Supporting Information

Quantification of Short-Chain Chlorinated Paraffins by Deuterodechlorination Combined with Gas Chromatography–Mass Spectrometry

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The Supporting Information contains 26 pages, and includes 8 Figures and 12 Tables.

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1. Chemicals and reagents.

Three kinds of SCCP mixture stock standard solutions ($C_{10–13}$; 51% Cl, 55.5% Cl and 63% Cl; 100 ng/μL in cyclohexane) together with four kinds of SCCP homologue stock standard solutions (C_{10}-CPs, 60.09% Cl; C_{11}-CPs, 55.2% Cl; C_{12}-CPs, 65.08% Cl; C_{13}-CPs, 65.18% Cl; 10 ng/μL in cyclohexane) were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). $^{13}C_6$-α-hexachlorocyclohexane ($^{3}C_6$-α-HCH) and $^{13}C_6$-hexachlorobenzene ($^{13}C_6$-HCB) were all purchased from Cambridge Isotope Laboratories (CIL, Andover, USA). Phenanthrene (purity 99%) was obtained from Merck (Darmstadt, Germany). Dichloromethane (DCM) and *n*-hexane of pesticide residue grade were purchased from J. T. Baker (Phillipsburg, USA). Nonane (purity >99.0% GC grade) was purchased from Fluka (Munich, Germany). Ethylene glycol diethyl ether (EGDE, Aladdin, Shanghai, China) was used as the solvent for the reduction of SCCPs with $LiAlD_4$ (Sigma-Aldrich, St. Louis, USA). Three commercial CP mixtures (CP-42, CP52 and CP-70) with chlorine contents of approximately 42%, 52% and 70% were obtained from a CP manufacturer in the northeast of China. Anhydrous Na_2SO_4 (Damao, China) was cleaned with *n*-hexane in an ultrasonic bath for 30 min and was dried at 300 °C for 2 h. Silica gel (63–100 μm) and basic alumina (Activity Super I, 63–200 μm, pH = 10) for column chromatography were purchased from Sunchrom (Friedrichshafen, Germany) and MP Biomedicals (Eschwege, Germany), respectively. Prior to use, the silica gel basic alumina were extracted with DCM by accelerated solvent extraction (ASE 350, Dionex, USA) at the temperature of 120 °C for three cycles, and then activated at 130 °C for 10 h. Acid silica gel was prepared by mixing 200 g activated silica gel and 56.4 g concentrated sulfuric acid, and stored in desiccator.

2. Synthesis of the calibration standards for method development

Table S1. Information on the synthetic SCCP calibration standards.

No.	Category	Carbon-chain length	Chlorine content (%)	Reaction time (min)
1	calibration standard	straight-chain C_{10}	41.1	60
2	calibration standard	straight-chain C_{10}	49.3	90
3	calibration standard	straight-chain C_{10}	57.8	120
4	calibration standard	straight-chain C_{10}	62.6	240

5	calibration standard	straight-chain C_{10}	66.2	480
6	calibration standard	straight-chain C_{11}	44.8	60
7	calibration standard	straight-chain C_{11}	51.0	70
8	calibration standard	straight-chain C_{11}	57.7	120
9	calibration standard	straight-chain C_{11}	59.8	240
10	calibration standard	straight-chain C_{11}	67.7	480
11	calibration standard	straight-chain C_{12}	45.6	60
12	calibration standard	straight-chain C_{12}	52.2	90
13	calibration standard	straight-chain C_{12}	59.7	120
14	calibration standard	straight-chain C_{12}	63.1	300
15	calibration standard	straight-chain C_{12}	66.4	480
16	calibration standard	straight-chain C_{13}	44.0	55
17	calibration standard	straight-chain C_{13}	55	90
18	calibration standard	straight-chain C_{13}	59.9	120
19	calibration standard	straight-chain C_{13}	65.4	300
20	calibration standard	straight-chain C_{13}	69.6	480
21	internal standard	branched-chain C_{10}	58.7	240
22	internal standard	branched-chain C_{12}	55.4	240

The chlorine content of the prepared SCCP calibration standards were calculated by the weight difference between the substrate alkane and the generated chlorinated alkane. The loss of stating materials or by-products could occur during the synthesis procedure. Therefore, we also determined the total chlorine of the synthetic SCCPs by oxygen flask combustion combined with ionic chromatogram.[1] In brief, 20 mg of the synthetic SCCPs was weighed on an ash-free filter. The filter was folded and fixed with a platinum wire. A flask containing 10 mL of deionized water was fed with oxygen for 1 min. Fire the filter and insert it in the flask immediately. The flask was then upended avoiding gas in the flask escaping. After the flame went out, deionized water was added as absorption liquid. A mixed solution containing

Na_2CO_3 and $NaHCO_3$ was used as eluent on an anion separation column. We determined four SCCP standards with chlorine contents ranging from 41.1–67.7%, and found that there are only small differences (0.5–1%) between chlorine contents determined by ionic chromatogram and those calculated from the weight loss. Therefore, the chlorine contents calculated from the weight differences were adopted in this manuscript for consistency.

3. Sample collection and pretreatment.

Three commercial CP mixtures (CP-42, CP-52 and CP-70) with labelled chlorine contents of 42%, 52% and 70% were obtained from a CP manufacturer in the northeast of China. Sediment and biological samples were all collected from the Liaohe River Basin. The collected samples were put into the precleaned self-sealing bags, and transported with ice to laboratory. Samples were freeze-dried, ground, homogenized and stored in amber glass bottles at –20 ^{o}C until analysis. Approximate 20 g of sediment sample were Soxhlet extracted with 250 mL of hexane /acetone (1:1, v/v) for 24 h. For biological samples, about 1.5 g of sample was homogenized with 2 g of anhydrous Na_2SO_4, and Soxhlet extracted as above. Prior to extraction, 5 μL of extraction internal standard (branched C_{10}-CPs with the concentration of 1 μg/μL nonane) was spiked into the sample. The extract was concentrated to about 2 mL using an evaporator, and then pretreated by gel permeation chromatography (GPC) for the removal of lipids and toxaphene.[2] DCM was used as the mobile phase at a flow rate of 5 mL/min. Silica gel column and subsequent basic alumina column were used for the further cleanup. Fractionation on silica gel column, packing with 5 g of anhydrous Na_2SO_4, 2 g of silica gel, 4.5 g of acid silica gel and 6 g of anhydrous Na_2SO_4 from bottom to top, was conducted with the solvent sequence: 50 mL of hexane, 100 mL of hexane/DCM (1:1) and 50 mL of hexane/DCM (1:2). The second and third fractions containing SCCPs were collected. A further fractionation was carried out on alumina column, packing with 5 g of anhydrous

Na_2SO_4, 5 g of alumina and 6 g of anhydrous Na_2SO_4 from bottom to top, with 60 mL of hexane and 90 mL of DCM. The DCM fraction containing all SCCPs was collected, concentrated to about 1 mL using an evaporator, and transferred to a micro-reaction vial. 5 μL of the reaction internal standard (branched C_{12}-CPs with the concentration of 1 μg/μL nonane) was spiked into the micro-reaction vial, and then concentrated to near dryness by a gentle stream of N_2.

