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The quantification of chlorinated paraffins in environmental samples by ultra-high-performance liquid chromatography coupled with Orbitrap Fusion Tribrid mass spectrometry

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ABSTRACT

As high-production-volume chemicals, chlorinated paraffins (CPs) have raised an increasing environmental concern in recent years. However, their accurate analysis and quantification is still a huge challenge due to the high complexity of their technical formulations and the interference from CPs congeners and other polychlorinated products. In this study, a novel method for the simultaneous analysis of short-chain (SC) and medium-chain (MC) CPs in a single injection has been developed using ultra-high-performance liquid chromatography coupled with Orbitrap Fusion Tribrid mass spectrometry (UHPLC-Orbitrap Fusion TMS). Compared with other analytical methods for CPs, this novel method can greatly shorten the measurement time and provides a lower limit of detection. A high resolution of 120,000 FWHM was set to avoid the self-interference of CPs congeners and to eliminate interferences from chlorinated olefins (COs). Accuracies for SCCPs and MCCPs standards were evaluated at 75–103% and 83–118%, respectively. The developed method was further validated by determining CPs in sediment, soil, and indoor dust samples. This novel method gives higher CPs concentrations than those achieved by gas chromatography-electron capture negative ionization low-resolution mass spectrometry (GC-ECNI-LRMS), with factors of 1.1–12.5 for SCCPs and 0.7–2.7 for MCCPs, respectively. Some new CPs, such as C_8Cl_{7-8} and C_9Cl_{5-8}, have been determined in soil samples for the first time, indicating great potential of this novel method for routine CP analysis in various environmental samples.

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1. Introduction

Chlorinated paraffins (CPs) are highly complex halogenated mixtures formed by the direct free radical chlorination of *n*-alkane feedstocks with molecular chlorine. According to their carbon chain length, technical CPs formulations are generally classified as short-chain (C_{10}–C_{13}, SCCPs), medium-chain (C_{14}–C_{17}, MCCPs), and long-chain (C_{20}–C_{30}, LCCPs) [1–3]. CPs is mainly used as additives in cutting oils, lubricants, and flame retardants, and as plasticizers in rubbers, plastics, paints, coatings, sealants, and adhesives [4]. Since the 1970s, the global production of CPs has increased significantly, and exceeded 1 million tons per year by the end of 2013 [5]. Dur-

ing the past decades, CPs have raised an increasing environmental concern due to their ubiquitous detection in various environmental matrices, including water, sediment, soil, air, dust, biota [4], and even human breast milk [6] and blood [7]. SCCPs have been listed in Annex A as a new group of POPs in May 2017 [8]. This global regulation underpin a commitment to phase out the production of SCCPs and to shift towards the use of MCCPs. Considering the facts that MCCPs are similar to SCCPs in terms of physicochemical properties, coexist in the environment, and MCCPs can be transformed into SCCPs through environmental processes such as combustion, equal or even more attention should be paid to the analysis of MCCPs as compared to that of SCCPs in further study [2,8,9].

However, the quantification of CPs in environmental samples is still an extremely challenging task because of the high degree of complexity of industrial mixtures, and self-interference among the individual CP congeners and between CPs and their polychlo-

rinated transformation compounds, such as chlorinated olefins (COs) [4,9,10]. To date, a number of methods have been developed for the determination of SCCPs and MCCPs in a variety of environmental matrices. In general, the most commonly used method is gas chromatography coupled with electron capture negative ionization low-resolution quadrupole mass spectrometry (GC-ECNI-LRMS), because it can provide information regarding the chain length and degree of chlorination of CPs [3,11–13]. Nevertheless, GC-ECNI-LRMS has always suffered from an overestimation of total CP concentrations, due to mass overlaps of some ions with very similar exact masses, such as $C_{11}H_{15}{}^{35}Cl_6{}^{37}Cl_2$ (m/z 396.9) and $C_{16}H_{27}{}^{35}Cl_5{}^{37}Cl$ (m/z 397.1). To address this problem, several researchers have begun to utilize time-of-flight high-resolution mass spectrometry (TOF-HRMS) to eliminate matrix interferences and to significantly improve selectivity, and have thereby succeeded in simultaneously profiling and quantifying SCCPs and MCCPs [7,9,14,15]. Unfortunately, even if TOF-HRMS has a high resolution of 10,000–15,000, this is still not enough to separate interfering ions of the same nominal masses of CPs and chlorinated olefins (COs). The latter are potential CP transformation products that may be formed in used metal-working fluid and atmospheric samples. They have similar carbon chain lengths and degrees of chlorination as CPs, and hence their peaks strongly overlap with those of CPs in mass spectra [10,16]. For example, the required resolving power for separating CPs ($C_{11}H_{16}Cl_8$–Cl, $[{}^{12}C_{11}{}^1H_{16}{}^{35}Cl_6{}^{37}Cl_1]^-$, m/z 394.9048 amu) from COs ($C_{11}H_{14}Cl_8$–Cl$^-$, $[{}^{12}C_{11}{}^1H_{14}{}^{35}Cl_5{}^{37}Cl_2]^-$, m/z 394.8862 amu) is at least 21,230.

In recent years, Orbitrap high-resolution mass spectrometry (HRMS) in full-scan acquisition mode has been increasingly applied to analyze drugs and metabolites [17,18] and other environmental contaminants (tetrabromobisphenol-S derivatives, perfluorinated and polyfluorinated compounds, organophosphate flame retardants etc.) [19–23]. Compared to TOF-HRMS, Orbitrap HRMS can provide even higher specificity and sensitivity, with a reliable high resolution of up to 450,000 FWHM at m/z 200 [19]. Although application of Orbitrap HRMS coupled with GC has been reported for the identification and quantification of CPs in a recent study [24], it is more generally coupled with reversed-phase high-performance liquid chromatography (RP-HPLC) [17,19,22], because the latter greatly reduces interferences and thus offers enhanced analytical sensitivity [7]. Recently, Schinkel et al. provided an analytical guide for dealing with the severe mass interferences of CPs and their transformation products [25]. To the best of our knowledge, there have been no further efforts to analyze CPs by means of HPLC combined with Orbitrap HRMS.

