

# Chlorinated Paraffins in Sediments from the Pearl River Delta, South China: Spatial and Temporal Distributions and Implication for Processes

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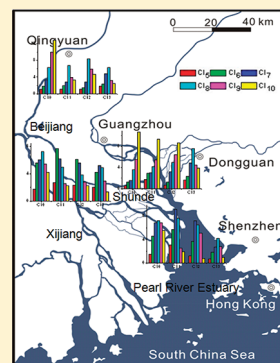
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**S** Supporting Information

**ABSTRACT:** Short-chain and medium-chain chlorinated paraffins (SCCPs and MCCPs) were measured in sediments from ponds, rivers and tributaries, and an estuary, as well as a sediment core in the Pearl River Delta (PRD), South China, to comprehensively investigate the spatial and temporal distributions of CPs. The concentrations of SCCPs and MCCPs in sediment were varied from 320 to 6600 ng/g and from 880 to 38 000 ng/g, respectively. Elevated CP concentrations were found in pond sediments (means of 2800 and 21 000 ng/g for SCCPs and MCCPs) in the e-waste recycling area and in river sediments (means of 1200 and 3900 ng/g for SCCPs and MCCPs) in the highly industrialized areas. The significant positive correlations between SCCP concentration and MCCPs/SCCPs in the highly industrialized areas reflected the emission of local industry activities, while the significant negative correlations in the low industrial activity areas could be linked to long-range transportation of CPs. An increased abundance of short chain and low chlorinated congeners was observed in the low industrial activity areas compared to the industrialized areas. The preferred transportation of short chain and low chlorinated congener CPs and the dechlorination of higher chlorinated congeners CPs were the most likely reasons. The vertical profile of CPs in the sediment core indicated a rapid increase in the usage of CPs and a shift to more MCCPs in recent years. The decreased chlorine content of CPs with increasing sediment depth indicated the possibility of dechlorination of higher chlorinated congeners (Cl<sub>9</sub> and Cl<sub>10</sub>) after deposition in sediments with greater dechlorination potential for short chain CPs than long chain CPs.



## INTRODUCTION

Chlorinated paraffins (CPs) with the formula (C<sub>n</sub>H<sub>2n+2-z</sub>Cl<sub>z</sub>) are subdivided into short-chain (C<sub>10</sub>–C<sub>13</sub>, SCCPs), medium-chain (C<sub>14</sub>–C<sub>17</sub>, MCCPs) and long-chain (C > 17, LCCPs) according to their carbon chain length, where chlorine content ranges from 10% to 72%.<sup>1</sup> Because of their chemical and thermal stability, CPs were widely used as additives in lubricants, as cutting fluids for metal working, as plasticizers and flame retardants in plastics, sealants, and leather.<sup>2</sup>

As high production volume chemicals, CPs are inevitably released into the environment during their production, transportation, and usage. CPs have been detected in various environmental matrices including water, sediment, air, soil, biota, and human beings.<sup>1</sup> It is also suggested that CPs are bioaccumulated and biomagnified in food webs.<sup>3</sup> CPs, especially SCCPs, have attracted increasing attentions in the past decade as they represent a potential “new” category of persistent organic pollutants (POPs).<sup>4</sup> The European Union restricted the usage of SCCPs via the Water Framework Directive based on the SCCP risk assessment.<sup>5,6</sup> Furthermore, SCCPs have been banned for use in Germany since 2003.<sup>1</sup>

Many studies have reported the concentrations of SCCPs in sediment around the world.<sup>7–11</sup> However, few studies have been conducted to investigate the environmental behavior of CPs during their transport and aging in the sediment. Previous studies have demonstrated that SCCPs could biodegrade under aerobic condition and usually biodegradation occurred in chlorinated paraffins with low degree of chlorination.<sup>12–15</sup> Recently, Thompson and Noble (2007)<sup>16</sup> investigated the biodegradation of SCCPs in both freshwater and marine sediments under aerobic and anaerobic conditions. The results showed that although mineralization of the testing substance occurred under aerobic conditions, the rate of mineralization was low, with a mean half-life of around 1630 days in freshwater sediment and around 450 days in marine sediment. Mineralisation was not evident under anaerobic conditions over the time frame of this study. In above studies, no parent compound

