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# Distribution, homologue pattern, sources, and environmental behavior of short-chain chlorinated paraffins in multi-media environments within the petrochemical industry of the Yangtze River Delta†

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Short-chain chlorinated paraffins (SCCPs) are widely found in the environment. However, limited information exists on the inter-media exchange and migration of SCCPs in the same region. In this study, a comprehensive survey of SCCPs was performed on various environmental substrates (including the surface soil, groundwater, and air) from a large petrochemical park in the Yangtze River Delta, and a total of 24 congener groups were measured. The SCCP concentrations, spatial variations, congener group profiles, and environmental behaviors during the water–land–atmosphere cycle in a typical industrial area were investigated. The  $\Sigma$ SCCP concentrations in the surface soil and groundwater within the petrochemical factory and in the atmosphere in the petrochemical factory perimeter were 108–745 ng g<sup>-1</sup>, 1133–2994 ng L<sup>-1</sup> and 12.1–30.5 ng m<sup>-3</sup>, respectively. The concentrations and homologue patterns of SCCP significantly varied across different sampling sites, which was attributed to the distances between the sampling sites and workshops, as well as the diverse CP products or byproducts involved in the processing activities. The congener profile revealed that C<sub>10</sub>Cl<sub>8,9</sub> and C<sub>13</sub>Cl<sub>8,9</sub> were the major SCCP homologue groups in the soil within the petrochemical park, whereas C<sub>10</sub>Cl<sub>5–7</sub> and C<sub>13</sub>Cl<sub>5–7</sub> were the predominant congeners in the groundwater, and C<sub>12,13</sub>Cl<sub>7,8</sub> was the dominant SCCP congener group in the atmosphere around the petrochemical park. With respect to the air–soil and soil–water exchange behaviors, the majority of fugacity fraction values for the air–soil and soil–groundwater samples were less than 0.3 and greater than 0.7, respectively, indicating the dominant deposition of SCCP congeners from the air to the soil and permeation into groundwater from the soil within the petrochemical park. To date, the preliminary risk assessments have indicated that SCCPs pose a low ecological risk in the petrochemical zone and pose a low risk to humans through dust ingestion and dermal contact.

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## Environmental significance

Short-chain chlorinated paraffins (SCCPs) are a global concern because of their high persistence in the environment, long-range transport potential, bio-accumulation and toxic characteristics. However, current researches have mainly focused on SCCPs using a single substrate with small sample sizes and narrow dispersion of research samples. The overarching data on the concentrations, distribution patterns, and compositions of homologue groups of SCCPs in various environmental substrates in the same region and during the same period, as well as the interfacial exchange behaviors between different substrates, are limited but vital for understanding SCCP migration in terrestrial environments. This research comprehensively investigates the contamination levels and potential sources of SCCP congener groups in multi-media environments, environmental behaviors in the water–land–atmosphere cycle, and the potential preliminary ecological and human health risks within a petrochemical park.

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## 1. Introduction

Chlorinated paraffins (CPs) are complex mixtures of chlorinated chain *n*-alkanes that contain tens of thousands of congeners, enantiomers, and diastereomers.<sup>1</sup> Commercial CPs are classified according to carbon chain length into short-chain chlorinated paraffins (SCCPs, C<sub>10–13</sub>), medium-chain chlorinated paraffins (MCCPs, C<sub>14–17</sub>), and long-chain chlorinated paraffins



(LCCPs, C<sub>18–30</sub>), with the degree of chlorination varying between 30% and 70%.<sup>2,3</sup> Owing to their high chemical and thermal stability, CPs are widely applied as flame retardants in plastics and textiles, as well as additives in cutting oils, paints, lubricants, rubber, and sealants.<sup>4</sup> With massive production and widespread usage, CPs have been detected in water,<sup>3,5,6</sup> soil,<sup>7–9</sup> sediments,<sup>5,10,11</sup> the atmosphere,<sup>12–14</sup> dust,<sup>15,16</sup> biota,<sup>6,17</sup> and even human tissue samples worldwide.<sup>7,18,19</sup> Since there are no known natural sources of CPs in the environment, almost all CPs observed in the environment are released during the manufacturing life cycle of CPs.

Compared to MCCPs and LCCPs, SCCPs have garnered more global concern because of their high persistence in the environment, long-range transport potential, bioaccumulation, and toxic characteristics.<sup>7,20–22</sup> Based on the above characteristics, SCCPs were listed in the Stockholm Convention as a new candidate category of persistent organic pollutants (POPs) in 2006, annexed as Annex A by the Conference of the Parties in 2017, and included in China's "List of Emerging Contaminants under Key Control (2023 edition)" released in December 2022.<sup>23,24</sup> With increasing industrial demand, the annual production of CPs in China has increased rapidly since 1978, which has made China become the largest producer and consumer of CPs in the world.<sup>21</sup> Moreover, due to chlorinated paraffin production enterprises span a wide range of industries, SCCPs can be released into the environment *via* various pathways.<sup>5</sup> For example, SCCPs released during the processing of solid wastes containing CPs can adsorb particles in the air and then settle into the soil and water *via* atmospheric deposition. Subsequently, SCCPs can be volatilized from the soil, landfills or water into the air and diffuse into the environment through subsurface flow and air movement.<sup>25,26</sup> In addition, SCCPs collected in sewer systems can accumulate in sewage sludge at wastewater treatment plants and be transferred to aquatic environments,<sup>27</sup> where they may ultimately enter the human body through various pathways, such as through food intake and dermal contact, posing potential risks to both the environment and human health.

Although many studies have reported the pollution levels of SCCPs in water, sediments, soil, the atmosphere, and organisms across China, there are some shortcomings in previous studies, including small sample sizes, narrow dispersion of research samples, and studies that have focused primarily on a single substrate. The overarching data on the concentrations, distribution patterns, and compositions of homologue groups of SCCPs in various environmental substrates in the same area and during the same period, as well as the interfacial exchange behavior between different substrates, are still scarce but vital for understanding SCCP migration in terrestrial environments. Therefore, comprehensive studies on the occurrence and potential sources of SCCP congener groups in multi-media environments in typical industries, along with potential ecotoxicological risk assessments, are needed.

In this study, groundwater samples, surface soil samples and air samples were collected from a typical industrial park in China. The contamination levels of SCCPs in various environmental substrates (including the soil, groundwater, and air) from the same industrial zone was investigated. The SCCP

concentrations were determined with the objective of (1) describing the spatial variations, homologue patterns, and potential sources in the petrochemical park; (2) characterizing their environmental characteristics in the water–land–atmosphere cycle; and (3) evaluating the preliminary ecological and human health risks around the zone.

