Supporting Information

Behavior, Fate and Mass Loading of Short Chain Chlorinated Paraffins in an Advanced Municipal Sewage Treatment Plant

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Standards and Reagents

Commercial standards of SCCPs (C_{10-13}, 51.5%, 55.5% and 63.0% chlorine content, 100 ng/μL; C_{10}, 50.2%, 55.0%, 60.1% and 65.0% chlorine content, 10 ng/μL; C_{11}, 50.2%, 55.2%, 60.5% and 65.3% chlorine content, 10 ng/μL; C12, 50.2%, 55.0%, 65.1% and 70.0% chlorine content, 10 ng/μL; C_{13}, 50.2%, 55.0%, 60.0% and 65.2% chlorine content, 10 ng/μL) and MCCPs mixtures (C_{14-17}, 42.0%, 52.0% and 57.0% chlorine content, 100 ng/μL) in cyclohexane as well as ε-hexachlorocyclohexane (ε-HCH, solution in cyclohexane, 10 ng/μL) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). $^{13}C_{10}$-*trans*-chlordane (99%) in *n*-nonane was purchased from Cambridge Isotope Laboratories (Andover, USA). All organic solvents (acetone, cyclohexane, dichloromethane, *n*-hexane) were pesticide residue grade and purchased from Fisher Scientific (Hampton, NH). Silica gel (63-100 μm) and Florisil (60-100 mesh) were obtained from Merck (Whitehouse Station, NJ). Anhydrous sodium sulfate and copper powder were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Silica gel was activated at 550 °C for 12 hours, Florisil at 140 °C overnight, and anhydrous sodium sulfate at 660 °C for 6 hours prior to use. The 44% acid silica gel was prepared by mixing 100 g of activated silica gel and 24 mL of concentrated sulfuric acid.

Sample Extraction and Cleanup

In the present study, a more elaborate cleanup technique was employed according to our improved procedure in the recent work,[1] in order to avoid interferences from other organic pollutants not removed by the routine clean-up procedure, such as PCB, toxaphene and certain organochlorine pesticides, with similar mass-to-charge ratios and retention time range.[2-4] Briefly, a homogenized sludge sample of 0.1 g was mixed with 10 g anhydrous sodium sulfate, spiked with 1.0 ng surrogate standard $^{13}C_{10}$-*trans*- chlordane for accelerated solvent extraction (ASE). Activated copper powders were added to the extract to remove sulfur-containing compounds. The extract was cleaned and concentrated to approximate 1 mL. Then the extract was cleaned and fractionated on a 1.5 cm i.d. silica-Florisil composite column packed, from the bottom to top, with 14 g of Florisil (deactivated with 1.5% of water), 2 g of

neutral silica gel, 10 g of acid silica gel (44%) and 4 g anhydrous sodium sulfate. The column was conditioned with 50 mL of *n*-hexane and the sample was eluted with 60 mL of *n*-hexane and 6 mL dichloromethane (first fraction, containing PCBs and toxaphenes), followed by 60 mL of dichloromethane (second fraction, containing CPs and a part of HCHs). The second fraction was further concentrated to near dryness under a gentle stream of N_2 and then reconstituted in 50 μL of cyclohexane. Prior to GC-MS analysis, ε-HCH was added to determine the recoveries.

The water samples were extracted by liquid-liquid extraction. Briefly, 1 L of filtered water samples was spiked with 1.0 ng $^{13}C_{10}$-*trans*-chlordane as recovery standard and subjected to extraction with 3 × 200 mL dichloromethane for three times. All three extracts were combined and concentrated, then subjected to anhydrous sodium sulfate column to remove residual moisture. Blanks were made from distilled water and put through the same manipulation. The subsequent cleanup steps followed the same procedure as for the sludge samples described above.

Quality Assurance and Quality Control (QA/QC)

Strict quality assurance and control measures were implemented to ensure the identification and accurate quantification of the analysis. All glassware were rinsed with dichloromethane and heated overnight at 450 ºC before use. Each batch of 8 samples included one procedural blank to check possible contamination. No SCCPs were detected in the procedural blanks, therefore the quantitative results were not blank corrected in this study. The recoveries of the surrogate standards $^{13}C_{10}$-*trans*-chlordane and SCCPs were determined by three replicates with spiked samples, and in the range 80–105% and 75–98%, respectively. Accuracy was controlled with spiked samples and deviated less than 10% from the expected values. The method limits of detection (LOD) were calculated as three times the standard deviation of the average procedural blanks or based on three times the signal-to-noise ratio. The LOD for SCCPs was determined at 1–2 ng/g. Repeatability of analysis was assessed by analyzing three duplicate samples with relative standard deviation below 6%.

