Distributions, transports and fates of short- and medium-chain chlorinated paraffins in a typical river-estuary system

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HIGHLIGHTS

- MCPs and SCCPs were widely detected in water and sediment of Xiaqing River.
- CPs in Xiaqing River were among the highest worldwide.
- SCCPs were the dominant species in the dissolved phase of river water.
- Cities were the most important sources of CPs.
- ETM detains long-chained and more chlorinated CPs into sediment.

GRAPHICAL ABSTRACT

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ABSTRACT

Chlorinated paraffins (CPs) are widely employed in a variety of domestic and industrial products, and are ubiquitously detected in the environment. Short-chain chlorinated paraffins (SCCPs) have been listed in the Stockholm Convention as persistent organic pollutants (POPs), but not medium-chain chlorinated paraffins (MCCPs), even though they exhibit physicochemical properties and environmental behaviors similar to SCCPs. However, very limited data are available regarding their environmental behaviors and fates in river-estuary systems. China is the major producer of chlorinated paraffins (CPs), and Shandong Province is the main producer of CPs in China. Here, we investigated the distribution, transport, and fate of SCCPs and MCCPs in a heavily polluted river in Shandong Province, aiming to explore the distributions of CPs between dissolved and particulate phases, and between water and sediment phases, as well as the transport of CPs from river headwaters to estuaries and the roles of the estuarine turbidity maximum zone (ETM) on the fate of CPs. CP concentrations in sediments were 9.1–16,000 ng/g dw (mean value: 1000 ng/g dw) for SCCPs and 2.4–27,000 ng/g dw (mean value: 4400 ng/g dw) for MCCPs. In the water column, CP concentrations were 7.4–470 ng/L for SCCPs (mean value: 43 ng/L) and 4.0–120 ng/L for MCCPs (mean value: 27 ng/L). CP concentrations in riverine sediments were among the highest worldwide. SCCPs accounted for 95% of CPs (sum of SCCPs and MCCPs) in the dissolved phase. Cities around the river basin were found to be important pollution sources for CPs. Long-chained and more chlorinated congeners with larger LogKow values might be more likely to be 'salted-out', and thus, will be sequestered in sediments in the ETM, while those lighter congener groups with relatively high water solubility were prone to be transported by water flow to larger distances.

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1. Introduction

Chlorinated paraffins (CPs) are among the most complex halogenated contaminants, featuring large variations in carbon chain lengths (C_{10} – C_{37}) and chlorination degrees (40–70 m/m %Cl) (Brits et al., 2020). Based on their chain lengths, CPs can be subdivided into short-chain (SCCPs, C_{10} – C_{13}), medium-chain (MCCPs, C_{14} – C_{17}), and long-chain (LCCPs, C_{18} – C_{37}) paraffins. CPs have been widely used as lubricants, plasticizers, and additives in a great variety of industrial and consumer products due to their broad chemical properties. As a result, they have been widely detected in various environmental compartments (Bayen et al., 2006; Wei et al., 2016). A large number of industrial CP applications have attracted scientific concern and regulatory scrutiny of SCCPs. Numerous literature shows that SCCPs match the definition of persistent organic pollutants (UNEP, 2016). In May 2017, the POPs review committee of the Stockholm Convention (SC) decided to list the SCCPs in Annex A as a group of new POPs at its eighth meeting. Owing to the ban on SCCPs, a shift to MCCPs in manufacturing and consumption has been underway, resulting in widespread contamination of wildlife (Du et al., 2018). MCCPs have also been detected in foodstuff as well as indoor dust, and pose a potential threat to human health (Glüge et al., 2018; Huang et al., 2018; Sprengel et al., 2019). However, even though their chemical structures, environmental behaviors, and toxicities were similar to those of SCCPs, the production and usage of MCCPs have not been restricted (Glüge et al., 2018).

China has emerged as the largest producer and consumer of CPs worldwide. Annual production volumes have increased rapidly from 515,000 tons in 2007 to 1,124,000 tons in 2013 and are estimated to grow at an annual rate of 10.9% or higher in the future (Zhang et al., 2017). However, no rigid measures have been taken in the CP commercial market in China until now. Shandong Province is one of the largest producers of CPs in China, which also results in largest emissions into the air and water (Jiang et al., 2017; Zhang et al., 2017). Laizhou Bay is a semi-enclosed bay surrounded by the Shandong Province, extending from Qimu Cape to the Yellow River Estuary, with a length of 320 km on the coastline. It is severely polluted by anthropogenic pollutants discharged from more than fifteen rivers and numerous wastewater pipelines. Our previous studies have reported the pollution by several toxic substances in the rivers and in the marine environment of the Laizhou Bay area (Pan et al., 2011; Zhang et al., 2012; Zhao et al., 2013; Zhong et al., 2011).