## 2. Materials and methods

### 2.1. Sample collection

To comprehensively understand the contamination status of SCCPs in multi-media environments in the petrochemical industry, the surface soil, groundwater, and air samples were collected from a large petrochemical park in a city in the Yangtze River Delta (YRD), China, in December 2023. A total of 39 industrial surface soil samples (0–20 cm) were collected from thirteen sites (T1–T13), and three parallel samples were collected at each site. Additionally, a total of 18 agricultural surface soil samples (0–20 cm) were collected from six sites (TS1–TS6) in the green belt outside the petrochemical park, and three parallel samples were collected at each site. At each site, more than five discrete subsamples were collected and homogenized to form a composite surface sample. The soil samples were sealed in a pre-cleaned aluminum foil bag and stored at –20 °C until further analysis. The total organic carbon (TOC) content of the surface soil samples was determined *via* the potassium dichromate titrimetric method.<sup>28</sup> A total of 21 groundwater samples (0–3 m) from seven sites (W1–W7) were collected in brown bottles, and three parallel samples were collected at each site. After being transported to the laboratory, the water samples were filtered through a glass fiber filter (Whatman GF/F, 0.7 µm, 47 mm) and stored in a clean brown bottle at 4 °C prior to analysis. The dissolved organic carbon (DOC) content in the water samples was determined with a total organic carbon (TOC) analyzer (SHIMADZU, TOC-L CPH). The air samples were collected from factory perimeter sites using polyurethane foam-based passive air samplers (PUF-PASSs) (9.0 cm diameter, 5.0 cm thickness, and 0.03 g cm<sup>–3</sup> density). One site was upwind of the factory (A1), and two sites were downwind of the factory (A2 and A3). The samples were hung 1.5–2 m above ground in the open area, allowing the air to move freely. Each sample was collected over a 2 hour period, and the collection flow rate was 800 L min<sup>–1</sup>. After each sample was harvested, the PUF disk and filter membrane were wrapped, sealed, and transported to the laboratory and stored at –18 °C before analysis. The detailed geographical locations of the sampling sites are depicted in Fig. S1.†

### 2.2. Chemicals and materials

Standard SCCP solutions (C<sub>10–13</sub>, 51.5%, 55.5%, and 63% Cl) at 100 ng µL<sup>–1</sup> in cyclohexane and an epsilon-HCH solution at 10 ng µL<sup>–1</sup> in cyclohexane were purchased from Dr Ehrenstorfer, Germany. The <sup>13</sup>C<sub>10</sub>-*trans*-chlordan solution at 100 ng µL<sup>–1</sup> in cyclohexane was obtained from Cambridge Isotope Laboratories, USA. Dichloromethane (GC grade) and *n*-hexane (GC grade) were purchased from Anpel Laboratory Technologies



(Shanghai) Inc., China. Cyclohexane ( $\geq 99.9\%$ ) was purchased from Aladdin Reagent Co., Ltd (Shanghai), China.  $\text{H}_2\text{SO}_4$  and copper powder were purchased from Sinopharm Chemical Reagent Co., China. Silica gel (70–230 mesh, SiliCycle Inc. UltraPure Silica Gels and Chemistry, Canada) and neutral alumina (100–200 mesh, Sinopharm Chemical Reagent Co., China) were activated at 130 °C for 16 h prior to use, and then acidic silica gel (30%, w/w) was prepared by thoroughly mixing 100 g of silica gel with 44 g of concentrated sulfuric acid. Deactivated neutral alumina (6%, w/w) was prepared by adding ultrapure water and storing it in a desiccator. Florisil (100–200 mesh, Macklin Biochemical Technology Co., Ltd, China) and anhydrous sodium sulfate (Sinopharm Chemical Reagent Co., China) were heated at 450 °C for 6 h before use.

### 2.3. Sample extraction and cleanup

Due to the importance and challenges that arise with SCCP analysis, in particular the chromatographic separation within CPs and between CPs and other compounds, new and improved analytical methods for SCCPs have been developed.<sup>29–35</sup> However, gas chromatography, coupled to an electron capture negative ionisation mass spectrometry (GC/ECNI-MS), remains the most commonly applied method. In this study, short-chain chlorinated paraffins in groundwater samples were concentrated using liquid–liquid extraction (LLE), whereas in the soil and air samples, they were concentrated using accelerated solvent extraction (ASE), as reported in previous studies.<sup>26,36</sup> Briefly, 1 L of water was spiked with 10 ng of  $^{13}\text{C}_{10}$ -*trans*-chlordane surrogate standard and then subjected to liquid–liquid extraction with  $3 \times 80$  mL of a dichloromethane/*n*-hexane solution (3 : 1, v/v). The eluate was dried over anhydrous sodium sulfate and concentrated to 1–2 mL for clean-up. For the soil samples, the surface samples were freeze-dried, ground, homogenized, and then sieved through a stainless steel 100-mesh (0.154 mm) sieve. Briefly, an aliquot of a 10 g soil sample was mixed with 1 g of anhydrous sodium sulfate and 0.5 g of activated copper powder for sulfur removal. The sample was spiked with 10 ng of the  $^{13}\text{C}_{10}$ -*trans*-chlordane surrogate standard and extracted with an accelerated solvent extractor (Dionex ASE 350, Canada) at a temperature of 100 °C and a pressure of 1700 psi. The thermal equilibration time was 5 min, and static extractions were performed in three cycles, with 10 min per cycle, a rinse volume of 60%, and a purge time of 60 s. A solvent mixture of dichloromethane/*n*-hexane (1 : 1, v/v) was used as the extraction solvent. After extraction, the extract was concentrated to 1–2 mL for clean-up. For the passive air sample, the PUF disk and filter membrane were spiked with 10 ng of  $^{13}\text{C}_{10}$ -*trans*-chlordane as a surrogate and extracted using an accelerated solvent extractor (ASE, Dionex ASE 350, Canada) under the same conditions as those for the soil sample mentioned above. After extraction, the extract was concentrated to 1–2 mL for clean-up.

Subsequently, the filtrate was subjected to clean-up by a multilayer silica-Florisil composite column, which consisted of 3 g of anhydrous sodium sulfate, 3 g of florisil, 12 g of acid silica gel (30%, w/w), 2 g of activated silica gel, and 1 g of alkaline silica gel from bottom to top. The column was

successively eluted with 10 mL of *n*-hexane and with 120 mL of a dichloromethane/*n*-hexane mixture (1 : 4, v/v). The second fraction containing the SCCPs was collected, concentrated to near dryness under a gentle stream of  $\text{N}_2$ , and finally redissolved in 500  $\mu\text{L}$  of *n*-hexane containing 15 ng of  $\epsilon$ -HCH as a syringe standard before GC-ECNI-MS analysis.<sup>7</sup>