4. Instrumental analysis.

In order to develop and validate the deuterodechlorination combined with HRGC–EI/HRMS method for SCCP analysis, SCCPs in some samples were also analyzed by the traditional HRGC–ECNI/LRMS method, carbon skeleton reaction GC with flame ionisation detection (FID) method and the deuterodechlorination combined with HRGC–EI/LRMS method. The detailed conditions for instrumental analysis are shown as follows.

(1) <u>HRGC–ECNI/LRMS method</u>[3]

The chromatographic separation of SCCPs was performed on a Trace GC Ultra gas chromatograph (Thermo, USA) equipped with a capillary DB-5 column (15 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific, USA). A sample volume of 1 μL was injected in the splitless mode with an injector temperature of 260 °C. Helium was used as the carrier gas at a flow rate of 0.8 mL/min. The oven temperature program was as follows: 100 °C, isothermal for 1 min, then 7 °C/min to 260 °C, and then isothermal for 8 min. A Trace DSQ II mass spectrometer (Thermo, USA) in ECNI mode was used to identify SCCPs with methane (99.995% purity) as reagent gas at a flow rate of 2 mL/min. The electron energy was 70 eV, and the emission current was 100 μA. The ion source and transfer line temperatures were kept at 150 °C and 260 °C, respectively. The two most abundant isotopes of the

$[M-HCl]^{\bullet-}$ cluster for each SCCP congener (5–10 chlorine atoms) were monitored. The dwell time in the selected ion monitoring (SIM) mode was set to 75 ms for each ion.

The quantification of SCCPs by ECNI/LRMS followed the procedure described by Reth *et al.*[4], using linear correlation between the total response factors and chlorine contents.

(2) <u>Carbon skeleton reaction with GC/FID method</u>

A Hewlett-Packard GC (HP 5890 Series II) equipped with a capillary DB-5 column (30 m × 0.32 mm i.d. × 0.25 µm film thickness, J&W Scientific, USA) and FID detector was used. The Pd catalyst was prepared and installed in the GC injector as described in Koh *et al.*[5] Temperature program was as followed: maintain an initial oven temperature of 50 °C for 3 min, rise to 280 °C at the rate of 10 °C/min, and keep 14 min. The temperatures of the detector and injector were 280 and 300 °C, respectively.

(3) <u>HRGC–EI/LRMS method</u>

Trace GC Ultra gas chromatograph (Thermo, USA) equipped with a capillary DB-5 column (60 m × 0.25 mm i.d. × 0.25 µm film thickness, J&W Scientific, USA). A sample volume of 1 µL was injected in the splitless mode with an injector temperature of 260 °C. Helium was used as the carrier gas at a flow rate of 0.8 mL/min. The oven temperature program was as follows: 50 °C, isothermal for 0.5 min, then 20 °C/min to 80 °C, keeping 8 min, then 5 °C/min to 280 °C, and final isothermal for 20 min. The electron energy was 70 eV, and the emission current was 100 µA. The ion source and transfer line temperatures were kept at 220 °C and 260 °C, respectively. The most abundant isotopes of the molecular ions $[M]^-$ (Table S2) for each deuterated *n*-alkane were monitored in selected ion monitoring (SIM) mode.

Table S2. The m/z values of the molecular ions $[M]^+$ for the deuterated alkanes generated from the deuterodechlorination of SCCPs.

Number of D	m/z values

atoms	deuterated decane	deuterated undecane	deuterated dodecane	deuterated tridecane
13	155.2538	169.2694	183.2851	197.3007
12	154.2475	168.2631	182.2788	196.2944
11	153.2412	167.2568	181.2725	195.2881
10	152.2349	166.2506	180.2662	194.2819
9	151.2286	165.2443	179.2599	193.2756
8	150.2224	164.2380	178.2537	192.2693
7	149.2161	163.2317	177.2474	191.2630
6	148.2098	162.2255	176.2411	190.2568
5	147.2035	161.2192	175.2348	189.2505
4	146.1973	160.2129	174.2286	188.2442
3	145.1910	159.2066	173.2223	187.2379
2	144.1847	158.2004	172.2160	186.2317
1	143.1784	157.1941	171.2097	185.2254