Table S1. The water flow and regularly measured parameters in the STP During the sampling period *.

	Raw sewage	Primary effluent	Anaerobic	Anoxic	Aerobic	Internal recirculation	Secondary effluent	Return sludge	Excess sludge	Supernatant of excess sludge	Dewatered sludge
Water flow (m^3/d)	2.0×10^5	2.0×10^5	4.0×10^5	10.0×10^5	4.0×10^5	6.0×10^5	1.2×10^5	1.99×10^5	5.3×10^3	5.2×10^3	-
TSS (mg/L)	282	254	4.1×10^3	4.1×10^3	4.1×10^3	4.1×10^3	11	8.3×10^3	10×10^3	-	-
COD (mg/L)	476						41.3				
BOD_5 (mg/L)	230						9.05				
DO (mg/L)							3.52				
TP (mg/L)	5.9						0.22				
NH4-N (mg/L)							0.67				
NO3-N (mg/L)							10.8				
Mass flux of TSS (Kg/d)	5.64×10^4	5.08×10^4	1.64×10^6	4.1×10^6	1.64×10^6	2.46×10^6	1.32×10^3	1.65×10^6	5.3×10^4	-	5.9×10^4

***** The water flow for tertiary treatment of hyperfiltration, ozonation and chlorination was about 80000 m^3/d.

Table S2. Measured concentrations of chlorine congener groups in sewage water (dissolved phase, ng/L) and sludge (adsorbed phase, µg/g d.w.) at various stages of the treatment process in the STP.

		Raw sewage	Primary effluent	Anaerobic	Anoxic	Aerobic	Secondary effluent	Hyperfiltration	Ozonation	Tertiary effluent (Chlorination)	Dewatered sludge
5Cl	**dissolved**	16 ± 4	9 ± 1	9 ± 1	11 ± 1	10 ± 1.8	7.0 ± 0.6	6 ± 1	5 ± 0.5	5 ± 1.2	
	adsorbed	0.8 ± 0.1	0.8 ± 0.0	0.4 ± 0.1	0.5 ± 0.1	0.4 ± 0.1	0.1 ± 0.1	-	-	-	0.6 ± 0.0
6Cl	**dissolved**	56 ± 7	39 ± 4	34 ± 2	26 ± 2	21 ± 4	16 ± 1	15 ± 2	11 ± 1	11 ± 3	
	adsorbed	3.7 ± 0.3	3.8 ± 0.3	1.6 ± 0.2	1.6 ± 0.1	1.5 ± 0.1	0.3 ± 0.1	-	-	-	2.0 ± 0.2
7Cl	**dissolved**	62 ± 5	57 ± 5	36 ± 2	19 ± 1	14 ± 3	10 ± 1	9 ± 1	7 ± 1	8 ± 2	
	adsorbed	8.7 ± 0.6	7.7 ± 0.9	3.9 ± 0.2	3.8 ± 0.1	3.9 ± 0.1	0.8 ± 0.3	-	-	-	6.0 ± 0.5
8Cl	**dissolved**	32 ± 3	31 ± 3	13 ± 1	6 ± 0.3	5 ± 1	3 ± 0.3	2 ± 0.4	2 ± 0.3	2 ± 0.5	
	adsorbed	5.6 ± 0.6	4.8 ± 1.0	2.4 ± 0.1	2.4 ± 0.0	2.4 ± 0.1	0.5 ± 0.2	-	-	-	4.4 ± 0.4
9Cl	**dissolved**	14 ± 3	14 ± 2	3 ± 0.2	2 ± 0.1	2 ± 0.4	1 ± 0.1	1 ± 0.1	1 ± 0.1	1 ± 0.1	
	adsorbed	2.4 ± 0.2	2.0 ± 0.5	1.1 ± 0.0	1.1 ± 0.1	1.0 ± 0.2	0.2 ± 0.1	-	-	-	2.0 ± 0.2
10Cl	**dissolved**	5 ± 1	4 ± 0.3	1 ± 0.1	1 ± 0.1	1 ± 0.1	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	
	adsorbed	0.7 ± 0.1	0.5 ± 0.1	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.1	0.1 ± 0.1	-	-	-	0.6 ± 0.2

Table S3. Mean mass flux (g/d) of SCCP congener groups categorized by carbon and chlorine atoms in the STP.