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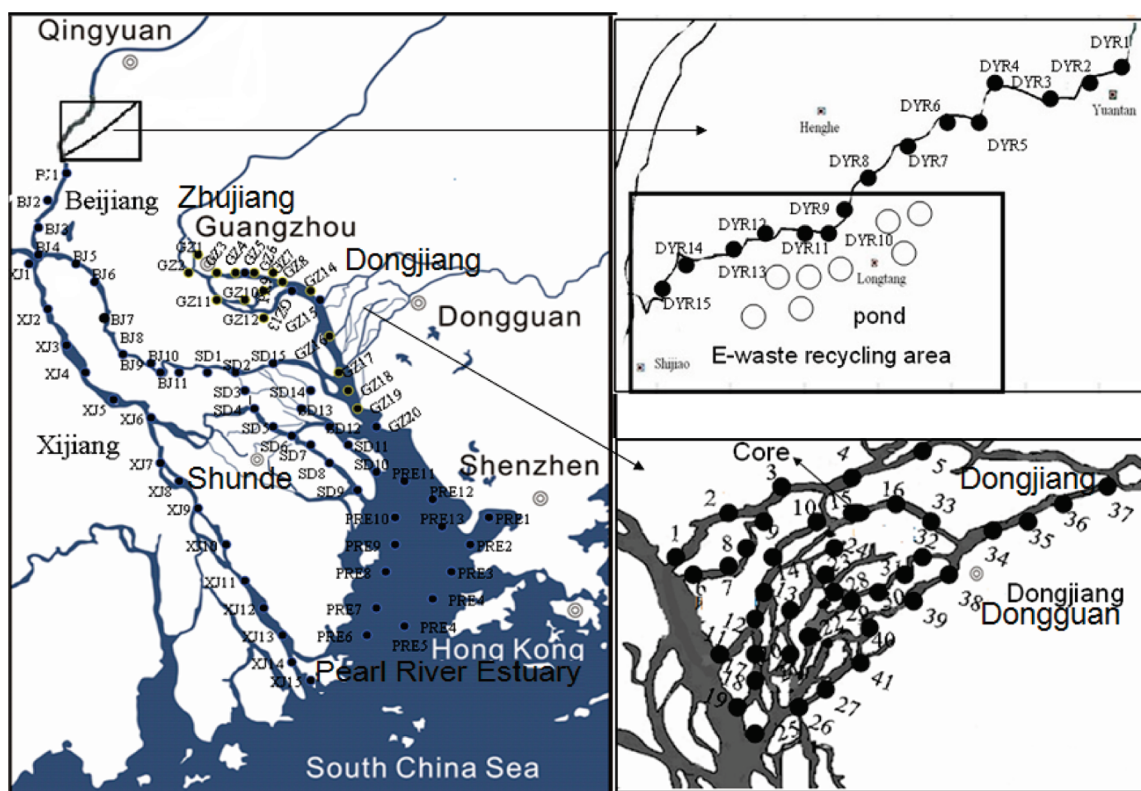


Figure 1. Map of the sampling areas.

analysis was carried out to investigate biodegradation and so the extent of primary degradation was not determined. Few studies have reported the environment fate of CPs in sediment. Tomy et al.<sup>17</sup> observed a trend with enrichment of  $C_{10}$  congeners and decrease of  $C_{12}$  congeners at the lower layers of dated sediment cores from Fox Lake. Similarly, Zeng et al.<sup>18</sup> found the increase of short chain and low chlorinated congeners ( $C_{10}Cl_{5-6}$ ) and the decrease of long-chain and high chlorinated congeners ( $C_{11-12}Cl_{7-8}$ ) with depth of sediment core from Gaobeidian Lake, northern China. These studies suggested that possible microbial mediated transformation of SCCPs occurred in sediments.

China is the world's largest producer and consumer of CPs. The annual production of CPs was only a few thousand tons in China in the early 1990s, whereas it increased to about 1 000 000 tons in 2009.<sup>19</sup> However, very little information is currently available on the occurrence of CPs in the Chinese environment.<sup>18,20-22</sup>

As one of the fastest developing regions in China in recent decades, the Pearl River Delta (PRD) region is experiencing accelerated environmental deterioration. The emergence of e-waste recycling practices during the past decade has compounded these issues. Elevated levels of POPs, including organo-chlorine pesticides, flame retardants and polycyclic aromatic hydrocarbons, have been detected in both abiotic and biotic compartments in the PRD and the e-waste recycling regions.<sup>23-27</sup> The PRD region is a complex watershed characterized by a great number of tributaries and streams, forming three river networks called the Xijiang River (XJ, the West River), the Beijiang River (BJ, the North River), and the Dongjiang River (DJ, the East River) (Figure 1). The pollutants from the PRD region are discharged into the river networks and finally transported to the South China Sea via the Pearl River Estuary (PRE). To our

knowledge, no studies on CPs in the environment in the PRD have been conducted.

In the present study, surface sediments from the three river networks in the PRD, tributaries and ponds in an e-waste recycling area, and the PRE were collected. A sediment core from the DJ River was also collected. The levels and congener profiles of SCCPs and MCCPs were determined. The aim of the present study was to comprehensively examine the status of CP contamination and temporal trends in the aquatic environment of the PRD. The transport behavior was investigated by comparing the level and congener pattern of SCCPs and MCCPs in different sampling areas. The potential dechlorination of CPs in sediments was also assessed by examining the change in the abundances of different chlorinated congeners within each carbon chain group through-out the sediment core.