### 2.4. Instrumental analysis, identification, and quantification

Briefly, twenty-four homologue groups of SCCPs ( $\text{C}_{10-13}\text{Cl}_{5-10}$ ) were analyzed *via* gas chromatography coupled with a mass spectrometer (GC/MS, Agilent 8890/7000E GC/TQ) in electron capture negative ion (ECNI) mode with methane (99.995%) as the reagent gas. An aliquot of 1 mL of the final extract was injected into an HP-5MS (15 m  $\times$  250  $\mu\text{m}$   $\times$  0.25  $\mu\text{m}$ ) capillary column in splitless mode at an injector temperature of 250 °C. Helium was used as the carrier gas at a constant flow rate of 1.4 mL min<sup>−1</sup>. The oven temperature program for chromatographic separation was as follows: 2 min isothermal at 80 °C, increased to 300 °C at 10 °C min<sup>−1</sup>, and held for 10 min. The two most abundant isotopes of the  $[\text{M}-\text{Cl}]^-$  cluster for individual CP congener groups with 5–10 chlorine atoms were monitored in selected ion monitoring (SIM) mode, while the highest and second most abundant isotope ions of  $[\text{M}-\text{Cl}]^-$  were used for quantification and confirmation,<sup>37,38</sup> respectively, as listed in Table S1.† To minimize the interferences from MCCP congeners with five carbon atoms more and two chlorine atoms less, SCCP and MCCP congeners were simultaneously detected at each injection using the chemical calculation method described by Zeng *et al.*<sup>39</sup> All monitored ions of SCCPs and MCCPs were divided into four groups by mutual combination:  $\text{C}_{10}$  and  $\text{C}_{15}$ ,  $\text{C}_{11}$  and  $\text{C}_{16}$ ,  $\text{C}_{12}$  and  $\text{C}_{17}$ , and  $\text{C}_{13}$  and  $\text{C}_{14}$  (Table S1†), requiring four separate injections per sample. The most abundant isotopes of the  $[\text{M}]^-$  ( $m/z = 419.9$ ) and  $[\text{M}-\text{Cl}]^-$  ( $m/z = 254.8$ ) ions were selected for the surrogate standard  $^{13}\text{C}_{10}$ -*trans*-chlordane and recovery standard  $\epsilon$ -HCH, respectively. The representative chromatograms and mass spectra of the reference substances and samples are shown in Fig. S2 and S3.†

The identification of the SCCP congener groups was performed by comparing the retention times, chromatographic signal shapes, and corrected isotope ratios.<sup>40,41</sup> The quantification of SCCPs followed the procedure described by Reth. A linear correlation was observed between the total response factors of reference SCCP mixtures and their chlorine contents, which allowed for the compensation of the influence of chlorine content on the total response factors between environmental samples and reference SCCP mixtures.<sup>42</sup> The calibration curve was plotted based on three SCCPs standards and their mixtures with varying chlorine contents (Fig. S4†).

### 2.5. Quality control and quality assurance (QA/QC)

Strict quality assurance and control measures were implemented to ensure the correct identification and accurate quantification of data. All glassware and sodium sulfate were solvent-rinsed and heated at 450 °C for 6 h before use. Each batch of ten samples included one procedural blank to verify



the absence of possible cross-contamination. The quantitative results in this study were, therefore, not blank-corrected. The recoveries of SCCP standards (51.5%, 55.5%, and 63.0% chlorine content) and  $^{13}\text{C}_{10}$ -*trans*-chlordane from the spiked samples ranged from 78–96% and 58–106%, respectively. The recoveries of  $^{13}\text{C}_{10}$ -*trans*-chlordane from all environmental samples ranged from 68% to 102%. The method detection limits (MDLs) for SCCPs in soil, water, and air were estimated to be  $7.5 \text{ ng g}^{-1}$ ,  $0.06 \mu\text{g L}^{-1}$ , and  $0.5 \text{ ng m}^{-3}$ , respectively. The accuracy was controlled with spiked samples and was within 10% of the expected values. The reliability of the method was verified by repeated measurements of spiked blank soil and water samples. The relative errors for SCCPs at  $2 \mu\text{g}$  and  $5 \mu\text{g}$  levels were within acceptable ranges (soil:  $-4.0\%$  and  $-11.0\%$ ; water:  $-9.0\%$  and  $-6.1\%$ ), confirming the robustness and accuracy of the SIM-based quantification using  $[\text{M}-\text{Cl}]^{-}$  ions.

## 2.6. Statistical analyses

The sampling location distribution graphs were drawn *via* ArcGIS 10.8. Spearman correlation analysis was performed to characterize the significant relationship between the SCCP concentration and organic carbon content. The composition, distribution, and source of SCCP homologue groups were determined *via* principal component analysis (PCA). The fugacity fraction (ffs) values were calculated *via* fugacity model theory. Finally, the environmental risks and human health risks in different regions were evaluated *via* the quotient value method and the human exposure model.<sup>16,43</sup> All statistical analyses were conducted using IBM SPSS v27 and Origin 2019 software.

## 3. Results and discussion

### 3.1. Concentration levels of SCCPs in multi-media environments

The concentrations of SCCPs and their carbon homologues in multi-media environments (surface soil, groundwater, and air

samples) collected from a petrochemical park in a city in the Yangtze River Delta, China, are presented in Table 1. SCCPs were detected in all the environmental samples collected in and around the petrochemical zone (Fig. 1 and S5†). The total concentrations of SCCPs ( $\Sigma\text{SCCP}$ ) in surface soil inside the petrochemical factory ( $\Sigma\text{SCCP}_{\text{T}}$ ), surface soil outside the petrochemical factory ( $\Sigma\text{SCCP}_{\text{TS}}$ ), groundwater in the petrochemical factory ( $\Sigma\text{SCCP}_{\text{W}}$ ) and atmosphere in the petrochemical factory perimeter ( $\Sigma\text{SCCP}_{\text{A}}$ ) were  $108\text{--}745 \text{ ng g}^{-1}$  (median:  $233 \text{ ng g}^{-1}$ ),  $95\text{--}178 \text{ ng g}^{-1}$  (median:  $119.5 \text{ ng g}^{-1}$ ),  $1133\text{--}2994 \text{ ng L}^{-1}$  (median:  $1389 \text{ ng L}^{-1}$ ) and  $12.1\text{--}30.5 \text{ ng m}^{-3}$  (median:  $14.6 \text{ ng m}^{-3}$ ), respectively. The chlorine contents of the above SCCPs ranged from 61.39 to 65.35% (mean: 63.34%), 60.57 to 63.69% (mean: 61.75%), 59.66 to 62.47% (mean: 61.20%) and 62.97 to 63.23% (mean: 63.13%), respectively.

