

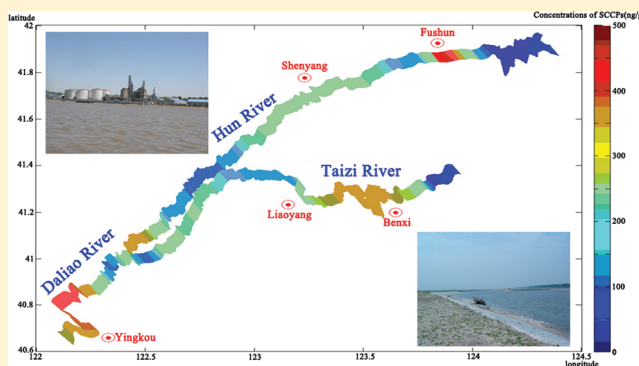
Environmental Occurrence and Distribution of Short Chain Chlorinated Paraffins in Sediments and Soils from the Liaohe River Basin, P. R. China

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S Supporting Information

ABSTRACT: Chlorinated paraffins (CPs) are industrially produced in large quantities in the Liaohe River Basin. Their discharge inevitably causes environmental contamination. However, very limited information is available on their environmental levels and distributions in this typical industrial region. In this study, short chain CPs (SCCPs) were analyzed in sediments, paddy soils, and upland soils from the Liaohe River Basin, with concentrations ranging from 39.8 to 480.3 ng/g dry weight. A decreasing trend in SCCP concentrations was found with increasing distance from the cities, suggesting that local industrial activity was the major source of SCCP contamination. A preliminary sediment inventory of SCCPs indicated approximately 30.82 tonnes of SCCPs residual in the sediments from the Liaohe River. The average discharge of SCCPs was estimated to be about 74.4 mg/tonne industrial wastewater. The congener group profiles showed that the relative abundances of shorter chain and lower chlorinated CP congeners (C_{10} –CPs with 5 or 6 chlorine atoms) in soils in rural areas were higher than in sites near cities, which demonstrated that long-range atmospheric transportation could be the major transport pathway. Environmental degradation of SCCPs might occur, where higher chlorinated congeners could dechlorinate to form the lower chlorinated congeners.



INTRODUCTION

Chlorinated paraffins (CPs) are industrial mixtures with chlorine contents ranging from 30% to 70% by mass.^{1,2} In the past three decades, CPs have been produced in high quantities as lubricant additives, cutting fluids, plasticizers, and flame retardants.³ The annual worldwide production of CPs was reported to be 300 000 tonnes in 1985, and increased by up to 1% per year between 1989 and 1998.⁴ CPs can be subdivided according to their carbon chain length 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_{30}).⁵ Among these, SCCPs have attracted considerable attentions due to their potential for long-range transport, persistence in the environment and high toxicity to aquatic organisms.^{6–8} Studies in F344/N rats and B6C3F1 mice exposed for two years have demonstrated that the SCCPs are carcinogenic.⁹ Furthermore, SCCPs have been found in a variety of environmental matrices including air, water, sediments, and biota.^{10–14} Even in remote areas such as a Canadian Arctic lake, Hazen Lake and the European Arctic, SCCPs have been found to accumulate in biota.^{6,14–16} In 2007, the European Community and its member states proposed classifying SCCPs as candidate persistent organic pollutants (POPs) in the Stockholm Convention.¹⁷ A similar action was also taken by the European Union, which included SCCPs in the list of priority hazardous substances under the Water

Framework Directive for the protection of the aquatic environment.¹⁸

The analysis of SCCPs is extremely difficult owing to their complex composition containing thousands of homologues and isomers, and data on the regional environmental levels of SCCPs are very scarce compared with other POPs such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans and polychlorinated biphenyls.^{1,19} Almost all available data on the temporal and spatial distribution of SCCPs in the environment are focused in North America, Europe, and Japan.^{2–4} China is the largest producer of CPs in the world, and the annual production has increased rapidly to about 600 000 tonnes in 2007 owing to high demand from the plastics industry.²⁰ Consequently, investigations on regional environmental levels and potential sources of SCCPs are urgently required in China. To date, very limited studies have focused on SCCP contamination in China. Zeng et al. investigated the distribution of SCCPs in topsoil from wastewater irrigated farmlands,²¹ and in an aquatic ecosystem receiving effluents from the Gaobeidian Sewage Treatment Plant (STP), China.²⁰ High SCCP concentrations were found in the vicinity of the