## EXPERIMENTAL SECTION

**Sampling Area and Sample Collection.** Sediment samples were collected in the PRD region from July 2009 to October 2010. Twenty-three surface sediments were collected in the e-waste recycling region (Qingyuan County) (Figure 1). Of those samples, 15 samples were collected from the Dayan River (DYR), a tributary of the BJ River, which runs through three towns in Qingyuan County (Yuantan, Longtang, and Shijiao towns). The e-waste recycling industry is the pillar industry in the later two towns. The remaining 8 samples were collected from ponds scattered throughout the e-waste recycling region (Longtang town). The e-waste recycling practices in this area have been previously described in detail.<sup>24</sup> A total of 102 surface sediment samples were collected in the three river networks in the PRD. Of the 102 samples, 15 samples were collected in the

main stream of the XJ River; 11 samples were collected in the main streams of the BJ River; and 76 samples were collected in the lower river drainages of the BJ and the DJ Rivers. These river drainages are composed of a number of tributaries and run through three heavily industrialized and urbanized cities in the PRD: Guangzhou (GZ), Shunde (SD), and Dongguan (DG). Thus, samples in these areas were considered as highly industrialized area samples. On the other hand, the main streams of the BJ and XJ Rivers flow through the northwest part of the PRD where the levels of urbanization and industrialization are low. Samples collected in these two main streams were representative of low level industry activity regions. Thirteen estuarine sediments were collected from the PRE, which is regarded as an important reservoir of pollutants from the PRD. A sediment core (E 113°37'01", N 23°04'24") at the DJ River within DG city, the largest manufacturing base of electronic products in the PRD, was also collected to investigate the temporal trend of CPs in the PRD.

The sediment samples were collected using a Van Veen stainless steel grab sampler. The top 5 cm sediment was taken with the sampler. The sediment core was collected using a gravity corer, and the core was sliced at 4 cm intervals at the site. The depth of the core was approximately 68 cm. A previous study obtained sedimentation rates of 4–6 cm/yr after the 1990s near our sampling locations.<sup>28</sup> Therefore, the top 68 cm of sediment was expected to encompass about 15 years of depositional records corresponding to the time period when electronic industries experienced growth in DG city. All samples were immediately transported in icebox to the laboratory, where they were stored at –20 °C until analysis was performed.

**Extraction and Clean-Up.** A homogenized dry sediment (approximately 10 g) was spiked with the surrogate standards (25 ng of <sup>13</sup>C<sub>10</sub>-trans-chlordane) and Soxhlet extracted with 200 mL of dichloromethane for 24 h. Activated copper granules were added to the extraction flasks to remove elemental sulfur. The extract was concentrated and the solvent changed to hexane, and further reduced to approximately 1 mL. The extract was cleaned and fractionated on a 10 mm i.d. silica column packed, from the bottom to top, with florasil (14 g, 3% water deactivated), neutral silica (2 g, 3% water deactivated), acid silica (10 g, 44% sulfuric acid), and anhydrous sodium sulfate (2 g). The column was eluted with 80 mL of *n*-hexane (first fraction) followed by 60 mL of dichloromethane (second fraction). The second fraction containing CPs was concentrated to near dryness and then reconstituted in 500 μL of isooctane. *ε*-HCH was added as an internal standard for GC/MS analysis.

**Instrumental Analysis, Identification, and Quantification.** The CPs (C<sub>10</sub>–C<sub>17</sub> with Cl<sub>5</sub>–Cl<sub>10</sub>) were quantified using gas chromatograph/electron capture negative ionization/low resolution mass spectrometry (GC-ECNI-LRMS) as described by Oehme et al.<sup>29</sup> Briefly, analyses were performed on a gas chromatograph QP-2010 coupled to a 1200 L triple quadrupole mass spectrometer (Shimadzu). The gas chromatograph was equipped with a split/splitless injector and a DB-5 HT (15 m × 0.25 mm) (J&W Scientific, Folsom, CA) capillary column. The injector temperature was set to 250 °C, the transfer line temperature was 280 °C, and the ion source temperature was 200 °C. The temperature program was as follows: 80 °C for 3 min, increasing at 25 °C/min to 160 °C and held for 6 min, then increasing at 20 °C/min to 280 °C and held for 15 min. The mass spectrometer was employed in the ECNI mode with methane as moderating gas at an ion source pressure of 730 Pa. The mass-to-charge

ratios used for their quantification and identification were published elsewhere.<sup>9</sup> The most abundant isotope was used for quantification, and the second most abundant isotope was used for identification of possible interferences from CPs themselves or from interfering compounds. To improve the instrument sensitivity, all monitored ions of CPs were divided into four groups: C<sub>10</sub> and C<sub>11</sub>, C<sub>12</sub> and C<sub>13</sub>, C<sub>14</sub> and C<sub>15</sub>, and C<sub>16</sub> and C<sub>17</sub>. Therefore, there are four individual injections were executed for each sample. The method developed by Zeng et al.<sup>18</sup> has been applied to identify and minimize mass interferences by simultaneous detection of SCCPs and MCCPs.

The applied quantification procedure was described by Tomy et al.<sup>30,31</sup> A reliable quantification can be achieved if the degree of chlorination of the samples was similar to those of the standards. In this study, the calculated chlorine contents were approximately 62.7–66.1% for SCCPs and 58.0–59.6% for MCCPs. Therefore, we used SCCPs with chlorine content of 63.0% and MCCPs with chlorine content of 57.0% as standards for quantitative work which closely resembled the analytes of sediments. The quantification method of SCCPs and MCCPs in the analytes and standards is given by following formula.

$$\text{inj massCP(an)} = \frac{\text{SIM(an)}}{\text{SIM(st)}} \times \frac{m/z_{\text{ab}}(\text{st})}{m/z_{\text{ab}}(\text{an})} \times \frac{\text{formab(st)}}{\text{formab(an)}} \\ \times \frac{\text{molar mass(an)}}{\text{molar mass(st)}} \times \text{inj massCP(st)}$$