5. Condition optimization for the deuterodechlorination reaction of SCCPs.

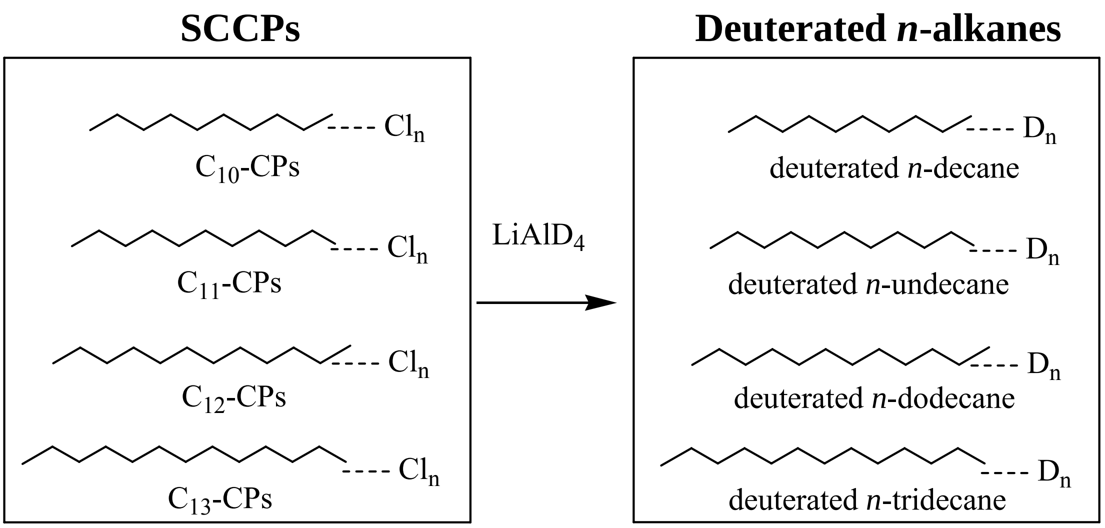

Figure S1. Reduction of SCCPs with $LiAlD_4$. C_{10}-CPs, C_{11}-CPs, C_{12}-CPs, and C_{13}-CPs represent the four groups of SCCP homologues with chlorine atom substitution (n) from 1 to 13. The generated corresponding deuterated *n*-alkanes consist of deuterated *n*-decane (C_{10}), deuterated *n*-undecane (C_{11}), deuterated *n*-dodecane (C_{12}), deuterated *n*-tridecane (C_{13}). D_n represent the deuterium atom number from 1 to 13.

Table S3. Deuterodechlorination rate and calculated chlorine content of SCCPs in the mixture standard with chlorine content of 51% under different reaction conditions.

Entry	Reaction temperature (^{o}C)	Reaction time (h)	Deuterodechlorination rate (%)	Calculated chlorine content (%)
1	110	4	10.7	49.6
2	110	15	9.5	49
3	110	72	18.1	50.3
4	90	4	5.9	48.1
5	90	13	11.3	50.2
6	90	25	37.9	50.4
7	90	48	36.6	50.2
8	90	54	50.2	50.8
9	90	96	56.4	50

Table S4. Deuterodechlorination rate and calculated chlorine content of SCCPs in the mixture standard with chlorine content of 63% under different reaction conditions.

Entry	Reaction temperature (^{o}C)	Reaction time (h)	Deuterodechlorination rate (%)	Calculated chlorine content (%)
1	110	4	17.3	61.5
2	110	15	7.1	58.9
3	110	25	14.4	61
4	110	72	15.4	61.8
5	90	4	15	57.5
6	90	13	9.9	59.1
7	90	25	13.5	59
8	90	48	24.5	61
9	90	54	43.6	60.1
10	90	96	48	60.6

6. Generation of deuterated *n*-alkenes and low-chlorinated deuterated *n*-alkanes during the deuterodechlorination reaction of SCCPs with $LiAlD_4$.

During the deuterodechlorination reaction of SCCPs with $LiAlD_4$, deuterated *n*-alkenes were generated (Figure S2), suggesting chlorine elimination also occurred. With chlorinated *n*-alkanes manufactured by free-radical chlorination of *n*-alkane feedstocks,[6] chlorine for hydrogen substitution at a secondary carbon atom was discriminated against although low positional selectivity[7]. However, vicinal chlorines must be present as the chlorine contents increase, which is apt to yield olefinic bonds during the reaction. In Figure S2, 1,2,5,6,9,10-hexachlorodecane was used to react with $LiAlD_4$ at 110 ^oC for 4 h. It was indicated that olefinic bonds ($C_{10}H_{16}D_4$) had been generated. The relative abundance of the deuterated *n*-alkenes decreased with the decreasing of the reaction temperature.

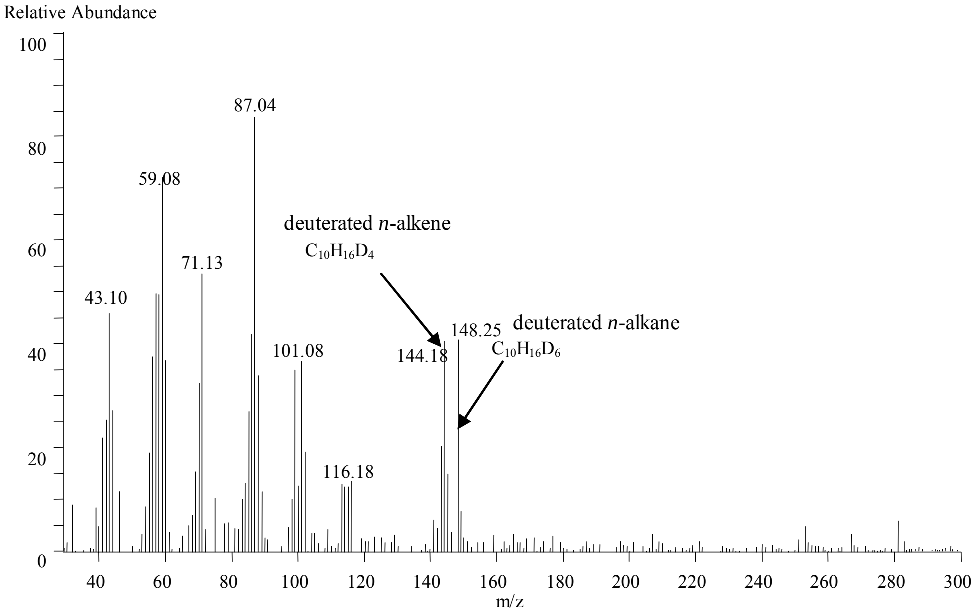

Figure S2 Mass spectra of the products from the deuterodechlorination of 1,2,5,6,9,10-hexachlorodecane with $LiAlD_4$ at 110 ^oC for 4 h.

Meanwhile, a small quantity of low chlorinated deuterated *n*-alkanes can be also generated during the deuterodechlorination reaction. Figure S3 showed the HRGC–EI/LRMS chromatogram of the products from 1,2,9,10-tetrachlorodecane reacted with $LiAlD_4$ at 60 ^oC for 72 h. Monochloro-, dichloro- and trichloro- decanes were detected out.

To increase the yielding efficiencies of deuterated *n*-alkanes and depress the other products, deuterodechlorination conditions for SCCPs have been optimized as described above.