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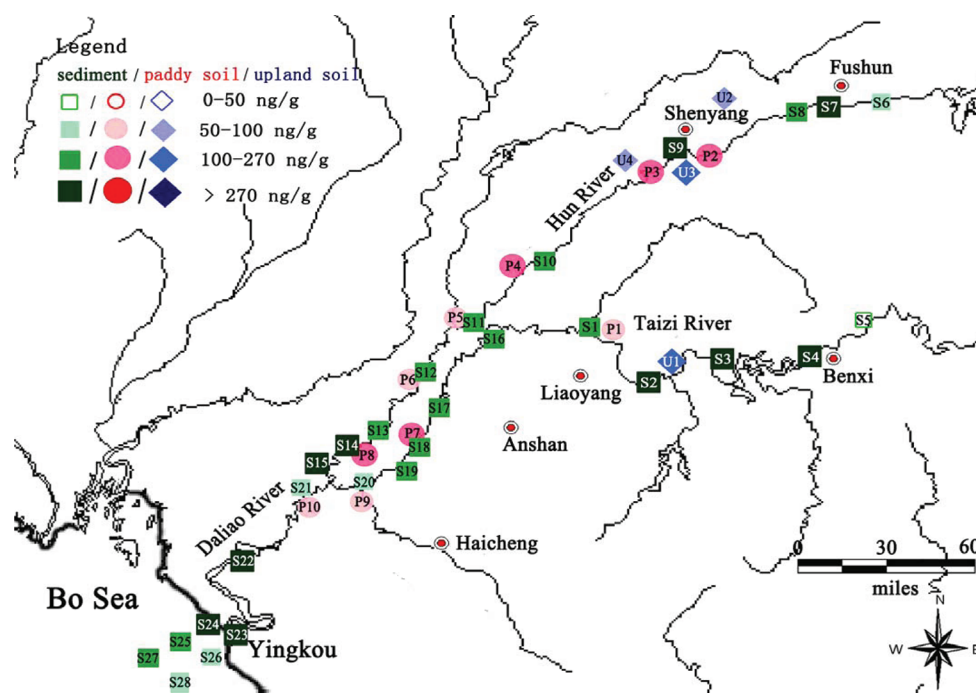


Figure 1. Spatial distribution of SCCPs (ng/g dry weight) in sediments (□), paddy soils (○) and upland soils (◇) from the Liaohe River Basin. Data for sediment samples S23–S28 collected from the mouth of the Daliao River taken from ref 24.

STP, and SCCPs were found to accumulate in soils and biomagnify through the food chain.^{20,21} Chen et al. determined the concentrations of SCCPs and MCCPs in sediments from the Pearl River Delta in South China, and found a wide range of concentrations from 320 to 6600 ng/g and from 880 to 38 000 ng/g, respectively.²² Long-range transportation was indicated as being the major input pathway for SCCPs in sediments from low industrial activity areas.²²

The Liaohe River, which includes the Taizi, Hun and Daliao rivers, is one of the most heavily polluted rivers in China.²³ The Taizi and Hun rivers flow into the Daliao River at their confluence, before finally entering the Bo Sea (Figure 1). The Liaohe River Basin is the largest industrial region in northeastern of China, with metallurgy, machinery, and the petrochemical, electronic, and building material industries since the 1950s. There are also more than one million acres of irrigated paddy fields in the basin. Until 2000, most industrial wastewater was directly discharged into the rivers without effective treatment. Up to 2011, about five CP manufacturers had been established in the Liaohe River Basin, and at least two of them were still producing CPs. In 2010, an investigation conducted by our research group indicated high contamination levels of SCCPs in sediments from the mouth of the Daliao River in the range of 64.9–407.0 ng/g.²⁴ A further investigation into the occurrence and distribution of SCCPs in the Liaohe River Basin was considered necessary to assess their ecological and human health risks.

The primary objective of this study was to gain an overview of the spatial distribution and congener group profiles of SCCPs in sediments from the Liaohe River and ambient environmental matrices such as paddy soils and upland soils. From these survey data, the potential contamination sources and transportation pathway for SCCPs were further explored. An attempt was also made to develop an inventory of SCCPs in the Liaohe River sediments and obtain correlations with local industrial wastewater emissions. It is hoped that this work will

be helpful in creating a SCCP inventory for China and developing a strategy for future reduction of SCCPs in the environment in China.

MATERIALS AND METHODS

Chemicals. Three SCCP technical mixtures (100 ng/μL in cyclohexane) with chlorine contents of 51%, 55.5%, and 63% were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). An internal standard and recovery standard of ¹³C₆-α-hexachlorocyclohexane (¹³C₆-α-HCH) and ¹³C₆-hexachlorobenzene (¹³C₆-HCB), respectively, in *n*-nonane were purchased from Cambridge Isotope Laboratories (Andover, MA, U.S.). Acetone, *n*-hexane, and dichloromethane (DCM) for pesticide residue analysis were obtained from J. T. Baker (Phillipsburg, NJ, U.S.). Three commercial CP mixtures (CP-42, CP-52, and CP-70) with chlorine contents of approximately 42%, 52%, and 70% were kindly provided by the Jiangxi Chemical Plant, Lvshun, China. Silica gel (63–100 μm) and basic alumina (Activity Super I, 63–200 μm, pH 10) were purchased from Sunchrom (Friedrichshafen, Germany), and MP Biomedicals (Eschwege, Germany), respectively. These two adsorbents, i.e., silica gel and basic alumina were extracted with DCM by accelerated solvent extractor (Dionex ASE 350, Sunnyvale, CA, U.S.) at 120 °C for three cycles, and then activated at 130 °C for 10 h prior to use. Acid silica gel was prepared by mixing 200 g of activated silica gel and 56.4 g of concentrated sulfuric acid. Anhydrous Na₂SO₄ (Damao, China) was cleaned with *n*-hexane in an ultrasonic bath for 30 min and then dried at 300 °C for 2 h before use.