The objective of this study was to develop a novel analytical method for the determination of SCCPs and MCCPs, based on ultra-high-performance liquid chromatography coupled with negative-ion electrospray ionization Orbitrap Fusion Tribrid mass spectrometry (UHPLC-Orbitrap Fusion TMS). With this novel analytical procedure, 48 different CPs congeners ($C_{10–17}Cl_{5–10}$) could be simultaneously determined in a single injection by extracting accurate masses at a resolution of 120,000 FWHM. The method also proved suitable for eliminating the interferences from COs and for screening CPs with carbon chain lengths shorter than C_{10} in environmental matrices. Finally, the method was successfully applied to analyze CPs in sediment, soil, and indoor dust samples.

2. Experimental

2.1. Standards, materials, and reagents

SCCP standards (51.5%, 55.5%, and 63% chlorine contents, 100 ng μL^{-1} in cyclohexane) and MCCP standards (42%, 52%, and 57%

chlorine contents, 100 ng μL^{-1} in cyclohexane) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). As a recovery standard, $^{13}C_{12}$-labeled α- Hexbromocyclododecane (HBCD) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

All solvents used in extraction and analytical procedures were HPLC grade. Hexane, methanol, and acetonitrile were obtained from Merck (Darmstadt, Germany). Dichloromethane was purchased from CNW Technologies GmbH (Düsseldorf, Germany). Deionized water (18.2 MΩ·cm) was produced by an FBZ2002-UP-P water purification system (FlOM, Qingdao, China). Silica gel (70–230 mesh) was purchased from Merck (Darmstadt, Germany) and florisil (60–100 mesh) was purchased from CNW Technologies GmbH (Düsseldorf, Germany). Prior to use, neutral silica gel (70–230 mesh) and alumina (100–200 mesh) were soxhlet extracted with methanol and dichloromethane, respectively, for 48 h. Sodium sulfate was baked at 450 °C for 4 h and stored in a sealed desiccator.

2.2. Sample collection, extraction, and clean-up procedures

Four sediment samples (SD1–SD4) and three topsoil samples (SO1–SO3) were collected in Dongguan, Guangdong province, in September 2011. Four indoor dust samples (ID1–ID4) were collected in Wuhan, Hubei province, in 2013 (Detail sampling information please see the supplementary materials). Portions of 10 g of sediment/soil samples (dry weight) or 0.25 g of indoor dust samples were spiked with the recovery standard and soxhlet extracted with 200 mL of dichloromethane for 72 h. After concentration to around 1 mL, the extracts were subjected to clean-up according to a previously described procedure [26], with minor modification. Briefly, the extracts was first fractioned on a multilayer silica/alumina column (i.d. 1 cm) that had been wet-loaded sequentially with 6 cm of neutral silica gel (130 °C), 10 cm of acidic silica gel (44% concentrated sulfuric acid, 130 °C), 1 cm of neutral alumina (3% H_2O, 250 °C), and 2 cm of anhydrous Na_2SO_4, from bottom to top. Two fractions were collected from the column; the first consisted of 20 mL hexane (discharged), and the second was eluted with hexane: dichloromethane (1:1, v/v; 70 mL) and then concentrated to 1 mL.

The concentrated eluate was subjected to clean-up on a multilayer silica/florisil column (i.d. 1 cm) that was packed with 6 cm of florisil (550 °C), 6 cm of neutral silica gel (550 °C), 10 cm of acidic silica gel (30% concentrated sulfuric acid, 550 °C), and 2 cm of anhydrous Na_2SO_4, from bottom to top. Hexane (50 mL) and hexane: dichloromethane (1:1, v/v; 70 mL) were used to elute successive fractions, and the second fraction was concentrated to near dryness under a gentle nitrogen stream and redissolved in methanol (400 μL).