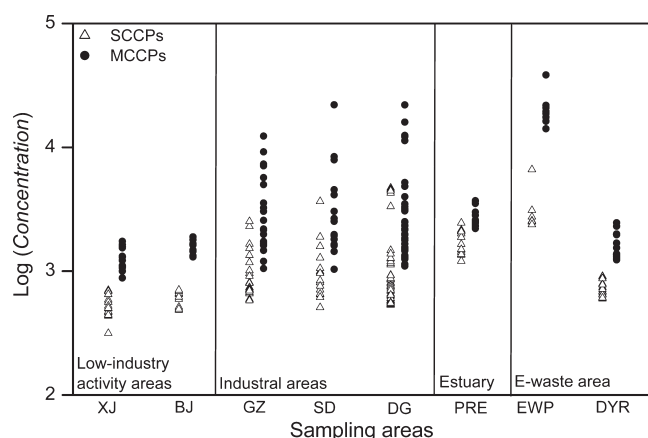
From this equation, inj mass CP (an) is the concentration of CP in the environment sample, and inj mass CP (st) is the concentration of standard; SIM is the integrated ion signal of the monitored *m/z* peak; *m/z* ab is the fractional relative abundance of the monitored *m/z* species in the ion formula; form ab is the fractional relative abundance of the molecular formula in the CPs; and molar mass is the average molar masses of standard (st) or analyte (an).

**QA/QC.** Quality assurance was performed by analyses of procedural blanks, spiked blanks and sample duplicates. Procedural blanks were processed for each batch of samples. No CPs were detected in the procedural blanks. Three spiked blanks and three spiked matrixes were processed, in which 25 μg commercial CP mixtures and 25 ng <sup>13</sup>C<sub>10</sub>-trans-chlordane were spiked in blank solvent and pre-extracted sediments. The recoveries of SCCPs and MCCPs in the spiked blanks ranged from 85.5–98.0% and 90.7–97.6%, respectively, with relative standard deviations less than 10%. The recoveries of CPs in spiked matrix ranged from 85.5–98.6%, and the relative standard deviations were less than 15% for all targets. The recoveries of surrogate standards (<sup>13</sup>C<sub>10</sub>-trans-chlordane) ranged from 90.6% to 101%. As for sample duplicates, the relative standard deviations were less than 8% with the exception of C<sub>16</sub>H<sub>28</sub>Cl<sub>6</sub> (8.6%) and C<sub>17</sub>H<sub>31</sub>Cl<sub>5</sub> (9.3%). The limit of quantification (LOQ) was set as a signal-to-noise ratio of 3 with a sample size of 10 g. LOQs ranged from 0.144 to 3.47 ng/g for SCCPs and from 0.530 to 2.24 ng/g for MCCPs, respectively.

**Total Organic Carbon Analysis.** The sediment samples were determined for total organic carbon (TOC) with a total organic carbon analyzer (Vario EL III from Elementar, Germany). Prior to the TOC measurements, about 1 g samples were treated with 1 mol/L HCl to remove carbonate residues.

**Data Analysis.** CP concentrations were reported on a dry weight basis (dw). Concentrations below the LOQ were considered to be zero. Simple linear regression analysis was used to





**Figure 2.** Concentrations (log) of SCCPs and MCCPs in sediments from the Pearl River Delta. XJ: Xijiang River; BJ: Beijiang River; GZ: Guangzhou section; SD: Shunde section; DG: Dongguan section; PRE: Pearl River Estuary; EWP: ponds in e-waste area; DYR: Dayan River.

examine the correlation between the levels of MCCPs and SCCPs, and the correlation between the ratios of MCCPs/SCCPs and log (SCCPs) in different sampling areas. All statistical analyses were conducted with SPSS software. The level of significance was set at 0.05 throughout the present study.

## RESULT AND DISCUSSION

**CP Spatial Distribution.** As shown in Figure 2, the concentrations of SCCPs were displayed in the following order of: ponds in the e-waste recycling region (EWP, mean of 2800 ng/g) > the PRE (mean of 1700 ng/g) > DG section (mean of 1200 ng/g), GZ section (mean of 1100 ng/g), and SD section (mean of 1100 ng/g) > DYR (mean of 830 ng/g) > the BJ River (mean of 610 ng/g) and the XJ River (mean of 530 ng/g).

It was not a surprise that the highest SCCPs level was found in the ponds in the e-waste recycling areas. Recycling of plastics could be a source of CPs depending on the extent of dust control at the facility.<sup>32,33</sup> The discarded electronic, electrical and plastics products were stacked in the ponds or on the bank of the ponds in the e-waste recycling area. Thus, CPs were released into the surrounding environment and resulted in high CPs in the pond sediments. The SCCP levels (600–690 ng/g) in the upper reaches of the DYR (sites DYR1 to DYR 8) were much lower than those (910–1100 ng/g) in the lower reaches (sites DYR9 to DYR15). The DYR runs through the e-waste recycling area in its lower reaches. Obviously, e-waste recycling activities were the main cause for the elevated CP levels in the lower reaches. Yuan et al.<sup>21</sup> also found relatively high levels of SCCPs in the soil (2.9 mg/g) from an e-waste dismantling area in China, confirming releases from e-wastes were important source of CPs in the environment.

