Abundances, Depositional Fluxes, and Homologue Patterns of Polychlorinated Biphenyls in Dated Sediment Cores from the Pearl River Delta, China

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Despite the recent efforts to investigate the distribution and fate of persistent organic pollutants in the tropical and subtropical regions of Asia, very little was known about the temporal change of polychlorinated biphenyls (PCBs) in the environmental ecosystem of China. In this study, three dated sediment cores collected from the Pearl River Delta of southern China were analyzed for a large suite of PCB congeners, from which the temporal profiles of PCB abundances, fluxes, and homologue patterns were constructed. The sedimentary inventories of total PCBs at the sampling sites ranged from 480 to 1310 ng/cm², at the low end of the worldwide figures. Although production and use of PCBs have been banned or highly restricted in China since the early 1980s, the fluxes of total PCBs continued to increase in the Pearl River Delta sediments. There was a concurrent increase of PCB fluxes and gross domestic product per capita in the region from 1980 to 1997, and a decline of agricultural land use was evident at the same time. Apparently, large-scale land transform since the early 1980s as well as emissions from the PCB-containing electrical equipments were responsible for the sharp rise of PCB fluxes in the recent sediments. The difference in the PCB homologue patterns from 1940 to the mid-1970s was probably indicative of the different timelines of PCB usage in Macao/Hong Kong and mainland China and the different types of technical PCBs commercially used. PCBs were detectable in sediments deposited well before the time frame when production of PCBs began (before 1930) and were relatively enriched in the less chlorinated homologue groups (3Cl and 4Cl PCBs), suggesting

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the downward mobility of lightly chlorinated PCB congeners in the sediment column.

Introduction

Polychlorinated biphenyls (PCBs) were first manufactured commercially in 1929, and serious concerns about the distribution of PCBs in the global environment were raised in the 1960s when PCBs were found in soil, water, and animals (*1*). The production/usage of PCBs have been banned/restricted worldwide since the early 1970s (*2*), but a large amount of PCBs was already produced. A recent study pegged the total global production of PCBs at about 1.3 million t (*3*). In addition to industrial syntheses, PCBs are also byproducts from a number of combustion processes (*4*) such as municipal solid waste incineration (*5*), domestic burning of coal and wood for residential heating (*6*), and domestic and public bonfires (*7*). PCBs were also present as impurities in other chemicals such as chlorinated phenols (*8*).

PCBs have remained detectable in environmental samples from around the globe despite the ban/restriction on their production and usage. There are, however, conflicting reports on the temporal trends of PCB concentrations in atmosphere. While some studies showed declining concentrations of PCBs in the atmosphere of Europe (United Kingdom and Norway) and North America (mainly around the Great Lakes) since the 1980s (*9−12*), others suggested no significant change in the PCB concentrations in Norway and Canadian Arctic (*13, 14*) or even reported a slight increase of PCB concentrations in air near the Great Lakes since the mid-1990s (*15, 16*). In the later case, the Great Lakes were suggested as the source for the concentration increase of atmospheric PCBs (*16*).

One well-established strategy to document the temporal trends of contaminant inputs is to analyze dated sediment cores collected from locations near suspected input sources (*17, 18*). Many previous studies concerning PCBs in dated sediments obtained sedimentary PCB profiles similar to the historical trends for the production and usage of PCBs that typically declined since the early 1980s (*19−24*). However, several previous studies illustrated that PCB levels or fluxes continued to increase or flattened in top sediment layers dated as the time period from the 1980s to present. Specific examples include analyses of sediment/peat cores from Narragansett Bay and Santa Monica Bay of the United States (*25, 26*), Lake Ontario of Canada (*27*), Esthwaite Water of the United Kingdom (*28*), Flaxmere bog of the United Kingdom (*29*), and mid-latitude locations of the northeastern United States (*30*). More recently, Barra et al. (*31*) reported a sharp increase of PCB fluxes over the last 10 yr in a salt-marsh sediment core from south−central Chile, although use of PCBs was banned in 1982. Apparently, the postdepositional behavior of PCBs in the global environment remains to be fully understood. Another pitfall with the current knowledge about the temporal variability of PCBs is that data were largely acquired from North America, Europe, and the Artic (*19, 20, 22−25, 27−30*). Only one study was conducted in Asia, which acquired the historical profiles of PCBs in a sediment core collected from Tokyo Bay of Japan (*21*).

