Short- and medium-chain chlorinated paraffins in sediments from the Laizhou Bay area, North China: Implications for transportation from rivers to marine environment*

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The concentrations of short- and medium-chain chlorinated paraffins (SCCPs and MCCPs) were measured for riverine and marine sediments from the Laizhou Bay area in order to investigate their spatial distributions, possible sources and transport behaviors. Concentrations of SCCPs and MCCPs in riverine sediments varied from 8.4 to 2000 ng g⁻¹ dw and from 1.8 to 3200 ng g⁻¹ dw, respectively. Higher concentrations were found exclusively at industrial sites. Emissions from local factories were the main source of CPs in river sediments of this region. It was 5-22 ng g⁻¹ dw and 6-63 ng g⁻¹ dw with an average value of 11 ng g⁻¹ dw and 9 ng g⁻¹ dw for SCCPs and MCCPs in marine sediments of Laizhou Bay, respectively. In addition to riverine input, ship related emissions are suggested to be another important source of CPs in the Laizhou Bay. MCCPs/SCCPs values and compositional profiles of SCCPs were found to vary along with CP concentrations. A distinct shift to congener groups with shorter carbon chains and lower chlorination from emission sources to remote areas was noticed. The role of log octanol-water partition coefficient (LogKow) values indicated decisive in their transportation from emission sources to remote areas in the Laizhou Bay area.

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1. Introduction

Chlorinated paraffins (CPs), are industrial product with the general formula CₙH₂ₙ₋₂Clₙ, consisting of 10–30 carbon atoms and chlorine content from 30% to 70% by mass. Three groups — short chain (C₁₀ - C₁₃, SCCPs), medium-chain (C₁₄ - C₁₇, MCCPs), and long-chain (C₁₈ - C₃₀, LCCPs) are included according to the length of their carbon chain. CPs have been widely used in industries, such as high-temperature lubricants in metal-working machinery and flame-retardant plasticizers. Many other new applications are being developed and rapidly popularized, for example, as additives in adhesives, paints, rubber and sealants (Feo et al., 2009).

The release of CPs into the environment could occur during various processes, among which production and consumption for the PVC, flame retardant and metal cutting fluid industries are thought to be the major ones (Tomy et al., 1999; Wei et al., 2016). CPs are ubiquitous in the environment and they have high bio-accumulation and biomagnification potentials due to their high Kow values. SCCPs have shown carcinogenic potential in rats and chronic toxicity in aquatic and soil organisms (Bezchlebová et al., 2007; Geng et al., 2015; Warnasuriya et al., 2000). SCCPs were listed in Annex A to curtail its production and use worldwide by the Eighth Conference of the Parties of Stockholm Convention in 2017. In contrast, reports on eco-toxicity tests of MCCPs are very limited; however, they were reported to possibly be more bioaccumulative than SCCPs because of their reduced biotransformation resulting from the longer carbon chain lengths (Fisk et al., 2000). There is scientific concern that exposure to MCCPs may be associated with increased risk of kidney toxicity (Cherrie and Semple, 2010). Studies have revealed that MCCPs are also persistent in the environment and their concentration levels experienced an increase due to the regulation of SCCPs (Yuan et al., 2017).

China is the world’s largest producer and consumer of CPs. The annual production volumes have increased rapidly to about 1,050,000 ton in 2013 (UNEP/POPS/POPRC.12/11/Add.3, 2017). However, according to Wei et al. (2016), there are no restrictive
regulations on the production and use of CPs in China to date. As a result, relatively high CP concentration levels were found ubiquitous in a variety of environmental matrices in China. Laizhou Bay is a typical estuary-bay ecosystem and one of the three main bays of the Bohai Sea. The Laizhou Bay area has experienced rapid urbanization and industrialization, which has led to excessive water contamination in the last few decades. Various industries, including petro-chemical, marine chemical, paper, textile, gold mining, and manufacturing, are located in this area. Several rivers flowing through cities and industrial districts are discharging into the bay (Zhang et al.; Pan et al., 2011a; Zhang et al.). Besides, Laizhou Bay is surrounded by Shandong Province, which is a major CP-product supplier and has been proven to emit the highest levels of SCCPs into the atmosphere in China from 2008 to 2012 (Jiang et al., 2017; Zhang et al., 2017).

