	n.d.
Y6	62.8	70.2	21.8	3.99	4.05	20.7	59.2	88.8	8.13	1.52	1.51	2.85
Y7	63.1	82.5	10.6	3.31	3.60	33.9	56.9	66.2	17.6	8.23	7.96	3.93
Y8	61.8	65.8	22.3	4.70	7.18	32.2	55.8	59.4	17.2	14.6	8.85	14.6
Y9	62.0	87.3	9.09	2.23	1.42	10.5	55.2	–	–	–	–	n.d.
Y10	63.1	78.6	13.3	4.50	3.55	4.19	57.1	–	–	–	–	n.d.
Y11	62.4	80.7	13.9	3.22	2.10	32.2	57.3	57.3	21.0	8.86	12.9	1.94
Y12	63.5	71.4	16.2	6.97	5.44	7.74	54.6	–	–	–	–	n.d.
Y13	62.7	73.2	15.7	3.89	7.18	16.1	57.9	76.7	13.8	7.24	2.20	3.08

(Chen et al., 2011), and in the Czech Republic (18–5575 ng/g dw) (Pribylova et al., 2006).

The SCCP concentrations were generally higher in the sediments collected close to downtown areas, such as in the cities of Yichang, Yidu, Songyi, and Jingzhou (Fig. 1). This may be because many industries, including electronics manufacturing, plastics factories and petrochemical plants, are located in these areas. In addition, increased use and disposal of CPs because of higher population density compared with less-urban areas may be another contributor to the increased CP levels in sediments collected from these sites. Besides, MCCP concentrations in the sediments tended to decrease from urban to rural areas, which was similar to the spatial distribution of SCCPs.

The TOC content is considered to play a role in the accumulation of organic compounds into sediments. Significant relationships between CP concentrations and TOC contents have been found in some previous studies, suggesting the TOC content is an important factor influencing the accumulation level of CPs (Chen et al., 2011; Zeng et al., 2013). However, other studies found this relationship was not significant, and instead, emission sources were important (Gao et al., 2012). For the present sediment samples, TOC contents were in the range of 0.88–3.36% (Table S1). No significant correlation was found between SCCP concentrations and TOC values via Spearman correlation analysis ($P > 0.05$), and a similar result was observed for MCCPs (Table S2). Therefore, variations in the SCCP and MCCP concentrations in sediments from the middle reaches of the Yangtze River did not only depend on the organic matter contents. This also suggested that CPs probably be still introduced into the sediments at present, and the equilibrium partitioning of CPs between sediment and air or water has not been well established.

3.2. Congener group profiles and source apportionment of SCCPs and MCCPs in the sediments

The homolog patterns of SCCP and MCCP in sediments from the middle reaches of the Yangtze River were analyzed. Overall, C_{10} -CPs was the most abundant, followed by C_{11} -CPs. These two homolog groups contributed to 80.4–96.6% of Σ SCCPs. The dominant chlorine homolog groups were Cl_6 - and Cl_7 -CPs, which accounted for 25.8–55.5% and 34.6–54.8% of the Σ SCCPs, respectively. For the MCCPs, Cl_7 - and Cl_8 -CPs were the major chlorine homolog groups contributing 44.6–79.2% of the Σ MCCPs, and C_{14} -CPs (57.3–88.8% of Σ MCCPs) was the main carbon chain. The homolog patterns of SCCP were consistent with those found in sediments from the East China Sea and Liaohe River Basin

(Gao et al., 2012; Zeng et al., 2012b). However, they were different from those found in highly industrialized areas (Chen et al., 2011), in which C_{10} -, C_{11} -, C_{12} - and C_{13} -CPs contributed to similar proportions of the total SCCPs. The homolog patterns of MCCPs in the investigated sediments were similar to those found in sediments from the Pearl River Delta (Chen et al., 2011) and the Czech Republic (Pribylova et al., 2006). They were all dominant by $C_{14}Cl_{7-8}$, while the proportion of C_{14} -CPs in the Yangtze River was higher than that in other regions.