In China, the total amount of technical PCBs, named as PCB3 and PCB5, produced from 1965 to 1974 was approximately 10 000 t, accounting for 0.6% of the total global production (*21*). In addition, an unknown number of PCB-containing transformers and capacitors were imported from industrialized countries from the 1950s to the 1970s or later (*21*). The industrial production of technical PCB formulations began to decline since 1974 and discontinued in the early 1980s, but the use of PCBs-containing transformers and
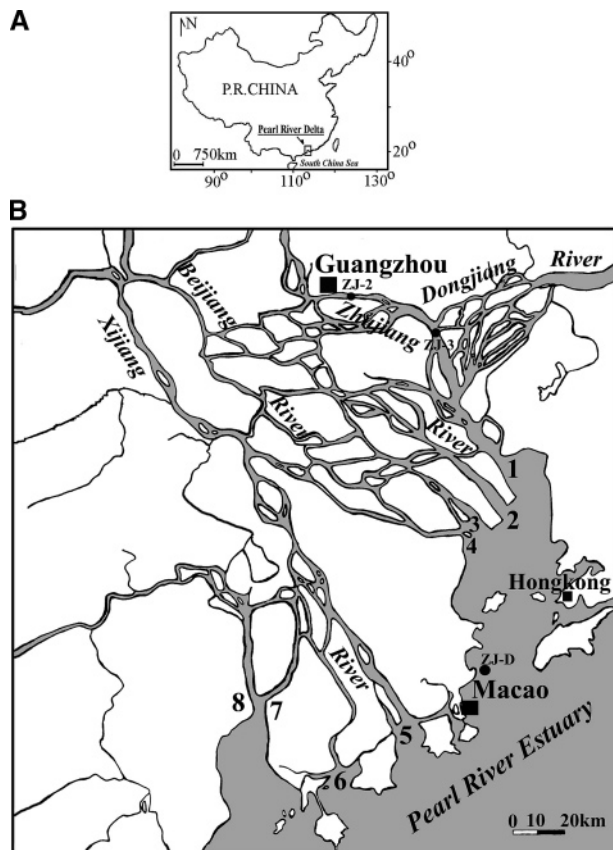
FIGURE 1. (A) Schematic showing the geographical locality of the Pearl River Delta in China. (b) Map of the general study area and sampling sites (●) around the Pearl River Delta and Estuary with the numbers 1–8 indicating the eight major runoff outlets: 1, Humen; 2, Jiaomen; 3, Honqilimen; 4, Hengmen; 5, Modaomen; 6, Jitimen; 7, Hutiaomen; and 8, Yamen.

capacitors continued until the late 1990s (*32*). The occurrence of PCBs has been found widespread throughout the country (*33–42*). However, no study has been conducted to assess the temporal trends of PCBs in the environment of China. By comparison, temporal trends of several other types of persistent organic contaminants (such as DDTs, HCHs, and PAHs) have been investigated (*43–48*).

The present study, the first of its kind to assess the historical trends of PCBs in China, was intended to provide an important link to a better understanding of the postdepositional dynamics of PCBs globally. This objective was accomplished by measuring a large suite PCBs in dated sediment cores collected from the Pearl River Delta, a highly urbanized and populated coastal region (21°50′–23°25′ N/112°33′–114°10′ E) in southern China (Figure 1). The Pearl River Delta is one of the most economically prosperous regions in China with an annual gross domestic product (GDP) increase rate of 12.3% in comparison with 8.9% for the nation from 1978 to 1990 (*49*). Because it is in the northern subtropical zone, the mild temperatures and frequent rainfalls all year around facilitate the transport of contaminants to the aquatic environments. Riverine and estuarine sediments have been regarded as the ultimate environmental destiny for anthropogenic pollutants in this region (*37, 43, 48, 50–52*). Therefore, core sediments were expected to preserve the historical records of pollution in the Pearl River Delta and to be suitable for the present study.

