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# Spatial and temporal trends of short- and medium-chain chlorinated paraffins in sediments off the urbanized coastal zones in China and Japan: A comparison study<sup>☆</sup>



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## ABSTRACT

To examine the impacts of urbanization and industrialization on the coastal environment, and assess the effectiveness of control measures on the contamination by chlorinated paraffins (CPs) in East Asia, surface and core sediments were sampled from the urbanized coastal zones in China and Japan (i.e., Pearl River Delta (PRD), Hong Kong waters and Tokyo Bay) and analyzed for short-chain (SCCPs) and medium-chain CPs (MCCPs). Much higher concentrations of CPs were found in the industrialized PRD than in adjacent Hong Kong waters. Significant correlation between CP concentration and population density in the coastal district of Hong Kong was observed ( $r^2 = 0.72$  for SCCPs and  $0.55$  for MCCPs,  $p < 0.05$ ), highlighting the effect of urbanization. By contrast, a relatively lower pollution level of CPs was detected in Tokyo Bay. More long-chain groups within SCCPs in the PRD than in Hong Kong waters and Tokyo Bay implied the effect of industrialization. Comparison of temporal trends between Hong Kong outer harbor with Tokyo Bay shows the striking difference in historical deposition of CPs under different regulatory situations in China and Japan. For the first time, the declining CP concentrations in Tokyo Bay, Japan, attest to the effectiveness of emissions controls.

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## 1. Introduction

Chlorinated paraffins (CPs) are a complex mixture of polychlorinated n-alkanes with chlorine content ranging from 30 to 70% (De Boer et al., 2010). Because of their excellent thermal and chemical stability, over 200 CP formulations have been applied in a wide variety of consumer products and industrial processes, including use as metal-working lubricants, plasticizers, flame retardants, adhesives, paints, rubber, and sealants, and as softeners in various materials (Bayen et al., 2006). Based on their chemical structures, the substances are divided into short-chain (SCCPs, C<sub>10–13</sub>), medium-chain (MCCPs, C<sub>14–17</sub>) and long-chain chlorinated

paraffins (LCCPs,  $C_{>17}$ ) (Feo et al., 2009). With the wide applications and huge amounts of production, CPs have been found in different environmental compartments including air (Diefenbacher et al., 2015; Chaemfa et al., 2014; Li et al., 2012), soil (Wang et al., 2013; Halse et al., 2015), water (Ma et al., 2014), sediment (Iozza et al., 2008; Pribylova et al., 2006; Gao et al., 2012; Tomy et al., 1999; Marvin et al., 2003), dust (Friden et al., 2011), food (Iino et al., 2005; Harada et al., 2011; Cao et al., 2015) and biota (Basconcello et al., 2015; Luo et al., 2015; Houde et al., 2008; Reth et al., 2006) over the past decade. Of all the CPs, SCCPs are of great environmental concern because they are highly persistent (Iozza et al., 2008), bioaccumulative (Ma et al., 2014; Houde et al., 2008), toxic (Warnasuriya et al., 2010; Geng et al., 2015), and ubiquitous in the environment (Santos et al., 2006). SCCPs are currently being evaluated by the Stockholm Convention, and research of CPs has been an emerging scientific endeavor (UNEP/POPS/POPRC.11/4, 2015). The European Union, USA, Canada and Japan have begun to restrict the production and usage of CPs (De Boer et al., 2010; UNEP/POPS/POPRC.11/4, 2015; Eljarrat and Barcelo, 2006; van Mourik et al., 2016). However, China is now the largest producer, consumer, and exporter of CPs in the world. With the rapidly increasing production in the past decade, the annual production volume of CPs reached 1050 kilotonnes in 2013 (De Boer et al., 2010; [http://www.eurochlor.org/media/88258/20140908\\_icaia\\_newsletter\\_03\\_final.pdf](http://www.eurochlor.org/media/88258/20140908_icaia_newsletter_03_final.pdf)), but there are no regulations of CPs in China now. To date, there is still a lack of data on the levels and fate of CPs in many parts of the world. Especially, more attention should be paid to CP pollution in China.

Anthropogenic CPs can be distributed extensively into the ambient environment through two pathways, riverine runoff and atmospheric transport (Zeng et al., 2012, 2013; Zhao et al., 2013). In both cases, coastal sediment is a key sink for terrestrially derived CPs. Wastewater discharges are recognized as a main source of CPs in land-based aquatic system (Zeng et al., 2011a, 2011b). The majority of CPs can bond to suspended particles and end up forming part of sediments. Therefore, investigation of sediment core profile is very useful for reconstructing the historical inputs of CPs, evaluating the effectiveness of emission control, and improving future management strategies.

Rapid economic development has taken place in China in the past few decades. Since the establishment of Special Economic Zones (SEZ) in 1979, China's coastal zones have become the primary sites for industrial production; meanwhile, the coastal environment is undergoing accelerated deterioration. The Pearl River Delta (PRD), located on the southern coast of China, is one of the highly industrialized manufacturing bases for electronic products, textiles and plastic products in China. With domestic and industrial wastewater treatment plants failing to keep step with the growth in population and rapid development of industries in the area, the PRD is facing serious environmental pollution challenges. Large amounts of industrial and municipal effluents are discharged into the Pearl River Estuary (PRE) and finally transported to the South China Sea (SCS). Elevated levels of POPs, including CPs have been found in the sediment of the PRE (Chen et al., 2011). Shenzhen, situated north of Hong Kong, is the fastest-developing SEZ and a densely populated metropolis. Developed industries including electronics manufacturing and chemicals production, also pose a potential pollution risk to the coastal ecosystem. Hong Kong is one of the most developed and highly urbanized cities in China, situated at the southeastern end of the PRD, with a population of 7.2 million residing on around 25% of its 1104 km<sup>2</sup> land area. Since the 1980s, the dominant industries have shifted from manufacture to services with many factories and plants having been relocated to the adjacent PRD region (Liu et al., 2014). Previous studies indicated that POPs, such as polybrominated diphenyl ethers (PBDEs) and novel

halogenated flame retardants, have been detected in sediment from the urbanized coastal zone of Hong Kong (Liu et al., 2014; Muller et al., 2002; Terauchi et al., 2009; Richardson and Zheng, 1999).

In Japan, CPs were extensively used as additives to metal-working lubricants and to other various materials (e.g. flame retardant additives, plasticizers for polyvinyl chloride) from the beginning of production in about 1950, but there are no specific data on the production and use of CPs before 2000 (De Boer et al., 2010). Considering the environmental and health risk, Japan has listed SCCPs under the Pollutant Release and Transfer Register Law (PRTR), and the controls and regulations for SCCPs have been implemented in recent years ([http://www.eurochlor.org/media/88258/20140908\\_icaia\\_newsletter\\_03\\_final.pdf](http://www.eurochlor.org/media/88258/20140908_icaia_newsletter_03_final.pdf)). It is reported that production and use of CPs in Japan have constantly declined after 2001 (Harada et al., 2011). Tokyo Bay is the major region of CP use in Japan (De Boer et al., 2010), surrounded by Tokyo and Yokohama, which have been seriously contaminated by industrial and urban wastes in its history. Many POPs have been found in Tokyo bay (Tsui et al., 2015; Ahrens et al., 2009; Yamashita et al., 2000), but there are no reports on CPs to date.