		C10	C11	C12	C13	5Cl	6Cl	7Cl	8Cl	9Cl	10Cl
Raw influent	**dissolved**	14.4	10.0	6.4	6.1	3.3	11.1	12.3	6.4	2.7	1.0
	adsorbed	327.1	377.9	270.7	253.8	44.0	211.1	488.0	316.4	135.6	37.2
Primary effluent	**dissolved**	10.7	9.5	5.7	4.8	1.8	7.9	11.4	6.3	2.7	0.7
	adsorbed	272.2	307.7	213.2	204.6	38.0	194.3	387.9	244.8	101.6	27.1
Raw sludge	**dissolved**	-	-	-	-	-	-	-	-	-	-
	adsorbed	43.3	41.2	23.4	23.0	9.0	34.6	52.6	25.7	7.4	1.7
Anaerobic	**dissolved**	17.3	11.4	5.7	4.0	3.6	13.5	14.1	5.3	1.2	0.5
	adsorbed	4820.6	4981.2	3418.8	2860.7	718.2	2649.0	6398.1	3999.6	1787.9	527.8
Anoxic	**dissolved**	31.6	19.1	8.3	5.6	11.3	25.6	18.4	6.1	2.4	0.8
	adsorbed	12059.4	12382.0	8239.8	6676.9	1963.5	6631.9	15626.7	9556.7	4299.5	1281.7
Aerobic	**dissolved**	10.5	5.7	2.7	2.0	4.1	8.3	5.5	1.9	0.9	0.3
	adsorbed	4721.0	4973.9	3202.5	2681.9	687.6	2516.6	6447.7	3856.6	1583.4	488.2
Internal recirculation	**dissolved**	15.8	8.5	4.1	3.0	6.1	12.4	8.2	2.9	1.4	0.5
	adsorbed	7081.5	7460.9	4803.7	4022.8	1031.4	3774.8	9671.6	5784.8	2375.1	732.2

		C10	C11	C12	C13	5Cl	6Cl	7Cl	8Cl	9Cl	10Cl
Secondary effluent	**dissolved**	3.7	2.1	1.0	0.5	1.4	3.1	1.9	0.6	0.2	0.0
	adsorbed	1.3	1.4	1.0	0.8	0.2	0.7	1.8	1.1	0.5	0.1
Return sludge	**dissolved**	6.0	3.2	1.6	1.2	2.3	4.7	3.1	1.1	0.5	0.2
	adsorbed	4774.5	5030.4	3238.8	2712.3	695.3	2545.0	6520.6	3900.1	1601.3	493.7
Excess sludge	**dissolved**	0.3	0.2	0.1	0.1	0.1	0.3	0.2	0.1	0.0	0.0
	adsorbed	246.7	263.2	172.9	147.2	30.5	108.0	315.1	238.2	107.3	30.9
Supernatant of excess sludge	**dissolved**	0.3	0.1	0.1	0.0	0.1	0.2	0.1	0.1	0.0	0.0
	adsorbed	-	-	-	-	-	-	-	-	-	-
Hyperfiltration	**dissolved**	1.4	0.7	0.3	0.2	0.5	1.2	0.7	0.2	0.1	0.0
	adsorbed	-	-	-	-	-	-	-	-	-	-
Ozonation	**dissolved**	0.9	0.6	0.3	0.2	0.4	0.8	0.6	0.2	0.0	0.0
	adsorbed	-	-	-	-	-	-	-	-	-	-
Tertiary effluent (Chlorination)	**dissolved**	1.0	0.7	0.3	0.2	0.4	0.9	0.6	0.2	0.0	0.0
	adsorbed	-	-	-	-	-	-	-	-	-	-
Dewatered sludge	**dissolved**	-	-	-	-	-	-	-	-	-	-
	adsorbed	261.5	298.2	198.8	163.5	36.7	119.5	354.6	260.1	118.8	32.2

Table S4. The congener-specific solid-water partition coefficients (K_d) at different treatment stages in the STP.

