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Sedimentary records of polychlorinated biphenyls in the East China Marginal Seas and Great Lakes: Significance of recent rise of emissions in China and environmental implications☆

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ABSTRACT

Polychlorinated biphenyls (PCBs) in dated sediment cores from the East China Marginal Seas (ECMSs) and the chronology of the net fluxes to sediments were analyzed. The accumulation of 27 PCBs (ΣPCBs) in the ECMS sediments is about 5–26 ng cm^{-2}, with the net depositional fluxes of ΣPCBs 10 times lower than those observed in the Great Lakes during the 1960s–1970s. Exponential increases in PCB deposition to the ECMS sediments since the 1990s were observed, which closely follows the fast growth of PCB emissions from industrial thermal processes and e-waste related sources in China. Recent PCB fluxes to the study sites in the ECMSs and the Great Lakes are comparable; the former surged forward with a rising tendency, while the latter showed continued decline after the late 1970s. Due to the different PCB application histories and sources between the two regions, the ECMS sediments may remain as a net sink for land-derived PCBs, while sediments in the Great Lake may have been acting as a secondary source releasing PCBs to water. A higher proportion of trichlorobiphenyls in the ECMS sediments than the Great Lakes was indicated, which may imply the net transport of atmospheric PCBs from China.

1. Introduction

Polychlorinated biphenyls (PCBs) were manufactured and utilized heavily from the early 1930s to the late 1970s in developed countries, with global production of >1 million metric tonnes (Breivik et al., 2007, 2002; Gioia et al., 2013). The histories of PCB pollution in the United States, Europe, and Japan have been naturally recorded in well-preserved sediment cores. In cores collected during the 1980s from waters near emission sources, PCB inputs to sediments often peaked around 1970 when intentional production (IP) of PCBs peaked, followed by declines toward recent years (Eisenreich et al., 1989; Sanders et al., 1992; Sugiura et al., 1986). The current PCB levels in North America and Europe are linked to environmental cycling and remobilization of previously deposited PCBs in sediments and soils (Khairy et al., 2015; Li et al., 2010).

In China, about 7000 to 10,000 tonnes of PCBs were produced from 1965 to the early 1980s, and most of their applications were in East China (China SEPA, 2003). PCB pollution in China is in general much lower than that in the developed countries, as demonstrated by the relatively low PCB levels in nation-wide soils (Ren et al., 2007). Nevertheless, PCB fluxes to sediment layers deposited in the 1970s were found to be elevated, suggesting a peak input of PCBs that was temporally coherent with the trend observed in industrialized countries (Mai et al., 2005; Yang et al., 2012, 2009). In recent years, China has seen an increasing trend of PCB pollution in

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the atmosphere (Cui et al., 2013; Hogarh et al., 2012; Wu et al., 2017). The increased inputs of PCBs to the environment are also evidenced by spikes observed in the upper layers of sediments collected from some heavily industrialized areas (Mai et al., 2005; Yang et al., 2012). PCBs can be unintentionally produced (UP) as byproducts in industrial thermal processes and fuel combustion (Lee et al., 2005; Li et al., 2017; Richards and Agranovski, 2017). The UP-PCB emissions have been continuously augmented through China's booming industrial and urban development (Zhao et al., 2017). PCB pollution has been exacerbated by the emissions from primitive e-waste recycling activities in Eastern China since the 1980s (Breivik et al., 2016; Lu et al., 2015).

The present study was to track the historical and recent environmental pollution by PCBs in China through retrieving sediment cores in marine environment. Concentrations of PCBs in these dated core segments were measured, and inventories and depositional fluxes were estimated. To highlight the differences in chronology of PCB pollution between China and industrialized countries, previously obtained data from the Great Lakes of North America were used for comparison purposes (Li et al., 2018). The results allowed us to gain insights into the combined effects of historical usage and emerging emission on regional accumulation and release of PCBs in sediments from a source-to-sink perspective.

2. Materials and methods

2.1. Study area

The East China Marginal Seas (ECMSs) are composed of the Bohai Sea (BS), Yellow Sea (YS), and East China Sea (ECS), from the north to the south. Along the coast of the ECMSs are the most economically prosperous and highly industrialized areas of China (i.e., Bohai Rim and Yangtze River Delta Economic Zone). Propelled by prevailing eastward winds, the long-range transport of airborne PCBs from source regions of mainland China to the ECMSs takes place, especially in spring and winter when westerly winds dominate. As ocean margins, the ECMSs are receptive to terrestrial organic pollutants from both riverine input and atmospheric deposition. The sedimentary records of polycyclic aromatic hydrocarbons, organochlorine pesticides and polybrominated diphenyl ethers (PBDEs) in this region accord well with the known histories of emissions of these pollutants in China (Guo et al., 2006; Li et al., 2016; Lin et al., 2016).

The Great Lakes of North America consist of Lakes Superior, Michigan (LM), Huron, Erie (ER) and Ontario (ON), forming the largest freshwater system on Earth by total surface area. Within its watershed, there are densely populated and highly industrialized areas. PCBs have been continuously detected in the lakes since the late 1960s (Hornbuckle et al., 2006). A recent estimate for the total accumulation of PCBs in the sediments of the five lakes amounts ca. 500 metric tonnes (Li et al., 2018).