The marine systems of China include the Bohai Sea (BS), Yellow Sea (YS), East China Sea (ECS), and SCS. In the past several years, a large-scale study of spatiotemporal distribution, transport and sources of CPs in Chinese marine ecosystem was carried out. This study builds on and continues from the previous investigations on the ECS (Zeng et al., 2012; Zhao et al., 2013), BS and YS (Zeng et al., 2013; Yuan et al., 2012), and extends to the SCS (Zeng et al., 2015) and other coasts in East Asia. In this study, surface sediment and sediment core samples were collected from several typical industrialization- and urbanization-impacted coastal zones in China and Japan (including the PRD, Shenzhen coast, Hong Kong and Tokyo Bay, Figs. 1 and 2) and analyzed for SCCPs and MCCPs. The aims of this study were to determine the current levels and spatial distribution off the important coastal zones in East Asia, to assess the magnitude of sediment contamination through a worldwide comparison, to reveal the impacts of urbanization and industrialization on the coastal environment, and to compare the temporal trends of CP contamination between China and Japan. This study mainly aimed at examining the effectiveness of emission controls by a comparison study under different regulatory situations in China and Japan.

## 2. Materials and methods

### 2.1. Sample collection, extraction, and cleanup

A total of 16, 8, 35 and 8 surface sediments were collected from the PRD, Shenzhen coastal waters, Hong Kong waters and Tokyo Bay of Japan, respectively, during 2012 and 2013 (Figs. 1A and 2). The top 5 cm of sediment was taken using a stainless steel scoop, packed in aluminum foil and stored in Ziplock bags. The sampling sites in Hong Kong waters corresponded to the Environmental Protection Department's (EPD) regular sediment monitoring stations (Marine Water Quality in Hong Kong). Detailed coordinates of all sampling sites are listed in Table S1 of Supporting Information (SI). One sediment core was collected from Hong Kong waters in 2004 (Core HK1: N22°12'17.76", E114°6'39.39") and the other two from Tokyo Bay of Japan in 2012 (Core J1: N35°35'39.12", E139°54'24.48"; Core J2: N35°28' 14.52", E139°45'23.04"). The sediment cores mainly were made up of clayey silt and the grain size variation was small, suggesting a stable sedimentary environment in selected sampling locations. The cores were sectioned at 2 cm intervals aboard ship immediately after collection. All samples were immediately transported in ice-cooled boxes to the laboratory

and freeze-dried and stored at  $-80\text{ }^{\circ}\text{C}$  until analysis. The details of extraction and cleanup procedure, sediment core dating, sedimentation rate and flux calculations can be found in the SI.

2.2. Instrumental analysis, identification and quantification

SCCPs ( $\text{C}_{10}\text{--}\text{C}_{13}\text{Cl}_{5}\text{--}\text{Cl}_{10}$ ) and MCCPs ( $\text{C}_{14}\text{--}\text{C}_{17}\text{Cl}_{5}\text{--}\text{Cl}_{10}$ ) were simultaneously analyzed by gas chromatography/electron capture negative ionization/low resolution mass spectrometry (GC-ECNI-LRMS). The two most abundant isotopes of  $[\text{M}-\text{Cl}]^{-}$  ions of the CP congener groups were monitored. Detailed instrumental parameters are published in our previous works (Zeng et al., 2011a, 2011b). Qualitative identification was performed by comparing retention time, signal shapes and isotope ratios with the standards (Reth and Oehme, 2004). SCCPs always interfere with MCCPs with five carbon atoms more and two chlorine atoms less due to similar mass fragments during quantitative analysis. The developed chemical calculation procedure was used to attempt to avoid interference

(Zeng et al., 2011a). The quantification method was based on Reth et al. (2005). Three SCCP standards (51.5%, 55.5% and 63% Cl) and three MCCP standards (42.0%, 52.0% and 57.0% Cl) together with their respective mixtures were used to set up linear relationship between chlorine content and the total response factor. The coefficients ( $R^2$ ) of linear regression of five-point calibration curves for SCCP and MCCP standards were  $\geq 0.97$ .

2.3. Quality assurance and quality control

A procedural blank was processed for each batch of eight samples to check for possible interference or contamination. CPs in procedural blanks were below or close to the detection limits. The recoveries of surrogate standard  $^{13}\text{C}_{10}\text{-trans-chlordane}$  and target analytes in spiked samples (CP free sediments from Nam Co Lake in Tibetan Plateau, China) were 79–108%. The recoveries of surrogate standard in field samples were 76–105%. Chlorine contents of SCCPs and MCCPs in field samples were 57.5–63.4% and