2.3. Instrumental analysis

Chromatographic separations were performed on a Thermo Ultimate 3000 UHPLC system equipped with a UHPLC reversed-phase column (Hypersil Gold, 1.9 μm particle diameter, 2.1 × 100 mm, Thermo Scientific) interfaced with an Orbitrap Fusion™ Tribrid™ mass spectrometer (Orbitrap Fusion TMS, Thermo Fisher Scientific, USA). The injection volume was 1 μL. Gradients of (A) water (pH adjusted to 4.8–5 with 0.02% acetic acid and 5 mmol ammonium acetate), (B) methanol, and (C) acetonitrile at a flow rate of 300 μL·min^{-1} (DGP3600 pump, Thermo Scientific) were used to analyze samples. The initial conditions were 70% B and 30% A from 0 to 1 min, linear gradient to 100% B from 1 to 5 min, maintained at 100% B from 5 to 8.5 min, linear decrease to 50% B and 50% C from 8.5 to 9 min, maintained for 5 min, followed by a
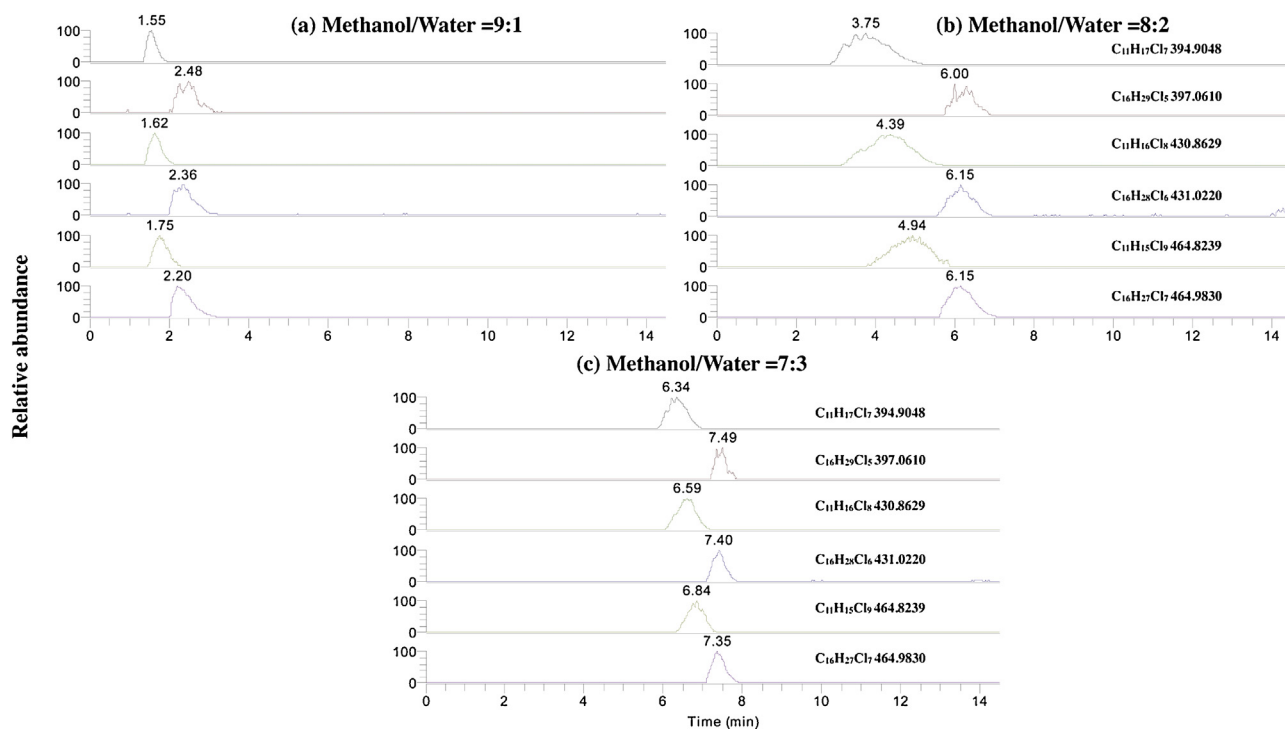
Fig. 1. UHPLC-Orbitrap Fusion TMS chromatograms of CPs congener using different mobile phases: (a) methanol/water (9:1), (b) methanol /water (8:2), (c) methanol/water (7:3).

return to the initial composition over 3 min and kept for 8 min (see Table S1). Electrospray ionization (ESI) was used as the ionization method and operated in negative-ion mode. The most abundant m/z signals of $[M–H]^-$ of CPs and $^{13}C_{12}$-labeled α-HBCD were used for quantification with 5 ppm mass tolerance. The optimized parameters used for the mass spectrometer were as follows: spray voltage, 3900 V; ion transfer tube temperature, 275 °C; vaporizer temperature, 300 °C; sheath gas flow rate, 25 respective arbitrary units; auxiliary gas flow rate, 5 respective arbitrary units; no sweep gas; detector type, Orbitrap; MS resolution, 120,000 FWHM; MS scan range, 200–700 m/z; MS maximum injection time, 100 ms; MS automated gain control (AGC) target, 2.0×10^5; S-lens RF level, 60 V.

3. Results and discussion

3.1. Chromatographic separation of CPs

Due to the matrix effects could severely affect the peak shapes and sensitivities of CPs [7], it is necessary to use a chromatographic column with a gradient mobile phase to separate the matrix from CPs. In this study, we performed preliminary tests to investigate the effect of organic solvents on the retention times of CPs, and the results showed that pure organic solvents (acetonitrile, methanol, or mixtures thereof) have poor retention capacities for CPs; the retention times of all CP congeners are less than 1.5 min. Compared to methanol, acetonitrile tends to suppress the sensitivity of CPs with lower chlorine contents, especially for Cl_5 congeners, therefore methanol and water were chosen for the final mobile phase. Fig. 1 illustrates how the initial mobile phase affects the retention times and peak widths of CPs. For initial mobile phases of methanol/water, as the ratio thereof was varied from 9:1 to 7:3 (Fig. 1), the retention time increased. According to these observations, we established a gradient mobile phase (listed in the Experimental Section) based on methanol, water, and acetonitrile. The aim of adding acetonitrile after the elution of CPs was to better

remove the nonpolar matrix and other pollutants remaining in the column, thus ensuring cleanliness of the column. Meanwhile, 0.02% acetic acid and 5 mM ammonium acetate as mobile phase modifiers were added to provide the maximum signal response of CPs in the method development.

3.2. Relative total response factors (RFs), instrumental detection limits (IDLs), and linear range of CP standards

Table 1 lists the instrumental responses towards different CP congeners. As can be seen, the response sensitivities of the UHPLC-Orbitrap Fusion TMS method for both SCCPs and MCCPs increased with increasing chlorine content (Table 1). The relative response factors (RFs) for SCCPs ranged from 1.0 to 3.6 as the chlorine content increased from 51.5% to 63%, comparable to those obtained by the UPLC-QTOF-MS method [7], but much lower than those obtained by the APCI-qTOF-HRMS method (1–50 between 49% Cl and 70% Cl) [14]. The RFs for MCCPs obtained by the UHPLC-Orbitrap Fusion TMS method were between 0.5 and 1.8 for 42% Cl, 52% Cl, and 57% Cl, markedly lower than those obtained by the UPLC-QTOF-MS method [7]. Evidently, the sensitivity for SCCPs and MCCPs is less dependent on the Cl content by the UHPLC-Orbitrap Fusion TMS method.