Sampling of Sediments and Soils. Sediment samples were collected from the Liaohe River using a grab sampler in June 2010. Soil samples were collected using a stainless steel scoop. Five separate soil samples were taken from each site, and then mixed together to form one composite sample for each sampling site. The distribution and detailed location information for the sampling sites are shown in Figure 1 and

Table 1. Relative Concentrations of SCCPs and Their Congeners in Sediment, Paddy Soil, and Upland Soil Samples from the Liaohe River Basin

		concentration ng/g (dw)							concentration ng/g (dw)				
sample no.	Cl%	ΣC_{10}	ΣC_{11}	ΣC_{12}	ΣC_{13}	$\Sigma SCCPs$	sample no.	Cl%	ΣC_{10}	ΣC_{11}	ΣC_{12}	ΣC_{13}	$\Sigma SCCPs$
sediment													
S1	59.8	51.5	48.5	22.4	6.3	128.7	S15	61.3	119.3	139.6	77.7	31.2	367.8
S2	59.0	115.1	108.6	46.4	11.5	281.6	S16	57.7	71.1	72.9	16.1	2.9	163.0
S3	59.1	132.4	138.5	64.7	18.0	353.6	S17	59.5	69.8	93.0	37.9	11.3	212.0
S4	59.4	108.5	105.2	54.0	24.6	292.3	S18	61.4	67.2	74.6	44.5	15.4	201.7
S5	58.6	17.0	16.4	5.2	1.2	39.8	S19	59.0	103.8	108.7	34.5	14.0	261.0
S6	59.1	27.3	24.1	7.8	3.0	62.3	S20	59.4	35.2	36.7	14.0	4.2	90.1
S7	60.0	151.8	145.1	138.5	44.9	480.3	S21	57.8	39.3	42.9	11.5	2.5	96.3
S8	58.0	69.7	54.2	13.4	2.7	140.0	S22	58.4	140.5	212.4	46.2	16.5	415.6
S9	60.0	121.4	101.6	38.3	12.7	274.0	S23 ^a	58.9	181.5	161.7	51.3	12.5	407.0
S10	57.7	102.4	63.0	12.9	2.9	181.3	S24 ^a	59.4	115.4	112.9	42.3	11.3	281.9
S11	58.3	55.9	31.8	9.9	4.2	101.8	S25 ^a	60.4	29.2	30.8	41.3	8.5	109.8
S12	59.2	40.7	47.8	15.7	5.2	109.4	S26 ^a	60.3	25.3	21.5	21.4	6.2	74.4
S13	60.6	75.4	64.9	35.8	8.0	184.1	S27 ^a	59.3	62.3	69.5	32.4	14.5	178.7
S14	60.9	107.1	129.8	57.0	18.4	312.3	S28 ^a	59.8	19.6	24.1	15.5	5.7	64.9
paddy soil													
P1	59.4	31.4	26.5	10.9	2.9	71.7	P6	58.6	30.8	27.9	7.4	2.5	68.5
P2	58.5	77.2	58.0	15.1	4.2	164.5	P7	59.2	62.0	60.3	26.4	7.7	156.4
P3	59.5	62.7	69.3	28.4	10.7	171.1	P8	58.7	39.9	43.7	18.4	5.5	107.5
P4	59.2	46.5	55.6	18.7	8.4	129.2	P9	58.8	27.9	20.3	8.2	1.5	56.9
P5	58.8	28.5	23.2	7.7	2.1	61.5	P10	58.6	52.8	42.5	13.3	3.4	112.0
upland soil													
U1	58.9	82.7	70.9	30.8	4.9	189.3	U3	59.1	56.5	57.3	17.3	6.2	137.3
U2	59.1	43.2	30.6	11.7	1.9	87.4	U4	59.6	33.9	32.8	11.7	5.1	83.5

^aData for sediment samples S23–S28 collected from the mouth of the Daliao River taken from ref 24

Table SI-1 of the Supporting Information, SI, respectively. The collected samples were put into precleaned self-sealing aluminum/polyethylene bags with zippers, and transported to the laboratory on ice. Samples were freeze-dried, ground and homogenized by passing a stainless steel 60 mesh sieve. Finally, subsamples were stored in amber glass bottles at <4 °C until analysis. The sediment and soil samples were analyzed for their total organic carbon (TOC) contents, which are presented in Table SI-1 of the SI.