	C10	C11	C12	C13	5Cl	6Cl	7Cl	8Cl	9Cl	10Cl
Raw influent	22.7	37.8	42.3	41.6	13.3	19.0	39.7	49.4	50.2	37.2
Primary effluent	25.4	32.4	37.4	42.6	21.1	24.6	34.0	38.9	37.6	38.7
Anaerobic	278.6	436.9	599.8	715.2	199.5	196.2	453.8	754.6	1489.9	1055.6
Anoxic	381.6	648.3	992.7	1192.3	173.8	259.1	849.3	1566.7	1791.5	1602.1
Aerobic	449.6	872.6	1186.1	1341.0	167.7	303.2	1172.3	2029.8	1759.3	1627.3

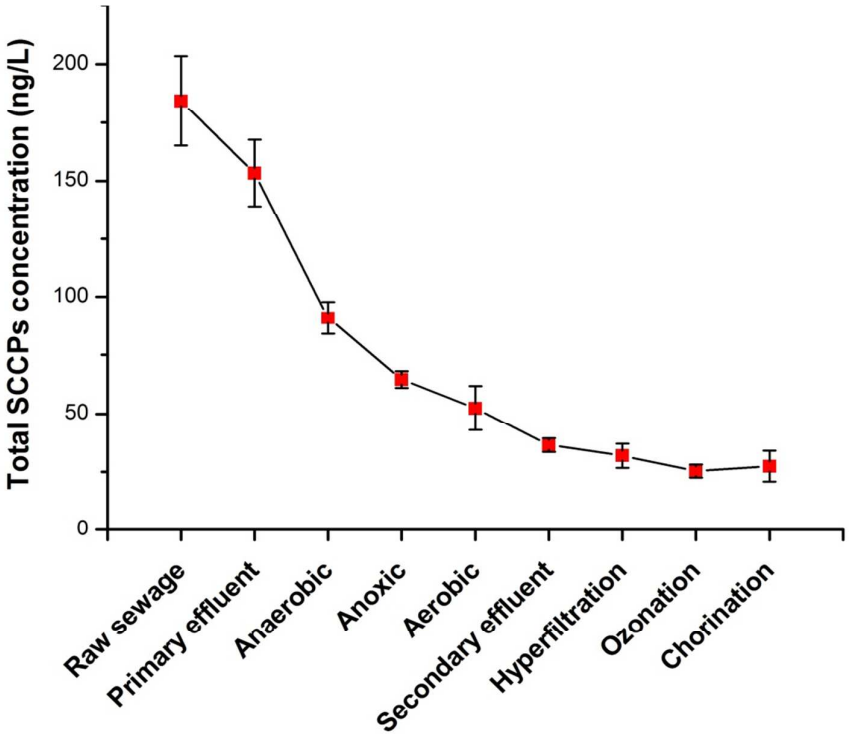

Figure S1. Variations of ∑SCCPs concentration (dissolved) in sewage water at various stages of sewage treatment in the STP.