The instrumental detection limits (IDLs) for SCCPs and MCCPs by the UHPLC-Orbitrap Fusion TMS method were in the ranges 3–27 ng/mL and 4–31 ng/mL, respectively (Table 1), both decreasing with increasing Cl contents. Compared with previous studies, the IDLs for SCCPs and MCCPs obtained in this study are significantly lower than those reported for a GC-ECNI-LRMS method (1000 ng/mL and 500–1000 ng/mL, respectively) [27] and an APCI-qTOF-HRMS method (100–1200 ng/mL and 80–200 ng/mL, respectively) [14]. They are also lower than those obtained by UPLC-ESI-QTOF-MS (70–200 ng/mL and 20–100 ng/mL, respectively) [7], NCI-TOF-HRMS (24–81 ng/mL and 27–170 ng/mL, respectively) [9], and GC × GC-HRTOF-MS methods (20 ng/mL and 100 ng/mL, respectively) [15]. The linearity ranges of mixed standard solutions of SCCPs and MCCPs in this study are 0.1–25 ng/μL (0.1, 0.25,

Table 1
The calculated chlorine content, instrumental detection limit (IDL, pg/μL), linear range (ng/μL), relative total response factor (RF) based on the total response of SCCPs 51.5%Cl (measured five times) of UHPLC-Orbitrap Fusion TMS.

CPs technical mixtures	calculated chlorine content	IDL	Linearity range	RF
SCCPs (51.5%Cl)	57.5 ± 0.01%	27	0.1–25	1.0
SCCPs (55.5%Cl)	59.4 ± 0.00%	10	0.1–25	1.7
SCCPs (63%Cl)	64.0 ± 0.01%	3	0.1–25	3.6
MCCPs (42%Cl)	51.4 ± 0.00%	31	0.1–12.5	0.5
MCCPs (52%Cl)	55.5 ± 0.00%	11	0.1–12.5	1.4
MCCPs (57%Cl)	58.2 ± 0.00%	4	0.1–12.5	1.8

0.5, 1.0, 2.5, 5.0, 12.5, and 25) and 0.1–12.5 ng/μL (0.1, 0.25, 0.5, 1.0, 2.5, 5.0, and 12.5), respectively (Table 1 and Fig. S1), narrower than those reported for APCI-qTOF-HRMS [14] and NCI-qTOF-MS methods [9]. Given that Orbitrap Fusion-TMS mainly serves as a screening tool [19,21], the results met our expectation.

3.3. Quantification of technical CPs and elimination of interference from COs

Quantification of CPs remains a challenging task due to interference from different CP congeners and other polychlorinated pollutants (such as polychlorinated biphenyls, organochlorine pesticides, and toxaphene) in their analysis [15]. In this study, our preliminary tests indicated that most polychlorinated pollutants could be separated from CPs through our developed clean-up procedures. The main interference stems from self-interference between individual CP congeners and their polychlorinated transformation compounds, such as chlorinated olefins (COs). Technical CP mixtures contain thousands of congeners with the general elemental composition $C_nH_{2n+2-m}Cl_m$, and so complete separation of individual CPs has not hitherto been achieved [28]. When we applied the UHPLC system for chemical separation, individual congeners having similar molecular weights, such as C_nCl_7 and $C_{n+5}Cl_5$ or C_nCl_8 and $C_{n+5}Cl_6$ ($n = 10$–12), could be almost separated on a Hypersil Gold column using our developed mobile phase. However, for most other CP congeners, a high-resolution mass spectrum ($R > 20,000$) was still needed. In general, the ion fragments of $[M–Cl]^-$ have been used to quantify SCCPs and MCCPs in conventional GC-based methods [1,9,11,15,29], whereas under chlorine-enhanced conditions in dichloromethane, $[M+Cl]^-$ ions have been used to quantify CPs in environmental and biological samples [7,14,30,31]. For other environmental contaminants, such as HBCDs, their $[M–H]^-$ ions have usually been quantified in ESI mode [32,33]. In this study, we compared the relative responses of the three abovementioned ions in the SCCP (55.5% Cl) and MCCP (52% Cl) standards. The results showed $[M–H]^-$ to be the predominant ions, with an average resolution of 24,064 for 5 ppm mass accuracy. In addition, a resolution of 120,000 FWHM was set for Orbitrap Fusion TMS to separate and ensure the scan rate (3.6 Hz) and sensitivity of similar molecular mass $[M–H]^-$ ions generated from SCCPs and MCCPs [19].

The quantification of SCCPs and MCCPs in this study followed the principles developed by Bogdal et al. [14], and a mathematical pattern deconvolution algorithm was used to eliminate the dependence on the amount of chlorine, although less dependence on the chlorine content was seen in the quantification of SCCPs and MCCPs by UHPLC-Orbitrap Fusion TMS (See detailed description in supplementary materials). The results showed that all 48 of the SCCP and MCCP formula congeners could be simultaneously analyzed in full-scan mode in one injection. For each CP formula congener, the most abundant isotope signal was used for quantification and the second one was used for identification. All of the selected quantification and qualification ions are shown in Table S1. Next, the percentage ratio of the measured and reference concentrations of CPs was applied to evaluate the accuracy of the quantification

method. As can be seen in Table 2, the measured concentrations of SCCPs (chlorination degrees: 51.5% Cl, 55.5% Cl, and 63% Cl) and MCCPs (chlorination degrees: 42% Cl, 52% Cl, and 57% Cl) were very close to the spiked concentrations, with accuracies of 75–103% and 83–118%, respectively. Compared to the single mixture standard, binary mixture standards of SCCPs and MCCPs showed a larger positive bias when measuring MCCP concentrations. The results were consistent with those obtained by the NCI-qTOF-MS method [9], whereby this phenomenon was partially attributed to the greater amount of impurities in the SCCP standard (4.6% MCCP content) than that in the MCCP standard (1.9% SCCP content).