Previous studies have suggested that river sediments are more or less contaminated by different organic pollutants (Zhang et al.; Pan et al., 2011a; Pan et al., 2011b; Zhang et al.; Zhao et al., 2013b; Zhong et al., 2011). Since there is a limited amount of existing data on CPs in the Laizhou Bay area, we collected sediment samples from the bay and 12 tributaries flowing into the bay. The sampling details are described in our previous studies (Pan et al., 2011a). The purpose of this work is to get an overview of the concentration levels and congener profiles in this area and discuss the possible transport pathways of CPs from emission sources to the marine environment.

This article aims to offer a sight into the ecosystem risk evaluation of CPs and guide the further development of regulations for environmental control of CPs in the Laizhou Bay area.

2. Materials and methods

2.1. Sample pretreatment

The extraction and purification procedure of CPs in sediments was similar with that of polychlorinated naphthalenes (PCNs) and polybrominated diphenyl ethers (PBDEs) which was reported in our previous paper (Pan et al., 2011a; Pan et al., 2011b). Freeze-dried sediment samples (approximately 20–40 g of riverine samples and 80 g of marine samples) were spiked with 10 ng surrogate standard ([13C10]trans-chlordane, purchased Cambridge Isotope Laboratories) and soxhlet extracted with 500 mL dichloromethane (DCM). Activated copper granules were added to the extraction flasks to remove elemental sulfur. The extract was then concentrated and cleaned up with a multilayer silica composite column consisted of 3 cm pre-rinsed silica gel (3% deactivated), 3 cm acid silica gel (50%, w/w) and 1 cm anhydrous sodium sulphate from bottom to top. The extract was eluted in sequence with 15 mL of hexane (F1) and 15 mL of DCM/HEX (1:1, v/v) (F2), Fraction F2 which contained CPs was reduced and spiked with internal standard (20 ng of [13C6]mirex purchased from Ehrenstorfer GmbH) before instrumental analysis.

2.2. Instrumental analysis, quantification and quality assurance

Instrumental analysis was performed by a high-resolution gas chromatograph coupled with electron capture negative ion-low resolution mass spectrometer (HRGC/ECNI-LRMS, Agilent, USA). The two most abundant isotopes of the [M–Cl]− ions with 5–10 chlorine atoms were monitored (lozza et al., 2009; Reth and Oehme, 2004). In order to reduce interferences between SCCP and MCCP congener groups, all monitored ions were divided into two groups (Table S1). Each sample was subjected to analysis by two individual injections. For each injection, the corresponding SCCPs and MCCPs were simultaneously monitored. SCCP and MCCP congener groups were identified by comparing retention time and chromatographic peak shapes of monitored [M–Cl]− ions. The quantification of CPs in sediment samples was based on the procedure described by Reth et al. (2005) to compensate the influence of chlorine contents on the total response factors between environmental samples and CP standards. Commercial references of SCCP/MCCP (C10–13, 51.5%, 55.5% and 63.0% chlorine content; C14–17, 42.0%, 52.0 and 57.0% chlorine content) were mixed in different proportions to establish the calibration curves of total response factor (RF) versus Cl content for the quantitation purpose (Table S2). Good linear correlations were obtained as shown in Fig. S1. Chemical calculation using an algebraic equation group was conducted to reduce the interference from mass overlap between SCCPs and MCCPs (Zeng et al., 2011a). Congener group abundance profiles were established using the actual relative integrated signals, followed by chemical calculation to determine the relative concentrations of the commercial component in the commercial standards and environmental samples (Tomy et al., 1997; Zeng et al., 2011a).

2.3. Quality assurance and quality control

Every effort was made to reduce blank levels. Glassware and sodium sulphate were heated at 450 °C for 12 h and solvent rinsed prior to use. Limits of detection (LOD) were defined as average method blank level plus three times the standard deviation, indicating that CPs were detectable in the blanks at concentrations relevant for real sample analysis. In this study, for each batch of 8 field samples one procedural blank and one sample duplicate was processed. LOD was calculated from the blank levels, and the obtained values were 38 ± 2.8 ng g−1 dw and 13 ± 2.7 ng g−1 dw for SCCPs and MCCPs, respectively. Average recoveries for the surrogate standard [13C9]trans-chlordane were between 79 and 106%. Duplicate samples reported relative standard deviation (RSDs) within 20% for all the target chemicals. All the samples were corrected by blanks but not by surrogate recoveries.