Among all the rivers flowing into Laizhou Bay, the artificial Xiaoqing River is a large contributor to pollution fluxes and runoff (Pan et al., 2011; Pan et al., 2018; Zhong et al., 2011). It originates from Jinan City and flows downstream through the heavily urbanized and industrialized cities of Zibo, Weifang, Binzhou, Dongying, and finally discharges into Laizhou Bay. Our previous study has revealed the heavily contamination by halogenated flame-retardants (HRFs) and perfluoroalkyl substances (PFASs) in the Xiaoqing River and the likely threats of riverine input to Laizhou Bay (Heydebreck et al., 2015; Zhen et al., 2018). The present study focused on the distribution and transportation of CPs from the Xiaoqing River to the marine environment. Both water and sediment samples were collected and analyzed to uncover the occurrence and fate of CPs from the Xiaoqing River in relation to the Laizhou Bay environment. From this analysis, we expected to determine the influence of human activities along a river basin on the water quality and further to obtain useful information about the control over emissions of CPs to ecosystems that would be useful for the protection of human health.

2. Materials and methods

2.1. Sample preparation and analysis

Twenty-two sediment samples and 30 water samples were obtained from the upper reaches to the estuary of the Xiaoqing River in April

2014 (Fig. 1). Freeze-dried sediment samples (40 g) and filters (from 20 to 40 L water per sample) containing suspended CPs were spiked with 10 ng of surrogate standard ($[^{13}C_{10}]trans$ -chlordane, purchased from Cambridge Isotope Laboratories) and then extracted by dichloromethane (DCM) by Soxhlet method for 24 h. The dissolved phase (20–40 L water) CPs were allowed to pass through an Amberlite® XAD-2 resin column (30×4 cm i.d) and then extracted in a modified Soxhlet apparatus for 24 h using DCM. Elemental sulfur was removed by adding activated copper granules into the extraction flasks. All the extracts were further concentrated and subjected to a cleanup procedure. The eluent was concentrated to ~100 μ L in isooctane and spiked with 20 ng of $[^{13}C_8]mirex$ (as an internal standard) before injected. More details about the sample pretreatment are presented in the supplementary information (SI). Detailed sampling information has been described in our previous study (Zhen et al., 2018).

A gas chromatograph coupled with an electron capture negative ion – mass spectrometer (GC/NCI-MS, Agilent 7890-5975C, USA) was used to monitor the two most abundant isotopes of the $[M-Cl]^-$ ions of SCCPs and MCCPs with 5–10 chlorine atoms (Iozza et al., 2009; Reth and Oehme, 2004). Three SCCPs (51.5%, 55.5%, and 63.0%Cl), three MCCP references (42.0%, 52.0%, and 57.0%Cl) from Dr. Ehrenstorfer (Augsburg, Germany) and their mixtures (Table S1, Supporting Information) were used to establish a linear correlation between chlorine content and total response factor (see Fig. S1, Supporting Information (SI)) (Reth et al., 2005). Two individual injections were needed for each sample owing to the number of ions. Simultaneously comparing the retention time and chromatographic peak shapes of monitored $[M-Cl]^-$ ions could prove the identification of SCCP and MCCP congeners.

2.2. QA/QC

To ensure accurate identification and quantification of the target compounds, strict quality controls (SI) were employed. All the blank levels were negligible with 22.8 ± 3.2 ng for SCCPs and 17.7 ± 3.8 ng for MCCPs. The method detection limits (MDLs) were defined as the mean of all the blanks plus three times the standard deviation. The MDLs of SCCPs and MCCPs were estimated at 1.3 and 0.87 ng/g for sediments, 1.4 and 0.93 ng/L for filters, and 1.2 and 1.0 ng/L for the dissolved phase. The recoveries of $^{13}C_{10}$ -*trans*-chlordane from all environmental samples were 76–107%. All the samples were corrected by blanks, but not by surrogate recoveries. Detailed information about the analytical method is described in the supplementary information and in our latest study (Pan et al., 2018).