Extraction and Cleanup. The extraction and cleanup of SCCPs were carried out as according to our previous paper.²⁵ In brief, a 20 g subsample was spiked with 0.2 ng of ¹³C₆-α-HCH and then Soxhlet extracted with 250 mL of *n*-hexane/acetone (1:1, v/v) for 24 h. The extract was concentrated to ~1 mL for cleanup. Gel permeation chromatography was used for the removal of sulfur-containing compounds and toxaphene. The eluent was then concentrated before a two-step cleanup procedure using a silica gel column and a subsequent basic alumina column. Fractionation on the silica gel column packed with silica gel (2 g) and acid silica gel (4.5 g) was achieved with the solvent sequence: 50 mL of *n*-hexane, 100 mL of *n*-hexane/DCM (1:1) and 50 mL of *n*-hexane/DCM (1:2). The second and third fractions, containing SCCPs and HCH along with some other organochlorine compounds such as endrin ketone, endrin aldehyde, and *trans*-chlordane, were collected. A further fractionation was carried out on 5 g of basic alumina with 60 mL of *n*-hexane (discarded) and 90 mL of DCM. The DCM fraction contained all SCCPs and HCH, which were separated from the other interfering substances. After evaporation, the solution was further concentrated to near dryness under a gentle stream of N₂. A 0.2-ng portion of ¹³C₆-HCB in 10 μL of

n-hexane was added to the vial as a recovery standard before analysis.

The three commercial CP mixtures (CP-42, CP-52, and CP-70) were diluted to 100 mg/L in *n*-hexane, and 10 μL of each solution was added to a vial along with 0.2 ng of ¹³C₆-α-HCH and ¹³C₆-HCB in 10 μL of *n*-hexane as the internal and recovery standard, respectively.

Instrumental Analysis of SCCPs. The SCCPs were analyzed using high resolution gas chromatography/electron capture negative ion–low resolution mass spectrometry (HRGC/ECNI–LRMS) as previously described.²⁵ In brief, the chromatographic separation of SCCPs was performed on a Trace GC Ultra gas chromatograph (Thermo, U.S.) equipped with a capillary DB-5 column (15 m × 0.25 mm i.d. × 0.25 μm film thickness, J&W Scientific, U.S.). 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 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, U.S.) in ECNI mode was used to identify the SCCP congeners 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 and 260 °C, respectively. The two most abundant isotopes of the [M–HCl][–] cluster for each SCCP congener (5–10 chlorine atoms) were monitored. The [M–Cl][–] and [M][–] ions of the internal standard and recovery standard were selected as the monitoring ions. The dwell time in the selected ion monitoring mode was set to 75 ms for each ion, as described in detail elsewhere.²⁵

Method of Identification and Quantification. Identification of the SCCP congeners was performed by comparison of retention time, signal shape, and correcting isotope ratio. The congener group abundance profiles were obtained by correcting the relative integrated signals for isotopic abundance and response factors. The quantification of SCCPs in sediment and soil samples followed the procedure described by Reth et al.²⁶ A linear correlation was obtained between the total response factors of reference SCCP mixtures and their chlorine contents, which was allowed to compensate the influence of chlorine contents on the total response factors between environmental samples and reference SCCP mixtures.²⁶ In addition, interferences from MCCP congeners with five carbon atoms more and two chlorine atoms less could be effectively minimized by the chemical calculation methods described by Zeng et al.²¹

Quality Assurance and Quality Control. Precautions were taken in the use of glassware, solvents, and adsorbent materials. Before use, glassware was rinsed in triplicate with *n*-hexane. Adsorbent materials were pretreated as described above.

Method blanks were performed by analyses of blank samples subjected to the extraction and cleanup procedure described above. The method detection limit (MDL) for total SCCPs was determined by measuring the mean of the background signals from blank samples, and was reported as the mean plus three times the standard deviation. The MDL was determined at 14 ng/g ($n = 4$ samples). The recoveries of the internal standard and SCCPs were determined using four replicates with spiked samples. Mean recoveries for ¹³C₆- α -HCH and SCCPs were calculated as 92.2% and 92.7%, respectively. The run-to-run precision was tested, with relative standard deviations less than 5.3% for SCCPs.

■ RESULTS AND DISCUSSION

Concentrations of SCCPs in Sediments. All concentrations of SCCPs in sediments, paddy soils, and upland soils in the Liaohe River Basin were reported based on a dry weight (dw) basis and normalized with TOC. The results are shown in Table 1 and Table SI-2 of the SI, respectively. SCCPs were detected in all 22 sediment samples from the Liaohe River. The chlorine contents of SCCPs in the sediment samples were calculated to be in the range of 57.7–61.4%. The SCCP concentrations in sediments ranged from 39.8 to 480.3 ng/g with an average value of 212.2 ng/g, as shown in Table 1. Compared with previous studies of SCCPs in river sediments analyzed by HRGC/ECNI–LRMS, the contamination level in sediments from the Liaohe River was similar to that in sediments collected from a river in a typical industrial region with rubber, tanning, and textile industries in the Czech Republic (16.30–180.75 ng/g).²⁷ Parera et al. reported SCCP concentrations in river sediments from the Besòs River close to industrial effluents in Spain, which ranged from 270 to 3260 ng/g.²⁸ In the United Kingdom, Nicholls et al. found the highest SCCP levels in river sediments from industrialized areas in the Midlands and the north of England, with concentrations ranging from <0.2 to 65.1 μ g/g.¹¹ River sediments from the Pearl River Delta, China, exhibited higher concentrations of SCCPs than sediments from the Liaohe River in our study, ranging from 320 to 6600 ng/g.²²

In the upper reaches of the Liaohe River, the SCCP concentrations in sediment samples from the Taizi River (S5) and the Hun River (S6) were only 39.8 and 62.2 ng/g,

respectively. These relatively low SCCP concentrations in sediments may be considered as being environmental background values in view of the fact that there are low anthropogenic emissions of SCCPs upstream of these two rivers. As the Liaohe River flowed through industrial areas, the SCCP concentrations in the river sediments obviously increased.