A comparison of the concentrations of SCCPs in soil samples from around China, as reported in recent studies, is given in Table S2.† The  $\Sigma\text{SCCP}_{\text{T}}$  values observed in the surface soil within the petrochemical factory in the present study were lower than those reported in the CP production plant from the e-waste dismantling area,<sup>44</sup> a contaminated area in Zhoushan,<sup>45</sup> the Liaohe River Basin,<sup>46</sup> the national farmland in China,<sup>7</sup> agricultural soil irrigated by Gaobeidian sewage,<sup>27</sup> soil in Dongguan,<sup>11</sup> and a chemical industry park in Jiangsu, China;<sup>47</sup> however, the  $\Sigma\text{SCCP}_{\text{T}}$  values were higher than those reported in the green belt outside the same petrochemical factory in the present study, outside the CP production plant from the Liaohe River Basin,<sup>46</sup> Chongming Island,<sup>48</sup> the intertidal zone of the Shandong Peninsula,<sup>3</sup> the Pearl River Delta, China,<sup>49</sup> background soil in the United Kingdom and various land use types in Switzerland.<sup>50,51</sup> The high concentration of SCCPs from the e-waste dismantling area in Taizhou is closely related to garbage dismantling activities,<sup>44</sup> whereas the high level of SCCPs in soil from the Liaohe River Basin may be because the Liaohe River Basin is one of the largest industrial areas in China, and most industrial wastewater is discharged into it.<sup>52</sup> In addition,

**Table 1** Concentrations of SCCPs and their homologue groups in surface soil ( $\text{ng g}^{-1}$  dw), groundwater ( $\text{ng L}^{-1}$ ) and air ( $\text{ng m}^{-3}$ ) from a petrochemical park in a city in the Yangtze River Delta, China

	Range	Mean	SD	Median	DF%		Range	Mean	SD	Median	DF%
<b>Soil</b>						<b>Soil</b>					
<b>In the petrochemical park</b>						<b>In green belt outside the petrochemical park</b>					
Cl%	61.39–65.35	63.34	1.1	63.13	100	Cl%	60.57–63.69	61.75	0.8	61.66	100
C <sub>10</sub>	31.9–165.8	70.3	27.3	67.2	100	C <sub>10</sub>	35.6–68.4	50.2	7.2	49.2	100
C <sub>11</sub>	20.9–279.7	72.3	62.2	49.6	100	C <sub>11</sub>	13.8–42.7	25.7	7.8	25.8	100
C <sub>12</sub>	20.0–183.1	58.6	37.8	50.3	100	C <sub>12</sub>	10.6–26.4	18.7	5.7	18.5	100
C <sub>13</sub>	28.6–275.7	89.8	70.2	63.8	100	C <sub>13</sub>	17.3–59.3	31.7	11.5	27.7	100
$\Sigma\text{SCCP}_{\text{T}}$	108–745	290.9	173.9	233	—	$\Sigma\text{SCCP}_{\text{TS}}$	95–178	126.4	24.1	119.5	—
TOC ( $\text{g kg}^{-1}$ )	2.7–22.3	11.9	6.3	9.3	—	TOC ( $\text{g kg}^{-1}$ )	3.2–7.4	5.0	1.8	4.4	—
<b>Groundwater</b>						<b>Air</b>					
Cl%	59.66–62.47	61.20	0.008	61.45	100	Cl%	62.97–63.23	63.13	0.001	63.18	100
C <sub>10</sub>	679.5–1679.6	783.3	247.1	682.2	100	C <sub>10</sub>	2.8–7.4	4.5	2.5	3.4	100
C <sub>11</sub>	190.7–553.2	283.6	100.9	252.8	100	C <sub>11</sub>	3.1–7.6	4.8	2.5	3.6	100
C <sub>12</sub>	135.9–540.0	232.9	99.1	195.4	100	C <sub>12</sub>	3.2–7.7	4.9	2.4	3.7	100
C <sub>13</sub>	182.6–693.1	295.8	128.9	240.4	100	C <sub>13</sub>	3.0–7.8	4.9	2.6	3.9	100
$\Sigma\text{SCCP}_{\text{W}}$	1133–2994	1374.7	437	1389	—	$\Sigma\text{SCCP}_{\text{A}}$	12.1–30.5	19.1	9.9	14.6	—
DOC ( $\text{mg L}^{-1}$ )	1.5–89.8	21.6	33.8	4.2	—						







Fig. 1 Spatial distributions of SCCPs in (a) surface soil, (b) groundwater and (c) air from a petrochemical park in a city in the Yangtze River Delta.

Gaobeidian Lake is a receiver of effluents from the Gaobeidian sewage treatment plant; hence, agricultural soil irrigated with Gaobeidian sewage has a high SCCP content.<sup>27</sup> In conclusion, the high concentration of SCCPs is typically associated with the heavy industries, production, usage, and recycling activities of electronic, electrical and plastic products.

Compared with other recent reported worldwide studies (Table S3†), the  $\Sigma\text{SCCP}_w$  values observed in the groundwater samples from the petrochemical park in this work were lower than those detected in water samples from the middle reach of the Yangtze River, China,<sup>53</sup> sewage treatment plants from Gaobeidian with heavy industries,<sup>27</sup> and urban snow cover from Gothenburg, Sweden.<sup>54</sup> In contrast, snow had a good ability to capture and accumulate SCCPs as a “container” for pollutants. However, the  $\Sigma\text{SCCP}_w$  values were higher than those in the Bohai Sea,<sup>55</sup> rivers in Shanghai,<sup>5</sup> the Lao-Jie River, Taiwan, China,<sup>56</sup> rivers and lakes in Beijing, China,<sup>57</sup> rivers in industrial areas from the United Kingdom,<sup>58</sup> and the Arc River and Berre Lagoon, France.<sup>59</sup> On the whole, when the water source is closer to heavy industries or CP production/usage factories, the concentration of SCCPs is higher in the water.

In addition, a comparison of the atmospheric concentrations of SCCPs reported in studies worldwide is given in Table S4.† The atmospheric concentrations of  $\Sigma\text{SCCP}_a$  in the petrochemical factory perimeter obtained from this study were lower than those reported from Xi'an,<sup>60</sup> a district in Beijing in summer,<sup>61</sup> Jinan<sup>15</sup> and India,<sup>62</sup> yet higher than those reported by Lhasa and Shergyla Mountain in the Tibetan Plateau, China,<sup>63</sup> Japan,<sup>59</sup> the United Kingdom,<sup>64</sup> Bear Island, Norway<sup>65</sup> and the Pearl River Delta, China.<sup>49</sup> In general, the atmospheric concentrations of SCCPs are usually higher when the sampling site is closer to the heavy industry production area.

### 3.2. Spatial distribution of SCCPs in multi-media environments

As shown in Fig. 1, the concentrations of SCCPs obtained from this study revealed apparent spatial variations in SCCPs among the different sampling sites for all environmental substrates.

For surface soil inside the petrochemical park, higher levels of SCCPs were observed at sites T10, T1, T6 and T11, with maximum concentrations of  $745 \text{ ng g}^{-1}$  (mean:  $675 \text{ ng g}^{-1}$ ),  $736 \text{ ng g}^{-1}$  (mean:  $541 \text{ ng g}^{-1}$ ),  $519 \text{ ng g}^{-1}$  (mean:  $427 \text{ ng g}^{-1}$ ) and  $416 \text{ ng g}^{-1}$  (mean:  $347 \text{ ng g}^{-1}$ ), respectively (Fig. 1a). Among them, Site T10 was located close to the petroleum hydrogen production plant. Thus, the high concentration of SCCPs at site

T10 might be ascribed to CP products or byproducts involved in the process of producing hydrogen from petroleum. Sites T1 and T11 were both located near the hydrocracking workshop, indicating that the high levels of SCCPs at these sites may be related to CP-containing products used in hydrocracking processes. Moreover, lower levels of SCCPs were observed at sites T5, T2, T12, T7 and T8. The low levels of SCCPs at sites T5, T12 and T7 were all near wax tanks/xylene tanks, whereas site T2 was located close to the hazardous waste dump, and site T8 was near the delayed coking workshop.