Methods

Field Sampling. A detailed description of the sampling area within the Pearl River Delta (Figure 1) was given elsewhere

(*51*). The river network mainly comprises Beijing (North River), Zhujiang (the main stream of the Pearl River), Dongjiang (East River), and Xijiang (West River) and merges into the Pearl River Estuary via eight outlets (Figure 1). Three locations with various levels and types of exposure were chosen for sampling (Figure 1 and Table 1). ZJ-2 is located at Zhujiang within the city of Guangzhou, the most urbanized and heavily populated district in the Pearl River Delta. ZJ-3 is downstream of ZJ-2 and situated at the confluence of Zhujiang and Donjiang. Intensive urbanization of the Zhujiang and Dongjiang watersheds began in the 1980s and 1990s, respectively. ZJ-D is located at the southwestern end of the Pearl River Estuary off Macao, which receives fluvial suspended particles from the delta water network and effluents from Macao and Hong Kong. Due to a southwestward coastal current (called the South China coastal current), originating from the counterclockwise Coriolis force in the Northern Hemisphere and the prevailing westward wind in the region, freshly discharged materials tend to be transported from north and east to southwest. As a result, the sedimentation rate in the west coast of the estuary is 1.52–3.85 cm/yr, higher than that (0.86 cm/yr) in the east coast (*48*). Three sediment cores were collected in summer 1997 with a stainless steel static gravity corer (8 cm i.d.). Efforts were made to minimize disturbance of surface sediment layers. The cores were sectioned at 2-cm intervals aboard ship immediately after collection using a stainless steel blade. Sectioned sediment samples were packed into solvent-rinsed aluminum boxes and immediately stored at −20 °C until analyzed.

Chemical Analysis and Quality Assurance. The procedures for extraction, purification, and measurement of PCBs in sediment samples were detailed elsewhere (*37, 50*), and only a brief description is given here. A sample of freeze-dried sediment, spiked with surrogate standards (2,4,5,6-tetrachloro-*m*-xylene and decachlorobiphenyl), was Soxhlet-extracted with a 1:1 acetone and hexane mixture for 72 h. Activated copper granules were added to the sample beaker during the extraction to remove elemental sulfur. The extract was concentrated and purified on a 10 mm i.d. silica column packed, from the bottom to top, with 10% silver nitrate silica gel (6 cm), neutral silica gel (10 cm, 3% deactivated), 50% sulfuric acid silica (12 cm), and anhydrous sodium sulfate. The fraction containing PCBs was eluted with 50 mL of hexane and collected. The volume of the PCB fraction was reduced to 50 μL under a gentle stream of N_2. A known amount of internal standard (pentachloronitrobenzene) was added to the extract prior to instrumental analysis.

The sample extracts were analyzed with a Hewlett-Packard (HP) 6890 gas chromatograph (GC) equipped with an electron capture detector (ECD) and a DB-5 fused silica capillary column (60 m × 0.25 mm i.d. with 0.25 μm film thickness). Operating conditions were the same as described previously (*50*). Identification of PCB congeners was confirmed with an HP 5890 GC/5972 MS system at selective ion monitoring (SIM) mode, with the GC conditions identical to those used for GC/ECD analysis. A total of 70 chromatographic peaks representing 112 individual or coeluting congeners (designated as domains) were quantified by a secondary Aroclors 1242/1248/1254/1260 mixture (1:1:1:1) standard, which was previously characterized with a set of 120 individual PCB congeners with an internal standard method (*53*). These congeners and domains according to the IUPAC nomenclature are 6, 8/5, 19, 16/23, 20/33/53, 22/51, 24/27, 25, 26, 28/31, 37/42/59, 40/103, 41/64, 44, 45, 46, 47/48/49/75, 52, 56/60/92, 63, 66/95, 70, 74, 77/110/154, 81/87/115, 82/151, 83, 84, 85/136, 90/101, 91, 97, 99, 105/132, 107, 118, 122/131, 123/149, 126/129/178, 128/167, 130/176, 134, 135, 138/158/160, 141/179, 146/165, 153, 156/171/202, 157/173/200, 169, 170/190, 172, 174, 177, 180, 183, 185, 187, 189, 191, 193, 194, 195/208, 196/203, 198, 199, 201, 205, 206, and 207. $\sum$PCB is