In the Hun River, heavy SCCP contamination was found in the Fushun and Shenyang reaches as well as downstream. Sediment sample S7, collected near the Fushun STP mainly receiving industrial wastewater, had the highest SCCP concentration of 480.3 ng/g, which was about eight times higher than in sample S6, upstream of the STP. This implies that effluents from the Fushun STP might be a potential source of SCCPs in the surrounding environment. Sediment sample S9 was collected from the vicinity of Shenyang, and also had a relatively high SCCP concentration of 274.0 ng/g. In the middle reach of the Hun River, the concentrations of SCCPs (samples S10–S13) were relatively low, ranging from 101.8 to 184.1 ng/g. However, sampling sites located in the lower reaches of the Hun River showed relatively high levels of SCCPs. As shown in Figure 1, the concentrations of SCCPs in sediment samples S14 and S15 exceeded 300 ng/g, suggesting the existence of an important SCCP emission source nearby.

In the Taizi River, high SCCP concentrations were found in the Benxi and Liaoyang reaches (Figure 1), which is an industrial base for the production of steel and iron. The individual sediment samples collected near Benxi (samples S2–S4) had relatively high SCCP concentrations (all >280 ng/g). The SCCP contamination in the middle and lower reaches of the Taizi River was less, with concentrations ranging from 90.1 to 261.0 ng/g.

In the Daliao River, the SCCP concentrations in sediments collected from the upper and middle reaches were 96.3 and 415.6 ng/g, respectively. Sediment samples from the mouth of the Daliao River were analyzed previously by our research group, with concentrations ranging from 64.9 to 407.0 ng/g (Figure 1 and Table 1).²⁴ The relatively high SCCP concentrations were found in sediments from the mouth of the Daliao River, and the concentrations decreased from the mouth of the river to more remote locations. This may be attributed to the midestuarine maximum phenomenon arising from the intrusion of seawater into the upper-estuary region.²⁹ This involves the rapid deposition of fine sediment particles, resulting in high concentrations of sediment-associated SCCPs in the deposition zone.

It should be noted that the SCCP concentrations in sediments tended to decrease with increasing distance between the sampling sites and cities. Therefore, discharge of industrial wastewater was inferred to be responsible for the high levels of SCCP contamination in sediment samples collected near the cities. To evaluate the effects of industrial wastewater emissions on the spatial distribution of SCCPs in river sediments, the Liaohe River was gridded with 1 \times 1 km cells for spatial discretization over a total length of about 560 km. The spatial-temporal discharge amounts of industrial wastewater from cities along the Liaohe River were available in the Collection of Environmental Statistical Data of Liaoning Province (1980–2008), as shown in Figure SI-1 of the SI.³⁰ Taking the data from 2008 as an example, the highest annual discharge of industrial wastewater occurred in Shenyang with about 180 000 000 tonnes, followed by Benxi, Fushun, Liaoyang and Yingkou. A total amount of 414 000 000 tonnes of industrial wastewater