2.3. Other parameters and statistical analyses

Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined for sediment and water samples, respectively. Other parameters, measured by a portable multi-parameter water quality meter (YSI Pro Plus, YSI Inc., USA), are presented in Table S2.

3. Results and discussion

Table S3 summarizes the concentrations of CPs in all the samples collected in the present study. The extract concentrate of the water phase sample at X_{14} was all split out during the pretreatment process, and no data were obtained. The calculated chlorine content for MCCPs in the dissolved phase and the sediments at X_{16} were far below the scope of the calibration curve. Even the smallest chlorine content could result in a large overestimation of the MCCP content. The sediment sample at site X_{13} exhibited similar values to those at X_{16} . Therefore, the MCCP concentration data were not obtained from these samples. Except for the samples described above, the samples in this study fit well in the calibration curve. Based on the station locations, the sampling area was divided into two sections: river (X_1 – X_{23}) and Laizhou Bay (X_{24} – X_{30}). The river section from site X_{10} to X_{23} was

Fig. 1. Map of the sampling stations in the Xiaoqing River Basin.

influenced by the convergence of seawater and freshwater according to the salinity.

3.1. CPs in sediments of the Xiaoqing River and Laizhou Bay

The spatial distribution of the CPs is shown in Fig. 2a. The concentration amounts spanned three orders of magnitude. SCCP concentrations varied from 48 to 16,000 ng/g dw along the river (sites $X_1 - X_{23}$) with a mean value of 1300 ng/g dw and ranged from 9.1 to 20 ng/g dw in the Laizhou Bay (sites $X_{26} - X_{30}$) with a mean of 13 ng/g dw. MCCPs concentrations ranged from 130 to 27,000 ng/g dw in the river (mean value: 6020 ng/g dw) and varied from 2.4 to 9.0 ng/g dw in the bay. MCCPs accounted for 52.0–98.4% of the summed CPs ($\sum \text{MCCPs} + \sum \text{SCCPs}$) with a mean level of 79.6% in the river, and 17.6–44.0% (mean value: 29.6%) in the bay. Three centralized peak concentrations appeared near X_3 , $X_{10} - X_{11}$, and $X_{17} - X_{19}$, which were located downstream of the cities of Jinan, Zibo, and in Yangkou Port (located in the estuary). Thus, the distinct influence of local discharge was clearly visible along the Xiaoqing River Basin.

The highest SCCP concentration occurred at site X_{10} (SCCP: 16,000 ng/g dw; MCCP: 17,000 ng/g dw). In our previous studies, high concentrations of halogenated flame retardants (HFRs), decabromodiphenyl ethane (DBDPE), and per- and polyfluoroalkyl substances (PFASs) also occurred at X_{10} (Heydebreck et al., 2015; Zhen et al., 2018). Site X_{10} is located downstream of the city of Zibo and was sampled in the Zhulong River (a branch of the Xiaoqing River), which flows through several industrial parks in Zibo city. These contaminants with high concentrations at X_{10} indicated industrial discharge from Zibo city. The use of metal-working fluids during thermal processing in the machine processing industry has been recognized as a major source of SCCPs, contributing to 47.4% of the total emissions and 77.8% of water emissions in China (Jiang et al., 2017; Zhang et al., 2017). Zibo city is famous for machinery and for the processing industry (up to one hundred processing enterprises are

located here), which might explain the high SCCP concentration at X_{10} . The highest MCCP concentrations were found near Yangkou port (X_{18} : 27,000 ng/g dw, X_{17} : 21,000 ng/g dw). Instead of industrial harbor, Yangkou port is a small-scale fishing and cargo port with a history of more than 100 years. Most of the moorings in Yangkou port are occupied by hundreds of traditional wooden fishing boats throughout the year. Several rubber tires hang on every boat just at the surface of the water. Waterproof and anticorrosive coatings are essential and brushed every year for repairment. CPs are commonly used as additives in the rubber industry, such as in marine coatings, rubber tires, and polyurethane materials (Tong et al., 2003; Wei et al., 2016). Many researchers have reported that compared to SCCPs, MCCPs are more prone to be adsorbed onto particles and settle in sediment instead of being transported by water over long distance (Chen et al., 2011; Ma et al., 2014; Pan et al., 2018; Zeng et al., 2013a). Thus, the mooring fishing boats might be a major contributor to MCCPs in the Xiaoqing River.