In order to identify the contamination sources of SCCPs in the sediments, correspondence analysis was performed basing on the relative abundances of SCCP congeners in thirteen sediment samples, three commercial CP mixtures (Gao et al., 2012) and two potential industrial sources (Lu et al., 2015; Zeng et al., 2012a) (Fig. 2). In the correspondence analysis plot, two main factors were extracted, which together explained a contribution of 82.7% (50.3% + 32.4%) to the most original variables. Most samples were found to be clustered with commercial mixtures CP-42 and CP-52. This result implied that the SCCPs in sediments were probably mainly from the production and use of CP-42 and CP-52. The commercial mixture CP-70 and the congeners $C_{10}Cl_9$ and $C_{10}Cl_{10}$ showed similar angles and close distances, suggesting that the use of CP-70 could contribute to these two SCCP congeners in the sediments. Similarly, the industrial processes of sewage treatment and e-waste dismantling were found to probably contribute to the accumulation of C_{12} and C_{13} homologs in the sediments. And it was in a good agreement with the previous discovery that high proportions of long chain congeners were detected in the environmental samples near these two kinds of plants (Lu et al., 2015; Zeng et al., 2012a).

Furthermore, principal component analysis was used to explore the relationship between SCCPs and MCCPs (Fig. 3). The first two principal components (PC1 and PC2) accounted for 85.6% of the total variances. From the factor loading plot, it can be inferred that SCCPs and MCCPs in sediments from the middle reaches of the Yangtze River probably have different sources. Data on MCCP homolog patterns in CP commercial mixtures (Fig. S2) and other potential emission processes are not enough, so the exact sources of MCCPs in the sediments are unable to be identified at present.

3.3. Quantification of chlorinated paraffins with nine carbon atoms in the sediments

The toxicities of CPs may increase as their carbon chains become shorter (De Boer et al., 2010). Many of the CP congeners have similar

Fig. 1. Spatial distributions of SCCPs and MCCPs in the sediments.

Fig. 2. Score plot of correspondence analysis from relative abundances of SCCP congeners in sediment samples and suspected sources. (The blue circle “n, m” represents “C_nCl_m”).

chromatographic retention characteristics, so that they cannot be separated and identified concretely using one-dimensional gas chromatography. Besides, different congeners that share similar mass-to-charge ratios cannot be distinguished using low resolution mass spectrometry. So far, C₁₀–C₁₃ with 5–10 chlorine atoms have been generally detected in most studies, but SCCPs with nine carbons have not been investigated in sediments. The GC × GC-HRTOFMS method used in this study can separate CP congeners more concretely due to high resolution and peak capacity. Because most of the C₉ congeners gave very low signals, only two C₉ congeners (C₉Cl₆ and C₉Cl₇) were determined. The relative abundance of these two C₉ congeners in all of the sediment samples ranged from 3.28% to 12.25%. The relative abundances of the C₉ congeners were even higher than those of C₁₂ or C₁₃ congeners at some sampling sites. Because C₉ and C₁₀ have similar characteristics, the percentage ratio of the relative abundance of C₉ over that of C₁₀ was also calculated. The results ranged from 4.97% to 16.22%. Therefore, the levels of C₉ congeners should not be neglected. The detection of C₉ CPs in the sediments suggests that they could be present in industrial CP products and released to the environment. This discovery of new CPs will improve our understanding of the composition of CPs. These C₉ homologs may be more toxic than other CPs, so their environmental behaviors and potential risks need to be further studied.

3.4. Risk assessment

Only a few studies have reported aquatic toxicity data for CPs, and very little data for sediment-dwelling organisms are available.

Fig. 3. Factor loading plot of eight carbon homolog groups in the sediments.