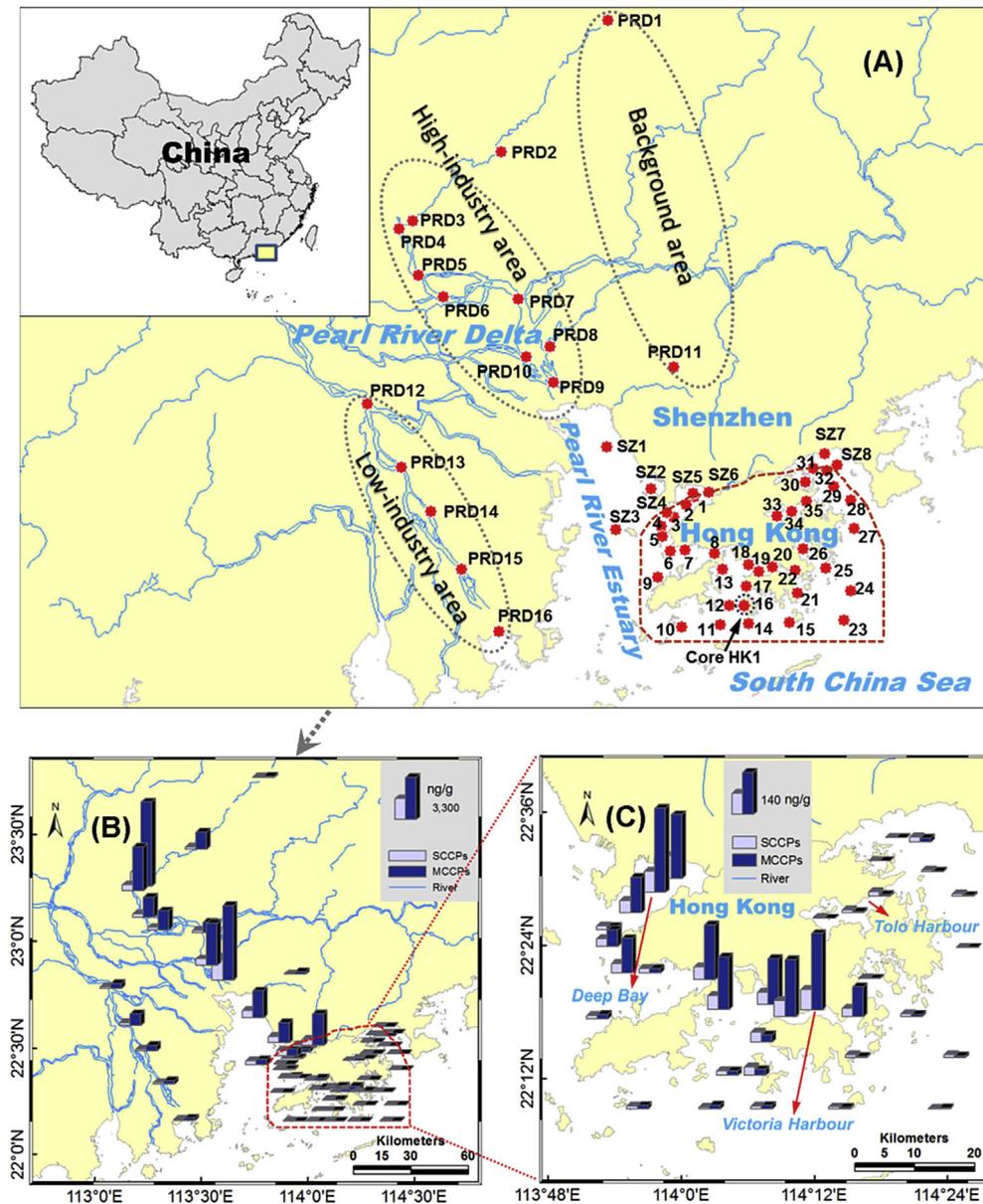


Fig. 1. Spatial distributions of SCCPs and MCCPs in surface sediment from PRD, Shenzhen and Hong Kong waters, China.

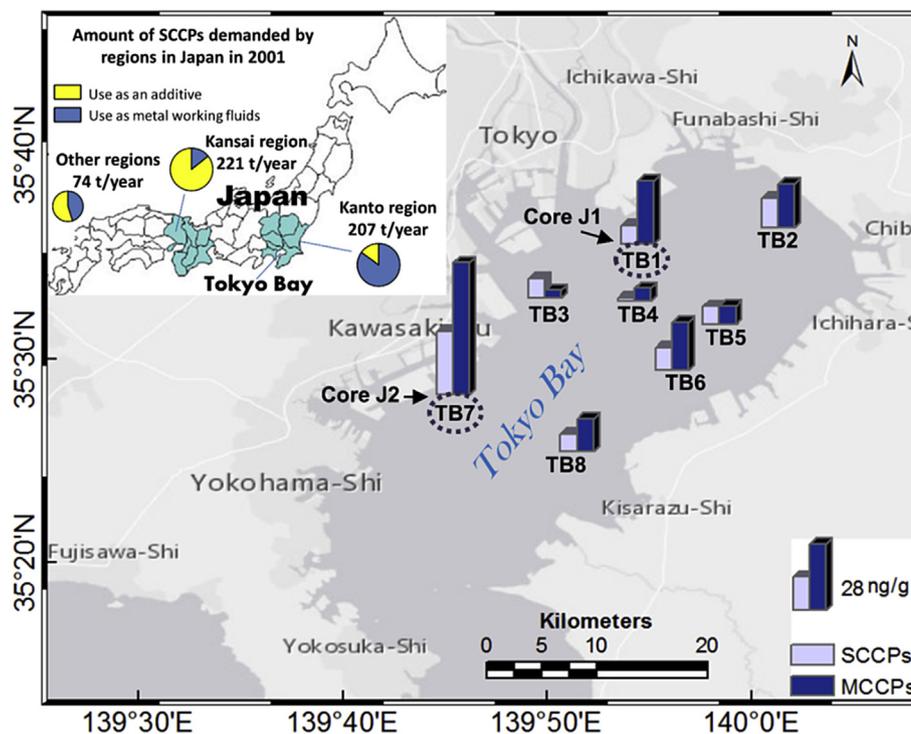


Fig. 2. Spatial distributions of SCCPs and MCCPs in surface sediment from Tokyo Bay, Japan.

51.0–58.6%, respectively, and were within the range of CP standards. The limit of detection (LOD) was defined as three-fold standard deviation of blanks. The LODs for SCCPs and MCCPs were estimated at 0.6 and 1.0  $\text{ng g}^{-1}$  dry weight, respectively. Concentrations below LOD were replaced by half of the LOD for data analysis. Accuracy was examined with spiked samples and deviated  $\leq 15\%$  from the expected values. Repeatability of the analysis was tested by analyzing duplicate samples, with a relative standard deviation  $\leq 12\%$ .

### 3. Results and discussion

SCCPs ( $\text{C}_{10-13}\text{Cl}_{5-10}$ ) and MCCPs ( $\text{C}_{14-17}\text{Cl}_{5-10}$ ) could be detected in most of the surface and core sediments from the typical urbanized and industrialized zones in China and Japan, suggesting a wide occurrence of CPs in the East Asia coastal environment. Concentrations are reported below on a dry weight basis with the unit of  $\text{ng g}^{-1}$ .

#### 3.1. Spatial trends of SCCPs and MCCPs in surface sediments off the coastal areas in China and Japan: association with urbanization and industrialization

Descriptive statistics of SCCP and MCCP concentrations in surface sediments from four representative coastal zones are summarized in Table 1. Individual SCCP and MCCP concentration and MCCP/SCCP ratio for each sampling site are presented in SI Table S1. Spatial distributions of CPs in the industrialized and urbanized areas in China and Japan are shown in Figs. 1 and 2, respectively.

To further illustrate the impacts of industrialization on the local environment and transport on the coastal environment, the sampling areas in the PRD which was previously considered to be the major source of SCCPs to the South China Sea (Chen et al., 2011), were categorized into high-industry, low-industry and background areas based on regional industrialized level by factor analysis (Xu