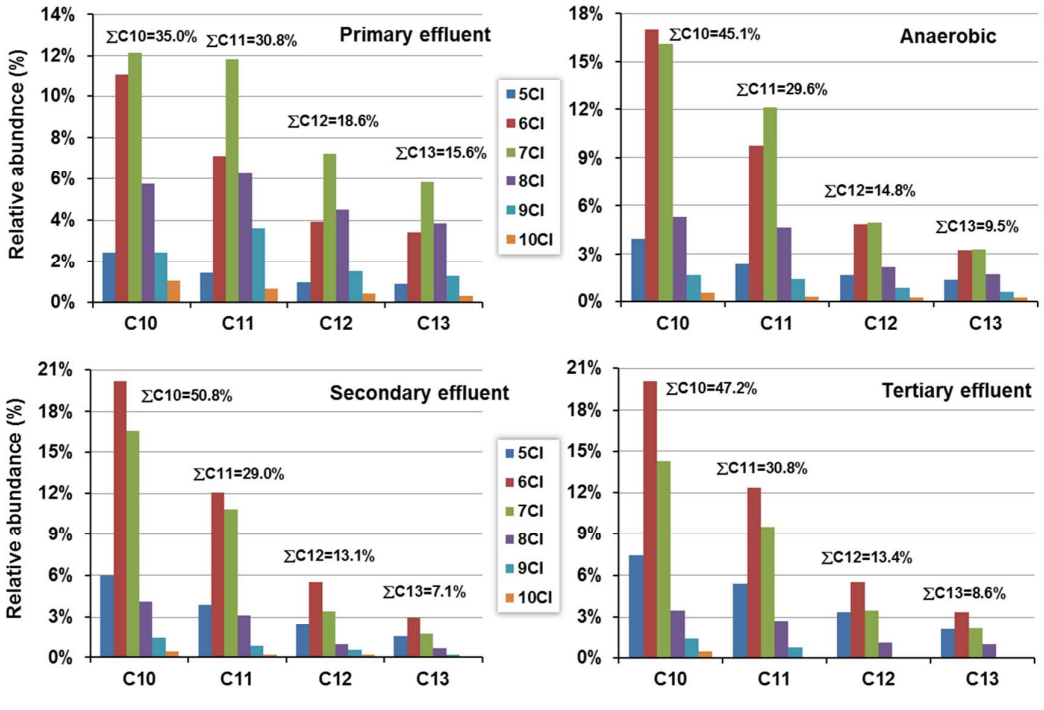

Figure S2. Comparisons of SCCP congener group abundance profiles among four typical sewage water samples at various stages of the treatment process**..**

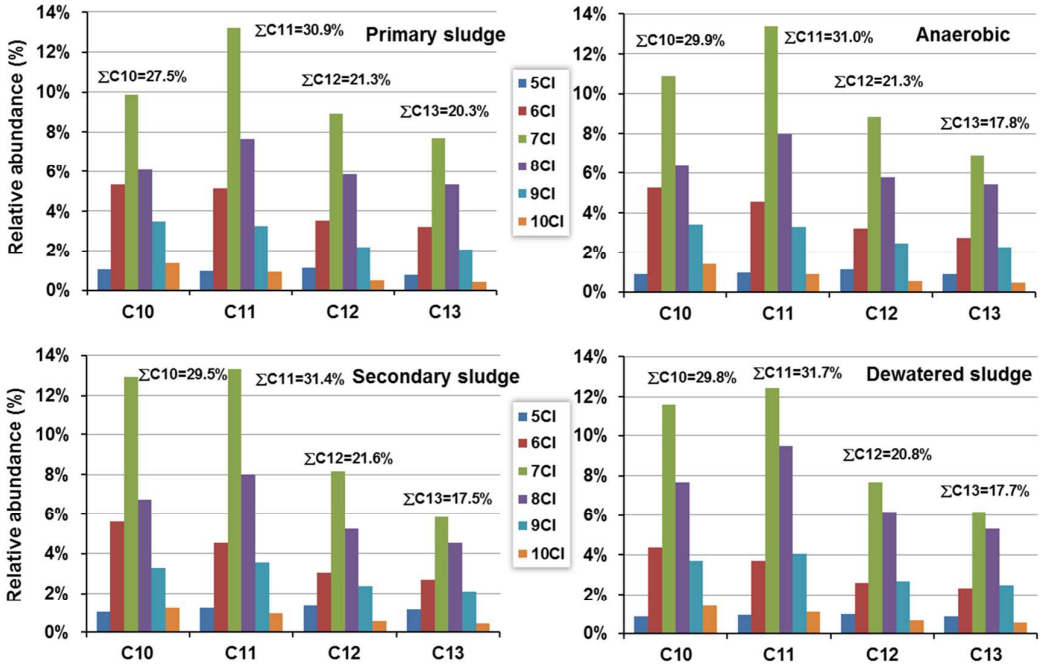

Figure S3. Comparisons of SCCP congener group abundance profiles among four typical sludge samples at various stages of the treatment process**..**