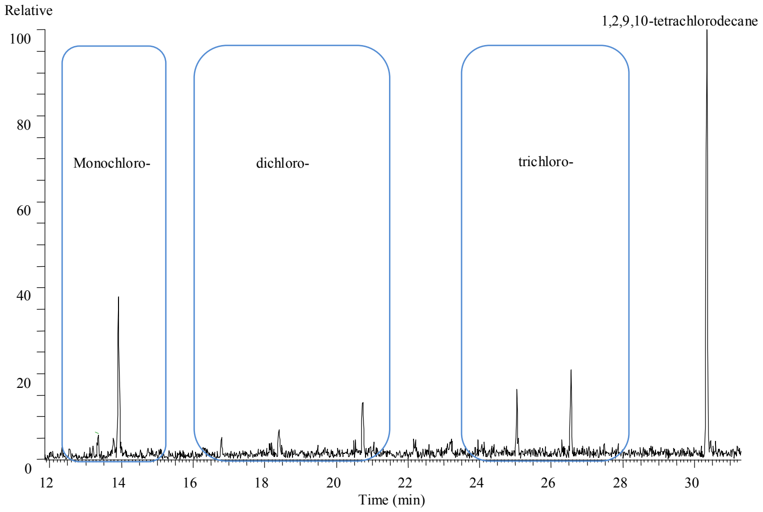

Figure S3 HRGC−EI/LRMS chromatogram of the products from the deuterodechlorination of 1,2,9,10-hexachlorodecane with $LiAlD_4$ at 60 °C for 72 h.

7. Calculation of the deuterodechlorination rates during condition optimization.

Preliminary experiments were carried out in order to investigate the influences of reaction temperature and reaction period on the deuterodechlorination rates of SCCPs. The generated deuterated *n*-alkanes were determined by external calibration using HRGC–EI/LRMS analysis. As illustrated in Figure S2, similar response factors between *n*-alkanes and deuterated *n*-alkanes were found in EI mode. Therefore, the calibration curves of individual *n*-alkanes (C_{10}–C_{13}) have been used by means of linear regression ($r^2>0.99$). Naphthalene was used as the injection internal standard before the instrumental analysis. The deuterodechlorination rate was calculated as the percentage of SCCPs reacted to the corresponding deuterated *n*-alkanes by the following equations:

$$ {}^{th}Q_{d-alk} = Q_{SCCP} \times \left(1 - \frac{M_{\mathrm{Cl}} - M_{\mathrm{D}}}{M_{\mathrm{Cl}}} \times K_{SCCP}\right) \qquad (1) $$

$$ {}^{ex}Q_{d-alk} = \sum_{i}^{10-13} {}^{ex}Q_{d-alk-i} \qquad (2) $$

$$ Deuterodechlorination\ rate = \frac{{}^{ex}Q_{d-alk}}{{}^{th}Q_{d-alk}} \times 100\% \qquad (3) $$

where ${}^{th}Q_{d\text{-}alk}$ and ${}^{ex}Q_{d\text{-}alk}$ are the theoretical and experimental determined masses of the total deuterated *n*-alkanes generated from SCCPs, respectively; ${}^{ex}Q_{d\text{-}alk\text{-}i}$ is the experimental determined mass of the individual deuterated *n*-alkanes (C_{10}–C_{13}); Q_{SCCP} is the mass of SCCPs; M_{Cl} and M_D are the molecular weights of Cl atom (average: 35.5) and D atom, respectively; and K_{SCCP} is the chlorine content (mass percentage) of SCCPs.

8. Fractionation and MS detection.

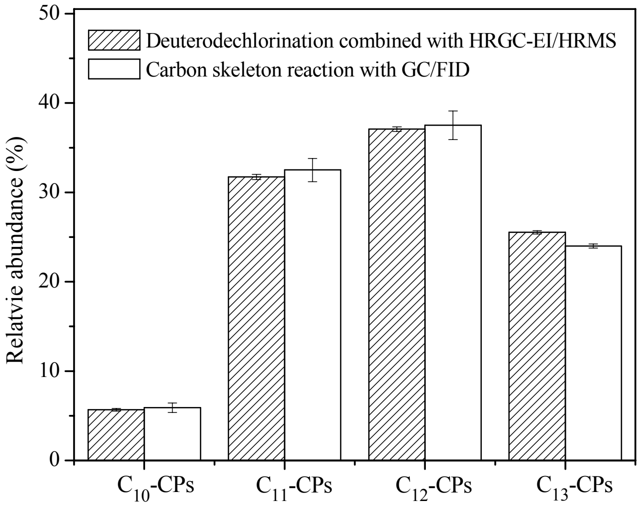

Figure S4. Comparison of the SCCP homologue profiles in the tested SCCP mixture standard (51% Cl) determined by deuterodechlorination combined with HRGC–EI/HRMS and by carbon skeleton reaction with GC/FID, respectively.

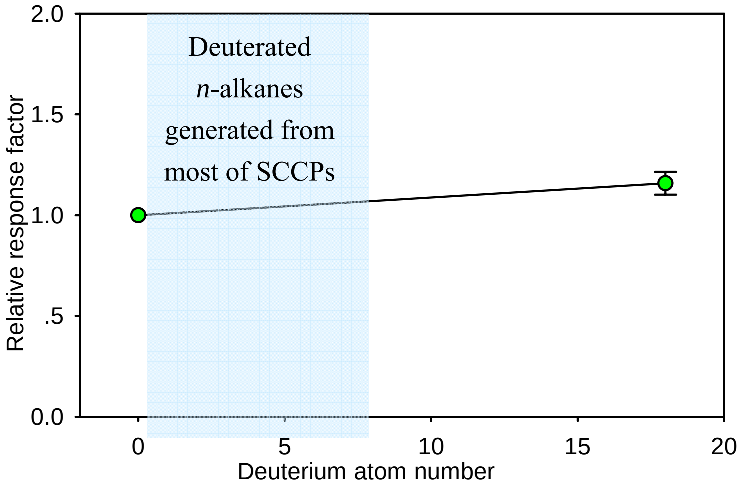

Figure S5. The relative response factors of *n*-octane and *n*-octane-d_{18} determined in EI mode, and the speculated variation range of the relative response factors for deuterated *n*-alkanes generated from SCCPs generally with 3−10 chlorine atoms.