et al., 2012). Samples (PRD2–10) collected from highly industrialized regions (factor > 0.6) were assigned as high-industry area samples. Samples (PRD12–16) collected from slightly industrialized regions ( $0 < \text{factor} < 0.6$ ) were representative of low-industry area samples. As reference sites, samples (PRD1, 11) were collected from the least industrialized regions (factor < 0). The population, automobile traffic, lifestyle, and socioeconomic status were similar among the sampling areas that were not categorized as various land use. As shown in Fig. 1B, SCCPs and MCCPs showed obviously spatial distributions in the PRD across the sampling areas. Concentrations of SCCPs and MCCPs in the PRD were in the range of 46.3–1540  $\text{ng g}^{-1}$  and 102–6650  $\text{ng g}^{-1}$ , with mean values of 334  $\text{ng g}^{-1}$  and 1720  $\text{ng g}^{-1}$ , respectively. The highest SCCP and MCCP concentrations were found in sites PRD9 (SCCP: 1540  $\text{ng g}^{-1}$ ) and PRD3 (MCCP: 6650  $\text{ng g}^{-1}$ ), from a high-industry area in the PRD. The pollution levels of CPs were of the same order of magnitude reported in a recent report in this region (Chen et al., 2011). Elevated CP levels are usually associated with the production, usage and recycling of electronic, electrical and plastic products (Luo et al., 2015; Chen et al., 2011). These substantial CP emission sources have resulted in the release of SCCPs and MCCPs into the surrounding receiving rivers through wastewater overflow and surface runoff. A relatively low CP concentration was found in site PRD2, the upper reaches of the river in the high-industry area. Lower pollution levels of CPs were found in sediment from Xijiang River (PRD12–16), a low-industry area in the PRD, with SCCP and MCCP concentrations in the range of 93.8–225 and 188–926  $\text{ng g}^{-1}$ , respectively. The lower CP concentrations were found in two background sites PRD1 and PRD11, with 60.9 and 46.3  $\text{ng g}^{-1}$  for SCCPs, respectively. The ratio of MCCPs/SCCPs in sediment from the PRD ranged from 1.7 to 7.8, which was obviously higher in high-industry areas (mean: 6.0) than low-industry areas (mean: 3.1) and background areas (mean: 2.9). Generally, MCCPs/SCCPs ratio can be used as an effective indicator for pollution intensity and direct industry emission of CPs in a regional

environment (Chen et al., 2011). Spatial distribution and the difference in MCCP/SCCP ratios between high- and low-industry areas ( $p < 0.05$ ) indicate that industry emission is a major source in regard to the environment, and the pollution level of CPs is directly associated with industrialization.

In Shenzhen coastal zone, the sediment concentrations of SCCPs and MCCPs were in the range of 14.7–574 ng g<sup>-1</sup> and 10.9–2500 ng g<sup>-1</sup>, respectively. Higher CP concentrations along with higher MCCP/SCCP ratios were found in the west (in the PRE, SZ1-6) than in the east region (SZ7-8). The heavy pollution levels in the PRE may be jointly attributed to the waterborne transport via river input from the PRD and local sewage discharge from the west coast of Shenzhen with high urbanization and industrialization.

In Hong Kong waters, sediment concentrations were between below the limit of detection (<LOD) and 75.9 ng g<sup>-1</sup> for SCCPs and between < LOD and 286 ng g<sup>-1</sup> for MCCPs. As presented in Fig. 1C, spatial distribution showed that the highest concentration occurred at sites 1 and 2 in the western waters, located at Deep Bay adjacent to the PRE. Deep Bay is shallow, poorly flushed with tides, and polluted by the discharge of domestic sewage from the Shenzhen River at the border of Hong Kong and Shenzhen, as well as from San Pui River in the New Territories of Hong Kong (Liu et al., 2014). Because high CP levels have been found at sites SZ5 and SZ6 of the Shenzhen River, it can be inferred that the direct effect from west Shenzhen coastal waters and the indirect transport from the PRE contribute to the relatively higher concentrations in Deep Bay of Hong Kong. The second highest concentration was found at site 20 in the Victoria Harbour, with SCCP and MCCP concentrations up to 67.5 and 258 ng g<sup>-1</sup>, respectively. Victoria Harbour is the major port of Hong Kong and home to the fourth largest container terminal in the world. It lies between the highly urbanized areas of Hong Kong Island and the Kowloon Peninsula, and receives approximately 1.4 million tonnes of wastewater from both sides of the harbour per day, which is now being impacted by intensive human activities (Liu et al., 2014). The southern and eastern sites including Tolo Harbour contained low concentrations of CPs, which might be due to their adjacent areas being less populated and less urbanized with low industrialization as well as there being relatively less marine traffic here. It is indicated that the western waters of Hong Kong adjacent to the mouth of the PRE are more contaminated by CPs than the southern and eastern waters, which also corresponds to the higher accumulation of CPs found in marine mammals dwelling in the northwest waters than in the southern and eastern waters of Hong Kong in our recent study (Zeng et al., 2015). Statistical analysis indicated that the correlation between total organic carbon (TOC) contents and CP concentrations in all Hong Kong sediments was poor ( $R^2 < 0.1$ ), suggesting a minor role of TOC in shaping the current spatial distribution pattern of sediment CPs in the study region, and implying the dominance of local sources from human activities contributing to the occurrence of CPs in sediments. Liu et al. (2014) reported halogenated flame

retardants (HFRs) in the same sediment samples. Correlation analysis indicated that significant positive correlations existed between concentrations of SCCPs vs HFRs ( $R^2 = 0.57$ ,  $p < 0.05$ ) and MCCPs vs HFRs ( $R^2 = 0.55$ ,  $p < 0.05$ ) in surface sediments (Table S2), showing that sediment co-contamination by organic pollutions in Hong Kong waters may be caused by the common impacts from human activities.

Since the dominant industries of Hong Kong shifted to the adjacent PRD region in the 1980s, industry emission is not the major factor contributing to water pollution in Hong Kong. The population densities along the shores of the Victoria Harbour on Hong Kong Island and Kowloon are much higher than in the New Territories and outlying islands (Muller et al., 2002). This uneven population distribution provides a unique opportunity to examine the impacts of urbanization on CP pollution along coastal zones. As shown in Fig. 3, significant positive correlations between the population densities and CP concentrations for the coastal council districts (excluding Yuen Long containing sites 1–3, which has suffered more influence from the PRE and Shenzhen River) were found ( $R^2 = 0.72$  for SCCPs and 0.55 for MCCPs,  $p < 0.05$ ). A similar correlation was also observed between the population densities and the concentrations of HFRs in Hong Kong surface sediments (Liu et al., 2014). This result further indicates that local sources from human activities, e.g., the use of CP-containing products, mainly contribute to the occurrence of CPs in Hong Kong's nearshore sediments, and also implies that CP pollution levels in Hong Kong's coastal zones are linked to urbanization.

In all surface sediments from the PRD and Hong Kong waters (Fig. 1), concentrations of SCCPs correlated well with those of MCCPs ( $R^2 = 0.93$ ,  $p < 0.001$ ), suggesting a similar emission resource/pathway for the two groups of CP contaminants. Similar positive relationships between SCCPs and MCCPs were also observed in marine mammals (Zeng et al., 2015) and in soil and sediment from other studies (Wang et al., 2013; Chen et al., 2011). This is because SCCPs and MCCPs are the two major components in Chinese commercial CP mixtures, and generally are not strictly grouped by chain length of *n*-alkane feedstock in the manufacture processes (Wang et al., 2010). Chen et al. (2011) and Gao et al. (2012) reported the SCCP and MCCP abundance profiles in some commercial CP mixtures (e.g. CP-52) that are widely used in China.