2.2. Sampling and ^{210}Pb dating

Sediment cores were collected in 2007–2013 from the central mud in the BS (core M7: 39°32′N, 120°27′E), the central mud in the south YS (core F0306: 34°59′N, 122°30′E), the wedge-shaped Min-Zhe coastal mud in the inner shelf of the ECS (core C0803: 27°38′N, 121°39′E), and the distal mud southwest off Cheju Island in the central shelf of the ECS (core FFJ103: 31°40′N, 125°52′E) (Fig. 1). The four cores were segmented at 1 cm intervals into a total of 145 samples using a pre-cleaned stainless steel blade. Each segment was packed in aluminum foil and freeze-dried. The sedimentation chronology was traced using ^{210}Pb gamma spectrometry. Further details on sediment collection, sample characterization, and dating are provided elsewhere (Li et al., 2016).

Dozens of sediment cores were collected from the Great Lakes from 2010 to 2014. For the purpose of this work, cores from six sites in Lakes Ontario, Erie and Michigan were used, including ON25 (43°25′N, 77°22′W), ON30 (43°32′N, 76°54′W), ER37 (42°6′N, 81°34′W), ER73 (41°58′N, 81°45′W), LM32 (44°22′N, 86°55′W) and LM09 (42°23′N, 86°35′W). These sites are in relatively tranquil depositional zones of the lakes, and the cores included segments dated before 1940, thus providing complete chronology of PCB inputs. Detailed information on sampling, sediment characterization, and ^{210}Pb dating is provided elsewhere (Bonina et al., 2018; Corcoran et al., 2018; Li et al., 2018).

2.3. Organic analysis

Processing procedures and analytical details of the ECMS samples are provided in the Supporting Information (SI). In brief, a ca. 10 g aliquot of freeze-dried and homogenized sediments were spiked with known amount of surrogate standards 2,4,5,6-tetrachloro-*m*-xylene (TcmX) and decachlorobiphenyl (PCB209), and then Soxhlet-extracted with dichloromethane (DCM) for 48 h. The concentrated extracts were purified through passage on an 8 mm i.d. alumina/silica column. The eluents were concentrated and solvent-exchanged, before the addition of pentachloronitrobenzene (PCNB) as internal standard. Quantification of PCBs was performed with gas chromatography (Agilent 6890 GC, Hewlett-Packard, USA) with a ^{63}Ni electron capture detector (ECD). Twenty seven PCB congeners with 3–8 chlorines (IUPAC Nos. 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 101, 118, 128, 132, 138, 151, 153, 158, 169, 170, 180, 183, 201 and 205) were routinely detected and analyzed. Analytical procedures and PCB determination for lake sediments from the Great Lakes are detailed elsewhere (Guo et al., 2014; Li et al., 2018). To facilitate the comparisons with data on marine sediments from the ECMSs, data for the same set of 27 PCB congeners are used in this paper.

2.4. Quality control

For each batch of 10 samples from the ECMSs, a procedural blank (only solvent), a spiked blank (standard mixtures of 27 PCBs) and a duplicate sample were processed. For the Great Lakes sediment samples, field and procedural blanks and duplicate samples were processed as well (Li et al., 2018). The average percent recoveries of surrogates in sediment samples in the ECMSs were 78.6 ± 10.3% for TcmX and 96.5 ± 12.8% for PCB209. The reported PCB concentrations were not adjusted for surrogate recoveries. The relative percent differences (RPDs) of ΣPCBs (sum of the 27 congeners) in duplicate samples were less than 15% for the ECMS samples. Though being different to electron impact triple quadrupole mass spectrometry-based instrumental analyses for PCBs in the Great Lakes (Li et al., 2018), determination of individual PCBs in the ECMSs was confidently identified by GC-ECD only when (1) the retention time of analyte was ±3 s of that observed for the corresponding standards, and (2) chromatographic peaks were at least 3 times higher than the noise. More information on quality control is provided in the SI.

2.5. Data calculation and analysis

Concentrations measured for sediment cores were used to estimate the flux of net deposition of chemicals to each segment (i) of the cores (Equation (1)):