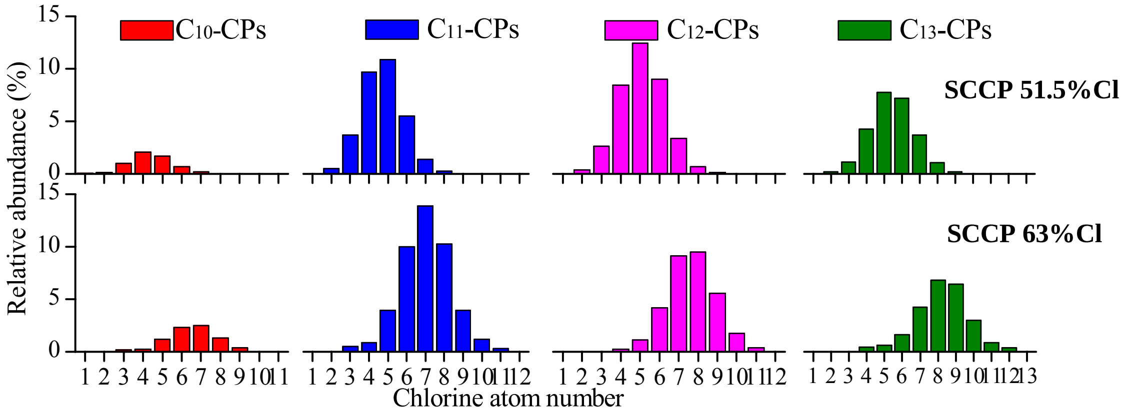

Figure S6. Relative abundances of individual SCCP congeners in two tested mixture standards with chlorine content of 51% and 63%, respectively, determined by deuterodechlorination combined with HRGC–EI/HRMS.

9. Interferences from deuterated *n*-alkenes, low-chlorinated deuterated *n*-alkanes and ^{13}C isotope.

In order to avoid the interferences from deuterated *n*-alkenes and low-chlorinated deuterated *n*-alkanes, HRGC–EI/HRMS was used because of the ultrahigh mass accuracy, and the molecular ion clusters $[M]^+$ of the formed deuterated alkanes were monitored in SIM mode. Therefore, both the deuterated *n*-alkenes and low-chlorinated deuterated *n*-alkanes were not detected out in this SIM mode. In addition, the retention times of deuterated *n*-alkenes and low-chlorinated deuterated *n*-alkanes were different from those of deuterated *n*-alkanes. However, background peaks, mainly originating from unknown chemicals and electrical signals, might appear in the SIM chromatogram due to the relatively low concentrations of the SCCP congeners ($D_{1\text{-}3}$-*n*-alkanes in Figure 1).

In addition, ^{13}C isotopes of $C_{10\text{-}13}$ alkanes might interfere with $[M+1]^+$ at 10% of $[M]^+$ when monitoring the molecular ion clusters by LRMS. In order to avoid the possible interference, the HRGC–EI/HRMS was adopted, and conducted in SIM mode with a mass accuracy of 0.001. The difference of the m/z values of the molecular ion between $^{12}C_{n-1}{}^{13}CH_{2n+2-m}D_m$ and $^{12}C_nH_{2n+1-m}D_{m+1}$ was 0.00292, where n and m are the numbers of carbon atoms and deuterium atoms. Therefore, the analytical interferences of ^{13}C isotopes of alkanes were prevented by HRMS. No obvious interference has been seen in the SIM chromatogram of the deuterated alkanes in Figure 1a. Some other peaks around $D_{1\text{-}3}$-*n*-alkanes might come from the background interferences, mainly originating from unknown chemicals and electrical signals. The relative signal intensities of background interferences can be largely reduced through increasing the concentration of deuterated *n*-alkanes and the mass resolution. However, some congeners in low concentrations could not be detected out with ultrahigh mass resolution. Based on the above, a mass resolution of 5000 was used in our study considering both the sensitivity and selectivity.

10. Performance evaluation of the extraction internal standard in sample extraction and cleanup procedure.

Commercial CPs are produced by radical chlorination of *n*-alkanes via petroleum feedstocks, so the amounts of branched SCCPs are very few. In recent years, we analyzed a series of commercial CPs produced in China, including CP-42, CP-52 and CP-70, as well as some petroleum feedstocks by carbon skeleton reaction with GC/FID. The amounts of branched alkanes were below the LOD values (15~19 μg/L at a S/N of 3: 1). Possibly because of the lack of industrial sources, the branched SCCPs have not been detected out in sediment and biota samples. The performance of the extraction internal standard in sample extraction and cleanup procedure has been evaluated. Four replicates of 5 g sodium sulfate spiked with the extraction internal standard at the mass fraction of 100 ng/g were pretreated by Soxhlet extraction, GPC and the two-step cleanup procedure, and then analyzed by the carbon skeleton reaction with GC/FID using external calibration. The average recoveries of branched C_{10}-CPs were calculated to be 92.5%.

11. Method development for the quantification of SCCP congeners by deuterodechlorination combined HRGC–EI/HRMS.

Table S5. Calculated chlorine content and RCF values of the synthetic SCCP calibration standards.

Carbon-chain length	Chlorine content (%)	Calculated chlorine content (%)	RCF values	Deuterodechlorination rate (%)
C_{10}	41.1	41.3	13.15	66.8
C_{10}	41.1	42.1	9.49	48.2
C_{10}	41.1	42.0	9.12	48.3
C_{10}	49.3	50.1	21.55	58.4
C_{10}	49.3	52.8	14.93	58.1
C_{10}	49.3	46.1	13.81	49.2
C_{10}	57.8	58.5	16.61	59.3
C_{10}	57.8	57.7	17.23	66.6
C_{10}	57.8	57.1	19.34	68.3
C_{10}	62.6	61.9	21.54	50.5
C_{10}	62.6	62.0	22.90	49.1
C_{10}	62.6	62.0	22.08	42.1
C_{10}	66.2	64.3	17.76	69.7
C_{10}	66.2	64.4	21.96	53.6
C_{10}	66.2	64.6	20.33	58.2
Average RCF values	17.45	Relative standard deviation (RSD) of RCF values (%)		26.0
C_{11}	44.8	44.7	16.00	66.8
C_{11}	44.8	46.7	13.00	48.2