The congener patterns of all SCCPs and MCCPs in six mixed standards are shown in Figs. S2 and S3. For the three standard SCCP mixtures, the congeners varied with the chlorine content and were dominated by $C_{12}Cl_6$, $C_{12}Cl_7$, and $C_{12}Cl_8$; their homologue distributions were $C_{12} > C_{13} > C_{11} > C_{10}$, $C_{12} > C_{13} \approx C_{11} > C_{10}$, and $C_{12} > C_{11} > C_{13} > C_{10}$ for SCCPs with 51.5% Cl, 55.5% Cl, and 63% Cl, respectively. The predominant congeners for standard MCCPs with 42% Cl, 52% Cl, and 57% Cl were $C_{14}Cl_6$, $C_{14}Cl_7$, and $C_{14}Cl_{7-8}$, respectively; their homologue profiles were dominated by C_{14} compounds, followed by C_{15}, C_{16}, and C_{17} compounds. Compared with the results obtained by GC-ECNI-LRMS in this study, the present method gave higher abundances of longer-chain SCCP congeners (Figs. S2 and S3). Similar homologue distributions have also been obtained by APCI-qTOF-HRMS [14] and UPLC-ESI-QTOF-MS [7]. The relatively high ionization efficiencies of ESI and APCI sources for longer carbon chain SCCPs and the high signal response of the ECNI source for shorter carbon chain SCCPs were considered to be responsible for these observations [7].

Interferences from COs were difficult to eliminate by conventional methods for determining CPs, because isotopomer mass differences between CPs and corresponding COs were only 0.0186; separation of these two groups of ions requires a mass resolution of $R > 25,000$ for CP molecular weights of about 500 [16]. In the present study, this serious obstacle was overcome by setting a resolution of 120,000 FWHM for the Orbitrap Fusion TMS. As shown in Fig.S4, when $\Delta m/z = 0.25$, a very narrow mass spectrum (m/z 408.80–409.05) of CP ($C_{12}H_{19}Cl_7$, 408.9196) and CO ($C_{12}H_{17}Cl_7$, 408.9120) was taken at the rentention time of 6.54 min, and complete baseline separation for CP and CO could obtain by the Orbitrap Fusion TMS at a resolution of 120,000 FWHM with a 5 ppm mass error. In addition, we adopted the rules proposed by Li et al. for the semi-quantitative determination of COs due to a lack of CO standards, assuming that the responses of COs were similar to those of CPs with similar carbon numbers and chlorine contents (quantitative and qualitative ions for COs listed in Table S2) [16]. The ratios of COs/CPs were 1.2–10.0% and 0.7–4.9% in the SCCP and MCCP standard mixtures, repectively. Both ratios increased with increasing chlorine contents. For commercial CP products, only CP42 and CP52 have been discussed, in which the ratios were quoted as 1.3–1.5% and 1.5–4.6% for SCCOs (short-chain chlorinated olefins)/SCCPs, and 2.1–3.7% and 1.6–5.9% for MCCOs (medium-chain chlorinated olefins)/MCCPs, respectively. Furthermore, we investigated the interference of COs on CPs in eleven environmental samples (four sediment samples, three soil samples,

Table 2
The repeatability and accuracy by UHPLC-Orbitrap Fusion TMS.

Performance test	Expected con. (ng/μL)	Calculated con. ± error (ng/ μL)	Accuracy	Binary mixtures	Expected con. (ng/μL)	Calculated con. ± error (ng/ μL)	Accuracy
SCCP 51.5% Cl	5.00	3.73 ± 0.01	75%				
	10.00	10.10 ± 0.03	101%				
SCCP 55.5% Cl				SCCP 55.5% Cl and MCCP 52% Cl (1:1, v/v)	2.50	2.57 ± 0.02	103%
	5.00	4.45 ± 0.06	89%		5.00	5.05 ± 0.11	101%
	10.00	8.32 ± 0.05	83%		10.00	9.63 ± 1.06	96%
SCCP 63% Cl	5.00	4.73 ± 0.04	95%				
	10.00	9.70 ± 0.03	97%				
MCCP 42% Cl	5.00	4.15 ± 0.00	83%				
	10.00	8.73 ± 0.06	87%				
MCCP 52% Cl				SCCP 55.5% Cl and MCCP 52% Cl (1:1, v/v)	2.50	2.85 ± 0.02	114%
	5.00	5.11 ± 0.01	102%		5.00	5.92 ± 0.22	118%
	10.00	10.93 ± 0.04	109%		10.00	11.51 ± 1.52	115%
MCCP 57% Cl	5.00	4.41 ± 0.01	88%				
	10.00	9.06 ± 0.10	91%				

and four indoor dust samples), in which ratios of SCCOs/SCCPs and MCCOs/MCCPs ranged from 2.2% to 14.3% and from 2.6% to 15.1%, respectively.

3.4. Method performance and its application to environmental samples

To validation of method performance, procedural blanks were analyzed alongside the field samples, the method detection limits (MDLs) of SCCPs and MCCPs were defined as their average concentrations in the procedural blanks plus three times the standard deviation, and amounted to 5.5 and 2.8 ng/g for SCCPs and MCCPs in sediment and soil samples, and 0.22 and 0.11 μg/g for SCCPs and MCCPs in indoor dust samples, respectively. The MDL in sediment and soil samples were comparable to those of GC × GC-HRTOF-MS methods (3.7 ng/g for SCCPs and 2.1 ng/g for MCCPs) [15]. The average recoveries of SCCPs (55.5% Cl) and MCCPs (52% Cl) spiked in blank solvent (hexane) were $103.8 \pm 5.1\%$ and $96.4 \pm 2.3\%$, respectively. Matrix effects were evaluated by the percentage of calculated concentration to spiked concentration, when SCCPs (55.5% Cl) and MCCPs (52% Cl) were spiked into pre-cleaned soil, sediment, and indoor dust extracts. The percentage was $80.3 \pm 2.1\%$ for SCCPs and $82.2 \pm 6.8\%$ MCCPs, respectively. A known amount (8 ng) of $^{13}C_{12}$-labeled α-HBCD was used as a surrogate standard to check the possible loss of CPs during the extraction and pretreatment of samples, and its average recovery was $93.7 \pm 7.9\%$.