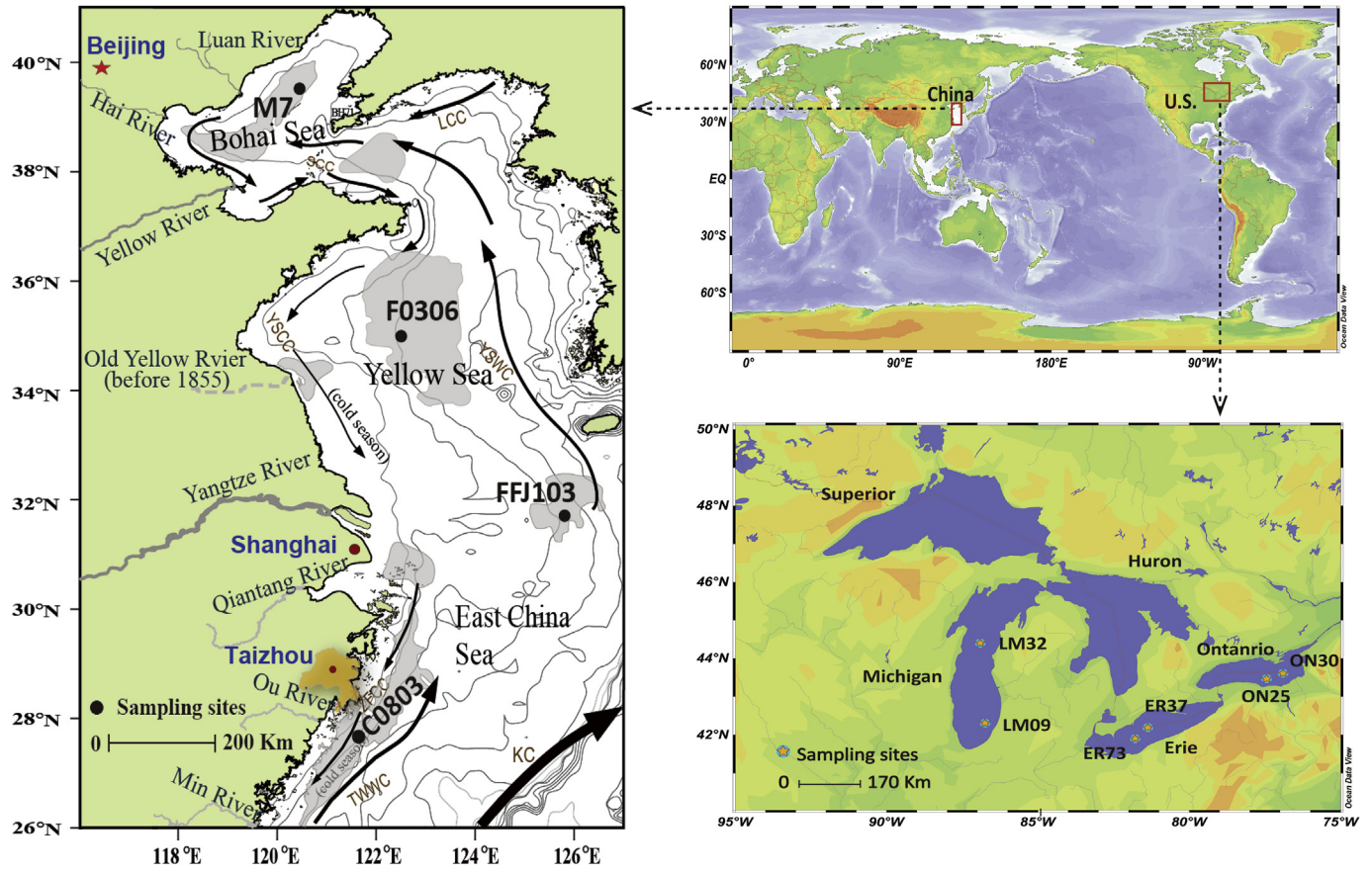

Fig. 1. Sampling locations for coring sites in the ECMSs and the Great Lakes. The arrows represent the flows of Kuroshio Current (KC), Taiwan Warm Current (TWWC), Zhejiang-Fujian Coastal Current (ZFCC), Yellow Sea Coastal Current (YSCC), Yellow Sea Warm Current (YSWC), Shandong Coast Current (SCC) and Liaonan Coast Current (LCC), respectively. Ocean circulations and mud areas are modified from Hu et al. (2011). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$$\text{Net fluxi}(\text{ng cm}^{-2}\text{y}^{-1}) = C_i \times R \times \rho_i / FF \quad (1)$$

where C_i (ng g^{-1}) is the measured PCB concentration, FF is the focusing factor of the coring sites, and ρ_i (g cm^{-3}) is the dry bulk density. R (cm y^{-1}) is the linear sedimentation rate obtained from ^{210}Pb dating (Fig. S1) (Li et al., 2016). For the Great Lakes sites, the sedimentation was nonlinear; thus mass sedimentation rate (g cm^{-2} y^{-1}) was used, which incorporates ρ_i (Li et al., 2018).

Chemical inventory represents the total accumulation of the chemical per unit area at a specified sampling site (Equation (2)):

$$\text{Inventory}(\text{ng cm}^{-2}) = \sum C_i \times \rho_i \times d_i \quad (2)$$

where d_i is the sample thickness (cm) of core segment i.

The recent annual loading rate of specific area was estimated based on surface net depositional flux (Equation (3)):

$$\text{Annual loading rate}(\text{kg y}^{-1}) = \text{net flux} \times \text{surface area} \quad (3)$$

3. Results and discussion

3.1. Abundance of PCBs in sediments of the ECMSs

Sum of the 27 targeted PCB congeners refers to ΣPCB hereafter. All concentrations are reported on a dry weight basis in Tables S1–S10. The concentrations and the net flux at their peaks and sediment surface, as well as the inventory at each site, are presented in Table 1.