C_{11}	44.8	46.0	14.01	48.3
C_{11}	51.0	51.4	16.07	58.4
C_{11}	51.0	51.8	16.59	58.1
C_{11}	51.0	53.5	13.34	49.2
C_{11}	57.7	55.7	23.17	59.3
C_{11}	57.7	56.0	23.13	66.6
C_{11}	57.7	55.6	20.59	68.3
C_{11}	59.8	58.8	27.80	63.6
C_{11}	59.8	58.8	27.45	64.0
C_{11}	59.8	58.8	24.00	53.8
C_{11}	67.7	65.0	18.05	69.7
C_{11}	67.7	65.1	26.27	53.6
C_{11}	67.7	65.1	20.17	58.2
Average RCF values	19.98	Relative standard deviation (RSD) of RCF values (%)		25.7
C_{12}	45.6	43.7	13.61	66.8
C_{12}	45.6	42.3	17.98	48.2
C_{12}	45.6	42.3	17.91	48.3
C_{12}	52.2	52.8	15.72	63.6
C_{12}	52.2	52.8	17.02	64.0
C_{12}	52.2	54.3	18.82	53.8
C_{12}	59.7	56.4	23.10	59.3
C_{12}	59.7	56.2	21.01	66.6
C_{12}	59.7	56.0	17.50	68.3
C_{12}	63.1	61.7	22.65	50.5
C_{12}	63.1	61.6	22.64	49.1
C_{12}	63.1	61.6	19.28	42.1
C_{12}	66.4	62.4	13.50	69.7
C_{12}	66.4	63.2	14.97	53.6
C_{12}	66.4	63.2	12.93	58.2
Average RCF values	17.91	Relative standard deviation (RSD) of RCF values (%)		18.9
C_{13}	44.0	42.6	25.11	69.9
C_{13}	44.0	41.5	24.93	56.1
C_{13}	44.0	41.1	30.98	69.2
C_{13}	55.0	53.7	27.32	57.9
C_{13}	55.0	54.1	31.01	53.6
C_{13}	55.0	60.0	26.53	56.5
C_{13}	59.9	60.2	24.88	59.3
C_{13}	59.9	60.1	24.74	66.6
C_{13}	59.9	62.2	18.75	68.3
C_{13}	65.4	62.1	20.21	63.6
C_{13}	65.4	62.0	23.20	64.0
C_{13}	65.4	65.3	15.69	53.8

C_{13}	69.6	65.4	21.31	69.7
C_{13}	69.6	65.4	16.53	53.6
C_{13}	69.6	44.7	13.15	58.2
Average RCF values	23.7	Relative standard deviation (RSD) of RCF values		20.0

Table S6. The $R_{i,\,j}$ values for individual deuterated *n*-alkane generated from SCCPs in three commercial CP mixtures (CP-42, CP-52 and CP-70).

CP-42	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0.145	0.161	0.126	0.093
2Cl	0.190	0.269	0.252	0.119
3Cl	0.189	0.290	0.258	0.231
4Cl	0.179	0.178	0.157	0.256
5Cl	0.119	0.074	0.119	0.209
6Cl	0.096	0.028	0.088	0.094
7Cl	0.058	0^{*}	0	0
8Cl	0.025	0	0	0
9Cl	0	0	0	0
10Cl	0	0	0	0
11Cl	0	0	0	0
12Cl	0	0	0	0
13Cl	0	0	0	0
14Cl				0
15Cl				0
CP-52	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0.006	0	0	0
2Cl	0.017	0.016	0.008	0.003
3Cl	0.057	0.052	0.079	0.032
4Cl	0.289	0.154	0.123	0.097
5Cl	0.308	0.301	0.226	0.189
6Cl	0.237	0.301	0.292	0.272
7Cl	0.074	0.139	0.194	0.245
8Cl	0.011	0.032	0.066	0.122
9Cl	0.001	0.004	0.012	0.034
10Cl	0	0	0.001	0.006
11Cl	0	0	0	0.001
12Cl	0	0	0	0
13Cl	0	0	0	0
14Cl				0

15Cl				0

CP-70	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0	0	0	0
2Cl	0	0	0	0
3Cl	0	0	0	0
4Cl	0	0	0	0
5Cl	0	0.119	0.027	0
6Cl	0.134	0.111	0.066	0
7Cl	0.152	0.184	0.203	0.054
8Cl	0.180	0.256	0.313	0.117
9Cl	0.250	0.177	0.163	0.127
10Cl	0.185	0.097	0.145	0.224
11Cl	0.068	0.046	0.057	0.255
12Cl	0.031	0.010	0.025	0.130
13Cl	0	0	0	0.067
14Cl				0.027
15Cl				0

*congeners were not detected out.

Table S7. The $R_{i,j}$ values for individual deuterated *n*-alkane generated from SCCPs in sediment and biota samples.

Sediment 1	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0*	0	0	0
2Cl	0	0.008	0.009	0.017
3Cl	0.041	0.098	0.104	0.129
4Cl	0.163	0.239	0.230	0.193
5Cl	0.344	0.232	0.198	0.178
6Cl	0.280	0.198	0.179	0.198
7Cl	0.117	0.139	0.172	0.161
8Cl	0.040	0.063	0.080	0.082
9Cl	0.011	0.018	0.023	0.031
10Cl	0.003	0.004	0.005	0.008
11Cl	0	0.001	0	0.002
12Cl	0	0	0	0
13Cl				0
14Cl				0

Sediment 2	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0	0	0	0

2Cl	0.003	0.011	0.021	0.017
3Cl	0.037	0.090	0.129	0.128
4Cl	0.291	0.251	0.252	0.206
5Cl	0.284	0.227	0.192	0.188
6Cl	0.230	0.190	0.163	0.184
7Cl	0.104	0.144	0.147	0.151
8Cl	0.037	0.063	0.070	0.083
9Cl	0.011	0.019	0.021	0.031
10Cl	0.003	0.004	0.005	0.009
11Cl	0.001	0.001	0	0.002
12Cl	0	0	0	0
13Cl				0
14Cl				0

Loach	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0	0	0	0
2Cl	0.018	0.033	0.078	0.062
3Cl	0.120	0.170	0.224	0.251
4Cl	0.368	0.360	0.377	0.369
5Cl	0.291	0.235	0.212	0.197
6Cl	0.104	0.108	0.072	0.073
7Cl	0.055	0.046	0.028	0.029
8Cl	0.033	0.030	0.007	0.013
9Cl	0.009	0.014	0.002	0.006
10Cl	0.002	0.004	0	0.001
11Cl	0	0	0	0
12Cl	0	0	0	0
13Cl				0
14Cl				0

Frog	C_{10}	C_{11}	C_{12}	C_{13}
1Cl	0	0	0	0
2Cl	0.034	0.019	0.099	0.036
3Cl	0.038	0.098	0.163	0.187
4Cl	0.207	0.198	0.313	0.309
5Cl	0.180	0.196	0.248	0.248
6Cl	0.140	0.131	0.115	0.124
7Cl	0.181	0.126	0.046	0.056
8Cl	0.149	0.133	0.014	0.025
9Cl	0.061	0.076	0.003	0.011

10Cl	0.009	0.020	0	0.003
11Cl	0	0.003	0	0.001
12Cl	0	0	0	0
13Cl				0
14Cl				0

*congeners were not detected out.