The concentrations of SCCP in the PRE sediments were higher than those in the river sediment except for some specific sites, which could be related to the brackish nature of water in the estuary. Due to the mixture of freshwater and seawater, the physicochemical properties of water in the estuary changed remarkably compared to freshwater, which result in the deposition of suspended particle and the salting out effect of hydrophobic organic pollutants.<sup>34</sup>

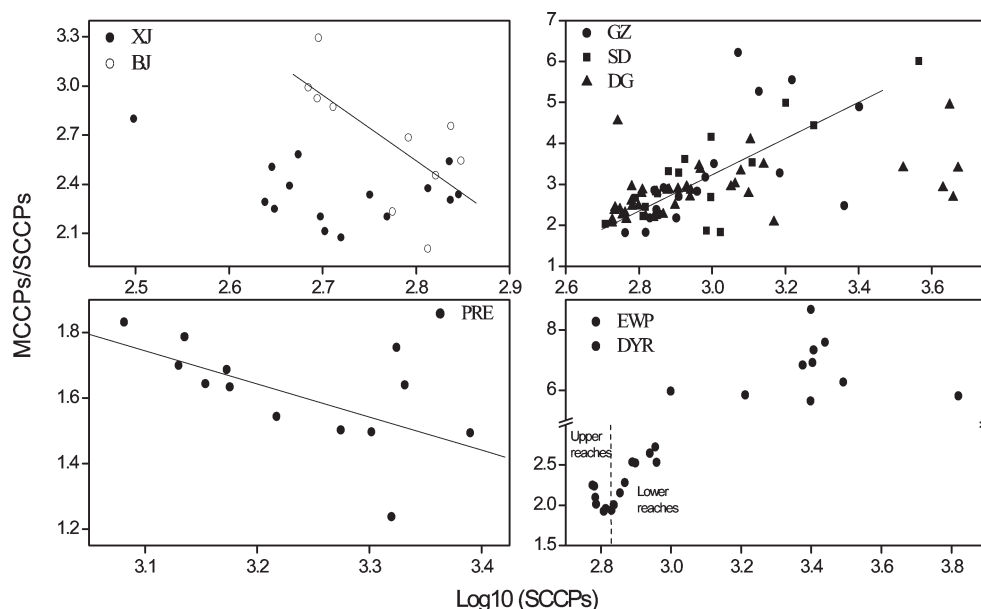
The spatial variations of CPs seen in the PRD sediments could be explained by the proximity of the sampling sites to industrial

and urban areas. The CPs in the XJ (320–700 ng/g) and BJ (480–810 ng/g) rivers were significantly lower than those in sediments from the tributaries running through GZ section (580–2500 ng/g), SD section (510–3700 ng/g), and DG section (530–4700 ng/g). As described above, the XJ and BJ rivers run through areas with low industrialized activity in the PRD. Previous studies showed that the XJ and BJ rivers received atmospherically transported pollutants such as polycyclic aromatic hydrocarbons and polybrominated diphenyl ethers from highly industrialized and urbanized area of the PRD.<sup>23,27</sup> Conversely the GZ, SD, and DG sites were three highly urbanized and industrialized areas in the PRD. Electronic and electrical manufacturing, plastics manufacturing and plastics packaging, all of which are heavy users of CPs, are important industries in these areas. The emission from usage and disposal of CPs in these industries could be the main cause for the elevated CP levels in the sediments. High concentrations of polybrominated diphenyl ethers, another important class of flame retardants, were also reported in GZ and DG sections in a previous study.<sup>27</sup>

Some individual sampling sites in DG (DG14–16, DG31, and DG39), GZ (GZ4, GZ13), and SD (SD7) showed significant CP levels compared to other sites (Figure 2). High TOC contents in sediment could be responsible for the high CP concentrations for most of above sites (all sites in DG section and site of GZ4). The TOC contents in these sites (from 2.9% to 5.8% for all sites in DG and 2.4% for GZ4) were high in the corresponding sampling area. A correlation analysis between TOC and SCCP level showed that significant positive correlations were found in sediments from these sampling areas ( $P < 0.05$ ), indicating that TOC plays an important role in determining the CP concentrations. For sites GZ13 and SD7, TOC content cannot explain the high CP concentrations due to their low TOC content (0.63% and 0.86%, respectively). GZ13 is near one of the largest wastewater treatment plants in Guangzhou city and SD7 is near a big paint company in Shunde. The emission from the wastewater effluent and industry activity could be the reasons for their high CP concentrations.

The concentrations of MCCPs in all sediments ranged from 880–38 000 ng/g. Significant positive correlations were found in all sampling areas, but with different slopes, between SCCPs and MCCPs. Thus, the spatial distribution of MCCPs was similar to that of SCCPs except that the MCCPs concentrations in the PRE were not higher than those in the sediments from the industrial and urban areas (Figure 2). The relative decrease of MCCPs in the PRE was possibly linked to the transport and deposition of CPs in the estuary. River runoff is the main transport mechanism for POPs in the PRE.<sup>25</sup> The solubility of MCCPs is lower than that of SCCPs, and as a consequence, relatively low amount of MCCPs were transported to and deposited in the estuary area.