The concentration ranges of ΣPCB were slightly higher in M7 (0.29–2.16 ng g^{-1}) and F0306 (0.27–2.20 ng g^{-1}) than in C0803 (0.17–1.21 ng g^{-1}) and FFJ103 (0.19–0.70 ng g^{-1}). The range of ΣPCB concentrations in the four cores from the ECMSs agrees well with a recent report in sediment cores collected in the continental shelf of the ECS (0.1–2.5 ng g^{-1} for 20 PCBs) (Cai et al., 2016) but is lower than those in the estuaries of the Yangtze River (maximum of ca. 15 ng g^{-1} for 22 PCBs) (Yang et al., 2012) and the Pearl River (1.5–32 ng g^{-1} for 112 PCBs) (Mai et al., 2005). In comparison with the PCB levels found in China, one or two orders of magnitude higher levels of ΣPCB were found in Lakes Michigan (1.21–121 ng g^{-1}), Ontario (1.70–165 ng g^{-1}) and Erie (0.11–46.4 ng g^{-1}), as well as in other waters in developed regions of the world, for example the western Adriatic Sea (<LOD–9 ng g^{-1} for 28 PCBs) (Combi et al., 2016), Tokyo Bay (3.39–151 ng g^{-1}) (Yamashita et al., 2000), and the Baltic Sea (0.71–74 ng g^{-1} for 7 PCBs) (Sobek et al., 2015). Overall, PCB levels in sediment of the ECMSs were at the low end of the global range (Table S11).

The inventories of ΣPCB in sites M7, F0306, C0803 and FFJ103 ranged from 5 to 26 ng cm^{-2}, which are consistently lower than the estimated 42–335 ng cm^{-2} at the six sites in the Great Lakes (Table 1). This indicates that the sediments at the four sites in the ECMSs have accumulated only a fraction of ΣPCB per unit area relative to the Great Lakes sites. The sheer contrast of PCB

Table 1
Comparison of ΣPCB among sites [a].

Site	Peak concentration before 1979 (ng g^{-1} dw) [b]	Concentration at core surface (ng g^{-1} dw) [b]	Net flux at core surface (ng $cm^{-2}y^{-1}$)	Peak flux before 1979 (ng $cm^{-2}y^{-1}$)	Inventory (ng cm^{-2})	Inventory ratio pre- to post-1979
M7	1.84	2.16	1.01	1.07	18	0.41
F0306	1.56	1.98	0.78	0.58	26	0.36
C0803	0.71	1.21	1.13	0.67	20	0.39
FFJ103	0.57	0.70	0.15	0.12	5	0.75
LM09	121	26.7	1.74	7.93	335	1.95
LM32	38.8	26.4	0.49	0.72	42	2.06
ON25	165	29.3	0.76	4.29	147	2.36
ON30	139	27.1	0.77	3.93	145	1
ER37	46.4	18.5	2.86	7.16	223	1.05
ER73	26.2	6.67	1.08	4.45	143	0.62

[a] ΣPCB = the sum of 27 PCB congeners with IUPAC Nos. 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 101, 118, 128, 132, 138, 151, 153, 158, 169, 170, 180, 183, 201 and 205.
[b] dw = dry weight.

accumulation in sediments reflects the remarkable differences in the historical IP-PCB productions and uses between North America and China. The U.S. is responsible for ca. 46% of the global consumption of PCBs, far exceeding that of China (<1%), in the mid-late 20th century (Breivik et al., 2002).

3.2. Temporal trend of PCBs in sediment cores

The ΣPCB fluxes to sites M7, F0306, C0803 and FFJ103 were in the range of 0.16–1.07, 0.11–0.78, 0.16–1.13 and 0.04–0.15 ng cm^{-2} yr^{-1}, respectively. A common temporal characteristics of ΣPCB depositional flux shared in the four sediment cores from the ECMSs was a trace level at the bottom sediments followed by an initial increase from the 1950s till a first peak in the 1970s, then another rise towards the surface (or subsurface) where the flux reached maximum (Fig. 2). Although varying in core length, all cores in this work reached PCB pre-production periods (before 1956). In the bottom of the cores, ΣPCB fluxes (0.16–0.27, 0.11–0.32, 0.16–0.26, 0.05–0.07 ng cm^{-2} y^{-1} in cores M7, F0306, C0803 and FFJ103, respectively) in the segments deposited before 1956 could be attributed to post-depositional downward diffusion over the past decades. Production of PCBs in China started in 1965 and ceased in the late 1970s. Reflected in the sediment segments deposited within this period, ΣPCB fluxes started to rise and progressively attained a first peak, reaching 1.07, 0.58, 0.67 and 0.12 ng cm^{-2} y^{-1} for cores M7, F0306, C0803 and FFJ103, respectively, in the mid-1970s (Table 1). The increases in ΣPCB fluxes from the mid-1950s to the peaks before 1979 were about 2–5 folds, and less at remote site FFJ103 than at coastal sites M7 and C0803. After the first peak occurred, ΣPCB fluxes were evidently declined in cores M7, C0803 and FFJ103 (Fig. 2), with the respective reduction of 82%, 65% and 71% before rebound. The dramatic declining trend was the response to the cessation of PCB production in the mid to late 1970s in China and other countries. The flux profiles of ΣPCB for core F0306 during the same time period fluctuated in a zigzag pattern followed by a flat. This pattern could be affected by the cyclonic circulation-dominated sedimentary processes in the area encompassing F0306 (Hu et al., 2011).