12. Method selectivity and linearity.

Sample preparation was conducted in a super clean laboratory to avoid background contamination, and the procedure blanks were run to verify the contamination of the solvents and glassware. Method performance of the whole analytical procedure was investigated according to EURACHEM and EPA guidelines.[8, 9] During the deuterodechlorination of SCCPs, the individual deuterated *n*-alkanes are specifically formed by the reduction of $LiAlD_4$. The generated deuterated *n*-alkanes can be further identified by EI/HRMS in the SIM mode, which avoids the interferences from some undesired products, such as low chlorinated deuterated *n*-alkanes and deuterated alkenes. For environmental and biota extracts, the selectivity of the analytical method was further ensured by removing other organochlorine compounds using column cleanup procedure. The application of HRGC−EI/HRMS method in SIM mode can also prevent the interferences from the deuterated products generated from these organochlorine compounds. The *n*-alkanes and deuterated *n*-alkanes have similar behavior on the EI/HRMS detection, and thus the detection linearity range of the deuterated *n*-alkanes can be evaluated by the *n*-alkanes. Four kinds of *n*-alkanes with diferent carbon chain lengths, *n*-decane, *n*-undecane, *n*-dodecane and *n*-tridecane, were spiked with phenanthrene (as the injection internal standard), and then used to evaluate the detection linearity range. There was a good correlation ($R^2 > 0.99$) between the *n*-alkane concentrations (range: 17−212 μg/L) and the relative peak area of the tested *n*-alkane to phenanthrene (Figure S7).

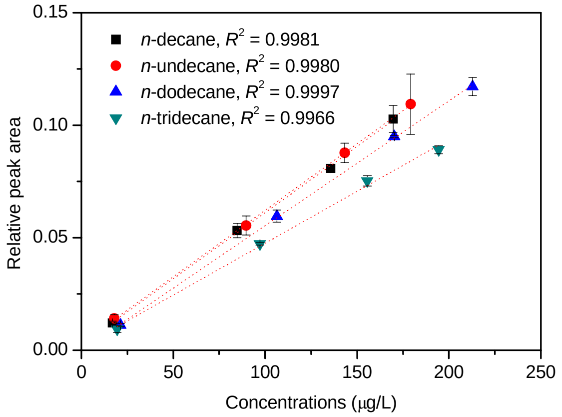

Figure S7. The linear correlation between the *n*-alkane concentrations and its relative peak areas determined by HRGC–EI/HRMS.

13. Instrumental detection limit (IDL) of *n*-alkanes and method detection limit (MDL) of SCCPs.

The blank sediment sample was matrix-matched, which was prepared using Soxhlet extraction until no detectable quantities of SCCPs analyzed by HRGC−ECNI/LRMS method. Eight replicates of blank sediment samples spiked with the internal standard solution were pretreated by Soxhlet extraction and the subsequent column cleanup procedure. The concentrated solution in the micro-reaction vial was spiked with the reaction internal standard, and then treated with $LiAlD_4$ as described in the experimental section. The method detection limit (MDL) for total SCCPs, calculated as 3-fold the standard deviation of SCCPs in blank sediment samples, was 33 ng/g (n = 8). The value was a little higher than that by ECNI/LRMS method (14 ng/g)[3], which was undoubtedly sensitive for high chlorinated SCCPs. The average chlorine content of SCCPs in blank sendiment samples was calculated to be 55.0%.

14. Repeatability and Precision.

Table S8. The quantitative results of SCCPs in different stock standard solutions.

Standard	Test times	Mass				Chlorine content				R_{re} (%)[g]
		Expected mass (μg)	Determined average mass (μg)	Relative standard deviation (%)[a]	Relative error (%)[b]	Labeled chlorine content (%)[c]	Calculated average chlorine content (%)[d]	Relative standard deviation (%)[e]	Relative error (%)[f]	
C_{10}-CPs	n =2	0.5	0.58	--	16.2	60.09	60.7	--	1.0	88.3
C_{11}-CPs	n =2	1	0.84	--	15.6	55.2	52.4	--	5.1	105.1
SCCP mixture	n =3	10	12.0	8.9	20.1	51.5	49.7	0.9	3.5	84.7

[a] Relative standard deviation for the determined mass. [b] Relative error between the expected mass and the determined average mass. [c] Chlorine content labeled by producer (Dr. Ehrenstorfer GmbH, Germany). [d] Chlorine content calculated from the determined chlorine distribution of SCCPs. [e] Relative standard deviation for the calculated chlorine content. [f] Relative error between the labeled chlorine content and the calculated average chlorine content. [g] Recovery of the extraction internal standard (chlorinated 2-methylnonane) throughout the sample pretreatment.

Table S9. The quantitative results of SCCPs in blank sediment samples spiked with different SCCP homologues.

Spiked standard	Test times	Mass				Chlorine content				R_{ex} (%)[g]	R_{re} (%)[h]
		Expected mass (μg)	Determined average mass (μg)	Relative standard deviation (%)[a]	Relative error (%)[b]	Labeled chlorine content (%)[c]	Calculated average chlorine content (%)[d]	Relative standard deviation (%)[e]	Relative error (%)[f]		
C_{10}-CPs	n =1	0.5	0.50	--	0.6	60.09	59.8	--	0.5	78.6	88.8
C_{11}-CPs	n =2	1	1.20	--	19.9	55.2	53.4	--	3.2	83.6	79.2
C_{12}-CPs	n =3	0.5	0.38	9.1	24.3	65.08	61.1	0.36	6.1	80.0	89.1
C_{13}-CPs	n =1	0.5	0.37	--	25.9	65.18	61.3	--	6.0	78.6	88.8

[a] Relative standard deviation for the determined mass. [b] Relative error between the expected mass and the determined average mass. [c] Chlorine content labeled by producer (Dr. Ehrenstorfer GmbH, Germany). [d] Chlorine content calculated from the determined chlorine distribution of SCCPs. [e] Relative standard deviation for the calculated chlorine content. [f] Relative error between the labeled chlorine content and the calculated average chlorine content. [g] Recovery rate of the extraction internal standard (chlorinated 2-methylnonane) throughout the sample pretreatment. [h] Recovery of the reaction internal standard (chlorinated 2-methylundecane) throughout the deuterodechlorination reaction.