3. Results and discussions

The calculated chlorine content for SCCPs of all the samples for the calculation of total response factors fell well in the linear scope (Table S2 - S3). For MCCP calculation, only three samples went out of the linear scope. The nearest chlorine content within the scope were introduced for the three samples. C15C15, C16C15 and C17C15 were not detected. SCCP concentrations at GLH2 is under LOD. There are some limitations of the method used in present study, such as that low chlorinated CPs (Cl1 – C14) cannot be detected with the method in present study. Information on CPs only with 5–10 chlorine atoms was obtained, which may cause underestimation of the concentration levels. Besides, only total concentrations of SCCPs/MCCPs were obtained instead of that of individual congener group (Gao et al., 2016; Hilger et al., 2013). Therefore, comparisons of concentrations levels and congener group patterns in following sections were conducted with other studies using similar analytical method.

3.1. Concentration levels of SCCPs and MCCPs

The spatial distributions are shown in Fig. 1. It can be seen that CPs concentrations varied greatly in riverine sediments. SCCPs concentrations were in the range of 8.4–2000 ng g−1 dw with a mean value of 160 ng g−1 dw. Over 75% of the riverine samples were below 50 ng g−1 dw. Samples ranging from 51 to 2000 ng g−1 dw were found exclusively at industrial sites, especially near their local discharges. Site DH2 (2000 ng g−1 dw), MH2 (1200 ng g−1 dw), YHH1 (510 ng g−1 dw), and YKG (350 ng g−1 dw) were sampled below 50 ng g−1 dw. Over 75% of the riverine samples were below 50 ng g−1 dw. Samples ranging from 51 to 2000 ng g−1 dw were found exclusively at industrial sites, especially near their local discharges. Site DH2 (2000 ng g−1 dw), MH2 (1200 ng g−1 dw), YHH1 (510 ng g−1 dw), and YKG (350 ng g−1 dw) were sampled
from the lower reaches of the paper mill and textile industries, from around a chemical plant, from the Shengli Oil Field, and from within an industrial river port, respectively. These results are similar to those obtained in our previous study of Polychlorinated naphthalenes (PCNs) and Polybrominated diphenyl ethers (PBDEs) in this region (Pan et al., 2011a; Pan et al., 2011b). Thus, it can be seen that emissions from local factories were likely the main source of SCCPs in river sediments of this region. The lowest concentrations at site HH2, GLE, and JLH3 were found on a vast saline and alkaline land relatively far from human activities. According to the general sampling groups (Pan et al., 2011b), the mean concentrations decreased by one magnitude in the following order: 320 ng g\(^{-1}\) dw (industrial group), 22 ng g\(^{-1}\) dw (urban group with less industries), 6.5 ng g\(^{-1}\) dw (the countryside group). We suggest that the distributions of CP concentrations are mainly controlled by the proximity of the sampling sites to industrial and/or local discharges.

The spatial distributions of MCCPs in rivers were similar to that of SCCPs. This can also be illustrated by the significant correlation between SCCP and MCCP concentrations (\(R = 0.809, p < 0.01\)), which are in the range of 1.8–3200 ng g\(^{-1}\) dw, with an average value of 360 ng g\(^{-1}\) dw. In over 70% of the riverine samples, MCCP concentrations were below 100 ng g\(^{-1}\) dw. A few samples with higher concentrations were found in the industrial area.

For marine sediments, there is a sharp decrease up to 1–2 orders of magnitude from riverine sediments located in the most industrialized areas. They were 5.1–22 ng g\(^{-1}\) dw and 2.2–63 ng g\(^{-1}\) dw with an average value of 11 ng g\(^{-1}\) dw and 9 ng g\(^{-1}\) dw for SCCPs and MCCPs respectively. The highest CPs concentrations occurred at site A5 near Longkou port in the east coast of Laizhou Bay and it was with very low TOC value. An ENVISAT ASAR image based on wide swath SAR was used to identify possible ship-related sources (Fig. 2). This image was scanned at 10:10:45 on 04-23-2011 with a spatial resolution of 150 m x 150 m. A dense concentration of white light spots in Longkou port anchorage indicated a large number of moored ships. Thus discharge from ports or ship-related activities is probably another important source of CPs in Laizhou Bay. The image also reveals that there are many moored ships anchoring in Weifang port, where site E3 (SCCP: 12 ng g\(^{-1}\) dw; MCCP: 12 ng g\(^{-1}\) dw) was located, with the concentration was two and three times higher than F2 (SCCP: 6.6 ng g\(^{-1}\) dw; MCCP: 3.8 ng g\(^{-1}\) dw). The ship-related activities discharge might also make contributions. The relatively higher concentrations in the central area from the south coast instead of a seaward decrease trend, such as site A2, A3, B2 and D3, is similar with distributions of PCNs and PBDEs in our previous studies (Pan et al., 2011a; Pan et al., 2011b), which could be attributed to a comprehensive influence by sedimentation type and hydrodynamic forces apart from different source input.