In the all ECMS cores, rebounds of ΣPCB fluxes were observed in core segments deposited from the mid-1980s (or the early 1990s) to the sampling dates. The exponential escalation in the recent sediments was more noticeable at near-shore sites M7 and C0803, paralleling fast increase in land-based PCB emissions (Fig. 3). At the open sea site (FFJ103), the increasing trends appeared more steady. Comparatively, the increases in flux appeared to be slower at these two remote sites than at sites M7 and C0803 which are more directly influenced by land sources from coastal runoff. Overall, ΣPCB fluxes in the surface segments of the cores averaged 60% higher than their peaks in the 1970s (Table 1). The rise in PCB deposition to the sediments of the ECMSs during the past decades, as revealed in this study, is in chronological accordance with the rapid industrialization in China. The currently increasing trend of PCB input has also been observed in waters near other developing countries in Southeast Asia (Kwan et al., 2014), where rapid urbanization and industrialization have been undergoing in recent decades.

Compared with the ECMS cores, significantly higher ΣPCB fluxes were exhibited in the cores from Lakes Ontario, Erie, and Michigan (Table 1), and the profiles with deposition years were less complex. As shown in Fig. 2, the fluxes of ΣPCB started rising and continued to increase after the onset of PCB production around 1930, and peaked in the late 1960s to the 1970s. During this period, the depositional flux of ΣPCB increased more rapidly at the six sites, as compared to the ECMS sites. In sharp contrast to the escalating trends in the ECMSs after the 1990s, the post-peak declines towards recent years at the Great Lakes sites are mostly monotonic (Fig. 2). The recent fluxes of ΣPCB in sediments from cores ON25, ON30, ER37, ER73, LM32 and LM09 registered reductions of 82%, 80%, 60%, 76%, 32% and 78% from their respective peak levels, based on the data in Table 1. The significant decrease of ΣPCB fluxes in recent decades to the Great Lakes is the response to reduced IP-PCB input (Breivik et al., 2016). Despite the confirmed occurrence of non-Aroclor sourced PCBs (e.g., paint pigment (Hu and Hornbuckle, 2010)) and continued diffusive emissions, the overall decline of PCB pollution is not retarded because the quantity of these PCBs may be much less than that of IP-PCBs produced historically. In the surface segments of the six cores from the Great Lakes, ΣPCB fluxes dropped to 32 ± 19% of their peak levels, demonstrating first order kinetics after 1970 (Fig. S2). If the trend continues, the net flux of ΣPCB to the sediment may drop below 5% of the peak level in ca. 28 (Lake Ontario) to 46 (Lake Michigan) years. Similar to the Great Lakes, deceasing PCB input was also observed at the waters in other developed countries, such as Western Europe, Japan and South Korea (Hong et al., 2003; Okumura et al., 2004; Sanders et al., 1992).

3.3. Implications for rise of recent PCB emissions in China

Despite the differences in abundance, inventory, and chronological trends between the two study regions, the recent ΣPCB fluxes to the coastal sites M7 and C0803 in the ECMSs are comparable with those at the Great Lakes sites (Fig. 2, Table 1). The increase in ΣPCB fluxes to the sediment of the ECMSs is expected to continue, given the continuous growth of industrialization in China. We anticipate that the differences in annual PCB input to the sediments of the ECMSs and the Great Lakes continue to diminish.