Up to date, there are very limited data on CP environmental concentrations from Japan. Total CP production volume in Japan was about 11.8 kilotonnes in 2001, and then gradually decreased to 1.4 kilotonnes in 2009 (Iino et al., 2005). As shown in Fig. 2, concentrations of SCCPs and MCCPs in eight sediment samples collected from Tokyo Bay, Japan, were in the range of 1.3–27.4 ng g<sup>-1</sup> and 3.2–56.8 ng g<sup>-1</sup>, with mean values of 10.3 ng g<sup>-1</sup> and 19.2 ng g<sup>-1</sup>, respectively. The SCCP concentrations in Tokyo Bay sediments collected in 2013 are apparently lower than those in river sediments collected in 2003 (range of 4.9–484.4 ng g<sup>-1</sup> ww with five out of the six samples having

**Table 1**  
Descriptive Statistics of SCCP and MCCP Concentrations (ng/g d.w.) in Surface Sediment of Different Coastal Zones from China and Japan.

Coastal Zone	SCCPs			MCCPs		
	mean ± SD	median	range	mean ± SD	median	range
PRD (n = 16)	334 ± 418	173	46.3–1540	1720 ± 2050	868	102–6650
Shenzhen (n = 8)	317 ± 232	401	14.7–574	960 ± 955	541	10.9–2500
Hong Kong (n = 35)	22.0 ± 21.2	12.2	< LOD - 75.9	58.7 ± 84.7	12.5	< LOD - 286
Tokyo Bay (n = 8)	10.3 ± 7.6	8.0	1.3–27.4	19.2 ± 17.2	16.6	3.2–56.8

concentrations greater than 196.6 ng g<sup>-1</sup> ww) (Iino et al., 2005). Current pollution levels of CPs in Tokyo Bay sediments are lower than those in Hong Kong's nearshore sediments, and are comparable to those in Hong Kong's offshore sediments. The relatively low contamination in Tokyo Bay by CPs indicates the effectiveness of emission controls in Japan in recent years (Harada et al., 2011).

### 3.2. Comparison of worldwide SCCP and MCCP levels in sediments

There is still a lack of environmental data regarding CPs in sediments among different countries/regions worldwide although great progress has been made in recent years. Until now, there have been only a few studies on SCCPs in sediments around the globe, but for MCCPs in sediment samples there are even less documented studies available. Table S2 shows a summary of worldwide CP concentrations in lake, river and marine sediments from previous to present studies.

On the basis of these global comparisons, it can be found that, on the whole, SCCP pollution levels in surface sediments follow the order of industrial area sediment > river/lake sediment > marine sediment. SCCP concentrations in the industrial area of the PRD in the present study are comparable to those previously reported in the same region (320–6600 ng g<sup>-1</sup>) (Chen et al., 2011). The selected industrial areas of the UK (<200–65,100 ng g<sup>-1</sup>) (Nicholls et al., 2001) and Spain (250–3260 ng g<sup>-1</sup>) (Castells et al., 2004; Parera et al., 2004) have higher levels than found in Liaodong Bay (65–541 ng g<sup>-1</sup>) (Ma et al., 2014) and Liaohe River Basin (39.8–480.3 ng g<sup>-1</sup>) (Gao et al., 2012) of China, Lake Ontario (19–410 ng g<sup>-1</sup>) (Marvin et al., 2003), Winnipeg, Nipigon, Fox, Ya Ya and Hazen Lakes (1.6–257 ng g<sup>-1</sup>) (Tomy et al., 1999) of Canada, the Rivers of the Czech Republic (4.6–347 ng g<sup>-1</sup>) (Pribylova et al., 2006; Stejnarova et al., 2005) and the North and Baltic Seas (4–500 ng g<sup>-1</sup>) (Huttig and Oehme, 2005), but were much greater than the values in Hong Kong (<LOD - 75.9 ng g<sup>-1</sup>), the Bohai and Yellow Seas (14.5–85.2 ng g<sup>-1</sup>) (Zeng et al., 2013), the East China Sea (5.8–64.8 ng g<sup>-1</sup>) of China (Zeng et al., 2012), Lake Thun of Switzerland (21 ng g<sup>-1</sup>) (Iozza et al., 2008), the Firth of Clyde of the UK (0.4–69 ng g<sup>-1</sup>) (Hussy et al., 2012), and Tokyo Bay of Japan (15.3–25.4 ng g<sup>-1</sup>) from this study. It is also indicated that industry emission is the major driver of SCCPs in the environment.

MCCP concentrations in the PRD from the present study were in the range of those previously reported in the same region (880–38,000 ng g<sup>-1</sup>) (Chen et al., 2011), and were comparable to the highest concentration (5574 ng g<sup>-1</sup>) in river sediment of the Czech Republic (Pribylova et al., 2006), but much higher than those in the North and Baltic Seas (22–149 ng g<sup>-1</sup>) (Huttig and Oehme, 2006), Lake Thun of Switzerland (26 ng g<sup>-1</sup>) (Iozza et al., 2008), the mouth of the Detroit River at Lake Erie of Canada (68 ng g<sup>-1</sup>) (Tomy and Stern, 1999), Hong Kong (<LOD - 286 ng g<sup>-1</sup>) and Tokyo Bay of Japan (3.2–37.9 ng g<sup>-1</sup>). Owing to the very limited data on pollution levels of MCCPs in the world's sediments, presently it is impossible to take a global perspective on sediment pollution by MCCPs in this study. In addition, it should also be noted that, there are possible discrepancies for CP comparison in general due to the different analytical techniques (e.g. GC/ECNI-HRMS, GC/ECNI-LRMS) used in these studies (van Mourik et al., 2015).

### 3.3. Composition profiles of SCCPs and MCCPs in surface sediments reflecting the usage patterns of CPs

Only CP homologues with more than five chlorine atoms are detected by using the GC-ECNI-LRMS technique. Fig. 4 illustrates the representative homologue profiles of SCCPs in sediment samples obtained from four selected regions in China and Japan: the PRD, Shenzhen, Hong Kong and Tokyo Bay. SCCP relative abundance

patterns of carbon number are in the order of C<sub>13</sub> > C<sub>12</sub> ≈ C<sub>11</sub> ≈ C<sub>10</sub> for the PRD and Shenzhen sediments. The C<sub>13</sub> was the most predominant carbon chain group, accounting for more than 30% of the total abundance. The SCCP patterns dominated by more long-chain groups in sediments from highly industrialized areas in the present study are fairly similar to those detected in Indo-Pacific humpback dolphins collected from the PRE (downstream of the PRD) in 2013–2014 (Zeng et al., 2015), but there are some deviations from the results in sediments earlier collected from the PRD in 2009–2010 (Chen et al., 2011), which may reflect a shift to the production and usage of CP technical mixtures containing more long-chain congeners at present. This inference can be confirmed by a temporal shifting trend of SCCP patterns in dolphins (2010–2014) from the South China Sea in our recent work (Zeng et al., 2015). Contrarily, SCCP composition profiles in Hong Kong and Tokyo Bay sediments were characterized and predominated by short-chain groups of C<sub>10–11</sub>Cl<sub>5–7</sub>, consistent with the ones in typical marine sediments (Zeng et al., 2012, 2013). The differences in SCCP patterns among different sampling areas may primarily depend on the commercial formula of used products, but the physicochemical properties and environmental process of congeners should not be neglected.