Therefore, it is difficult to thoroughly assess the ecological risks posed by CPs in sediments. But an elementary risk assessment can be carried out according to the CP concentrations in the present samples and toxicology thresholds reported. The estimated lowest observed effect concentration of SCCPs to benthic organisms was 35.5 mg/kg dw (UNEP, 2015). And the SCCP concentrations found in the sediments (4.19–41.6 ng/g dw) were lower than this value, suggesting that SCCPs in sediments from the middle reaches of the Yangtze River pose no significant ecological risk currently.

Despite the lack of significant risk at this stage, CP contamination levels in sediments and their ecological risks should be monitored continually because mass loads of SCCPs could increase over time and CPs could interact with other persistent organic pollutants to produce unexpected effects.

4. Conclusions

SCCPs and MCCPs in sediments from the middle reaches of the Yangtze River were analyzed by GC × GC-TOFMS. The concentrations of SCCP and MCCP in the sediments were at similar or lower levels compared with those found in other regions. Spatial distributions indicated that CP contamination levels in sediments were closely related to local human activities. The most abundant congener groups were C₁₀–C₁₁Cl_{6–7} and C₁₄Cl_{7–8}. SCCPs in the sediments probably came from the application of CP-42 and CP-52, and MCCPs may have different sources to the SCCPs. CPs with nine carbon atoms in sediment samples were quantitated for the first time. Results indicated that their occurrence should not be neglected, and the environmental behaviors of C₉ homologs need to be studied further. In addition, CPs in sediments from the middle reaches of the Yangtze River pose no significant ecological risk currently.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.09.193>.

References

- Bayen, S., Obbard, J.P., Thomas, G.O., 2006. Chlorinated paraffins: a review of analysis and environmental occurrence. *Environ. Int.* 32, 915–929.
- Chen, M.Y., Luo, X.J., Zhang, X.L., He, M.J., Chen, S.J., Mai, B.X., 2011. Chlorinated paraffins in sediments from the Pearl River Delta, South China: spatial and temporal distributions and implication for processes. *Environ. Sci. Technol.* 45, 9936–9943.
- Coelhan, M., 2010. Levels of chlorinated paraffins in water. *Clean: Soil, Air, Water* 38, 452–456.
- De Boer, J., El-Sayed Ali, T., Fiedler, H., Legler, J., Muir, D.C., Nikiforov, V.A., Tomy, G.T., Tsunemi, K., 2010. Chlorinated paraffins. In: De Boer, J. (Ed.), *The Handbook of Environmental Chemistry. Chlorinated Paraffins 10*. Springer-Verlag, Berlin/Heidelberg.
- European Commission, 2002. Directive 2000/45/EC of the European Parliament and of the Council of 25 June 2002. *Off. J. Eur. Communities* L 177/121–177/122.
- Fisk, A.T., Wiens, S.C., Webster, G.R.B., Bergman, W., Muir, D.C.G., 1998. Accumulation and depuration of sediment-sorbed C-12- and C-16-polychlorinated alkanes by oligochaetes (*Lumbriculus variegatus*). *Environ. Toxicol. Chem.* 17, 2019–2026.
- Fisk, A.T., Tomy, G.T., Cymbalisky, C.D., Muir, D.C.G., 2000. Dietary accumulation and quantitative structure-activity relationships for depuration and biotransformation of short (C-10), medium (C-14), and long (C-18) carbon-chain polychlorinated alkanes by juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* 19, 1508–1516.
- Gao, Y., Zhang, H.J., Chen, J.P., Zhang, Q., Tian, Y.Z., Qi, P.P., Yu, Z.K., 2011. Optimized clean-up method for the determination of short chain polychlorinated n-alkanes in sediments by high resolution gas chromatography/electron capture negative ion-low resolution mass spectrometry. *Anal. Chim. Acta* 703, 187–193.
- Gao, Y., Zhang, H.J., Su, F., Tian, Y.Z., Chen, J.P., 2012. Environmental occurrence and distribution of short chain chlorinated paraffins in sediments and soils from the Liaohai River Basin, P. R. China. *Environ. Sci. Technol.* 46, 3771–3778.