The usage of IP-PCBs in China and neighboring countries (e.g.,

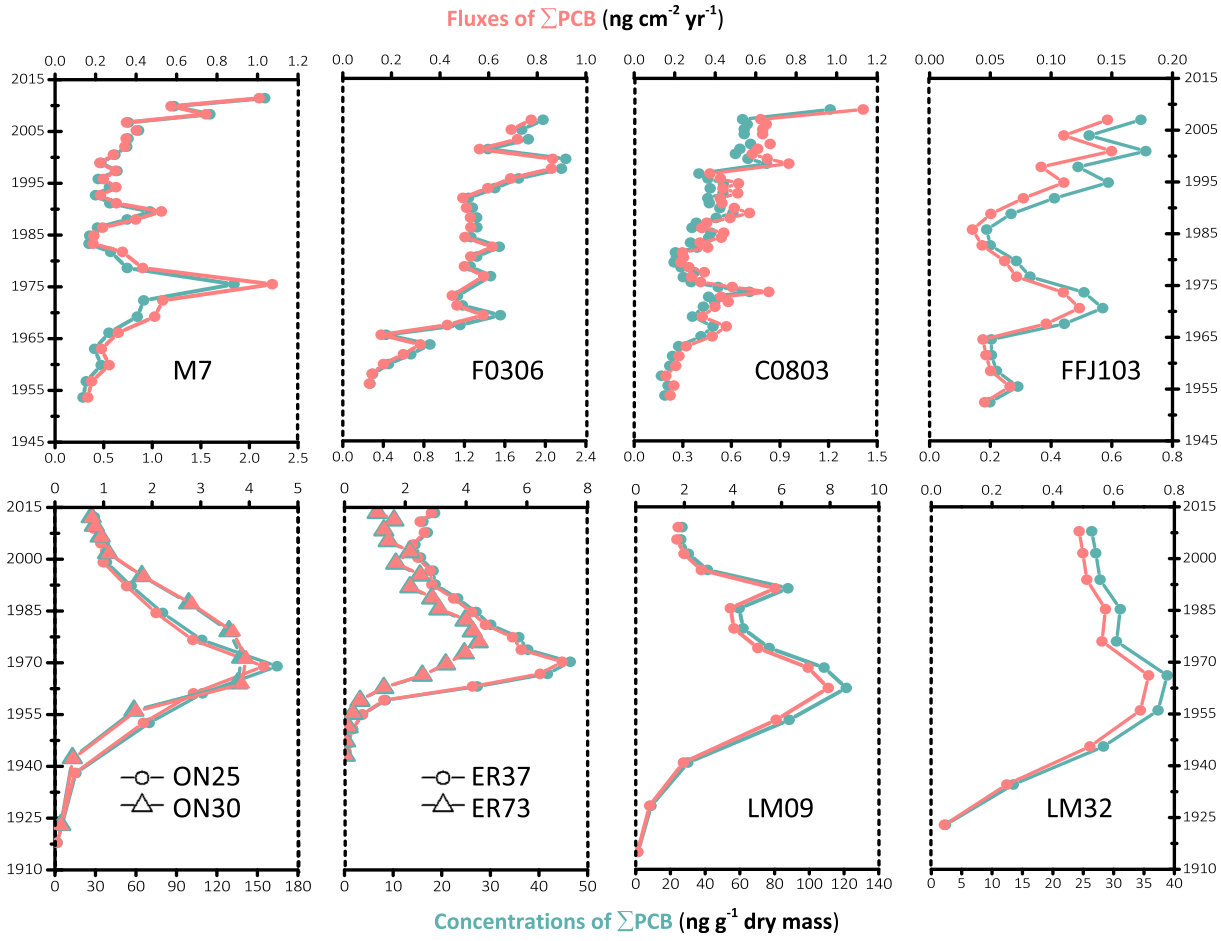

Fig. 2. Down-core profiles of ΣPCB concentrations and their deposition fluxes in the cores of the ECMSs and the Great Lakes.

South Korea and Japan) has been restricted since the 1970s (Kim et al., 2007; Shibata and Takasuga, 2007), therefore, the recent increases in PCB deposition to the sediment of the ECMSs are unlikely related to current release, if any, of legacy IP-PCBs. As indicated by modeling results, secondary sources in China have remained a low-level contribution to total PCB emission inventory since PCB production started (Zhao et al., 2017). Meanwhile, annual emissions of IP-PCB in China, based on the "baseline" estimate with 22 PCBs by Breivik et al. (2016), showed a long-term declining trend since the late 1970s (Fig. 3a). Therefore, as the IP-PCB emissions are incapable of impelling the rise of ΣPCB fluxes in upper sediment layers observed in the ECMSs, we consider that the ongoing PCB inputs are primarily due to increasing emissions, associated with industrial activities and e-waste disposal or recycling activities in modern China (Cui et al., 2015, 2013). As presented in Fig. 3c and d, the temporal trends of ΣPCB fluxes in cores M7, F0306, C0803 and FFJ103 match with those of Chinese cement and steel productions, with correlation coefficients r being 0.84, 0.57, 0.77 and 0.70 through Spearman correlation analysis ($p < 0.05$) for cores M7, F0306, C0803 and FFJ103, respectively. The data used in Fig. 3c for recent PCB emissions in China is mainly contributed from UP-PCB associated industrial sectors in contemporary China (i.e., cement, steel, lead and coking industries). Cui et al. (2013) estimated that the emission inventories of UP-PCB from cement and steel industries, in particular, were responsible for 91.3% and 7.1% of total UP-PCB emissions in 2008. Temporally, PCB emissions from cement and steel productions have grown by 33 and 22 folds, respectively, from 1978 to 2012 (Fig. 3d), in response to the demand from unprecedented growth in urbanization and industrialization in China. Some of the techniques currently used in these industrial processes are energy-intensive and outdated (Ba et al., 2009; Liu and Diamond, 2005). Many of those involving thermal processes are small-scale, primitive, and sporadically distributed in rural areas (Liu and Diamond, 2005). It has been shown that numerous PCBs form during the open combustion of solid fuels, with higher emission factors than other chlorinated persistent organic pollutants (Lee et al., 2005).

With the fast growing electronics industry in China, e-wastes have been imported from developed countries as a cheap source of needed raw materials. Trans-boundary shipment of e-waste to China represents a form of long-range transport of persistent organic pollutants including PCBs (Breivik et al., 2016). The bulk e-waste imports, under the "default" estimate, may have resulted in extensive emissions of PCBs in China, with cumulative emissions of more than 200 tonnes from the 1980s to 2012 (Fig. 3a) (Breivik et al., 2016). The rapid expansion of e-waste recycling activities occurs mostly in costal mainland China, aggravating emissions there (Li and Wania, 2018; Ni and Zeng, 2009; Zhao et al., 2017) and subsequent transport of PCBs to the ECMSs. It was estimated that PCB emissions increased 40 folds during 1930–2030 in Taizhou (Breivik et al., 2016), one of the largest e-waste processing centers in China. Sampling site C0803 was in close proximity (ca. 50 km) to Taizhou. The input of PCBs to the site is likely to be dominated by emissions from the e-waste related activities. Based on Spearman correlation analysis, the flux of ΣPCB correlates with the flux sum of 13 PBDE congeners in the ECMS cores (Li et al., 2016), with r values