**Ratios of MCCPs/SCCPs and Congener Profiles.** The MCCPs/SCCPs ratios in samples from different areas are given in Figure SI-1 in the Supporting Information. The average MCCPs/SCCPs ratio ( $6.7 \pm 0.98$ ) of EWP was higher than those in other sampling areas. This result indicates that e-waste recycling area contain more MCCPs than other areas. The e-wastes recycled in South China were mainly imported from Europe and North America. SCCPs have been listed as priority hazardous substances by the Europe Union, and the production of SCCPs has been voluntarily reduced from 13 000 tons in 1994 to 4000 tons in 1998 by the European Industry.<sup>5</sup> The high MCCPs/SCCPs ratio in the e-waste was consistent with the regulation of CPs in the developed countries. On the other hand, the usage of CPs in China is currently not



**Figure 3.** Relationships between MCCPs/SCCPs and log (SCCPs) concentration in sediments from the Pearl River Delta. XJ: Xijiang River; BJ: Beijiang River; GZ: Guangzhou section; SD: Shunde section; DG: Dongguan section; PRE: Pearl River Estuary; EWP: ponds in e-waste area; DYR: Dayan River.

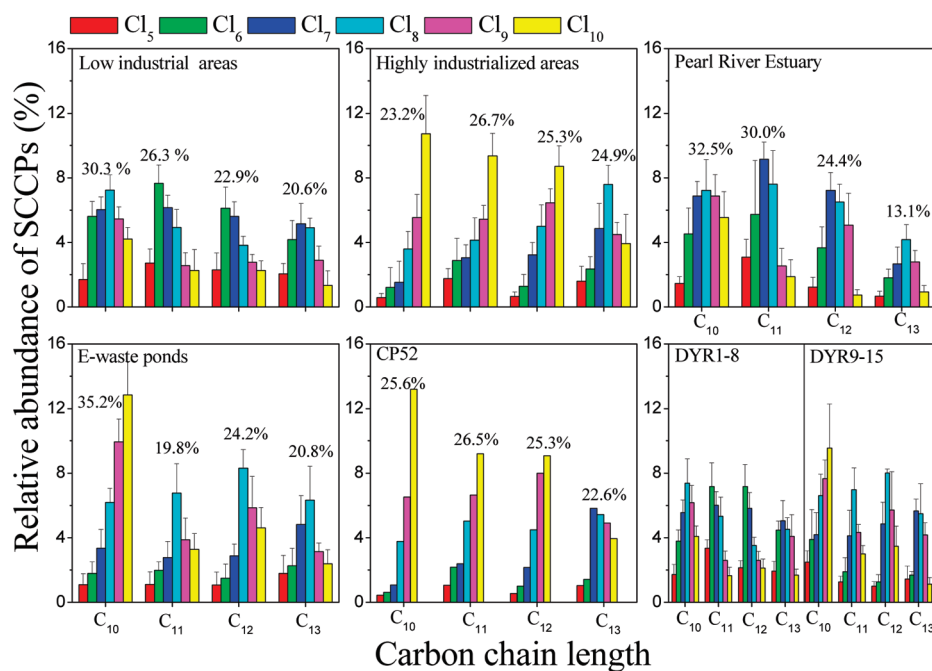
regulated and a great amount of SCCPs are still produced and used in industry activity.

The MCCPs/SCCPs ratios were higher in the high industrialized activity areas than in the low industrialized activity areas, and the MCCPs/SCCPs ratios in the PRE were the lowest among all sampling areas (Supporting Information Figure SI-1). Meanwhile, we found that high MCCPs/SCCPs ratios were often found along with high CP concentrations in the high industrialized activity area. To explore the significance of the MCCPs/SCCPs ratio, a correlation analysis between SCCPs concentrations (log (SCCPs)) and MCCPs/SCCPs ratios was performed. Interestingly, significant positive correlations between log (SCCPs) and MCCPs/SCCPs were found in the three sampling areas with high level of urbanization and industrialization. Conversely, significant negative correlations were observed in sampling areas with low urbanization and industrialization level and the PRE (Figure 3). These observations could likely be linked to the emission and transport of CPs in the environment. In the highly industrialized and urbanized areas, direct emission from industrial wastewater is an important source of CPs in the sediments. In the sites with high concentrations of CPs, sediments often received recent industry emission of CPs which have high MCCPs/SCCPs ratio due to the preceding discussion about a general ban of SCCPs in recent decades in European countries. On the other hand, long-range water and/or atmospheric transport were major input pathways for CPs into the sediments in the low industry activity area. SCCPs have relatively higher vapor pressures and solubility than MCCPs which make SCCPs more available for long-range transport than MCCPs. The difference in correlations between concentration of SCCPs and MCCPs/SCCPs in high and low industrialized activity areas were reinforced by the observation in the DYR. In the upper reaches of DYR, a significant negative correlation was found due to no direct industrial emission. However, a significant positive correlation was found in the lower section where e-waste activities contribute to the CPs in the sediment (Figure 3). Thus, we can conclude