Although great progress has been made in recent years, there is still a lack of environmental data regarding CPs especially MCCPs in sediments among different countries/regions worldwide. The concentrations in sediments worldwide were summarized in Table 1. Compared with sediments from freshwaters reported in other countries, SCCP concentrations in rivers around the Laizhou Bay area are much higher, such as Czech rivers of the Czech Republic (nd-347 ng g\(^{-1}\) dw), rivers in Japan including Arakawa, Tamagawa, and Yodogawa River (4.9–484.4 ng g\(^{-1}\) dw), and lakes in Canada (Iino et al., 2005; Ismail et al., 2009; Pribylová et al., 2006; Stejnarová et al., 2005). Compared with those from industrial areas in more developed regions, such as sediments in the marine coast near Barcelona (SCCPs: 840–2740 ng g\(^{-1}\) dw), Besos Fig. 1. Spatial distributions of SCCPs and MCCPs concentrations. Note: Red, brown and green bars are representative of industrial sites, urban sites and the countryside as described in our previous study (Pan et al., 2011b). The black and blue ones mean river estuaries and marine sites. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
River in Spain (SCCPs: 250–3040 ng g\(^{-1}\) dw), and the Pearl River Delta in south China (SCCPs: 320–6600 ng g\(^{-1}\) dw; MCCPs: 880–38000 ng g\(^{-1}\) dw), and those from aquatic Ecosystem receiving effluents from a Sewage Treatment Plant in Beijing of China (1100–8700 ng g\(^{-1}\) dw), CP levels in Laizhou Bay area are relatively lower (Castells et al., 2008; Castells et al., 2004; Chen et al., 2011; Zeng et al., 2011b). SCCPs in marine sediments of Laizhou Bay area are slightly lower than those found in Bohai and Yellow seas (14.5–85.2 ng g\(^{-1}\) dw), Liaodong Bay (65–541 ng g\(^{-1}\) dw), Liaohe River Basin (39.8–480.3 ng g\(^{-1}\) dw), East China Sea (5.8–64.8 ng g\(^{-1}\) dw), and Hongkong marine coast (<LOD - 75.9 ng g\(^{-1}\) dw) (Gao et al., 2012; Ma et al., 2014b; Zeng et al., 2013; Zeng et al., 2012). This slight difference on the same order of magnitude does not rule out the cause by the drawbacks of GC/ECNI-LRMS used in CP detection. Both SCCP and MCCP concentrations in marine sediments of Laizhou Bay area are similar with those found in North/Baltic Sea (SCCPs: 8–63 ng g\(^{-1}\) dw; MCCPs: 22–140 ng g\(^{-1}\) dw) (Huttig and Oehme, 2005). However, with the rapid development of CP production and usage in the last decade in Shandong Province (Jiang et al., 2017), CP concentrations in the Laizhou Bay area might undergo a big increase, which needs further attention and study.

3.2. Correlations among CPs and TOC

TOC has been considered a key factor influencing the accumulation of SCCPs in the sediment. In present study, Pearson’s correlation analysis was conducted between TOC and CP concentrations. Riverine and marine sediments were implemented respectively due to their huge concentration span and different sources. No significant correlations were observed between \(\Sigma\)SCCPs/\(\Sigma\)MCCPs and TOC in riverine sediments, which confirmed that local industrial emissions contributed mostly to the distributions of CPs in this area and this is consistent with that in the Liaohe River Basin (Gao et al., 2012). In marine sediments, significant correlations between \(\Sigma\)SCCPs and TOC were reported in a few studies (Chen et al., 2011; Zeng et al., 2013; Zeng et al., 2012). In present study however, there was no significant correlations between \(\Sigma\)SCCPs and TOC whereas \(\Sigma\)MCCPs and TOC were significantly positively correlated \((R = 0.633, p < 0.01)\). This is very interesting and could be concerned with possibly different sources in marine environment. In riverine sediments, local industrial emissions covered up the impact of TOC and other possible sources. In marine sediments however, CPs may come from a comprehensive contribution of riverine/coastal input, atmospheric dry/wet deposition and other sources such as discharge from ship-related activities. Due to the different physical-chemical properties between SCCPs and MCCPs, the contributions of different sources varied and the transport abilities and/or pathways were also probably different. The strong correlation between MCCPs and TOC in marine sediments of Laizhou Bay indicated the key role of TOC on the distribution of MCCPs in the sediments.