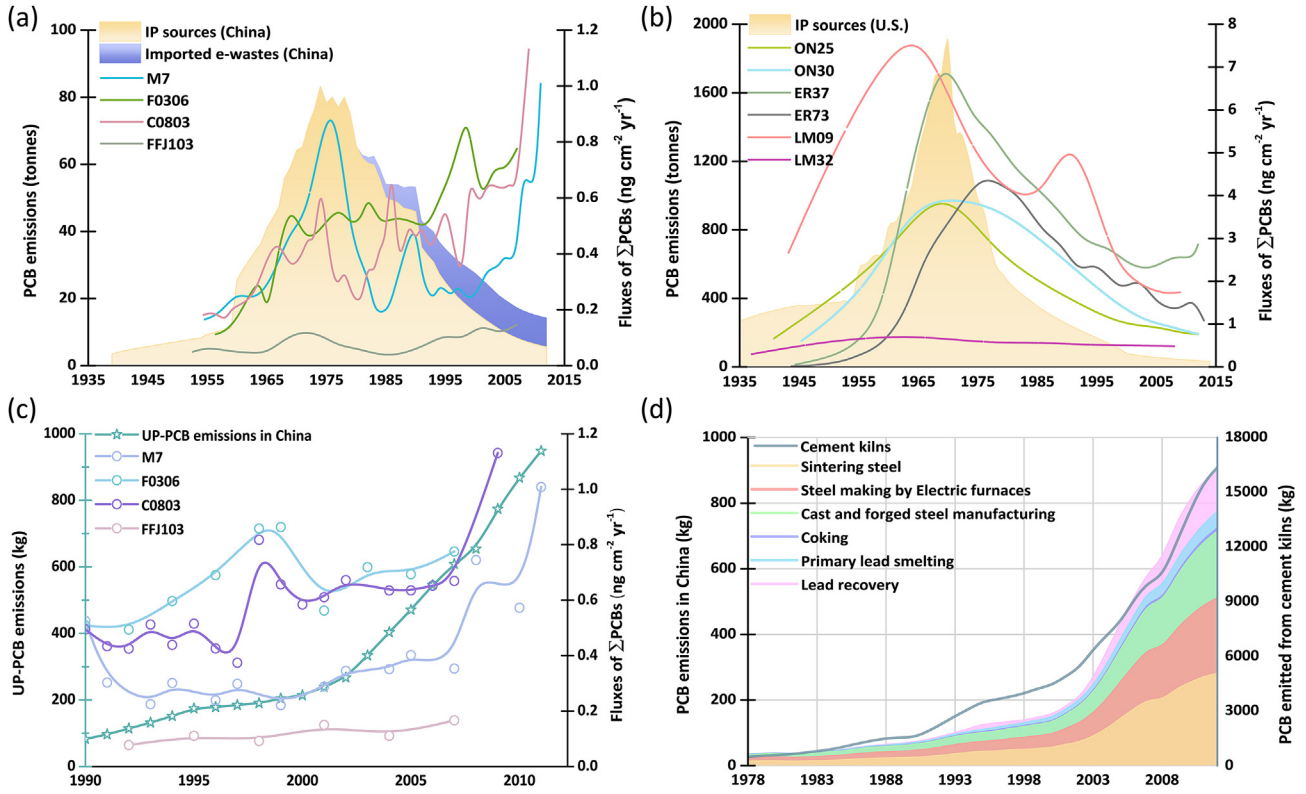

Fig. 3. Temporal variations of IP-PCB emissions in China (a) and the U.S. (b). Emissions from IP-PCB sources and China's e-waste imports were obtained from (Breivik et al., 2016). Temporal trend of ΣPCB fluxes in the cores of the ECMSs and UP-PCB emissions (c), and emission inventories from cement, steel and lead production, and coking (d). Emission factors of mentioned industrial processes were from (Cui et al., 2013), (Yamamoto et al., 2011) and (Toda, 2005). Annual production of cement, steel, lead and coke in China were collected from http://www.stats.gov.cn.

of 0.74, 0.86 and 0.91 ($P < 0.05$) for cores M7, C0803 and FFJ103, respectively.