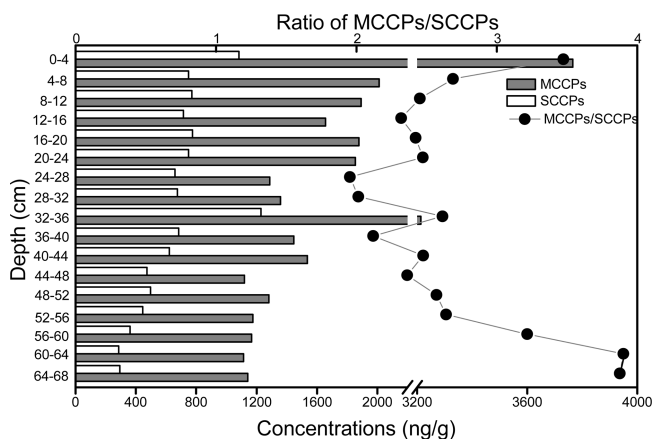
that the correlation between SCCP concentration and ratio of MCCPs/SCCPs can be used as an indicator to determine whether there is direct emission source of CPs in a given region in the PRD.

The congener profile of SCCPs in the high industry activity areas mostly resembles that of a technical mixture of CP52 (Figure 4). This finding suggested that CP52 was a major source of CPs in the PRD, which was in line with the usage of CP52 in China.<sup>35</sup> Compared to the high industrial activity areas, the abundance of short carbon chain ( $C_{10}$ ,  $C_{11}$ ) and lower chlorinated congeners ( $Cl_5$ – $Cl_8$ ) increased in the low industrial activity area and the PRE (Figure 4). Similar observations were previously reported in other studies. Marvin et al.<sup>7</sup> reported a higher relative abundance of  $C_{13}$  congeners in sediments potentially influenced by local industrial sources of SCCPs. Tomy et al.<sup>36</sup> found that marine mammal samples from urbanized and industrialized areas showed a higher relative abundance of less volatile congeners and a pattern closer to commercial CP mixtures. The likely reason for the congener profile difference between the high and low industrial activity areas was the different transport abilities between different congeners and/or degradation of CPs during transport. Short chain and low chlorinated congeners are more prone to migrate to sites farther from the emission sources than long chain and high chlorinated congeners due to their higher solubility and volatility. High chlorinated congeners ( $Cl_9$ – $Cl_{10}$ ) might dechlorinate to form low chlorinated congeners ( $Cl_5$ – $Cl_8$ ) during transportation, which will be discussed in detail in the following section.

The SCCP congener profile in the EWP was different from those in the PRD sediments with the highest abundance of  $C_{10}$  homologue group (35.2%) (Figure 4). The elevated contribution of  $C_{10}$  in the e-waste recycling area cannot be attributed to the segregation during transport of CPs in the environment because no long-range transport occurred for CPs in the EWP. Approximately 1.7 million tons of e-wastes were dismantled annually in this area and most of these e-wastes were imported from



**Figure 4.** SSCP congener profiles in different sampling areas: Low industrial areas: Beijiang River and Xijiang River; Highly industrialized areas: Guangzhou, Shunde, and Dongguan section; DYR: Dayan River; CP52: a commercial CP mixture used in China. The values above the bar represent the contribution of each homologue group to total SCCPs.



**Figure 5.** Vertical distributions of concentration of SCCPs and MCCPs and ratios of MCCPs/SCCPs in sediment core.

overseas.<sup>24</sup> Therefore, the high  $C_{10}$  abundance in the e-waste area was attributed to the differences in commercial CP mixtures used in developed countries and in China. The upper (sites 1–8) and lower (sites 9–15) reaches of DYR showed different SSCP congener profiles (Figure 4). The congener patterns of SCCPs were similar to those in the lowly industrial areas for DYR1–8 but were similar to those in the EWP for the DYR9–15. Elevated levels of CPs in the lower section of DYR and the similar pattern of DYR9–15 to those in the EWP suggested that e-wastes had become one major source of CPs in the environment of e-waste recycling area.

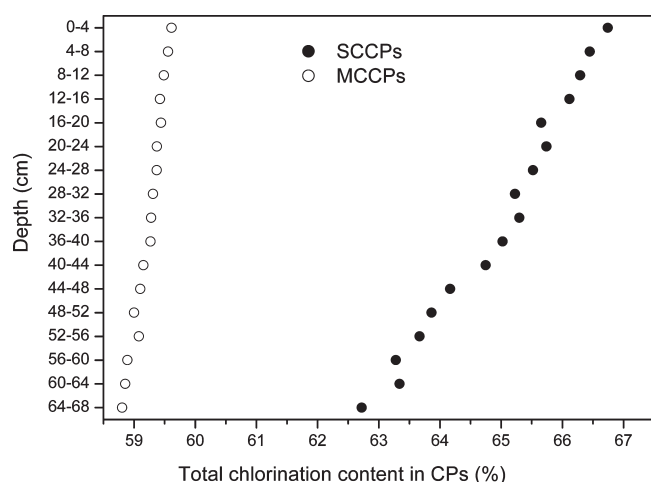
Similar to the congener profiles of SCCPs, the short chain ( $C_{14}$ ) homologue group abundance in MCCPs in the PRE (70.8%) and the low industry activity area (68.5%) were significantly higher than those in the high industry activity areas and the

e-waste area (59.8% and 58.4%, respectively) (Supporting Information Figure SI-2). This observation further supported that short carbon homologue groups have higher transport ability than that of long carbon homologue groups. The congener pattern of MCCPs in the industrial area were similar to that in the e-waste area indicating that the composition of MCCPs used in the e-waste from developed countries were same as those used in the China.