As shown in Fig. S1, MCCP composition profiles in all sediment samples showed some similarities with C<sub>14</sub> as the major contributors, followed by C<sub>15</sub>, C<sub>16</sub> and C<sub>17</sub>. It is noteworthy that the most abundant congeners are C<sub>14</sub>Cl<sub>7–9</sub> for the PRD and Shenzhen sediments, but C<sub>14</sub>Cl<sub>6–8</sub> for Hong Kong and Tokyo Bay sediments. Besides, a larger abundance proportion of C<sub>14</sub> homologue was observed in the PRD and Shenzhen zone than in Hong Kong and Tokyo Bay. The MCCP patterns are similar to those previously reported in sediment from the other regions (Iozza et al., 2008; Chen et al., 2011; Huttig and Oehme, 2006; Tomy and Stern, 1999), and also correspond well to the compositions of extensively used commercial CP products (e.g. CP-52) (Chen et al., 2011; Tomy and Stern, 1999).

### 3.4. Temporal trends of CP concentrations and fluxes in sediment cores related to industrializing process and emission controls: comparison of China with Japan

To reconstruct the pollution histories of CPs, reveal the influence of industrializing process, and assess the effectiveness of emission control, sediment cores collected from China and Japan were dated, analyzed and compared. The reliability of the core dating was acceptable based on a linear decline in logarithmic <sup>210</sup>Pb<sub>ex</sub> with increasing depth in the cores (Fig. S2). The constant initial concentration (CIC) model was used to determine the ages and sedimentation rates. The average sedimentation rates were 1.45 cm yr<sup>-1</sup> for Core HK1, 1.50 cm yr<sup>-1</sup> for Core J1 and 1.03 cm yr<sup>-1</sup> for Core J2. The 80 cm at Core HK1, 80 cm at Core J1 and 76 cm at Core J2 covered about 55, 53 and 74 years of sedimentation records, respectively. The sedimentation rates in Core J1 and J2 are similar to those reported in previous studies from the same site of Tokyo Bay (Ahrens et al., 2009).

Temporal trends of CP concentrations and fluxes in Core HK1 from Hong Kong, China are shown in Fig. 5A. The detailed information is presented in SI Table S5. Each data point represents a date to the mid-point of each slice. The profiles of CP concentrations and fluxes tracked each other closely, reflecting a stable depositional environment. SCCP concentrations and fluxes ranged from 0.9 to 29.0 ng g<sup>-1</sup> and 1.0–32.4 ng cm<sup>-2</sup> yr<sup>-1</sup>, respectively. SCCPs were detected in the bottom sediment dated 1951, an approximate time that corresponds to their initial usage in Hong Kong. The concentration of SCCPs started to increase in 1960, a time that coincided with the start of CP production in China at the end of the 1950s (De

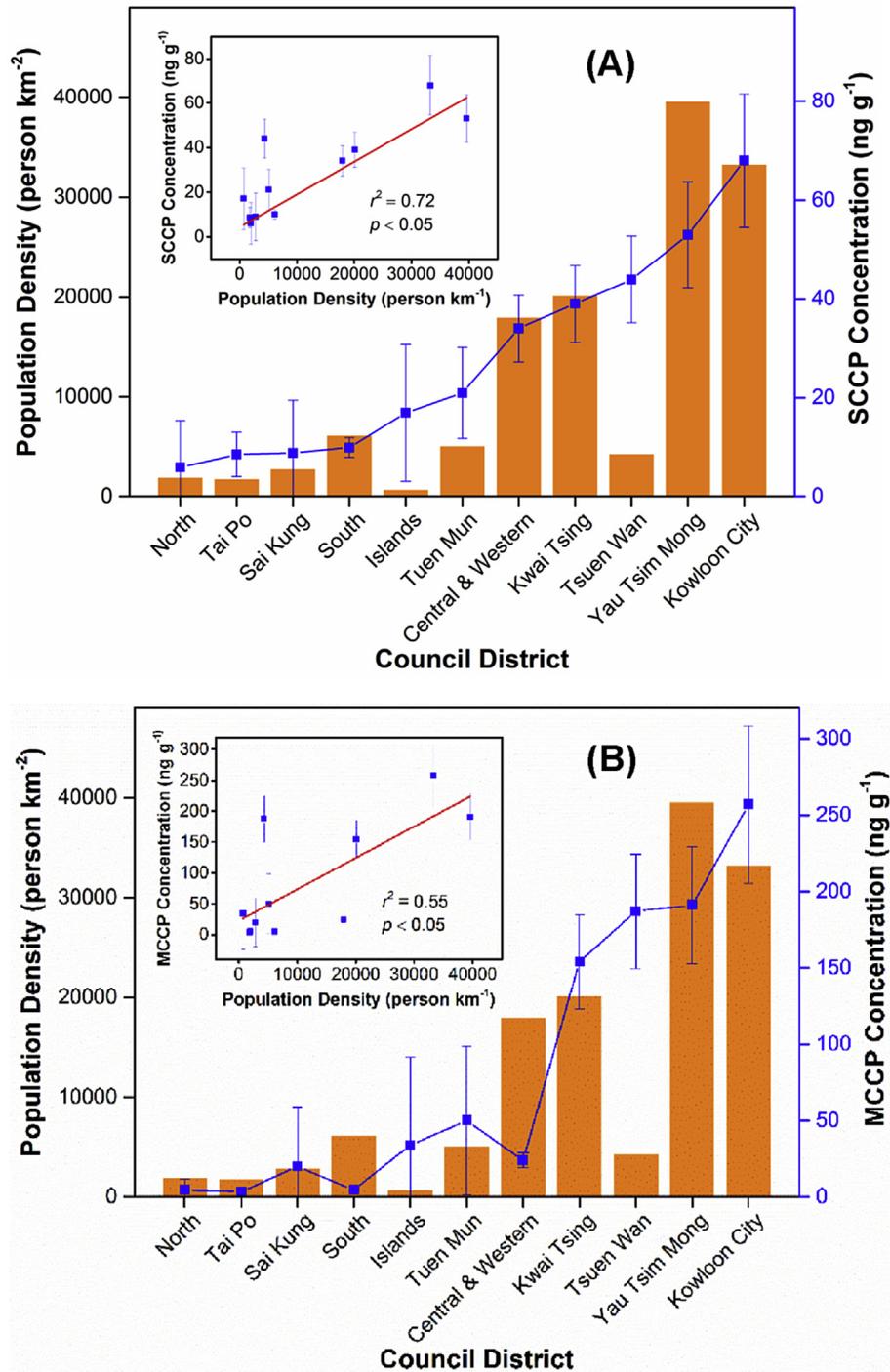


Fig. 3. Correlations between the population densities and SCCP (A) and MCCP (B) concentrations for the coastal council districts of Hong Kong.