3.4. Potential impact of rising PCB emissions in China

To gain insight on the potential impacts of rising PCB emissions in China, we estimated the recent annual loading rate of PCBs to the ECMS sediments using equation (3), assuming that the depositional flux to the mud area in each sea is spatially uniform. By multiplying the surface net flux at the core surface (Table 1) with the specific water surface area, the recent annual loadings of ΣPCB to the mud areas of the ECMSs were estimated to be 360, 490, 230 and 20 kg y^{-1} in BS mud, south YS mud, Min-Zhe coastal mud, and southwestern Cheju Island mud, where the mud areas are 36,000, 63,600, 20,000 and 10,000 km^2, respectively. The total loading to the entire mud areas of the ECMSs (water area c.a. 130,000 km^2) was therefore approximately 1100 kg y^{-1}. Despite the influence of oceanic dynamics, distribution of grain size and excess ^{210}Pb along core depth suggested sedimentation condition within these muds in the ECMSs were relatively stable over time (Fig. S1 and Fig. S3) (Li et al., 2016). Additionally, PCB levels at the sediment surface of the coring sites in the ECMSs were comparable to the large-scale investigations of PCB contamination in surface sediments of the ECMSs (in the three-digit pg g^{-1} to one- or two-digit ng g^{-1} concentration range) (Duan et al., 2013; Wang et al., 2015; Zhao et al., 2019), the estimated recent loadings of ΣPCB could thus yield a tenable information on PCB inputs from adjacent land. Based on Zhao et al. (2019), the annual inputs of Σ_{32}PCBs to sediments in the more polluted Yangtze River Estuary and the inner shelf of the ECS, covering an area of 85,000 km^2, were estimated to be 2600 kg y^{-1}. In comparison, the recent loading of ΣPCB to the three Great Lakes combined (water area c.a. 102,000 km^2) was estimated to be 1200 kg $year^{-1}$. This comparison hints that the recent mass loading rates to the two study regions are similar, and China is growing in global importance in PCB emission inventories. However, the dominant role played by sediments with respect to the environmental transport of PCBs may be different between the ECMSs and Great Lakes regions. Based on Lake Michigan mass budget modeling, contaminated sediments have shifted from being a significant reservoir toward acting as a secondary source releasing PCBs to the overlaying water and even air (Guo et al., 2017; McCarty et al., 2004). This is likely to be the case for the other Great Lakes. In the ECMSs, the recent net flux of ΣPCBs (1100 kg y^{-1}) to the sediments is only a minor portion of yearly PCB emissions from upwind area (32,000 kg y^{-1}). Due to abrupt increase of the marine biomarkers in the cores of the ECMS muds (Cao et al., 2017; Xu et al., 2018; Zhu et al., 2018), increasing marine primary productivity in the ECMSs is synchronized with the intensified human activities from the upstream, and in turn prompts vertical transport of PCBs (as a form of biological pump) somewhat causing the elevated deposition of PCBs to sediments (Nizzetto et al., 2012). Thus, sediments in the ECMSs have a large potential as a net sink with a continuously rising inputs of land-derived PCBs.

Homolog distribution patterns have assisted identifying emission sources and input pathways of PCBs (Li et al., 2009; Soonthornnonda et al., 2011). During the U.S. production of PCBs, there was a shift towards lighter PCBs from the 1950s to mid-1970s (McLearn, 1999). In China, IP-PCB manufacturing did not start until 1965, and tri-PCBs was the dominant homolog (Ren et al., 2007). In this work, we found that tri-PCBs are more enriched in sediments

of the ECMSs (27% of ΣPCB inventory) than in the Great Lakes (14%), but the opposite is true for hepta-PCBs (3% and 10% for the ECMSs and the Great Lakes, respectively) (Fig. S4). Tri-PCBs was the dominant homolog in background and rural soils in China, and this is attributed to the relatively larger historical use of lighter IP-PCB technical mixtures that was similar to Aroclor 1242 in homolog composition (Ren et al., 2007). Given that the PCBs emitted in recent decades are likely from diffusive sources, substantial proportion of PCBs in the sediment of the EMCSs could be via atmospheric transport and subsequent deposition to water. In contrast, Lakes Erie and Ontario received only 13% and 7%of PCBs from air deposition in the past, respectively (Strachan and Eisenreich, 1990).

Historical PCB manufacturing and consumption underlie high accumulation of legacy PCB, especially for the higher chlorinated PCBs, in sediments of industrialized countries. Re-emission from environmental reservoirs which previously received IP-PCBs, such as the contaminated sediments of the Great Lakes, may remain a significant source to the regional environment for years to come (Nizzetto et al., 2010). However, more alarming is the increasing primary emission of PCB from emerging developing economies, especially China. The outflow from East Asia and the long-range atmospheric transport of PCBs have been evaluated (Primbs et al., 2007). In these processes, less chlorinated PCBs (e.g., mono-, di, and tri-PCBs) are more prone to global redistribution as a result of long-range transport and volatilization from water to air. This could pose growing impact on atmospheric cycling of PCBs in the global environment. The global PCB spatial distributions or source−receptor relationships previously dominated by the usage and re-emitted IP-PCB may be re-established when the emissions of emerging PCBs continue to increase on a global scale in the long run.

4. Conclusion

This study for the first time provides extensive comparisons on the accumulations, historical patterns and environmental inputs of sediment PCBs in the ECMSs and the Great Lakes, the results of which clarify the different PCB pollution histories on a regional scale. Greater PCB levels and inventories in the Great Lake sediments than those in the ECMSs highlight the spatial divergences of IP-PCB manufacturing and use in China and North America. However, the pronounced increasing tendency in PCB deposition as well as the enhanced PCB accumulations to the ECMS sediments after the 1990s shows a close correspondence to rapid economic development in China. In contrast, the continuous reduction of PCB fluxes in the Great Lakes highly suggests the increasing impact of legacy IP-PCB re-emissions on longer-term PCB accumulation in North America. It is plausible, based on the rising PCB emissions in China and comparable annual loadings of ΣPCB between the study areas, that the fate processes and regional transport of PCBs would present a reverse in global environment.

Notes

The authors declare no competing financial interest.

Conflicts of interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “Sedimentary records of polychlorinated biphenyls in the East China Marginal Seas and Great Lakes: Significance of recent rise of emissions in China and environmental implications”.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2019.112972.

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