For groundwater inside the petrochemical park, higher levels of SCCPs were detected at sites W2 and W6, with maximum concentrations of  $2994 \text{ ng L}^{-1}$  (mean:  $2537 \text{ ng L}^{-1}$ ) and  $2201 \text{ ng L}^{-1}$  (mean:  $1733 \text{ ng L}^{-1}$ ), respectively (Fig. 1b). Sites W2 and W6 were near the hydrocracking workshop, while the high levels of SCCPs at these sites may also be attributed to the CP-containing products used in the hydrocracking process. Similarly, the lower levels of SCCPs at sites W7 and W3 were also located near the wax tanks/xylene tanks, and site W4 was located near the delayed coking workshop. In general, the concentrations of SCCPs in the soil and groundwater samples from adjacent sites were sequenced similarly in the same environmental substrate (T5/W3, T8/W4, and T11/W6), indicating that the SCCPs in the surface soil and groundwater within the petrochemical zone may have a similar source.

For the air at the perimeter of the petrochemical park, higher levels of SCCPs were observed at the downwind sites A2 and A3, with concentrations of  $14.6 \text{ ng m}^{-3}$  and  $30.5 \text{ ng m}^{-3}$ , respectively (Fig. 1c). Therefore, the higher concentrations of SCCPs in air at downwind of the boundary rather than it at upwind were nearly related to industrial activities.

DOC and TOC are important chemical parameters that might affect the desorption and adsorption of hydrophobic organic compounds in groundwater and soil. In this study, the DOC contents in the water ranged from  $1.5$  to  $89.8 \text{ mg L}^{-1}$ , with a mean value of  $21.6 \text{ mg L}^{-1}$  (Table 1). Spearman correlation analysis results suggested that the concentrations of  $\Sigma\text{SCCP}_w$  were not significantly correlated with the DOC content ( $p > 0.05$ ) (Table S5†). In addition, the TOC content of the surface soil within the petrochemical park ranged from  $2.7$  to  $22.3 \text{ g kg}^{-1}$ , with a mean value of  $11.9 \text{ g kg}^{-1}$ . Spearman correlation analysis results suggested that the concentrations of  $\Sigma\text{SCCP}_t$  were also not significantly correlated with the TOC content ( $p > 0.05$ ), which also indicates that the TOC content might not play an important role in the accumulation of SCCPs and local



industrial emissions might have a greater impact on the SCCP concentration in the surface soil.<sup>55,66</sup>

### 3.3. Homologue patterns of SCCPs in multi-media environments

The relative abundances of SCCP homologue groups in the multi-media environments (surface soil, groundwater, and air samples) are shown in Fig. 2. Among the surface soil samples collected from within the petrochemical park (surface soil<sub>in</sub>), the composition of the SCCP carbon congener groups was dominated by the C<sub>10</sub> and C<sub>13</sub> homologue groups, accounting for 29.1% and 28.2%, respectively, of the total abundance of SCCPs, followed by the C<sub>11</sub> (mean: 23.5%) and C<sub>12</sub> (mean: 19.2%) congener groups (Fig. 2a and S6†). Among the chlorine congeners, Cl<sub>8</sub> (mean: 21.4%) and Cl<sub>9</sub> (mean: 21.1%) were the most abundant congener groups. The lower chlorinated congeners (Cl<sub>5–7</sub>) accounted for only 39.3% of the total SCCP (Fig. 2b). This abundance pattern is consistent with that of the soil samples from the site located approximately 1.5 km outside a CP manufacturing plant<sup>3,57</sup> and corresponds to the composition of three major commercial CP products (CP-42, CP-52, and CP-70) manufactured in China,<sup>52</sup> suggesting that the carbon isogenic characteristics of SCCPs in surface soil may be related mainly to the regional migration and transport mode of industrial CP-containing products.

Compared with the SCCP composition of surface soil within the petrochemical park (surface soil<sub>in</sub>), the abundance ordering of carbon homologues (C<sub>10</sub> > C<sub>13</sub> > C<sub>11</sub> > C<sub>12</sub>) in the green belt outside the petrochemical park (surface soil<sub>out</sub>) was similar (Fig. 2a and S7†), and the abundance of C<sub>10</sub> increased slightly (mean: 38.6%), whereas that of C<sub>13</sub> decreased (mean: 26.1%). Several studies have shown that the C<sub>13</sub> content is relatively high in heavily polluted soil.<sup>67,68</sup> However, the chlorinated congener groups in the green belt outside the petrochemical park were different from those within the petrochemical park, whereas the lower chlorinated congener groups (Cl<sub>5–7</sub>) accounted for 54.6% of the major homologue groups (Fig. 2b). The differences in pollution sources between industrial (within the

petrochemical park) and agricultural areas (outside the petrochemical park) and the different transmission distances may influence the distribution patterns of chlorinated congener groups. In addition, SCCPs may undergo a variety of complex environmental processes, such as distribution, dechlorination, fractionation, and degradation, during their propagation,<sup>47</sup> which may also affect chlorine homologues in the surface soil inside and outside the park.

The carbon homologue profiles of SCCPs in the groundwater samples from the petrochemical park were quite similar to those in the surface soil samples (C<sub>10</sub> > C<sub>13</sub> > C<sub>11</sub> > C<sub>12</sub>) (Fig. 2a and S8†). Compared with the SCCP homologue profiles in the soil within the petrochemical park, the apparent discrepancy was that the relative abundance of C<sub>10</sub> in the groundwater increased significantly (mean: 51.2%), which might be due to its higher water solubility and greater potential for long-range transportation in comparison with other SCCP homologues.<sup>69</sup> The higher C<sub>10</sub> in the group distribution of SCCPs both in groundwater and soil outside the petrochemical park rather than in soil inside the petrochemical park indicates that the shorter carbon chain homologues have more potential to disperse from the industrial regions into the surrounding environment, and this phenomenon is referred to as the “Fractionation Effect”.<sup>70,71</sup> In contrast to the soil inside the petrochemical park, lower chlorinated congener groups (Cl<sub>5–7</sub>) accounted for 66.5% of the groundwater samples (Fig. 2b). The discrepancies may be attributed to the relatively high volatility and water solubility of chlorinated congeners, whereas CPs with longer chains and higher chlorination rates have higher octanol–water partition coefficient (*K*<sub>OW</sub>) and octanol–air partition coefficient (*K*<sub>OA</sub>) values, which lead to lower dispersal capacity in the atmosphere and are prone to accumulation in the soil.<sup>66,72,73</sup>