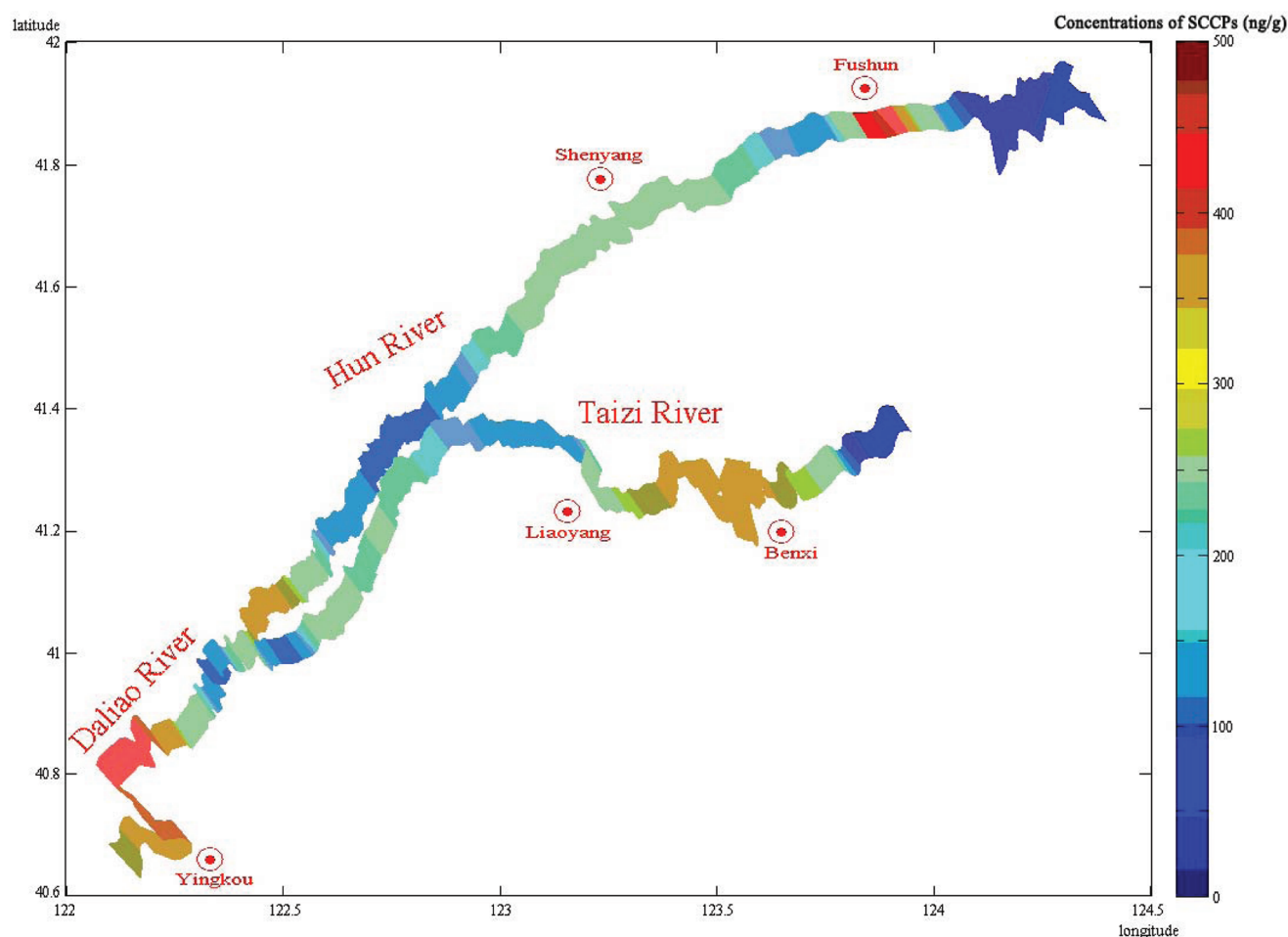


Figure 2. Spatial distribution of gridded (1×1 km) SCCP concentrations in sediments from the Liaohe River (including the Hun, Taizi, and Daliao rivers with a total length of about 560 km).

was discharged from these four cities into the Liaohe River. The SCCP concentrations in sediments from the Liaohe River were calculated using the piecewise cubic Hermite interpolating polynomial by the Matlab function. The calculation methods are shown in the SI. For locations that did not lie within the interval, an extrapolation method was used in the interpolating formula. Using this algorithm, gridded SCCP concentrations in the Liaohe River sediments were determined based on color gradients for each grid cell of the river (Figure 2). The spatial distribution pattern of SCCP concentrations in the Liaohe River sediments clearly showed a strong relationship with the distance from the cities and emission sources, as sites near the cities and emission sources had higher SCCP concentrations than sites in rural areas.

Both historical and current industrial activities appeared to influence the spatial trend of SCCPs in the river sediments. A surface sediment inventory for SCCPs was determined based on the gridded sediment areas and SCCP concentrations (Figure 2).³¹ The calculation equations are shown in detail in the SI. Approximately 30.82 tonnes of SCCPs accumulated in the Liaohe River sediments over the total length of 560 km. On the basis of the annual industrial wastewater discharge amounts in 2008, the average concentration of SCCPs in wastewater was estimated at about 74.4 mg per tonne of industrial wastewater (see the SI). The TOC normalized concentrations of SCCPs in sediments are shown in Table SI-2 of the SI, ranging from 2.0 to 147.3 $\mu\text{g/g}$. However, no significant relationships were

observed between the SCCPs and TOC concentrations in the sediment samples, suggesting relatively strong influence from local industrial emissions on the spatial distribution pattern of SCCPs. This result also indicated that the continuing discharge of SCCPs is happening.

Concentrations of SCCPs in Soils. A total of 10 paddy soil samples (P1–P10) and 4 upland soil samples (U1–U4) were collected and analyzed for SCCPs. As shown in Table 1, the total concentrations of SCCPs in paddy and upland soil samples were in the range of 56.9–171.1 ng/g and 83.5–189.3 ng/g, respectively. The chlorine contents of the SCCPs were calculated to range from 58.5% to 59.6%. In China, Zeng et al. investigated the SCCP concentrations in topsoils from a wastewater irrigated farmland using HRGC/ECNI–LRMS, and found a higher SCCP contamination level (159.9–1450 ng/g) than in this study.²¹

Similar to the distribution of SCCP concentrations in sediments, the soil samples collected near the cities and SCCP emission sources exhibited higher SCCP concentrations than in rural areas (Figure 1). This also suggested that the local industrial activity was the major source of SCCPs in soils. The TOC normalized concentrations of SCCPs in paddy and upland soil samples were in the range of 3.7–14.6 $\mu\text{g/g}$ and 4.6–15.0 $\mu\text{g/g}$, respectively, as shown in Table SI-2 of the SI. As with the sediment samples, no significant relationships were observed between the SCCPs and TOC concentrations in both paddy soils and upland soils, which indicated the strong