- Houde, M., Muir, D.C.G., Tomy, G.T., Whittle, D.M., Teixeira, C., Moore, S., 2008. Bioaccumulation and trophic magnification of short- and medium-chain chlorinated paraffins in food webs from Lake Ontario and Lake Michigan. *Environ. Sci. Technol.* 42, 3893–3899.
- Iozza, S., Muller, C.E., Schmid, P., Bogdal, C., Oehme, M., 2008. Historical profiles of chlorinated paraffins and polychlorinated biphenyls in a dated sediment core from Lake Thun (Switzerland). *Environ. Sci. Technol.* 42, 1045–1050.
- Lu, F.H., Chen, M.Y., Chen, Y.W., Liu, F.J., Luo, X.J., Mai, B.X., 2015. Distribution of chlorinated paraffins and polychlorinated biphenyls in e-waste, residues and sediment from e-waste areas of Qingyuan. *Environ. Chem.* 34, 1297–1303 (in Chinese).
- Ma, X.D., Chen, C., Zhang, H.J., Gao, Y., Wang, Z., Yao, Z.W., Chen, J.P., Chen, J.W., 2014a. Congener-specific distribution and bioaccumulation of short-chain chlorinated paraffins in sediments and bivalves of the Bohai Sea, China. *Mar. Pollut. Bull.* 79, 299–304.
- Ma, X.D., Zhang, H.J., Wang, Z., Yao, Z.W., Chen, J.W., Chen, J.P., 2014b. Bioaccumulation and trophic transfer of short chain chlorinated paraffins in a marine food web from Liaodong Bay, North China. *Environ. Sci. Technol.* 48, 5964–5971.
- Pribilova, P., Klanova, J., Holoubek, I., 2006. Screening of short- and medium-chain chlorinated paraffins in selected riverine sediments and sludge from the Czech Republic. *Environ. Pollut.* 144, 248–254.
- Reth, M., Zencak, Z., Oehme, M., 2005. New quantification procedure for the analysis of chlorinated paraffins using electron capture negative ionization mass spectrometry. *J. Chromatogr. A* 1081, 225–231.
- Reth, M., Ciric, A., Christensen, G.N., Heimstad, E.S., Oehme, M., 2006. Short- and medium-chain chlorinated paraffins in biota from the European Arctic – differences in homologue group patterns. *Sci. Total Environ.* 367, 252–260.
- Thomas, G.O., Farrar, D., Braekvelt, E., Stern, G., Kalantzi, O.I., Martin, F.L., Jones, K.C., 2006. Short and medium chain length chlorinated paraffins in UK human milk fat. *Environ. Int.* 32, 34–40.
- Tomy, G.T., Westmore, J.B., Muir, D.C.G., 1998. Environmental chemistry and toxicology of polychlorinated n-alkanes. In: Ware, G. (Ed.), *Reviews of Environmental Contamination and Toxicology* 158. Springer, New York, pp. 53–128.
- Tomy, G.T., Stern, G.A., Lockhart, W.L., Muir, D.C.G., 1999. Occurrence of C-10–C-13 polychlorinated n-alkanes in Canadian midlatitude and arctic lake sediments. *Environ. Sci. Technol.* 33, 2858–2863.
- UNEP, 2015. Risk Profile on Short-Chained Chlorinated Paraffins, UNEP/POPS/POPRC.11/10/Add.2. <http://chm.pops.int/Convention/POPsReviewCommittee/Chemicals/tabid/243/Default.aspx>.
- Wang, T., Han, S.L., Yuan, B., Zeng, L.X., Li, Y.M., Wang, Y.W., Jiang, G.B., 2012. Summer-winter concentrations and gas-particle partitioning of short chain chlorinated paraffins in the atmosphere of an urban setting. *Environ. Pollut.* 171, 38–45.