Both Pearson and Spearman correlations were performed between the MCCPs and SCCPs in the sediment samples. The results showed a significant correlation under Spearman analysis ($R = 0.988$, $p < 0.01$) and a moderate correlation under Pearson analysis ($R = 0.463$, $p < 0.05$). This suggested the coexistence of SCCPs and MCCPs emissions at each site, but with different MCCP/SCCP ratios, suggesting a mixture of various pollution sources and/or different transport pathways. There was no significant correlation between SCCPs and TOC in the sediment samples of the Xiaoqing River, nor between MCCPs and TOC, which is mainly attributed to industrial discharge. Similar results were also reported for both the Liaohe River Basin and the Laizhou Bay areas (Gao et al., 2012; Pan et al., 2018).

In comparison, CP concentrations in the sediments of the Xiaoqing River were similar to those in the Pearl River Delta (SCCPs: 46.3–1540 ng/g, mean value 334 ng/g; MCCPs: 102–6650 ng/g, mean value 1720 ng/g), but higher than those in the Liaohe River Basin (39.8–480.3 ng/g). They were also higher than the concentrations in

Fig. 2. Spatial distribution of SCCPs and MCCPs in the Xiaoqing River: (a) sediment; (b) SCCPs in dissolved and particulate phases; (c) MCCPs in dissolved and particulate phases.

the rivers of Japan, in the industrial area near Barcelona, Spain, in the rivers of the Czech Republic, and in all the reported coastal waters (Castells et al., 2008; Chen et al., 2011; Gao et al., 2012; Zeng et al., 2017). The highest SCCP concentration was found in rivers receiving industrial discharge in England (65,100 ng/g dw) (Nicholls et al., 2001), followed by that found at X₁₀ in the present study. The SCCP concentration at X₁₀ is the highest concentration reported in the last decade,

much higher than that in a wastewater receiving lake in Beijing, China (8700 ng/g dw) (Zeng et al., 2012). MCCP concentrations found in the Xiaoqing River are much higher than those found in sewage sludge in Australia (Brandsma et al., 2017), and second only to those found in the Pearl River Delta (38,000 ng/g dw) (Chen et al., 2011). High CP concentrations reflect the rapid industrial development, because the pollution level of CPs is reportedly directly proportional to industrialization (Zeng et al., 2017).

The compositional profiles of MCCPs varied little from the upstream to downstream and marine sediments (Fig. 3). The relative concentration of the congener groups declined with an increase in the carbon chain length, except for a few sites in the bay. C₁₄ was dominant, with a percentage of $46.2 \pm 6.3\%$. The dominant chlorinated groups were Cl₇₋₈, followed by the Cl₆ and Cl₉ congener groups. For SCCPs, however, along with the sharp decrease in CP concentration from the river to the bay, the CP congener group patterns also presented obvious differences between the river section (sites X₁–X₂₃) and the bay (sites X₂₆–X₃₀), as shown in Fig. 4. In the river section, C₁₃ groups dominated in all the samples; they were slightly higher than in the C₁₁ and C₁₂ groups, while C₁₀ had the lowest percentage of them. On average, the C₁₀–C₁₃ congener groups contributed by $17.1 \pm 11.6\%$, $25.3 \pm 6.7\%$, $24.2 \pm 7.0\%$, and $33.4 \pm 6.8\%$, respectively. This is consistent with the industrial groups reported in our previous study and resembles those in the PRD and Shenzhen coastal sediments (Pan et al., 2018; Zeng et al., 2017). In the Laizhou Bay sediments of X₂₆–X₃₀, however, the C₁₀ and C₁₁ groups predominate, accounting for an average abundance of 50.7% and 32.8% respectively. Among the chlorine groups, Cl₆₋₈ are the dominant congener groups in both the river section and the bay, accounting for 80% of the total. The Cl₅₋₆ groups were elevated in the headwaters compared to their values in the marine sediments, while the Cl₈₋₉ groups declined. Thus, for the sediments in the headwaters, the estuary, and in the bay, lighter congener groups with shorter carbon chains and lower chlorination tended to be transported for longer distances, while the heavier congeners were more likely to sink and deposit owing to larger K_{ow} values. These findings have been stated in previous studies (Pan et al., 2018).