station	longitude/latitude	water depth (m)	core length (cm)	^{210}Pb time (yr)	sedimentation rate[a] (cm/yr)	sedimentation flux (mg/cm^2 yr)
ZJ-2	113°22.66′ E/23°06.77′ N	6.0	58.5	1883	0.42−4.26 (1.17)	337−5140
ZJ-3	113°30.94′ E/22°59.96′ N	4.0	86.0	1887	0.26−3.85 (1.48)	470−1120
ZJ-D	113°37.98′ E/22°13.04′ N	4.8	181.0	1878	1.52	1522

[a] The numbers in parentheses are mean values.

defined as the sum of the concentrations of these congeners and domains. To calculate the contribution to the homologue groups from each congener in a domain, all congeners were considered equally abundant in the domain.

For each batch of 10 field samples, a procedural blank (solvent with a filter paper identical to that used to wrap the sediment), a spiked blank (24 PCB congeners spiked into solvent with the filter paper), a matrix-spiked sample (24 PCB congeners spiked into pre-extracted sediment), a matrix-spiked duplicate, a sample duplicate, and a National Institute of Standards and Technology (NIST; Gathersburg, MD) 1941 reference sample were processed. The concentrations of PCBs present in the appropriate procedural blank were subtracted from those in the sample extracts. A target analyte peak was reported only if the signal exceeded three times the baseline noise. The surrogate recoveries in 81 samples were 58.6 ± 10.6% for 2,4,5,6-tetrachloro-m-xylene and 115 ± 12.9% for decachlorobiphenyl, respectively. The relative percent difference for individual PCB congeners identified in paired duplicate samples ($n = 4$) was all <15%. Recoveries of 24 PCB congeners (IUPAC Nos. 8, 18, 29, 44, 50/28, 52, 66, 77/ 154, 87, 101, 104, 118, 126, 128, 153, 170, 180, 187, 188, 195, 200, and 206) in 16 spiked blank and matrix-spiked sample ranged from 65.3 ± 13.4% for PCB8 to 95.9 ± 15.9% for PCB206. Reported concentrations were not surrogate recovery corrected. Recoveries of all the PCB congeners in the NIST 1941 reference samples were between 75 and 120% of the certified values.

Organic Carbon Determination and Dating of the Sedimentary Cores. The determination of organic carbon (OC) was carried out with a CHN-O-RAPID elemental analyzer (Heraus, Gemany), after acidification for carbonate removal (51). The sediment cores were previously dated using a ^{210}Pb dating method (48, 54). Briefly, the ^{210}Pb activities in sediment subsamples were determined from analysis of α-radioactivity of its decay product ^{210}Po, with the assumption that the two were in equilibrium. The Po was extracted, purified, and self-plated onto silver disks at 75−80 °C in 0.5 M HCl, with ^{209}Po used as a yield monitor and tracer in quantification. Counting was conducted with computerized multichannel α-spectrometry with gold−silicon surface barrier detectors. Supported ^{210}Po was obtained by indirect determination of the α-activity of the supporting parent ^{226}Ra, which was carried by coprecipitated BaSO$_4$. A constant rate of ^{210}Pb supply (CRS) model was used to date sediment cores ZJ-2 and ZJ-3 to obtain sedimentation rates, and a constant initial ^{210}Pb concentration (CIC) model was used for core ZJ-D, which gives average sedimentation rate (54).

Data Analysis. All PCB concentrations were normalized to dry sample weights with the unit of nanograms per gram. OC data were presented as percent of dry sample weight. Inventory of ΣPCB was defined as the mass of ΣPCB per unit area, that is, $\Sigma(C_i - C_B)\rho_B d$, where C_i is the concentration of ΣPCB in sediment layer i, C_B is the background concentration of ΣPCB (in this study $C_B = 0$), ρ_B (g/cm^3) is the dry mass of the sediment layer i, and d (cm) is the thickness of the sediment layer i. The mass of contaminant for unanalyzed intervals was estimated by liner interpolation of adjacent measured intervals. Depositional flux estimates were obtained by using the calculated sedimentation rates as well

as the concentrations of PCBs in sediments. The PCB flux in mass/area/time unit was defined as flux = $C_i r_s \rho_B$, where C_i (ng/g) is the concentration of PCB in sediment layer i, r_s (cm/yr) is the sedimentation rate in the sediment layer i, and ρ_B (g/cm^3) is the dry mass of the sediment layer i.