Boer et al., 2010), and then fluctuated with a zigzag growth pattern until a relatively high concentration recorded in 1984. During the period from the 1960s–1980s, Hong Kong experienced a thriving manufacturing industry. Industrial activities together with uncontrolled disposal of domestic and industrial wastewater during the 1960s–1980s are reflected in the temporal profile of SCCP concentrations in this period (Shi et al., 2007). Since the 1980s, with the dominant industries of Hong Kong being relocated to the adjacent PRD region in succession (Liu et al., 2014), a declining trend of SCCP levels could be found from 1984 (16.2 ng g<sup>-1</sup>) to 1990 (1.3 ng g<sup>-1</sup>).

MCCPs could be only detected after 1957, and the concentrations and fluxes of MCCPs leveled off towards the end of the 1980s. After that, both SCCPs and MCCPs increased rapidly during 1990–2000 and thereafter escalated exponentially until 2004. The maximum fluxes and concentrations of CPs occurring in the surface layers correspond to 2004. As shown in SI Table S6, CP annual production in China has rapidly grown since the early 2000s. Therefore, the increasing trends of CPs during 1990–2004 could be due to a combined result of the increasing usage of CP-containing products in Hong Kong and uncontrolled emissions from mainland China,

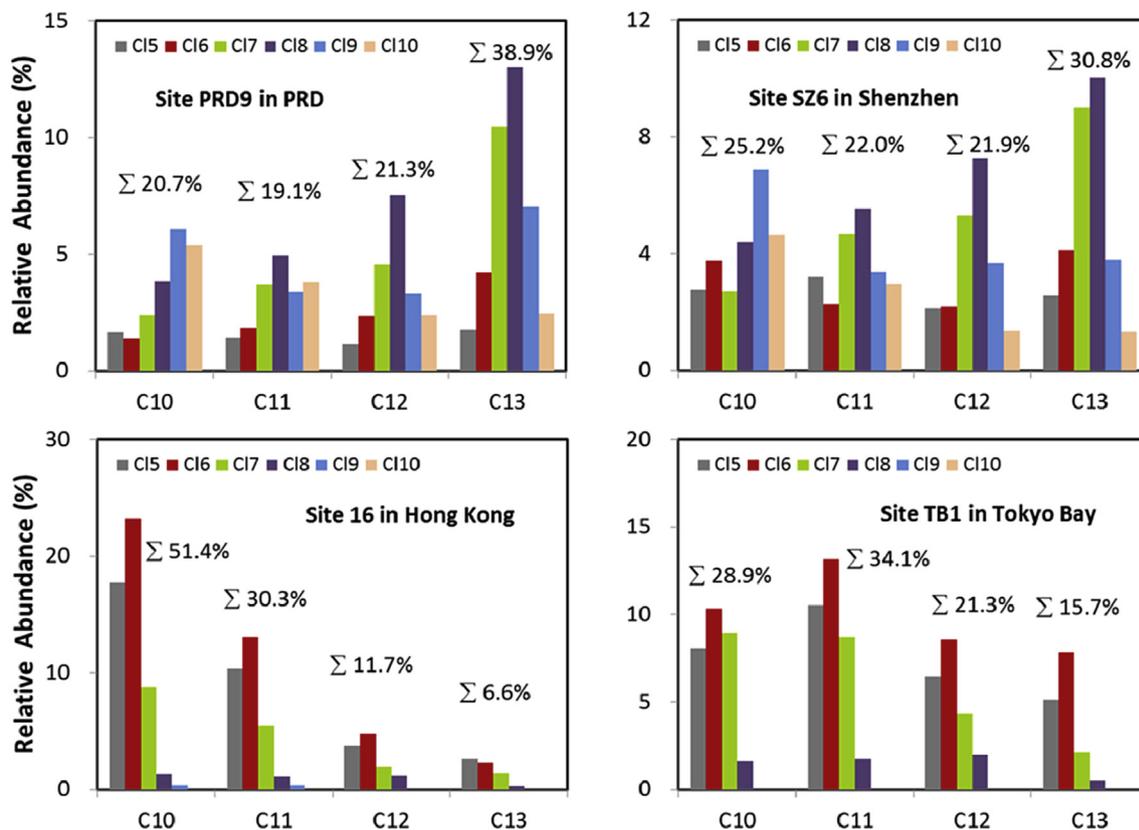


Fig. 4. The representative composition profiles of SCCPs in four coastal zones.

especially the outflow from the PRD region (Chen et al., 2011). Although the temporal trend of CPs ended in 2004 for Core HK1 owing to the limit of earlier collection, we can see a rapid increasing trend of CPs until 2010 in a sediment core from the PRD by the previous work (Chen et al., 2011). We can also deduce that the increasing trend of CPs in Chinese coastal sediments may still have been continuous over the past ten years due to there being no regulation and control measures in China (Zeng et al., 2015).

Temporal trends of CP concentrations in two sediment cores (Core J1 and J2) from Tokyo Bay, Japan are given in Fig. 5B and C. Detailed data are provided in SI Tables S7 and S8. The CP concentration profile shows a similar change to the flux profile in both cores, indicating a stable dynamic environment in the selected study locations. SCCPs and MCCPs could be found in all sediment slices of both cores. Core J2 ( $5.1\text{--}57.9\text{ ng g}^{-1}$  for SCCPs,  $7.9\text{--}180\text{ ng g}^{-1}$  for MCCPs) contained higher CP concentrations than Core J1 ( $1.3\text{--}26.4\text{ ng g}^{-1}$  for SCCPs,  $2.7\text{--}61.3\text{ ng g}^{-1}$  for MCCPs), but temporal trends of CP concentrations reflected in the vertical profiles of both cores are almost similar, indicating that the sources of CPs may be quite similar in Tokyo Bay. In both cores, SCCPs and MCCPs exhibited a similar trend with a higher level of MCCPs than SCCPs. Linear correlations were found between SCCP and MCCP concentrations ( $R^2 = 0.54$  and  $0.48$  for Core J1 and J2,  $p < 0.05$ ), suggesting their common release from some industrial applications. Higher levels of MCCPs than SCCPs in both cores could be the result of larger amounts of MCCPs had been used than SCCPs, which coincided with the historical data of reported production of CPs in Japan (SI Table S6). As shown in Fig. 5B, concentrations and fluxes of CPs in Core J1 showed no obvious changes from 1960 to 1981, but rapidly increased from 1982 to 1991. As seen from Fig. 5C, concentrations and fluxes of CPs in Core J2 showed a clearly continuous increase from 1950 to 1989. The peak concentrations of CPs in both

cores occurred synchronously in the period of the end of the 1980s to the early 1990s. About 3-fold higher concentrations of MCCPs than SCCPs in sediment layers were observed in this period. It is more important and noteworthy that both SCCPs and MCCPs in the cores showed a dramatic decline from 1990 to 2012. According to the estimated consumption of SCCPs during 1950–2002 (Fig. S3) (De Boer et al., 2010) and the reported production and usage information of CPs from 2001 to 2009 in Japan (Table S6), the consumption of SCCPs gradually increased from 1950 to 1980 with a peak of 1200 to 1400 tonnes per year from 1980 to 1990, which then decreased to 500 tonnes per year by 2000. After 2000, production and usage of CPs further declined and SCCPs were phased out by 2007.