The developed method was further applied to the analysis of four sediment, three soil, and four indoor dust samples. The quantified concentrations of SCCPs and MCCPs in four sediment samples were in the ranges 24.5–209 ng/g dry weight (dw) and 104–630 ng/g dw (Table 3). These concentrations were comparable to those in sediment from northeast China (SCCPs: 53.6–289 ng/g dw) [34], but higher than those in sediment from the North Sea and Baltic Sea (SCCPs: 8–63 ng/g; MCCPs: 22–149 ng/g dw) [35]. In the three soil samples, the concentrations of SCCPs (28.9–49.4 ng/g dw) and MCCPs (49.4–110 ng/g dw) were comparable to those found in soils from Switzerland (SCCPs: 3.0–35 ng/g; MCCPs: 5.1–160 ng/g dw) [36]. For the four indoor dust samples, the concentrations of SCCPs and MCCPs were 4.2–35.6 μg/g and 6.7–57.0 μg/g, respectively; the SCCP concentrations were lower than those from Munich, Germany (9–892 μg/g), but the MCCP concentrations were at the same level as those (4–27 μg/g) reported for the same region [37].

Fig. 2 shows the mean congener group patterns of SCCPs and MCCPs in all of the examined environmental samples. For SCCPs, the congener group patterns were dominated by C_{13} compounds (44.1–58.6%), followed by C_{12} (22.4–24.5%), C_{11} (13.3–22.4%), and

C_{10} compounds (3.7–11.2%). The profiles were similar to those reported in indoor dust from northeast China [38], but different from those in sediment and soil samples from the Liaohe River Basin, China, in which C_{10} and C_{11} SCCPs were predominant [3]. In profiles of MCCPs, the C_{14} compounds (61.9–69.0%) were the most prevalent, followed by C_{15} (18.8–21.3%), C_{16} (7.6–10.6%), and C_{17} (4.7–6.9%). Similar MCCP profiles were also found in sediments [39], soils [40], and indoor dust from China [41].
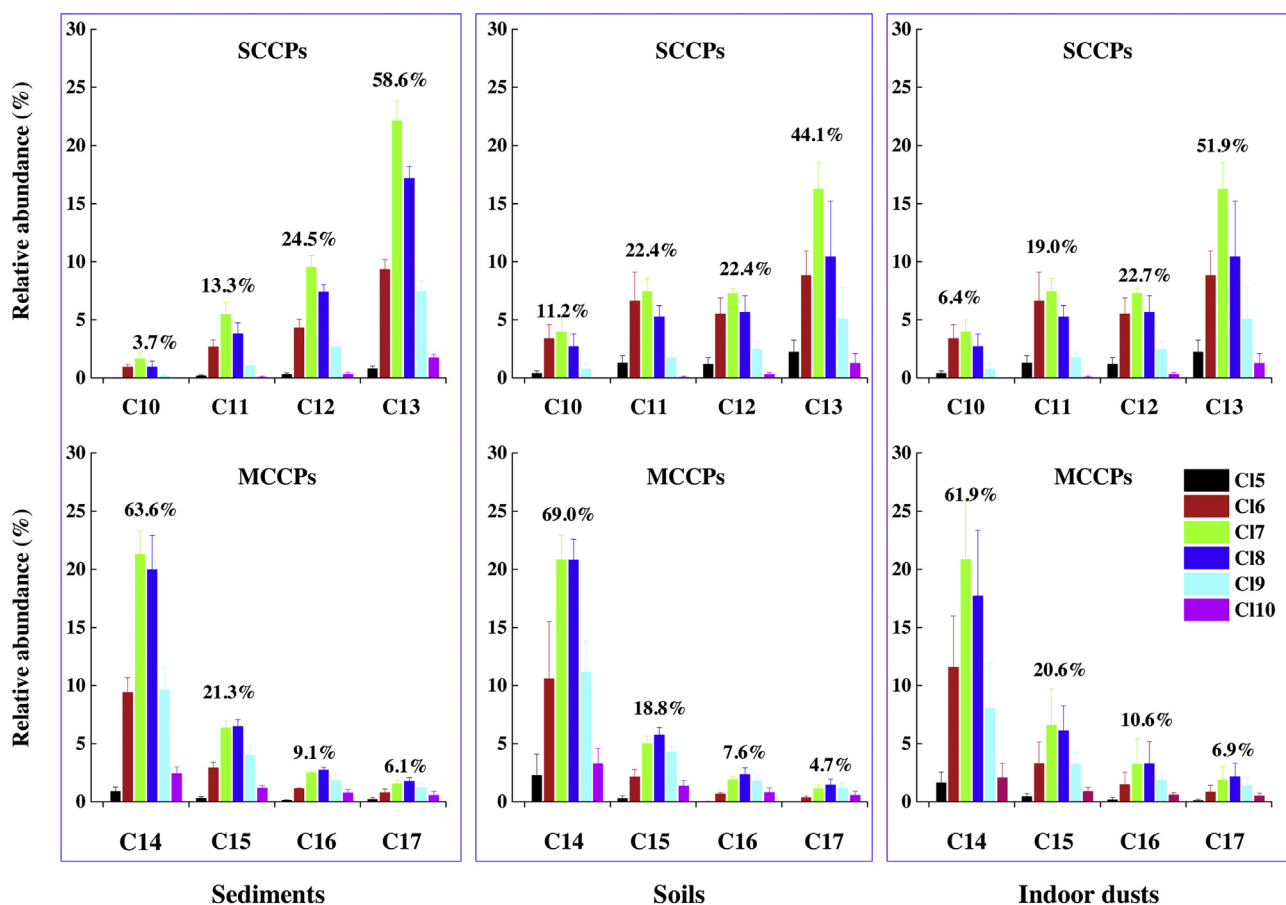
According to Bogdal et al., calculated CP concentrations are influenced by the goodness of fit (R^2) of the reconstructed CPs pattern, and $R^2 = 0.5$ would lead to discrepancy factors of 4 for SCCPs and 2 for MCCPs between the calculated and expected concentrations [14] (See detailed description in supplementary materials). In this study, R^2 values between the CP patterns in the technical mixtures and the sediment, soil, and indoor dust samples were in the ranges 0.66–0.79, 0.69–0.72, and 0.66–0.87 for SCCPs, and 0.97–0.98, 0.95–0.98, and 0.85–0.97 for MCCPs, respectively. These R^2 values for SCCPs and MCCPs would result in discrepancy factors of less than 1.5 (see Fig. S5), indicating that this novel quantification procedure was able to accurately characterize the uncertainty of the results, a great advantage in analysis of CPs in environmental samples.