The chemical distribution patterns of SCCPs in the atmosphere around the petrochemical park are shown in Fig. 2a and S9†. Overall, the compositions of all the carbon chains were similar, while the C<sub>12</sub> and C<sub>13</sub> homolog groups accounted for 25.9% and 25.6% of the total abundance of SCCPs, respectively,

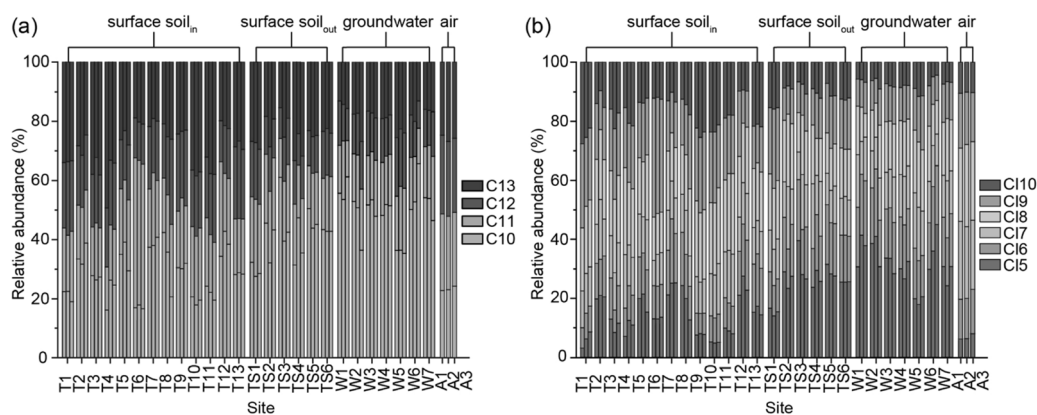


Fig. 2 Relative abundance patterns of SCCP (a) carbon congener groups and (b) chlorinated congener groups in surface soil samples from the petrochemical park (surface soil<sub>in</sub>), surface soil samples from the green belt outside the petrochemical park (surface soil<sub>out</sub>), groundwater samples from the petrochemical park and air samples from the petrochemical park.



followed by the  $C_{11}$  (mean: 25.2%) and  $C_{10}$  (mean: 23.3%) congener groups. The composition in the atmosphere was similar to that reported by Lancaster, United Kingdom, but significantly different from that reported in China and Japan, where  $C_{10}$  and  $C_{11}$  were the dominant components, respectively.<sup>60</sup> The dominant chlorine atoms were  $Cl_8$  and  $Cl_7$ , accounting for 26.4% and 24.7%, respectively, of the total chlorine content (Fig. 2b). Notably,  $Cl_8$  and  $Cl_7$  were the dominant groups in the air around the petrochemical zone, consistent with the surface soil samples collected from within the petrochemical park.

### 3.4 Factorial analysis of SCCPs in multi-media environments

To investigate the potential sources of SCCPs in surface soil, groundwater and the atmosphere, principal component analysis (PCA) was used in this study. PCA was performed on a dataset containing 63 surface soil or groundwater samples from within the petrochemical park or atmosphere samples from around the petrochemical park and 24 SCCP homologue groups ( $C_{10-13}Cl_{5-10}$ ). Two factors (F1 and F2) were extracted, and factor loading plots of the SCCP homologue groups are given in Fig. 3.

For the surface soil collected from within the petrochemical park, all the carbon chain homologues were divided into two parts, and the two dimensions explained a significant proportion of the original variance, with a cumulative contribution of 91.9% (Fig. 3a). F1 explained 80.0% of the total variance and was loaded by  $C_{10}$ -SCCPs,  $C_{12}$ -SCCPs and  $C_{13}$ -SCCPs, whereas F2 accounted for 11.9% of the total variance and was associated with  $C_{11}$ -SCCPs, suggesting similar sources for nearly almost of the carbon chain homologues of SCCPs and these SCCPs mainly originated from sources of commercial CP products due to their usage. The PCA of 24 chlorine homologues of SCCPs is shown in Fig. 3b, and the PCA results revealed that the first two factors

accounted for 85.5% of the total variance. F1 explained 68.8% of the total variance and was characterized by a large proportion of SCCP homolog groups. F2 accounted for 16.7% of the total variance and was highly associated with the lower chlorinated congener groups (including  $C_{10}H_{17}Cl_5$ ,  $C_{11}H_{19}Cl_5$ ,  $C_{12}H_{21}Cl_5$ ,  $C_{13}H_{23}Cl_5$ ,  $C_{13}H_{22}Cl_6$ ,  $C_{11}H_{16}Cl_8$ , and  $C_{11}H_{15}Cl_9$ ). These SCCP homologues with low molecular weights have higher subcooled-liquid vapor pressures than other CP homologues in commercial CP formulations,<sup>74</sup> indicating that they have a relatively high long-range atmospheric transport (LRAT) potential and are easily separated from other CP homologues in commercial CP formulations and CP-containing materials.

For groundwater within the petrochemical park, all the carbon chain homologues were roughly divided into two parts, with the first two factors accounting for 98.4% of the total variance (Fig. 3c). F1 explained 85.6% of the total variance and was loaded with  $C_{11}$ -SCCPs,  $C_{12}$ -SCCPs and  $C_{13}$ -SCCPs, whereas F2 accounted for 12.8% of the total variance and was associated with  $C_{10}$ -SCCPs, suggesting similar sources for nearly all of the carbon chain homologues of SCCPs. Furthermore, the PCA results revealed that the carbon chain homologues in groundwater were close to those in the soil outside the petrochemical park (Fig. S10a†), rather than to those in the soil within the petrochemical park (Fig. 3a), suggesting that the SCCPs deposited in the surrounding soil outside the petrochemical park were attributed mainly to subsurface flow. The PCA results of the 24 chlorine homologues of SCCPs revealed that the first two factors accounted for 77.2% of the total variance (Fig. 3d). F1 explained 65.3% of the total variance and was characterized by a large proportion of SCCP homolog groups, with the exception of lower chlorinated congener groups (including  $C_{10}H_{17}Cl_5$ ,  $C_{10}H_{16}Cl_6$ ,  $C_{12}H_{21}Cl_5$ , and  $C_{13}H_{23}Cl_5$ ). F2 accounted for 11.9% of the total variance and was highly correlated with