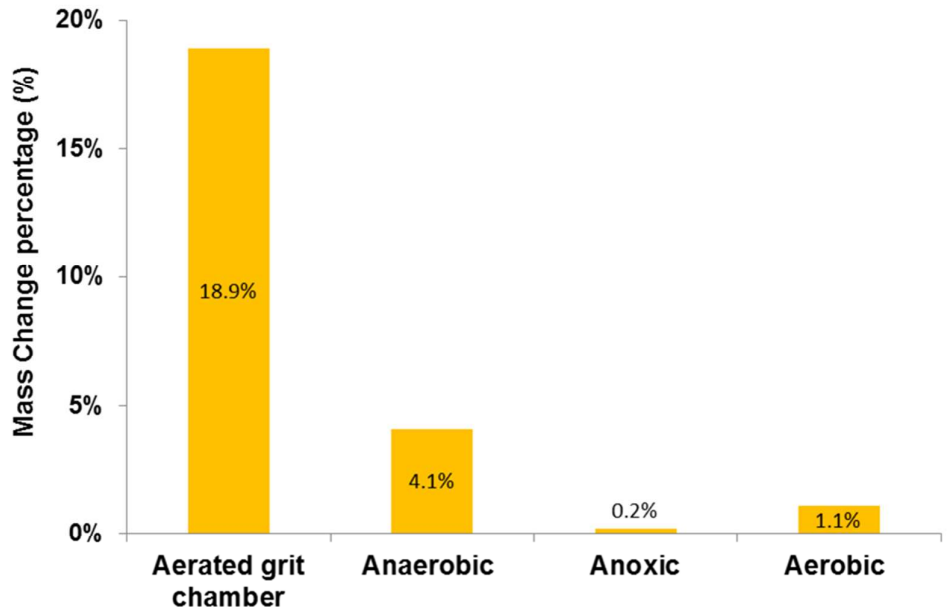

Figure S4. Total mass change percentages of ∑SCCPs (sum of dissolved and adsorbed) at the core treatment units calculated by comparing the total mass loading (aqueous and solid phases) in the inflow and outflow of individual treatment unit.

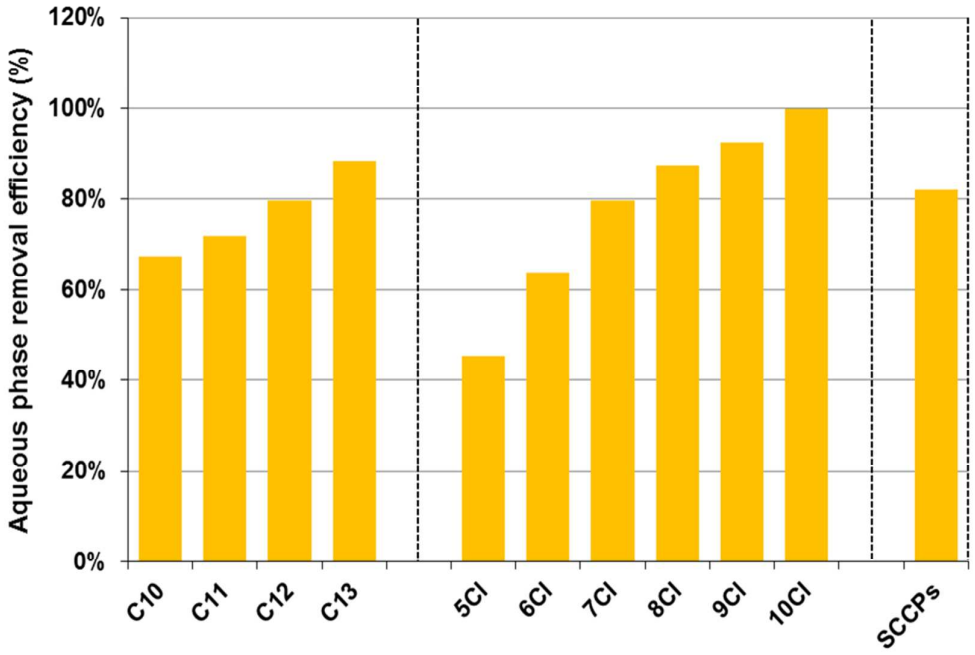

Figure S5. Removal efficiency (%) in aqueous phase of different SCCP congener groups and ∑SCCPs.

REFERENCES

(1) Zeng, L. X.; Zhao, Z. S.; Li, H. J.; Han, W. Y.; Liu, Q.; Xiao, K.; Du, Y. G.; Wang, Y. W.; Jiang, G. B., Distribution of Short Chain Chlorinated Paraffins in Marine Sediments of the East China Sea: Influencing Factors, Transport and Implications. *Environ. Sci. Technol.* **2012,** *46*, (18), 9898-9906.

(2) Tomy, G. T.; Stern, G. A.; Muir, D. C. G.; Fisk, A. T.; Cymbalisty, C. D.; Westmore, J. B., Quantifying C_{10}-C_{13} polychloroalkanes in environmental samples by high-resolution gas chromatography electron capture negative ion high resolution mass spectrometry. *Anal. Chem.* **1997,** *69*, (14), 2762-2771.

(3) Reth, M.; Oehme, M., Limitations of low resolution mass spectrometry in the electron capture negative ionization mode for the analysis of short- and medium-chain chlorinated paraffins. *Anal. Bioanal. Chem.* **2004,** *378*, (7), 1741-1747.

(4) Sverko, E.; Tomy, G. T.; Marvin, C. H.; Muir, D. C. G., Improving the Quality of Environmental Measurements on Short Chain Chlorinated Paraffins to Support Global Regulatory Efforts. *Environ. Sci. Technol.* **2012,** *46*, (9), 4697-4698.