3.2. CPs in waters of the Xiaoqing River and the bay

CP concentrations ranged from n.d. to 470 ng/L for SCCPs (mean value: 43 ng/L) and from n.d. to 120 ng/L for MCCPs (mean value: 28 ng/L) in the water column (sum of the dissolved phase and particulate phase), as shown in Fig. 2b and c. SCCPs accounted for 95% of CPs (sum of SCCPs and MCCPs) in the dissolved phase in the Xiaoqing River, ranging from n.d. to 230 ng/L with an average value of 23 ng/L. The MCCPs ranged from n.d. to 47 ng/L with an average value of 5.9 ng/L in the dissolved phase. MCCPs existed mainly in the particulate phase and were closely spearman-correlated with SCCPs ($r = 0.698$, $p < 0.01$). They were within the ranges of n.d. to 240 ng/L (mean value: 20 ng/L) and n.d. to 96 ng/L (mean value: 13 ng/L) for SCCPs and MCCPs in particulate phase, respectively. The highest concentration of SCCPs (470 ng/L) at X₂ was even much higher than that found in the influent waters of the municipal sewage treatment plants in Beijing (184 ng/L) and Japan (279 ng/L) (Wei et al., 2016; Zeng et al., 2013b). X₂ was located along the main stream of the Xiaoqing River just below Jinan city; therefore, it might be influenced by urban emissions. However, other industrialized contaminants, such as perfluoroalkyl substances and halogenated flame retardants, were detected at relatively low concentrations, as reported in our previous studies (Heydebreck et al., 2015; Zhen et al., 2018). In addition, SCCP concentrations at X₂ were more than 10 times higher than at X₁, which was also located downstream of Jinan City and only about 460 m upstream of X₂. When probing into the surroundings of sites X₁ and X₂, we found a drain outlet near site X₂ and determined that the discharged water was from a power plant used for refrigeration. SCCPs have been used as a polychlorinated biphenyl (PCB) substitute since PCBs were regulated in the 1970s (Fiedler, 2010), and have been widely used as an insulating

Fig. 3. Congener group patterns of MCCPs with C₁₄-C₁₇ and Cl₅-Cl₁₀ in sediments, particulate, and dissolved phases.

Fig. 4. Congener group patterns of SCCPs with C₁₀-C₁₃ and C₁₅-C₁₉ in sediments, particulate, and dissolved phases.

oil in transformers, capacitors, and other power equipment (Johnson et al., 1964). These may be the sources of SCCPs in the power plant.

The C₁₀ and C₁₁ groups were dominant congener groups in the dissolved phase, accounting for $81.6 \pm 9.2\%$ of the total (Fig. 4). Among the chlorine groups, Cl₆₋₈ accounted for $91.8 \pm 3.8\%$ on average. For MCCPs, only 30% of C₁₆ or C₁₇ groups were detected in the dissolved phase. The C₁₄ and Cl₇₋₉ groups were predominant in almost all the sites (Fig. 3). In particulate samples, the dominant groups were C₁₁ and C₁₃ groups, Cl₇ and Cl₈ groups (except X12), accounting for $38.5 \pm 7.1\%$ (C₁₁), $28.6 \pm 5.9\%$ (C₁₃), $35.1 \pm 5.2\%$ (Cl₇), and $29.2 \pm 4.2\%$ (Cl₈) respectively. The congener group patterns of MCCP in particulate samples varied little across the different sites. C₁₄ group was the predominant congener group, accounting for $87.6 \pm 4.6\%$, followed by the C₁₅ group. C₁₆₋₁₇ accounted for less than 20% of the most samples. Cl₇₋₉ groups were dominant, accounting for $58.7 \pm 9.8\%$. However, owing to the method limitations, congener groups with more than 10 chlorine atoms could not be detected (Casà et al., 2019). Thus, the overestimation of the relative abundances of the congener groups detected in the present study might occur.

3.3. Influence of environmental factors on the fate and transport of CPs along the estuary

Relatively high CP concentrations were observed below Jinan (X₂-X₃) and Zibo (X₁₀-X₁₁) cities, indicating urban sources to the Xiaoqing River. Relatively high concentrations in water samples also occurred around the two city clusters. However, at sites X₁₇-X₁₉ that were sampled near Yangkou port however, CP concentrations in sediments were the highest, while those in water samples, especially in particulate samples, were lower than those in other sites. This contrast indicated a sedimentation of a historical input from a local source rather than of a current input, and was also due to the dilution by seawater in the water phase.