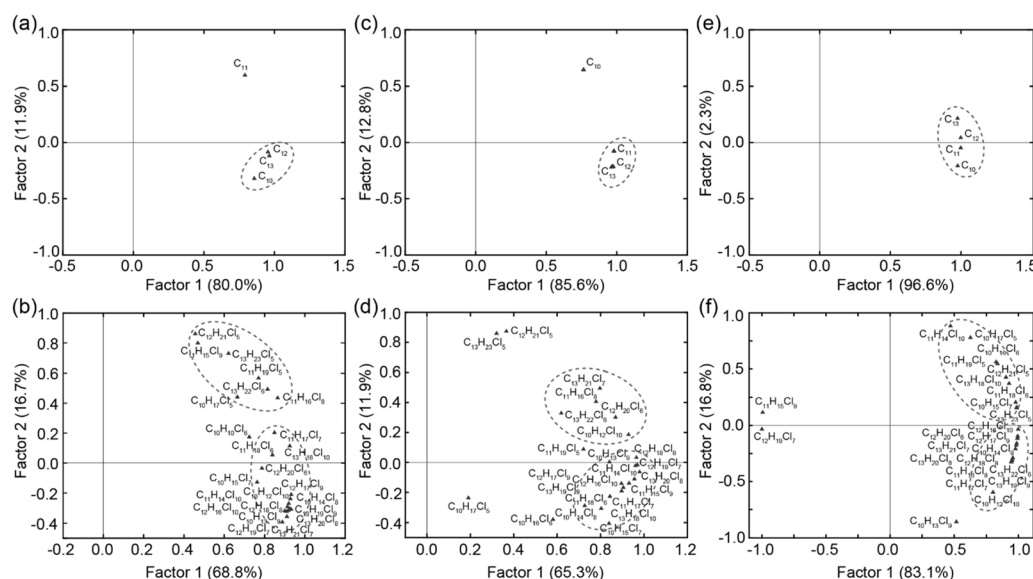


Fig. 3 Principal component analysis of SCCP carbon homologues and chlorinated congener groups in (a and b) surface soil within the petrochemical park, (c and d) groundwater within the petrochemical park, and (e and f) air in the perimeter of the petrochemical park.



$C_{12}H_{21}Cl_5$  and  $C_{13}H_{23}Cl_5$ , which had relatively high subcooled-liquid vapor pressures and relatively high LRAT potentials.

For air at the perimeter of the petrochemical park, the two dimensions accounted for 98.9% of the total variance for all the carbon chain homologues (Fig. 3e). F1 explained 96.6% of the total variance and was loaded by all the carbon chain homologues, whereas F2 accounted for 2.3% of the total variance, suggesting similar sources for the total carbon chain homologues of SCCPs. The PCA results of the chlorine homologues of SCCPs indicated that the first two factors accounted for 99.9% of the total variance (Fig. 3f). F1 explained 83.1% of the total variance and was characterized by most SCCP homolog groups except  $C_{11}H_{15}Cl_9$  and  $C_{12}H_{19}Cl_7$ , whereas F2 accounted for 16.8% of the total variance and was highly correlated with most  $C_{10}$ -SCCPs and  $C_{11}$ -SCCPs.

### 3.5 Environmental behavior of SCCPs

The directions (equilibrium states) of soil–air and soil–groundwater exchanges were investigated based on the fugacity model theory to study the environmental behaviors of SCCPs in soil, groundwater and air. Theoretically, a fugacity fraction ( $ff$ ) = 0.5 indicates that SCCPs are at soil–air or soil–water equilibrium. Owing to the uncertainties in data,  $0.3 < ff_{SA} < 0.7$  is typically considered the soil–air equilibrium, where  $ff_{SA} > 0.7$  indicates net volatilization and  $ff_{SA} < 0.3$  represents net deposition.<sup>13,75</sup> Similarly,  $0.3 < ff_{SW} < 0.7$  is considered as the soil–water equilibrium, whereas a value of  $ff_{SW} < 0.3$  indicates that SCCPs are deposited from water to soil, and  $ff_{SW} > 0.7$  indicates that SCCPs are released from soil to water.<sup>76</sup>

A box and whisker plot of the  $ff_{SA}$  for the soil–air exchange of SCCPs is shown in Fig. 4a. The majority of  $ff_{SA}$  values of SCCPs both inside and outside the petrochemical park were less than 0.3, indicating that the soil in the research area was nearly a net recipient of SCCPs from the atmosphere. The  $ff_{SA}$  for  $C_{10}Cl_5$  at site T7 exceeded 0.7, and the  $ff_{SA}$  values for  $C_{11}Cl_5$ ,  $C_{12}Cl_5$  and  $C_{13}Cl_5$  exceeded 0.5, demonstrating that the shorter carbon and lower chlorinated congeners were more water soluble and volatile. These findings are similar to those of studies near incinerators and shipyards in Zhoushan, China, in which

almost all the CPs, with the exception of one point, exhibited a settling state.<sup>45</sup> Overall, as shown by the spatial distribution (Fig. 4b), deposition from the atmosphere to the soil is the dominant process of SCCPs around the petrochemical zone.

In addition, the fugacity fraction values of the SCCPs between the soil and groundwater ( $ff_{SW}$ ) from within the petrochemical system were obtained, as shown in Fig. 5a and b. Except for  $C_{10}Cl_{5-7}$ , most of the  $ff_{SW}$  values of the SCCPs between the soil and groundwater samples from adjacent sites exceeded 0.7, which suggested that the SCCPs were deposited from the soil to the groundwater. Based on the above analysis, we infer the possible migration process of SCCPs: the SCCPs used/produced in industrial production first settle into the surface soil from the air within the petrochemical zone and then penetrate into the groundwater, followed by deposition into the surrounding soil outside the petrochemical zone with subsurface flow and air movement. However, here, we only calculated the exchange directions of SCCPs for soil–air and soil–groundwater, which are two separate compartments. In the future, we aim to develop an environmental multimedia fugacity model of SCCPs, which is often used to predict the distribution and migration processes of organic pollutants in large-scale environments, to predict the environmental fate of POPs. The model will consist of four main compartments (air, water, sediment and soil), and sub-compartments including the aerosol phase, suspended solid phase and biota phase. Mass transport between different compartments will also be modeled, considering volatilization, diffusion, deposition and runoff.<sup>77</sup>

### 3.6 Risk assessment of SCCPs

Risk quotient (RQ) is the most common method used to characterize the degree of ecological risk in soil and is often applied to assess the toxicological effects of individual compounds, whether quantitatively or semi-quantitatively.<sup>45</sup> Based on the concentration levels and toxicity data of SCCPs in the surface soil within the petrochemical park, the risks in the petrochemical park were classified into two risk levels for SCCPs (Table S7†). The RQ values of the SCCPs at T1 (the