Tokyo Bay is located in the downstream of the Kanto region, which is a major region of CP use in Japan. In 2001, the fraction of CPs used in metal-working fluids accounted for about 90% of total consumption volumes in the Kanto region (De Boer et al., 2010), and the usage of metal-working fluids containing CPs in the Kanto region accounted for 73% of the usage of CPs in Japan (De Boer et al., 2010). The production of CPs in Japan (including SCCPs, MCCPs and LCCPs) was 11,840 tonnes and 30% of the total volumes was used in metal working lubricants in 2001 (SI Table S5). Considering the environmental and health risk, some regulation and control measures have been implemented in Japan since 2001, leading to the declining production and use of CPs. For example, SCCPs were classified in Japan as Class I Chemical Substances Monitored in 2005. SCCPs were stopped producing in all domestic companies in Japan since 2006. SCCPs were withdrawn from metal-working fluids by 2007. In 2009, the volume of SCCPs imported was also reduced, but some manufactures and companies still use SCCPs as flame retardants and for other purposes (De Boer et al., 2010). Therefore, a substantial reduction of CP concentrations in sediment

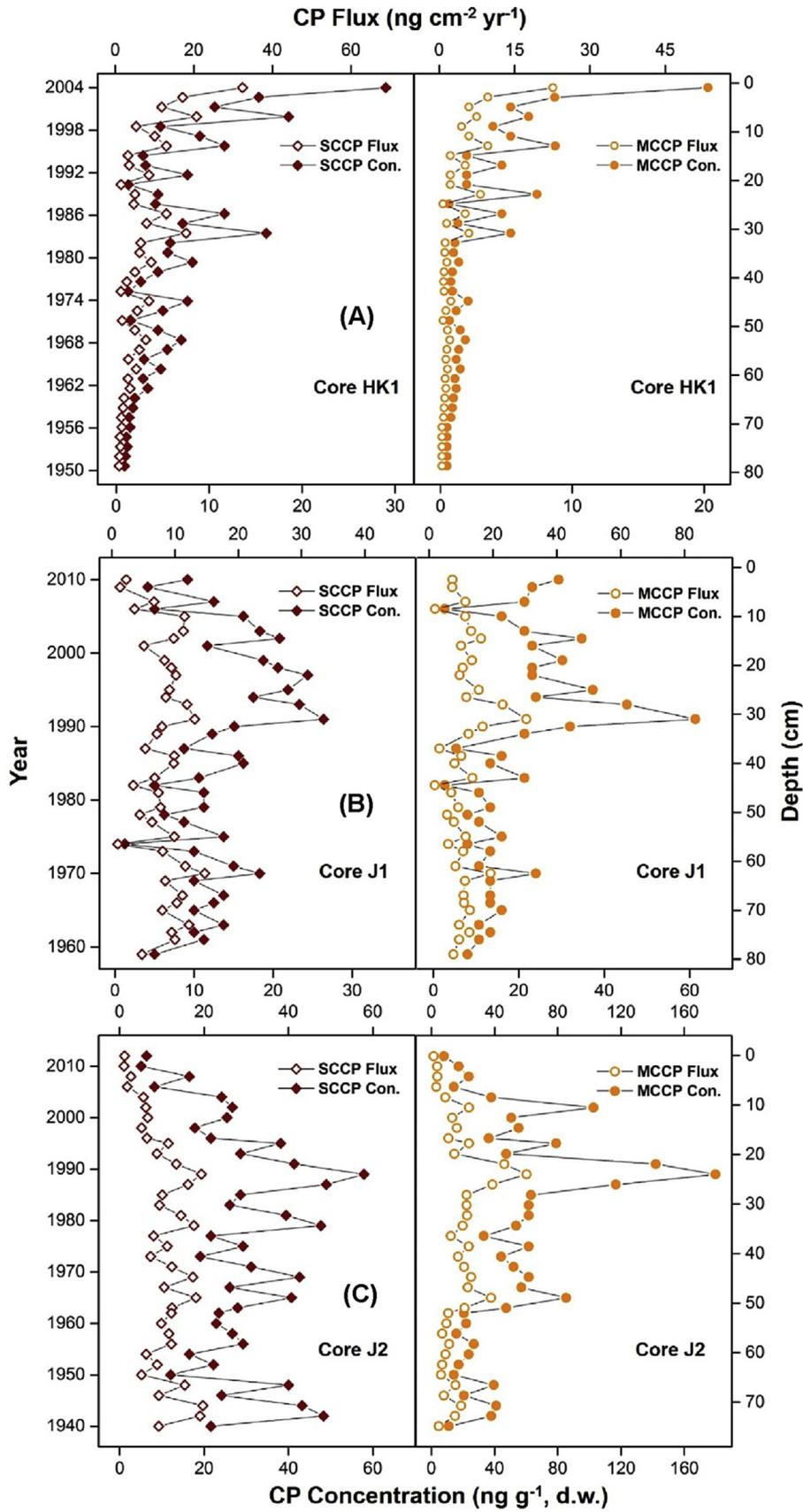


Fig. 5. Temporal trends of CP concentrations and fluxes in dated sediment cores from Hong Kong (Core HK1), China and Tokyo Bay (Core J1 and Core J2), Japan.

layers from 1990 to 2012 in Japan is largely the response to the controls on the manufacture and use of CPs, resulting in a large decrease of CP pollution in the Tokyo Bay. The results clearly indicate that temporal trends in CPs in Japan coincide well with the historical consumption associated with the industrializing process and control measures. In this study, we attest to, for the first time, the effectiveness of emission controls to reduce the environmental concentrations of CPs in Japan. Considering that there are no control policies in most Asian countries/regions, further studies with a view to assessing and managing risks of CPs should be carried out in the future.

#### 4. Conclusion

Spatial and temporal trends of CPs in sediments in the PRD/PRE and around Hong Kong and in Tokyo Bay were analyzed. Obviously higher CP contamination was found in industrial areas of the PRD/PRE. Significant correlations of coastal contamination of CPs with population density of the coastal areas in Hong Kong were demonstrated. It was indicated that CP contamination in the coastal environment was associated with urbanization and industrialization. The comparison between PRD/PRE and Hong Kong outer harbor with Tokyo Bay shows the striking difference in both concentrations and historical deposition. The declining SCCP and MCCP concentrations in sediment cores from Tokyo Bay, Japan, attest to the effectiveness of emissions controls.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2017.02.015>.

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