3.3. Ratios of MCCPs/SCCPs and compositional profiles

In this study, MCCPs/SCCPs ratios were found to decrease with CP concentrations. \(r_1\) was defined as \(r_1 = \text{MCCPs}/\text{SCCPs} - 1\) to give an intuitionistic description as shown in Fig. 3. The highest M/S values occurred at sites with significant high CPs concentrations sampled in industrial areas, varying from 1.1 to 5.6 with a mean value of 2.3. Lower M/S values were found in urban areas with less industry. They were fluctuating narrowly at 1.0 with the values of 0.97 ± 0.23. For samples collected from the countryside, including WH sites, HH sites and JLH sites, M/S values varied between 0.14 and 0.86, with an average value of 0.49. In marine sediments, M/S values varied between 0.18 and 1.0 in 28 out of 30 samples, with a

![Fig. 2. Geographic locations of marine sediments and mooring ships in Laizhou Bay. Note: It is ENVISAT ASAR images data and the white lightspots are representative of ships.](image-url)
mean value of 0.54, with two exceptions at site A5 (2.8) and site E3 (1.1). On the whole r1 values in surface sediments followed the order of industrial area sediment > urban sediment > countryside sediment > marine sediment. The relationship between CP concentrations and M/S values was firstly reported by Chen et al. (2011): they found M/S ratios were well correlated with SCCP concentrations and could be used as an indicator to determine whether there are direct emission sources of CPs in a given region. In the present work, the values of M/S ratios directly reflected the influence of emission sources on sampling sites. They also illustrated the replacement of MCCP products by SCCP in industries accompanied with the regulation of chlorine groups. Cl6 - C17 homologues were the most predominant carbon chain group, accounting for 33.2 ± 8.5% and 31.3 ± 2.1% to SCCPs respectively, followed by C12 at 18.9 ± 3.0%, and C13 homologue at 17.5 ± 4.6%.

The congener group patterns in the industrial category (Fig. 4a) highly resembled that in PRD and Shenzhen coastal sediments (Zeng et al., 2017). Chen et al. (2011) elaborated the compositional profiles in different areas of PRD. In comparison, the industrial category of present study differed from the highly industrialized areas in PRD and e-waste ponds, while the less industrialized category (Fig. 4b) resembled each other, and the remote group distant from industries (Fig. 4c) were similar with that in Pearl River Estuary (PRE).

In marine sediments, compositional profiles were consistent with each other, presenting small variations (except A5). C10 and C11 homologue were the most predominant carbon chain group, accounting for 33.2 ± 8.5% and 31.3 ± 2.1% to SCCPs respectively, followed by C12 at 18.9 ± 3.0%, and C13 homologue at 17.5 ± 4.6%.