15. Calculation of the recoveries.

Relative response factor ($\mathrm{RRF}_{\mathrm{ex}}$) for the extraction internal standard relative to the reaction internal standard and relative response factor ($\mathrm{RRF}_{\mathrm{re}}$) for the reaction internal standard relative to the injection internal standard can be calculated by eq. 4 and 5, respectively:

$$\mathrm{RRF}_{\mathrm{ex}} = \frac{Q_{\mathrm{d\text{-}RS}}}{Q_{\mathrm{d\text{-}IS}}} \times \frac{TA_{\mathrm{d\text{-}IS}}}{TA_{\mathrm{d\text{-}RS}}} \tag{4}$$

$$\mathrm{RRF}_{\mathrm{re}} = \frac{Q_{\mathrm{inj}}}{Q_{\mathrm{d\text{-}RS}}} \times \frac{TA_{\mathrm{d\text{-}RS}}}{A_{\mathrm{inj}}} \tag{5}$$

where $Q_{\mathrm{d\text{-}IS}}$ and $TA_{\mathrm{d\text{-}IS}}$ are the theoretical mass and the actually determined total peak area of deuterated 2-methylnonane generated from the extraction internal standard, respectively; $Q_{\mathrm{d\text{-}RS}}$ and $TA_{\mathrm{d\text{-}RS}}$ are the theoretical mass and the actually determined total peak area of deuterated 2-methylundecane generated from the reaction internal standard, respectively; and Q_{inj} and A_{inj} are the theoretical mass and the actually determined peak area of phenanthrene, respectively. Similar with RCF values, an average $\mathrm{RRF}_{\mathrm{ex}}$ and $\mathrm{RRF}_{\mathrm{re}}$ were calculated as ($\overline{\mathrm{RRF}_{\mathrm{ex}}}$) and ($\overline{\mathrm{RRF}_{\mathrm{re}}}$) for the recovery confirmation. The recoveries of the extraction and reaction internal standards (R_{ex} and R_{re}) can be calculated using the following equations:

$$R_{\mathrm{ex}} = \frac{Q_{\mathrm{d\text{-}RS}}}{Q_{\mathrm{d\text{-}IS}}} \times \frac{TA_{\mathrm{d\text{-}IS}}}{\overline{\mathrm{RRF}_{\mathrm{ex}}}} \times \frac{100\%}{TA_{\mathrm{d\text{-}RS}}} \tag{6}$$

$$R_{\mathrm{re}} = \frac{Q_{\mathrm{inj}}}{Q_{\mathrm{d\text{-}RS}}} \times \frac{TA_{\mathrm{d\text{-}RS}}}{\overline{\mathrm{RCF}_{\mathrm{re}}}} \times \frac{100\%}{A_{\mathrm{inj}}} \tag{7}$$

16. Concentrations and congener profiles of SCCPs in commercial CPs, sediment and biota samples.

Table S10. Congener concentrations and calculated chlorine contents of SCCPs in commercial CP products determined by deuterated carbon skeleton reaction combined HRGC–EI/HRMS.

Sample		CP-42	CP-52	CP-70
C_{10}-CPs	Concentrations (%)	2.3	10.3	0.5
	Chlorine content (%)	44.6	55.5	68.6
C_{11}-CPs	concentrations (%)	0.2	9.9	0.5
	Chlorine content (%)	37.6	55.1	60.8
C_{12}-CPs	concentrations (%)	0.5	10.7	0.4
	Chlorine content (%)	38.1	54.6	63.4
C_{13}-CPs	concentrations (%)	0.1	9.4	0.4
	Chlorine content (%)	40.1	54.2	67.6
Total concentrations (mg/g)		3.1	40.2	1.7
Average chlorine content (%)		42.9	54.9	65.2
R_{re} (%)		102.7	88.3	97.4

Table S11. Congener concentrations and calculated chlorine contents of SCCPs in sediment and biota samples determined by deuterated carbon skeleton reaction combined HRGC–EI/HRMS.

Sample		Sediment 1#	Sediment 2#	Loach extracts	Frog extracts
C_{10}-CPs	Concentrations (μg/g)	0.34	0.46	0.93	1.14
	Chlorine content (%)	57.9	56.8	53.8	58.8
C_{11}-CPs	Concentrations (μg/g)	0.60	0.60	0.96	1.10
	Chlorine content (%)	54.4	54.4	50.5	55.9
C_{12}-CPs	concentrations (μg/g)	0.76	1.02	1.38	1.10
	Chlorine content (%)	52.7	51.5	45.7	46.9
C_{13}-CPs	concentrations (μg/g)	1.01	1.20	1.64	1.15
	Chlorine content (%)	50.6	50.5	44.0	46.5
Total concentrations (μg/g)		2.71	3.28	4.92	4.49
Average chlorine content (%)		52.9	52.4	47.6	52.0
R_{ex} (%)		88.0	94.7	74.9	80.7
R_{re} (%)		79.3	78.1	84.6	88.1

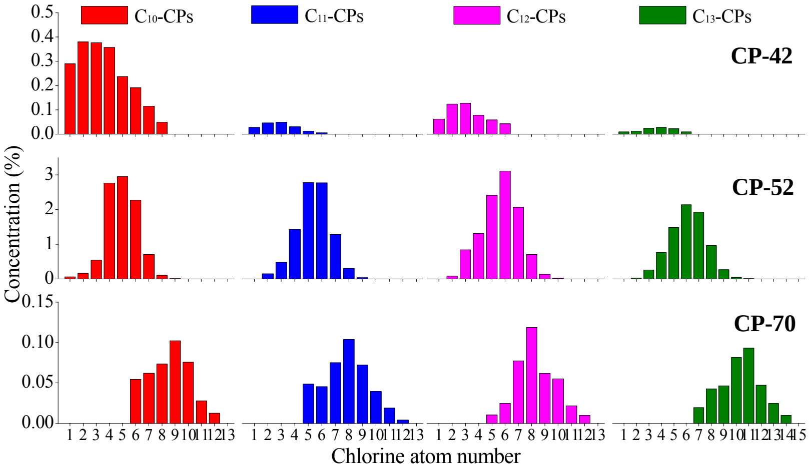

Figure S8. Congener profiles of SCCPs in three types of commercial CP products determined by the method of deuterodechlorination combined with HRGC–EI/HRMS.

Table S12. SCCP concentrations and their calculated chlorine contents in sediment and biota samples extracts analyzed by HRGC–ECNII/LRMS.

Sample	Concentrations (μg/g)	Chlorine content(%)
Sediment 1#	0.2	59.5
Sediment 2#	0.4	58.4
Loach extract	2.9	57.8
Frog extract	2.7	57.9

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