Results and Discussion

Sedimentation Rates and Fluxes. Estimated sedimentation rates and fluxes are summarized in Table 1. These data were used to estimate the fluxes of PCBs in the sampling area. The sediment cores used for the PCB measurements in this study had relatively high sedimentation rates as compared to other cores collected in this region (48) as well as discernible laminations in the sediment column and low abundance of burrowing benthic organisms. This suggests limited post-depositional mixing and diagenesis in the sediments (55), and the core samples were suitable for reconstructing the historical trends of contaminants due to their high temporal resolution.

Abundances and Inventories of PCBs. Total PCB concentrations were flat at the bottoms of the core sediments and began to rise in sediments deposited around 1940 in ZJ-2 and ZJ-3 and 1930 in ZJ-D (Figure 2). This period corresponds to approximately the time PCBs were first manufactured commercially in 1929 in the world. The production of PCB started in 1965 in China, but prior to 1965 PCB-containing transformers and capacitors were imported to China. The core ZJ-2 collected near Guangzhou contained slightly higher PCB concentrations (4.3−31.3 ng/g, mean = 17.7 ng/g) than ZJ-3 (3.1−32.0 ng/g, mean = 9.74) and ZJ-D (1.5−26.7 ng/g, mean = 8.84 ng/g), indicating that the metropolitan Guangzhou might be closer to the input source. The concentrations of ΣPCB in sediments deposited after 1940 were in the range of 10.9−31.3, 5.7−32.0, and 6.1−26.7 ng/g for ZJ-2, ZJ-3, and ZJ-D, respectively (Table 2). The top 2-cm layers of sediment generally had higher PCB concentrations (26.7−32.0 ng/g) than sediments inside the cores. These values were comparable to the concentration ranges in most surface sediments collected within the Pearl River Delta (11.5−48.3 ng/g) (37) and marine (10−26 ng/g) and costal sediments (3.5−25.1 ng/g) around Hong Kong (35, 56, 57) but much lower than the concentrations detected in sediments collected from several highly contaminated areas such as Fangcu Port of Guangzhou (485 ng/g), Macao Harbor near Macao (339 ng/g), and typhoon shelters in Hong Kong (170 ng/g) (35, 37). The PCB levels in most surface sediments of the Pearl River Delta (3.5−48.3 ng/g) were at the low end of the worldwide PCB concentration range (0.2−400 ng/g) in nearshore surface sediments (58). On the other hand, PCB concentrations (170−485 ng/g) in sediments from the highly urbanized regions, such as Guangzhou, Macao, and Hong Kong, were similar to those in sediments from moderately to highly contaminated locations, such as the Mediterranean Coast (181−401 ng/g) (59, 60).