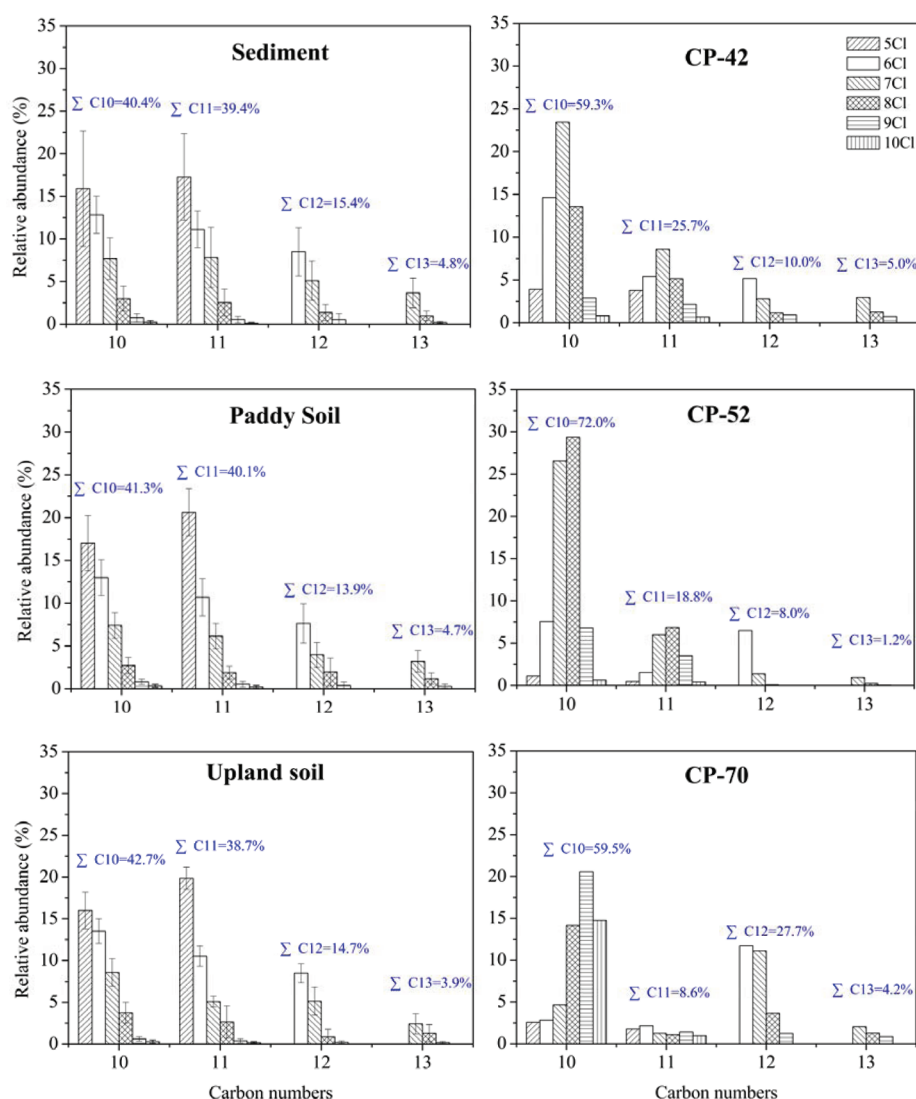


Figure 3. Average individual SCCP congener group profiles in sediment, paddy soil, and upland soil samples compared with three commercial CP mixtures (CP-42, CP-52, and CP-70).

influence of local emissions of SCCPs. In the Liaohe River Basin, rice is the main agricultural crop, and diverting river water for the irrigation of paddy fields is a common practice. Irrigation by river water is undoubtedly an important pathway for SCCP contamination of paddy soils. A correlation analysis between the SCCP concentrations in paddy soils and adjacent sediments showed no significant correlation ($R^2 = 0.49$ in Figure SI-2 of the SI), indicating that irrigation by river water was not the major transportation pathway for SCCPs. However, the SCCP concentrations in paddy soils were very similar to those in upland soils collected in the neighboring areas, in which no irrigation was used. As shown in Figure 1, the upland soil samples (U2–U4) and paddy soil samples (P2 and P3) collected around Shenyang had similar SCCP contamination levels. This is most likely due to long-range atmospheric transportation, via which SCCPs may migrate to sites in rural areas and deposit into the soils. Chen et al. also found SCCPs and MCCPs in sediments from low industrial activity areas, and considered atmospheric transportation to be the major pathway for SCCPs and MCCPs in the environment.²²