The estuarine turbidity maximum zone (ETM) is a typical characteristic of estuaries that determines water quality and influences the fate and transportation of pollutants. Fresh water and seawater converged at X₁₀₋₂₃, as shown by the salinity change curve, indicating that this section might be located within the ETM (Munoz et al., 2017). Studies have reported that the removal of contaminants from the water column may be enhanced at neap tides (low current velocities) as coarser particles settle on the bed sediment, and the 'salting-out' effects could be caused by a sharp increase in salinity (Munoz et al., 2017). Relatively higher concentrations of SCCPs were observed in the ETM of the Pearl River Estuary and the Liaohe Estuary than in the nearby upstream and downstream samples. These were related to a mixture of freshwater and seawater (Chen et al., 2011; Gao et al., 2012). In the present study, the mass distribution of lighter congener groups (C₁₀₋₁₁ and Cl₆₋₇ groups) of SCCPs in the ETM declined in the order: dissolved phase > particulate phase > sediment, while the concentrations of heavier congeners (C₁₃ and Cl₁₀ groups) increased. This variation within the ETM might be the result of both freshwater-seawater mixing and different physicochemical properties, such as LogKow values and solubilities. Long-chained and more chlorinated congeners with larger LogKow values might be more likely to be salted-out and thus be sequestered in sediments, while lighter congener groups with relatively high water solubility might be more prone to be transported further with the water flow. This is probably also the main reason for the sharp decrease in CP concentrations and for the variation in congener groups from the river to the sea in sediments.

Other parameters, including dissolved organic carbon (DOC), salinity, pH, oxidation-reduction potential (ORP), and vapor pressure, were simultaneously determined. It is interesting to note that CPs in the dissolved phase were significantly positively correlated with atmospheric pressure and that the coefficient for SCCPs was slightly higher than that for MCCPs. This result indicates the possible atmospheric input of the Xiaoqing River. Ma et al. (2018) reported the analysis of the net deposition in Liaodong Bay. They found that the diffusive inputs related to the concentrations and profiles of CPs in the dissolved phase in the

water column were larger than the diffusive inputs from dry deposition related to CPs in the particulate phase CPs (Ma et al., 2018). Air-water gas exchange might be an important source of dissolved CPs in the waters of the Xiaoqing River and was enhanced by the tide's ebb and flow. Dissolved organic carbon (DOC) has been considered a key factor affecting the transportation and fate of persistent organic pollutants (POPs). However, in this study however, no significant correlation was observed between CPs and DOC, as well as between individual congener groups and the DOC in the water column, indicating that SCCPs mostly belonged to the freely dissolved category. This also further proved the role of the atmospheric input in the waters of the Xiaoqing River.

Correlations between SCCPs and MCCPs in the dissolved phase were greatly weakened and reduced ($r = 0.39$, $p < 0.05$) compared to those in sediments and particles. The decline of the correlation coefficients from the sediment to the water phase reflected their different physicochemical properties and transfer-transformation behaviors. Compared with SCCPs, the congener patterns of MCCPs did not vary much from upstream to downstream and to the outer sea. There was only a slight decline in the C₁₄-MCCP group in the following order: dissolved phase, particulate phase, and the sediment samples, which may be attributed to its strong hydrophobicity and weak solubility.

3.4. Conclusion

We have reported the occurrence of SCCPs and MCCPs in the Xiaoqing River basin. Both water and sediment samples were analyzed to explore the transport behaviors and fate from the river to the Laizhou Bay. The results revealed that cities are an important pollution source of CPs pollution in the river environment. In the Xiaoqing River, relatively high concentrations occurred when the river passed by Jinan and Zibo cities. The highest SCCP concentration at X₁₀ is the highest concentration reported in the last decade, even higher than that in a wastewater-receiving lake in Beijing. MCCP concentrations exhibited the second highest values ever recorded, second only to those found in the Pearl River Delta. The mass distribution analysis indicated that long-chained and more chlorinated congeners with larger LogKow values (C₁₃ and Cl₁₀ groups) were more likely to be salted-out and be sequestered within the ETM, while the lighter congener groups (C₁₀₋₁₁ and Cl₆₋₇ groups), having relatively high water solubility, were prone to be transported further away with the water flow. This is probably an important influencing factor affecting the congener pattern differences from the river to the Laizhou Bay.

CRediT authorship contribution statement

Xiaohui Pan: Investigation, Methodology, Data curation, Software, Writing - original draft. **Xiaomei Zhen:** Investigation, Data curation, Visualization, Software, Validation. **Chongguo Tian:** Methodology, Validation, Writing - review & editing. **Jianhui Tang:** Conceptualization, Supervision, Data curation, Funding acquisition, Resources, Project administration, Writing - review & editing.

Declaration of competing 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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2020.141769>.

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