The PCB inventories were 750, 480, and 1310 ng/cm^2 at ZJ-2, ZJ-3, and ZJ-D, respectively. The highest inventory of PCBs in core ZJ-D among the three suggests that the western part of the Pearl River Estuary is an active area for deposition of sediment-bound contaminants. Schneider et al. (22)
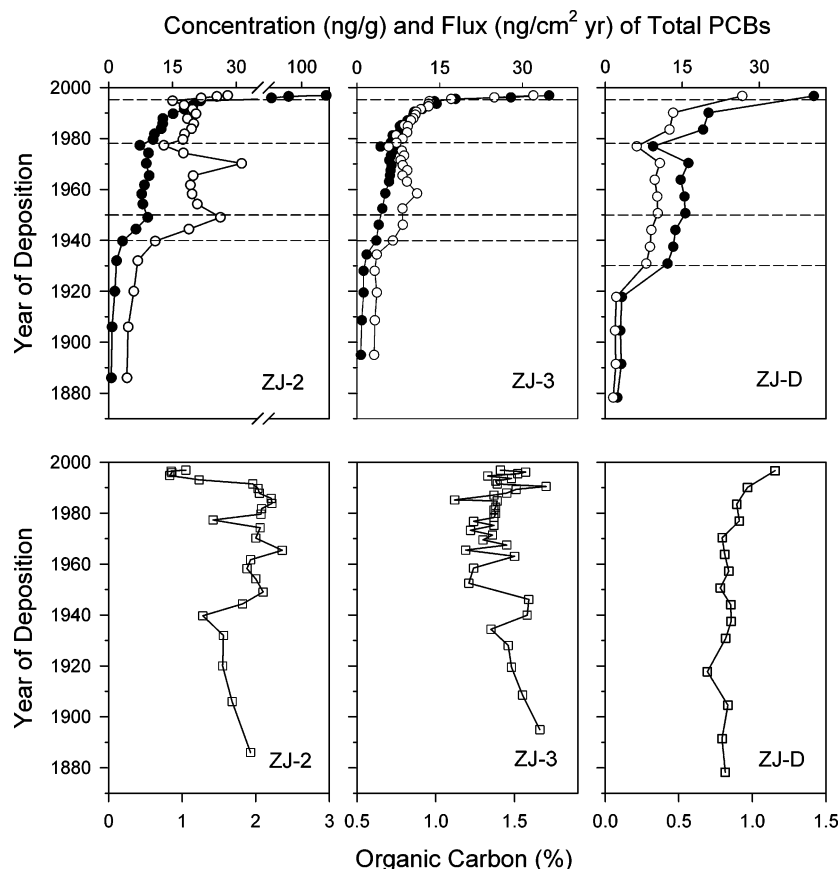
FIGURE 2. Down-core variations of $\sum$PCB concentrations (open circles, ng/g dry wt) and fluxes (closed circles, ng/cm^2 yr), and organic carbon content (open square, % dry wt) in sediments of the Pearl River Delta.

TABLE 2. Concentrations and Inventories of $\sum$PCB in Core Sediments from the Pearl River Delta, China

|	concentration range[a] (ng/g dry wt)		top layer concn[b] (ng/g dry wt)	inventory[c] (ng/cm^2)
core	before 1940[d]	after 1940[d]		
ZJ-2	4.3−6.8 (5.4)	10.9−31.3 (20.0)	28.0	750
ZJ-3	3.1−3.6 (3.4)	5.7−32.0 (10.8)	32.0	480
ZJ-D	1.5−2.1 (1.9)	6.1−26.7 (11.4)	26.7	1310

[a] The numbers in parentheses are average concentrations. [b] Top 2-cm layer. [c] Calculated by integrating the mass of $\sum$PCB per unit area (see text for details). [d] 1930 for core ZJ-D.

reported PCB inventories ranging from 24 to 205 ng/cm^2 in Lake Michigan and from 550 to 788 ng/cm^2 in more urbanized Lake Ontario, USA. PCB inventories as high as 28 000 ng/cm^2 were found in a reservoir core from Lake Harding, USA, where PCBs were predominantly derived from fluvial inputs (20). Another area with high PCB inventories ranging from 25 000 to 39 000 ng/cm^2 is on the Palos Verdes Shelf, California, where PCBs were mainly imported from municipal wastewater effluent (61). It is clear that the PCB inventories around the Pearl River Delta were at the low end of the worldwide figures.

The sediment profiles of OC and $\sum$PCB were quite different in cores ZJ-2 and ZJ-3 (Figure 2), indicating that the PCB concentrations and loadings within the main stream of the Pearl River were effectively independent of OC. Lack of correction between the PCB concentrations/fluxes and OC was also reported in a rural lake sediment core in the U.K. (62). Conversely, the correlation between the concentrations of OC and $\sum$PCB was significant ($r^2 = 0.67$) in the ZJ-D core sediments (Figure 2), emphasizing the role played by organic matter for transport and redistribution of PCBs within the Pearl River Estuary.