| Location/country | Sample type | Sampling year | Concentration (ng g⁻¹ d.w.) | Method of Analysis | Reference |
|------------------|-------------|---------------|----------------------------|-------------------|----------|
| Rivers (Labe, Bilina, Ohre, Vltava, Jihlava, Dyje, Svitava, Morava, Becva, Malá Becva, and Drevnice), Czech Republic | River sediment | 2003 | LOD - 347 | GC/ECNI-LRMS | Pribylova et al., 2006 |
| | | 2004 | LOD - 5574 | GC/ECNI-LRMS | | |
| The North and Baltic Seas | Marine sediment | 2003 | 8-63 | GC/ECNI-LRMS | Huttig and Oehme, 2006 |
| | | 2004 | 22-149 | GC/ECNI-LRMS | | |
| Industrial area near of Barcelona, Spain | River sediment | NR | 250 | GC/ECNI-LRMS | Castells et al., | |
| | | | 3260 | GC/ECNI-LRMS | 2008 | |
| Coastal area of Barcelona, Spain | Marine sediment | 2003 | 840 | GC/ECNI-LRMS | Castells et al., 2008 |
| | | | 2740 | GC/ECNI-LRMS | | |
| Bohai and Yellow Seas, China | Marine sediment | 2012 | 14.5 | GC/ECNI-LRMS | Zeng et al., 2013 |
| | | | 85.2 | GC/ECNI-LRMS | | |
| Bohai Sea Coast, China | Marine sediment | 2010 | 97.4 | GC/ECNI-LRMS | Ma et al., 2014a |
| | | | 1756.7 | GC/ECNI-LRMS | | |
| Liaodong Bay, China | Marine sediment | NR | LOD - 65-541 | GC/ECNI-LRMS | Ma et al., 2014a |
| Liaohe River Basin, China | River/estuary sediment | 2010 | 39.8 | GC/ECNI-LRMS | Gao et al., 2012 |
| | | | 480.3 | GC/ECNI-LRMS | | |
| East China Sea, China | Marine sediment | 2011 | 5.8-64.8 | GC/ECNI-LRMS | Zeng et al., 2012 |
| Pearl River Delta, China | River/estuary sediment | 2009 | LOD - 320 | GC/ECNI-LRMS | Chen et al., 2011 |
| | | 2010 | LOD - 880 | GC/ECNI-LRMS | | |
| Pearl River Delta, Coast of Shenzhen, China | River/coastal sediment | 2013 | LOD - 14.7 | GC/ECNI-LRMS | Zeng et al., 2017 |
| | | | LOD - 1540 | GC/ECNI-LRMS | | |
| Hong Kong, China | Marine sediment | 2013 | LOD - 75.9 | GC/ECNI-LRMS | Zeng et al., 2017 |
| Hong Kong, China | Marine sediment | 2013 | LOD - 26 | GC/ECNI-LRMS | Zeng et al., 2017 |
| Arakawa river, Tamagawa river and Yodogawa river, Japan | River sediment | 2003 | 4.9 | GC/ECNI-LRMS | Ino et al., 2005 |
| | | | 484.4 | GC/ECNI-LRMS | | |
| Tokyo Bay, Japan | Marine sediment | 2013 | 15.3 | GC/ECNI-LRMS | Zeng et al., 2017 |
| | | | 32.4-37.9 | GC/ECNI-LRMS | | |
| Laizhou Bay, China | Marine sediment | 2009 | 5-22 | GC/ECNI-LRMS | this study |
| | | | 6-63 | GC/ECNI-LRMS | | |
| Rivers around Laizhou Bay, China | River sediment | 2009 | 8.4 | GC/ECNI-LRMS | this study |
| | | | 1.8 | GC/ECNI-LRMS | | |
| | | | 2000 | GC/ECNI-LRMS | | |
were the predominant congener groups, accounting for \(34.0 \pm 4.5\%\) and \(34.9 \pm 3.5\%\) to \(\Sigma\)SCCPs respectively, followed by C18 group at \(16.0 \pm 3.5\%\), and they cumulatively accounted for \(69.5 \pm 4.1\%\). It is consistent with that found in Bohai Sea, Yellow Sea and East China Sea. But compared with Liaodong Bay, Tokyo Bay and Hongkong coastal zones, congener groups with 5 chlorine atoms were obviously lower. For MCCPs, their compositional profiles varied within a small
scale both in riverine and marine sediments. They were consistently predominant by 6Cl to 8Cl chlorinated congener groups and the C14 homologue group. On average, the relative mass abundance was 61.6 ± 11.1%, 20.3 ± 4.4%, 11.1 ± 4.7%, and 7.0 ± 3.3% in riverine sediments and 69.6 ± 4.5%, 17.5 ± 1.9%, 8.1 ± 2.1%, and 4.9 ± 1.5% in marine sediments for C14, C15, C16, and C17 groups respectively. Similar to SCCP congener group profiles, the lightest group - C14 homologue group were significantly higher in marine than riverine sediments. The congener group profiles of MCCPs were similar to that reported in other studies, except for that the abundance proportion of C14 homologue was at the highest level reported up to now (Chen et al., 2011; Iozza et al., 2008; Zeng et al., 2017).