**Temporal Trend of CPs.** Figure 5 shows the vertical distributions of SCCPs and MCCPs concentrations in the sediment core. The concentrations of SCCPs and MCCPs were significantly higher in the upper segments (670–1100 ng/g and 1400–3800 ng/g at 0–32 cm) than in the deeper segments (290–680 ng/g and 1100–1400 ng/g at 36–68 cm), except for the segment of 32–36 cm where had unusually high SCCP and MCCP concentrations. The high CP concentrations in the upper segments suggested that the consumption of CPs in the PRD region was increased in the most recent years (approximately 6–9 years according to the sediment rate), which were coincident with the production figures of CPs in China. The production of CPs in China has increased exponentially since 2003 (Supporting Information Figure SI-5).<sup>32</sup>

The vertical profiles of SCCPs and MCCPs in the lower segments were quite different from those in the upper segments. In the lower segments (68–36 cm), the SSCP concentrations show a gradually increasing trend but no obvious trend was observed for the MCCPs. On the contrary, a relatively constant level (approximately 700 ng/g) was found for the SCCPs in the upper segments (from 32 to 4 cm) but the MCCP levels rapidly increased from 1300 to 3800 ng/g from 28 cm to surface. These probably reflected the difference in usage of SCCPs and MCCPs in different periods, which can be seen on the vertical profile of ratio of MCCPs/SCCPs (Figure 5). The decreasing ratio of MCCPs/SCCPs from the bottom to the middle segments is





**Figure 6.** Vertical distributions of chlorination content in SCCPs and MCCPs in the sediment core.

coincident with the increased use of SCCPs in the early period in the PRD. On the other hand, the rapid increase of MCCPs levels and ratio of MCCPs/SCCPs in the upper segments of the sediment core indicated that more MCCPs were used in recent years in the PRD. This pattern could be attributed to the effect of the regulations of SCCPs under the EU Water Framework Directive and the preceding discussion about a general ban of SCCPs in 1996.<sup>5</sup> The vertical distribution of CPs in the present study was similar to that observed in Lake Thun in Switzerland although the sediment core in the present study was not dated. In the sediment core from Lake Thun, SCCPs rapidly increased in the early period of deposition (before 1990s) then shifted to more MCCP after 2000.<sup>37</sup>

A different homologue pattern was also observed for sediment slices between the upper segments (from 0 to 44 cm) and the lower segments (from 44 cm to bottom) (Supporting Information Figure SI-3 and Figure SI-4). The abundance of  $C_{10}$  and  $C_{11}$  homologue groups in SCCPs and  $C_{16}$  and  $C_{17}$  homologue groups in MCCPs were higher in the upper segment than in the lower segment. However, the contributions of  $C_{12}$  and  $C_{13}$  homologue groups in SCCPs and  $C_{14}$  homologue groups in MCCPs homologue groups were higher in the lower segment. The increase abundance of  $C_{12}$  and  $C_{13}$  homologues for SCCPs coincide with the decrease abundance of  $C_{16}$  and  $C_{17}$  homologues for MCCPs, indicating that the commercial CP mixture used recently might be different from those used in early decade in the sampling area.

The chlorine content of SCCPs and MCCPs showed a decreasing trend with increasing depth of sediment core (Figure 6), implying a dechlorination of CPs during the aging in the sediment. A regression analysis between the depth and abundance of each molecular formula to the total SCCPs or MCCPs revealed that the abundance of congeners with 9 and 10 chlorine atoms decreased with increasing depth while congeners with chlorine atom less than 8 increased with the depth of sediment (Supporting Information Table SI-1 and Figure SI-6). This result indicated that  $Cl_{10}$  and  $Cl_9$  congeners dechlorinated to low chlorine congeners in the sediments. The absolute values of slope of the regression line decreased with the increasing carbon chain for both  $Cl_{10}$  and  $Cl_9$  congeners indicating that long chain CPs had lower potential dechlorination ability than short chain CPs (Supporting Information Table SI-1). This finding could explain

why the change in degree of chlorine content of MCCPs was much less than that of SCCPs in the sediment core. Fisk et al.<sup>14</sup> found the long chain CP to have a low degradation rate in aerobic sediment, which was consistent with the present study. However, the degradation of CPs with greater chlorine content was lower than congeners with less chlorine in aerobic sediment,<sup>13–15</sup> which was different from the finding in the present study. This might suggest that the mechanism of aerobic degradation of CP is different to that of dechlorination in anaerobic sediments.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Detailed information for ratios of MCCPs/SCCPs (Figure SI-1), MCCP congener profiles in sampling areas (Figure SI-2), homologue pattern of SCCPs and MCCPs in sediment core (Figure SI-3), vertical distributions of abundance of  $C_{10}$  homologue group in SCCPs and  $C_{14}$  homologue group in MCCPs (Figure SI-4), production of CPs in China (Figure SI-5), vertical distributions of abundance of  $Cl_5$ – $Cl_{10}$  congeners in  $C_{10}$  homologue group (Figure SI-6), slopes of the regression lines between depth and abundance of each molecular formula to total SCCPs or MCCPs (Table SI-1). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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