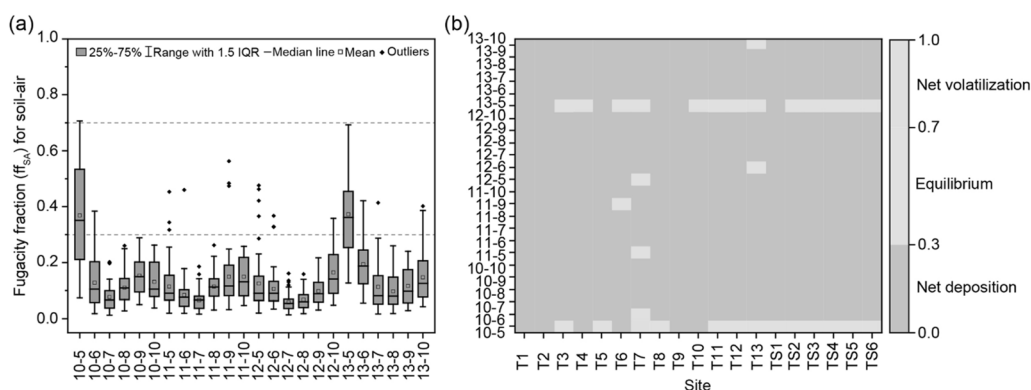


Fig. 4 (a) Box plot of the soil–air fugacity fraction ( $ff_{SA}$ ) for SCCP homologues inside and outside the petrochemical park. (b) Fugacity fraction of SCCPs between surface soil and air from different sites. Note: the congener labels indicate the number of carbon and chlorine atoms (e.g., 10–5 represents  $C_{10}H_{17}Cl_5$ ).





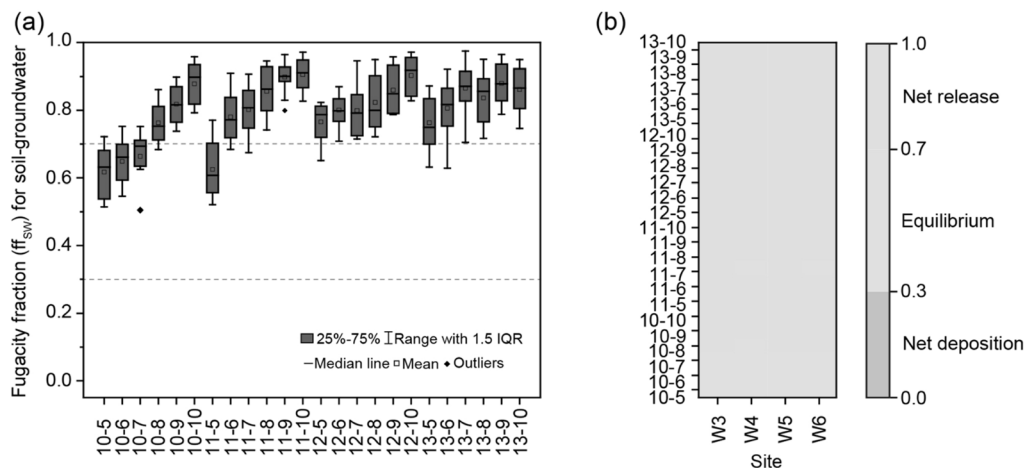


Fig. 5 (a) Box plot of the soil–water fugacity fraction ( $ff_{SW}$ ) for SCCP homologues inside the petrochemical park. (b) Fugacity fraction of SCCPs between surface soil and groundwater from different sites.

hydrocracking workshop) and T10 (the oil hydrogen production workshop) were 0.102 and 0.128, respectively, which were slightly higher than 0.1, both of which were at the medium risk level (0.1–1).<sup>40</sup> After the removal of T1 and T10, the RQ values of the SCCPs at the remaining sampling points were in the range of 0.025–0.081, all of which were at low risk levels (0.01–0.1). For comparison, the RQ values of SCCPs in the green belt outside the petrochemical park ranged from 0.019 to 0.026, indicating a low risk level. In general, the pollution of SCCPs in industrial areas poses a relatively low ecological risk to the surrounding environment, although it may harm the biological community within industrial areas to a certain extent.

Moreover, human exposure to SCCPs *via* ingestion and dermal contact around the petrochemical park was further assessed.<sup>78</sup> The exposure assessments revealed that the daily exposure rates of SCCPs *via* ingestion and dermal permeation for humans were  $2.87 \times 10^{-5}$ – $4.05 \times 10^{-3}$  and  $3.45 \times 10^{-5}$ – $2.53 \times 10^{-3}$   $\mu\text{g}$  per kg per day (Fig. S11 and Table S8†), respectively, which were below the tolerated daily intake of 10  $\mu\text{g}$  per kg per day outlined in the Canadian Environmental Protection Act,<sup>79</sup> indicating that the population in this area is not yet at risk of health exposure from SCCPs pollution. Collectively, SCCPs in the petrochemical zone pose a low ecological and health risk; however, more attention should be given to several key workshops, and effective measures should be taken to reduce the usage and discharge of CP products, thereby preventing further pollution by SCCPs.

## 4. Conclusion

In conclusion, SCCP homologues in multi-media environments (including surface soil, groundwater, and air samples) from a large petrochemical park were investigated. The SCCP concentrations markedly differed at the different sampling sites, which was attributed to the distances between the sampling sites and workshops, as well as the diverse CP products or byproducts involved in the processing activities. Higher

concentrations of SCCPs were detected in the soil within the petrochemical park than in the soil outside the petrochemical park. In addition to their concentrations, the homologue patterns of SCCPs also differ across various environmental substrates. Specifically,  $C_{10}Cl_{8,9}$  and  $C_{13}Cl_{8,9}$  were the major SCCP homologue groups in the soil within the petrochemical park, whereas  $C_{10}Cl_{5-7}$  and  $C_{13}Cl_{5-7}$  were the predominant congeners in the groundwater within the petrochemical park, and  $C_{12-13}Cl_{7,8}$  was dominant in the atmosphere around the petrochemical park. Furthermore, the environmental behaviors of SCCPs in the water–land–atmosphere cycle around the petrochemical zone were clarified by the soil–air and soil–groundwater exchange directions, in which the majority of SCCP homologues were deposited primarily from the air into the soil and then penetrated into the groundwater within the petrochemical park, followed by deposition into the surrounding soil outside the petrochemical zone owing to groundwater discharge and air diffusion. So far, SCCPs in the petrochemical zone pose a low ecological risk at most sampling sites. Both children and adults were exposed to SCCPs at levels below the tolerated daily intake of 10  $\mu\text{g}$  per kg per day, *via* different exposure pathways. Further work is recommended to study the distribution, homologue composition, and environmental dynamics of MCCPs and LCCPs in the same region, and to construct an environmental multimedia fugacity model to predict the distribution and migration processes of SCCPs in large-scale environments, as well as their ecological fate.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Jiaying Wang: conceptualization, investigation, methodology, validation, formal analysis, and writing – original draft. Xue



Wang: investigation, methodology, and formal analysis. Zai-hong Zhu: investigation and resources. Saixia Ying: supervision. Kashif Hayat: methodology, validation, and writing – review & editing. Xiaoxia Bai: validation. Shuren Liu: methodology and formal analysis. Xuexi Xiao: formal analysis and supervision. Chongwei Jin: supervision, validation, and writing – review & editing. Weiping Liu: supervision, conceptualization, and writing-review & editing.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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