- Wang, Y., Li, J., Cheng, Z.N., Li, Q.L., Pan, X.H., Zhang, R.J., Liu, D., Luo, C.L., Liu, X., Katsoyiannis, A., Zhang, G., 2013. Short- and medium-chain chlorinated paraffins in air and soil of subtropical terrestrial environment in the pearl river delta, South China: distribution, composition, atmospheric deposition fluxes, and environmental fate. *Environ. Sci. Technol.* 47, 2679–2687.
- Wang, X.T., Wang, X.K., Zhang, Y., Chen, L., Sun, Y.F., Li, M., Wu, M.H., 2014. Short- and medium-chain chlorinated paraffins in urban soils of Shanghai: spatial distribution, homologue group patterns and ecological risk assessment. *Sci. Total Environ.* 490, 144–152.
- Warnasuriya, G.D., Elcombe, B.M., Foster, J.R., Elcombe, C.R., 2010. A mechanism for the induction of renal tumours in male Fischer 344 rats by short-chain chlorinated paraffins. *Arch. Toxicol.* 84, 233–243.
- Wyatt, I., Coutts, C.T., Elcombe, C.R., 1993. The effect of chlorinated paraffins on hepatic enzymes and thyroid-hormones. *Toxicology* 77, 81–90.
- Xia, D., Gao, L.R., Zheng, M.H., Tian, Q.C., Huang, H.T., 2016. A novel method for profiling and quantifying short- and medium-chain chlorinated paraffins in environmental samples using GC×GC-ECNI-HRTOF-MS. *Environ. Sci. Technol.* <http://dx.doi.org/10.1021/acs.est.6b01404>.
- Zeng, L.X., Wang, T., Han, W.Y., Yuan, B., Liu, Q., Wang, Y.W., Jiang, G.B., 2011a. Spatial and vertical distribution of short chain chlorinated paraffins in soils from wastewater irrigated farmlands. *Environ. Sci. Technol.* 45, 2100–2106.
- Zeng, L.X., Wang, T., Wang, P., Liu, Q., Han, S.L., Yuan, B., Zhu, N., Wang, Y.W., Jiang, G.B., 2011b. Distribution and trophic transfer of short-chain chlorinated paraffins in an aquatic ecosystem receiving effluents from a sewage treatment plant. *Environ. Sci. Technol.* 45, 5529–5535.
- Zeng, L.X., Wang, T., Ruan, T., Liu, Q., Wang, Y.W., Jiang, G.B., 2012a. Levels and distribution patterns of short chain chlorinated paraffins in sewage sludge of wastewater treatment plants in China. *Environ. Pollut.* 160, 88–94.
- Zeng, L.X., Zhao, Z.S., Li, H.J., Wang, T., Liu, Q., Xiao, K., Du, Y.G., Wang, Y.W., Jiang, G.B., 2012b. Distribution of short chain chlorinated paraffins in marine sediments of the East China Sea: influencing factors, transport and implications. *Environ. Sci. Technol.* 46, 9898–9906.
- Zeng, L.X., Chen, R., Zhao, Z.S., Wang, T., Gao, Y., Li, A., Wang, Y.W., Jiang, G.B., Sun, L.G., 2013. Spatial distributions and deposition chronology of short chain chlorinated paraffins in marine sediments across the Chinese Bohai and Yellow Seas. *Environ. Sci. Technol.* 47, 11449–11456.
- Zeng, L.X., Lam, J.C.W., Wang, Y.W., Jiang, G.B., Lam, P.K.S., 2015. Temporal trends and pattern changes of short- and medium-chain chlorinated paraffins in marine mammals from the South China Sea over the past decade. *Environ. Sci. Technol.* 49, 11348–11355.
- Zhao, Z.S., Li, H.J., Wang, Y.W., Li, G.L., Gao, Y.L., Zeng, L.X., Lan, J., Wang, T., Jiang, G.B., 2013. Source and migration of short-chain chlorinated paraffins in the coastal East China Sea using multiproxies of marine organic geochemistry. *Environ. Sci. Technol.* 47, 5013–5022.