Congener Group Profile of SCCPs in Sediments and Soils. The average SCCP congener group profiles in the

sediment, paddy soil, and upland soil samples were compared with the congener group profiles in CP-42, CP-52, and CP-70 (Figure 3). These three commercial CP mixtures are produced in large quantities and are widely used in China, with CP-42 and CP-52 accounting for over 80% of the total production of CPs in China.³² In the sediment and soil samples, the relative abundances of the individual carbon chain groups were in the order of C_{10} -CPs > C_{11} -CPs > C_{12} -CPs > C_{13} -CPs. The C_{10} -CPs and C_{11} -CPs predominated, together accounting for more than 75% of the SCCP congener group profiles. This was consistent with the SCCP congener group profiles in CP-42 and CP-52, in which the C_{10} -CPs and C_{11} -CPs are the dominant congener groups. However, the dominant congener groups in commercial CP-70 are C_{10} -CPs and C_{12} -CPs, with a relative abundance of C_{12} -CPs at 27.3%, which is much higher than that of the C_{11} -CPs. The SCCP mass fractions in CP-42, CP-52, and CP-70 were determined to be 3.7%, 24.9%, and 0.5%, respectively. The relatively low content of SCCPs in CP-70, as well as its relatively low production amount, indicates that CP-70 is unlikely to be a major source of SCCPs in the environment. The SCCPs in the sediments and soils are likely

to mainly come from the production and use of CP-42 and CP-52.

The congener group profiles in the environmental samples differed substantially from those in the commercial CP mixtures (Figure 3). This is probably related to the differences in the physicochemical properties and environmental behaviors of the different congeners. Hilger et al. explored the effects of chain length on the log octanol–water partition coefficients ($\log K_{OW}$) of SCCPs and found that the $\log K_{OW}$ values increased almost linearly with increasing carbon atoms in the alkane chain.³³ Higher $\log K_{OW}$ values coupled with relatively higher log octanol–air partition coefficient ($\log K_{OA}$) values favor the accumulation of longer chain SCCP congeners in soils and sediments.⁹

The individual paddy soil samples collected in rural areas have higher relative abundances of shorter chain congener groups than samples collected near the cities. For example, in sample P3 near Fushun, the relative abundances of the C_{10} – to C_{13} –CPs were 36.6%, 40.5%, 16.6%, and 6.3% in order of increasing carbon atoms, while in sample P6, located distant from the cities and emission sources, the relative abundances were 44.9%, 40.7%, 10.8%, and 3.6%. The relative abundances of shorter chain congener groups (C_{10} –CPs) clearly increased while the relative abundances of longer chain congener groups (C_{12} – and C_{13} –CPs) decreased. A similar trend was also found in the individual upland soil samples. The possible reason for this trend is that the shorter chain SCCPs have a greater potential for long-range transportation owing to their higher vapor pressures and solubility compared with the longer chain SCCPs. These differences in congener group profiles between samples near the cities and in the rural areas further confirmed that the major pathway for SCCP migration to paddy soils and upland soils was via atmospheric transportation.

The relative average abundances of individual SCCP congener group based on the number of chlorine atoms in the sediment and soil samples were compared with those in the commercial CP mixtures as shown in Figure SI-3 of the SI. The SCCPs with 6 to 8 chlorine atoms were the predominant congener groups in CP-42 and CP-52, while in CP-70, the SCCPs with 7 to 10 chlorine atoms predominated. However, the predominant congener groups in the sediments and soils from the Liaohe River Basin were the SCCPs with 5 or 6 chlorine atoms. The significant differences in congener group profiles between the environmental samples and commercial mixtures indicated the dechlorination of the higher chlorinated SCCP congeners to the lower chlorinated congeners might occur in sediments and soils. This may be due to the differences in susceptibility to microbial and abiotic degradation between the different SCCP congeners.^{21,34} However, differences in the transportation abilities of SCCP congeners with different chlorine contents may also influence the SCCP congener group profiles in environmental samples, which should be investigated in detail in future studies.^{21,22,35}

This work demonstrated that industrial wastewater discharges into the Liaohe River have resulted in SCCP contamination of the environment. The production and use of commercial CP-42 and CP-52 are the major source of SCCPs in the Liaohe River Basin. Sampling sites near the cities and emission sources had the highest SCCP concentrations. An environmental inventory of SCCPs in surface sediments from the Liaohe River was developed, indicating that approximately 30.82 tonnes of SCCPs were residual in sediments along the 560 km river length. Atmospheric transportation could be the

major migration pathway for SCCPs into paddy soils and upland soils in rural areas. Transportation, i.e., adsorption and desorption, and transformation, i.e., environmental degradation, of SCCPs occurred in the environment, and these processes played an important role in the observed congener group profiles of SCCPs in the environment. Further detailed studies are needed to understand the environmental behavior of SCCPs and allow an evaluation of their ecological risk to the surrounding environment.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed location information for the sampling sites and TOC contents of the sediment, paddy soil, and upland soil samples (Table SI-1); the TOC normalized concentrations of SCCPs and their congeners in sediments, paddy soils and upland soils (Table SI-2); spatial-temporal discharge data of the regional industrial wastewater in the Liaohe River Basin in 1985–2008 (Figure SI-1); correlations between the SCCP concentrations in paddy soils and adjacent sediments (Figure SI-2); the calculation methods for the gridded SCCP concentrations and the inventory of SCCPs residual in the Liaohe River sediments; the comparison of average individual SCCP congener group profiles based on the number of chlorine atoms in environmental samples and commercial CP mixtures (Figure SI-3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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