3.5. Screening new CPs in environmental matrices

CPs with carbon chains shorter than C_{10} have been detected in environmental matrices, including indoor dust and sediments, and have even been found in fish samples in recent years [15,42,43]. These compounds have higher degrees of chlorination than SCCPs, MCCPs, and LCCPs, may thus be speculated as having higher toxicities [15], and therefore should be of greater concern to researchers. In this study, we screened a group of peaks with m/z 352.8582, 388.8167, 298.9518, 332.9130, 366.8745, and 402.8330 when analyzing the soil, sediment, and indoor dust samples. The retention times of these unknown ions were short and similar to those of SCCPs. After identification of the $[M–H]^-$ ion (<5 ppm), we finally characterized these compounds as $C_8H_{11}Cl_7$, $C_8H_{10}Cl_8$, $C_9H_{15}Cl_5$, $C_9H_{14}Cl_6$, $C_9H_{13}Cl_7$, and $C_9H_{12}Cl_8$, as detailed in Table S3. To the best of our knowledge, this is the first time that these CP compounds have been detected in soil samples, though they have been found in sediment and biota samples [15]. Xia et al. have summarized the possible sources of $C_9H_{14}Cl_6$ and $C_9H_{13}Cl_7$ as release from industrial CP products or generation through biotransformation or metabolism [15]. We are not aware of any further information about new CPs in industrial CP products or degradation in the environment. We then proceeded to determine 14 technical CP formulations, comprising three CP42, seven CP52, and four CP70,

Table 3
Concentrations of total SCCPs, MCCPs, the congeners and the goodness of fit (R^2) in the sediment (SD, ng/g), soil (SO, ng/g) and indoor dust (ID, μg/g).

Sample NO.	SCCPs concentration						MCCPs concentration					
	C10	C11	C12	C13	$\sum$SCCPs	R^2	C14	C15	C16	C17	$\sum$MCCPs	R^2
SD1	0.67	2.62	5.59	15.6	24.5	0.66	66.0	23.3	9.06	6.00	104	0.98
SD2	2.79	11.6	26.4	58.8	99.5	0.73	198	57.1	25.3	15.1	295	0.97
SD3	6.16	23.2	42.1	89.1	161	0.79	355	153	67.4	54.6	630	0.99
SD4	11.1	33.9	47.1	117	209	0.71	298	83.5	36.5	21.1	439	0.97
SO1	3.61	6.86	6.56	11.9	28.9	0.72	34.3	8.80	3.95	2.41	49.4	0.95
SO2	2.67	6.20	8.44	19.1	36.4	0.71	71.3	22.0	10.0	6.82	110	0.98
SO3	6.83	13.0	10.5	19.1	49.4	0.69	65.7	16.9	5.04	2.66	90.3	0.97
ID1	0.26	0.89	1.16	1.92	4.23	0.87	4.52	1.27	0.56	0.38	6.74	0.97
ID2	0.59	2.00	4.05	12.9	19.5	0.75	13.0	9.48	5.87	3.28	31.7	0.85
ID3	2.59	6.38	4.42	9.16	22.6	0.66	39.2	5.62	1.99	1.02	47.8	0.93
ID4	1.80	5.86	8.16	19.8	35.6	0.72	32.7	12.4	6.45	5.41	57.0	0.97

Fig. 2. Average congeners and homologue distribution of SCCPs and MCCPs in sediment, soil and indoor dust samples that detected by UHPLC-Orbitrap Fusion TMS.

obtained from domestic producers in China. The results showed that the proportions of SCCPs were 0.10–36.8% for CP42, 12.6–71.7% for CP52, and 0.001–0.003% for CP70, respectively. In one CP42 and one CP52 sample, we found the presence of $C_9H_{15}Cl_5$, $C_9H_{14}Cl_6$, $C_9H_{13}Cl_7$, and $C_9H_{12}Cl_8$. Considering the extensive production of CPs in China, it is possible that these compounds in soils, sediments, and indoor dust may have derived from technical CP products. More targeted research is needed to better understand the source of these compounds.

3.6. Comparison with the GC-ECNI-LRMS method

For determining the concentrations of CPs in environmental samples, we compared the UHPLC-Orbitrap Fusion TMS method with the GC-ECNI-LRMS method (Fig. 3). Except in the case of SD1

(with a factor of 12.5), the concentrations of SCCPs determined by UHPLC-Orbitrap Fusion TMS differed from those obtained by GC-ECNI-LRMS by factors of 2.3–2.6 in sediment samples. For the soil samples, differences by factors of 2.4–5.0 were observed in the concentrations of SCCPs determined by the two analytical methods. Higher SCCP concentrations in indoor dust samples were also provided by the UHPLC-Orbitrap Fusion TMS method as compared to those obtained by the GC/ECNI-LRMS method, albeit only by factors of 1.1–2.4. In a recent study by Bogdal et al., CP concentrations varied by factors of 1.5–2.8 between two urban air samples [14]. In a comparative study between NCI-qTOF-HRMS and GC-ECNI-LRMS methods, factors of 0.2–0.9 were reported for XAD-based air samples [9].