### 3.4. Implications for transport

A correlation analysis was performed between ln (SCCPs) concentrations in riverine sediments and the abundance ratio of congener groups with different carbon atoms (Fig. 5). Significant correlations were found. While Short carbon chain (C10, C11) congener groups decreased with the increase of SCCP concentrations (C10: \( R = -0.657, p < 0.01 \); C11: \( R = -0.399, p < 0.05 \)), C12 and C13 congener groups increased significantly (C12: \( R = 0.541, p < 0.01 \); C13: \( R = 0.548, p < 0.01 \)), especially for the shortest (C10) and the longest chain (C13) group. The parameter \( r^2 \) was defined as \( r^2 = (\Sigma C12 + \Sigma C13)/(\Sigma C10 + \Sigma C11) - 1 \) to visually simplify the profile variations, as shown in Fig. 3. It can be seen that longer carbon chain groups (C12 and C13) decreased and shorter ones (C10 and C11) elevated from emission sources to less-industrialized areas with lower SCCP concentrations. The parameter \( r_3 \) was defined as \( r_3 = (\Sigma 7Cl + \Sigma 8Cl)/(\Sigma 6Cl + \Sigma 7Cl) - 1 \) and it is consistent with \( r_2 \) distributions; there is also a shift from higher chlorinated congener groups near the emission sites to those with lower chlorination in remote areas and marine sediments (Fig. 3).

The fractionation of different CP components during the transportation from emission sources to remote areas is suggested from the discussion above. This is in agreement with a few other studies (Chen et al., 2011; Ma et al., 2014b; Zeng et al., 2012; Zhao et al., 2013a). The environmental behavior of organic pollutants is complicated and influenced by multiple factors. The log octanol-water partition coefficient (logKow) has been considered a key parameter for the measurement of organic pollutants in environmental fate modeling since it can be effectively correlated with water solubility and bioconcentration factors. A few studies reported the relationships between Kow values and the number of chlorine and carbon atoms, and/or their total numbers (Bettina et al., 2011; Drouillard et al., 1998; Mackay et al., 1993; Sijm and Sinnige, 1995). Hilger et al. (2013) probed the effects of chain length, chlorination degree, and chlorine substitution pattern on Log Kow values. The author found that while Log Kow values increased almost linearly with increasing carbon atoms in the
alkane chain (C10–C18) at given chlorine content, a polynomial effect was observed in dependence on the chlorination degree of an alkane chain. The function of Log $K_{\text{ow}}$ and chlorine content at an alkane chain, following a polynomial correlation of second order proposed by their study was used to get Log $K_{\text{ow}}$ value of SCCPs. Pearson correlations were made between SCCP concentrations ln(SCCPs) and the relative mass abundance of chloroalkanes for a further exploration of the transportation and environmental fate of CPs, shown in Table 2. Strong correlations were found for most individual congener groups with 5–8 chlorine atoms. They were negatively correlated when Log $K_{\text{ow}}$ values were no higher than 5.72, which means an increasing trend of the relative mass abundance from industrial areas to remote areas. While positive correlations were noticed when Log $K_{\text{ow}}$ values higher than 5.78, which means a declination from point sources nearby to faraway places. Congener groups with lower Log $K_{\text{ow}}$ values are likely to transport to longer places while those with higher Log $K_{\text{ow}}$ values tend to adsorb/absorb onto particles and sink to sediment. The compositional profiles of MCPPs is coincident with the variation trend of Log $K_{\text{ow}}$ of MCPPs, which was reported to level off at higher N$_{\text{tot}}$ (the sum of the number of chlorine and carbon atoms) when it is greater than approximately 20 (Sjömg and Sinninge, 1995). But for congener groups with 9 and 10 chlorine atoms, no significant correlations were noticed. There leaves a question open that whether it is due to the leveling off of Log $K_{\text{ow}}$ values at higher N$_{\text{tot}}$, or the impact of Log $K_{\text{ow}}$ values on their transportation had been greatly weakened. To thoroughly figure out this problem, further study as well as method with better sensitivity and accuracy might be needed.

4. Conclusion
Spatial trends and transport behaviors in riverine and marine sediments from the Laizhou Bay area were analyzed. Higher levels of CP contamination were found in sites near industrial areas. The CP contamination in rivers was mainly associated with emissions from local factories. In the marine sediments of the Laizhou Bay, apart from riverine input, ship related emissions are suggested to be an important source of contaminants. The correlations between relative mass abundance of CPs and CP concentrations were examined. A distinct shift to congeners with shorter carbon chains and lower chlorination from emission sources to remote areas as well as from rivers to marine environment was noticed. The role of Log $K_{\text{ow}}$ values on the transportation was assessed and indicated to be decisive in this area.

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Appendix A. Supplementary data
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