For the sediment and soil samples, the concentrations of MCCPs detected by the UHPLC-Orbitrap Fusion TMS method were higher
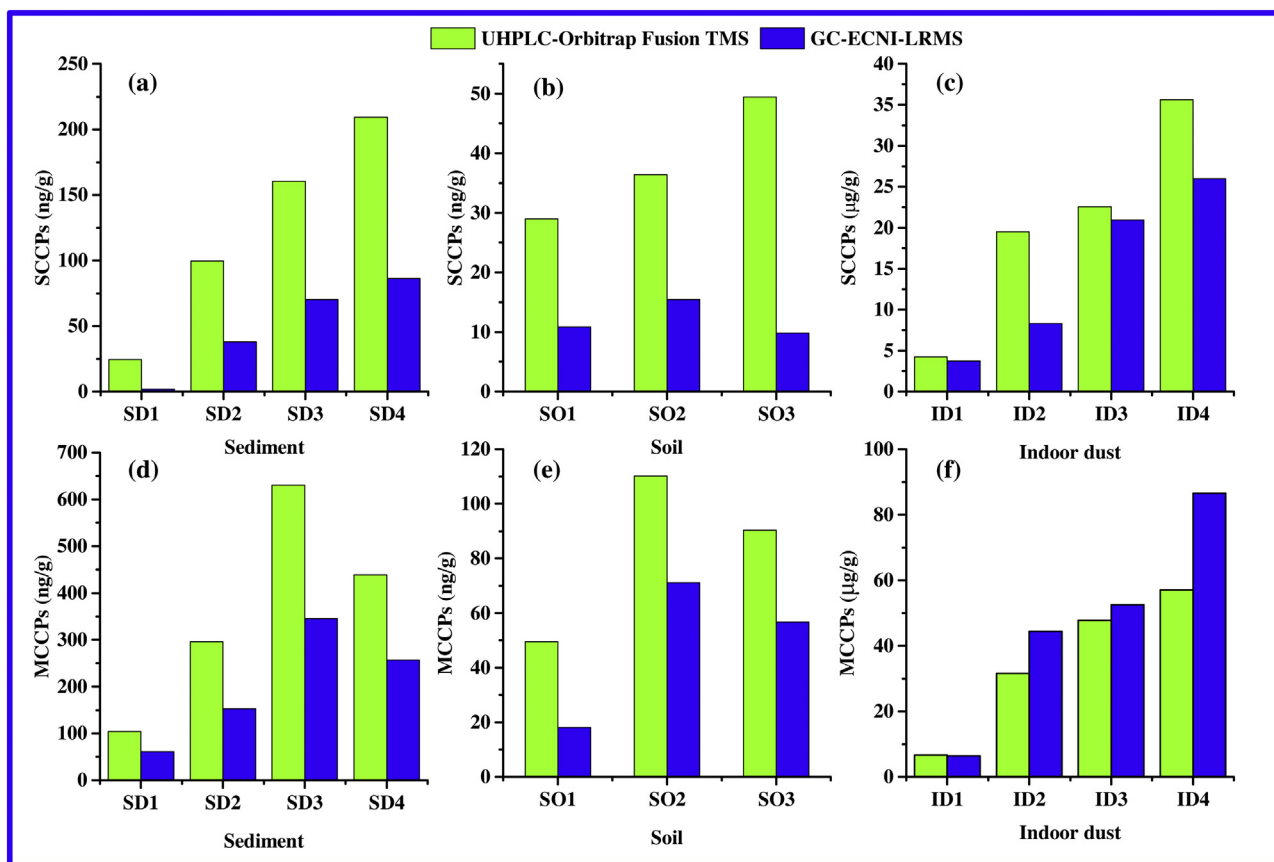
Fig. 3. Comparison of concentrations determined with the UHPLC-Orbitrap Fusion TMS method (green bars) and the GC/ECNI-LRMS method (blue bars) for (a) SCCPs in sediment samples, (b) SCCPs in soil samples, (c) SCCPs in indoor dust samples, (d) MCCPs in sediment samples, (e) MCCPs in soil samples, (f) MCCPs in indoor dust samples (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

than those obtained by the GC-ECNI-LRMS method by factors of 1.6–2.7. Differences by factors of 5.0–16 for MCCP concentrations in sewage sludges were determined by APCI-qTOF-HRMS and GC-ECNI-HRMS [14]. Notably, the MCCP concentrations determined by the UHPLC-Orbitrap Fusion TMS method in indoor dust samples (except ID1) were lower than those obtained by the GC-ECNI-LRMS method by factors of 0.7–0.9. It may be speculated that this different trend in MCCP concentrations determined by the GC-ECNI-LRMS and UHPLC-Orbitrap Fusion TMS methods in indoor dust samples was due to positive effects of the GC-ECNI-LRMS method and differences in matrix effects.

4. Conclusion

A novel sensitive method of UHPLC-Orbitrap Fusion TMS has been established for the simultaneous analysis of SCCPs and MCCPs. The entire quantification procedure was operated in full-scan mode with just a single injection. Compared to other developed analytical methods for CPs, the present method can greatly shorten the measurement time of the sample and provides a lower limit of detection. A resolution of 120,000 FWHM was set for Orbitrap Fusion TMS to overcome the obstacle of self-interference of CPs and to eliminate the interferences from COs. This novel method has been successfully applied to determine CPs in different environmental samples, and some new CPs with carbon chain length less than C_{10} have been screened in soil samples for the first time, indicating a great potential for routine analysis of CPs in various environmental samples.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.chroma.2019.01.077.

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