Temporal Trends of PCB Fluxes in Sediments. The temporal trends of $\sum$PCB fluxes were similar for the three sediment cores (Figure 2). $\sum$PCB fluxes began to rise in 1936−1943 at ZJ-2, 1937−1942 at ZJ-3, and 1930 at ZJ-D and progressively increased to 155, 384, and 387% of the background levels (pre-1940) in ~1950 at ZJ-2, ZJ-3, and ZJ-D, respectively. These increases were coincident with the increased use of PCBs in the region. Between 1950 and mid-1970s (about 1973) relatively constant fluxes were observed for ZJ-2 and ZJ-D, but the flux at ZJ-3 continued to increase at a steady pace. The difference between the onset times for ZJ-2/3 and ZJ-D could stem from the differences between CRS and CIC dating models. The difference between the onset times for ZJ-2/3 and ZJ-D also indicates that PCBs were used earlier in Macao or Hong Kong than in Guangzhou. The time period during which PCB fluxes remained constant at ZJ-2 and ZJ-D corresponded to the time frame for PCB application and production in China (32). Although the production of technical PCBs in China was commenced in 1965, PCB-containing electric equipments had been imported from industrialized countries prior to this date. Furthermore, Hong Kong and Macao were more developed and urbanized than mainland China for historical reasons and expected to use PCBs earlier than mainland China. As a result, there was a shift of time profiles of PCBs in sediment cores of the Pearl River Delta relative to the PCB production and application data in mainland China. At all three sediment cores, a small dip of PCB fluxes in the late-1970s (1976−1978) was evident (Figure 2), probably parallel to the first decline in the industrial production of technical PCBs in China (~1974). The PCB fluxes started to rise again after ~1980, from 10.4, 6.1, and
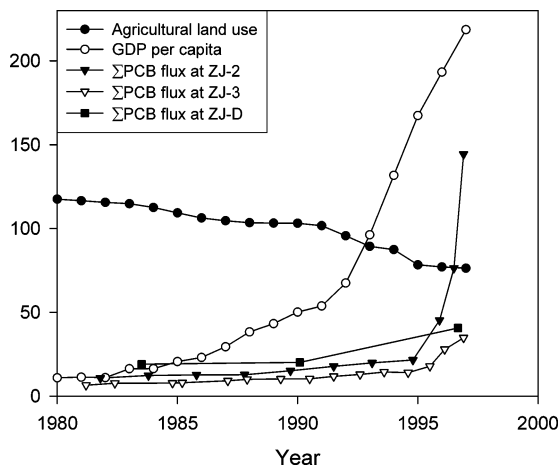
FIGURE 3. ΣPCB fluxes (ng/cm^2 yr) to the Pearl River Delta sediments compared to the agricultural land area ($\times$10000 ha) and the gross domestic production (GDP) per capita ($\times$100 RMB) in the Pearl River Delta from 1980 to 1997. (Date of agricultural land area and GDP per capita were excerpted from Guangdong Statistical Yearbook of 1980$-$1990 and 1990$-$2000, China Statistic Press, Beijing, China.)

9.3 ng/cm^2 yr in $\sim$1980 to 21.6, 14.4, and 20.1 ng/cm^2 yr in $\sim$1994 at ZJ-2 and ZJ-3, and in $\sim$1990 at ZJ-D, respectively, and finally escalated exponentially to the maximum values at the surface layers.

Core ZJ-D showed higher ΣPCB fluxes (14.7$-$16.2 ng/cm^2 yr) than cores ZJ-2 (7.8$-$9.5 ng/cm^2 yr) and ZJ-3 (4.6$-$6.6 ng/cm^2 yr) from the 1950s to the mid-1970s, suggesting that ΣPCB inputs from Hong Kong and/or Macao were a more predominant source than those from Guangzhou during that period of time. After 1980, the highest ΣPCB flux was recorded in core ZJ-2, indicating that inputs from Guangzhou became a main source of PCBs. Several previous studies observed decreases or not change of PCB residues over the time period of most recent 15$-$20 yr in several compartments of the aquatic ecosystem (20, 63$-$65). This pattern was not registered in the sediment cores analyzed in the present study, probably due to the fact that PCB-containing electric equipment is presently still in use in China. However, our previous study indicated that fluxes of DDTs also rose strongly in the top sediment layers at the same sampling sites (48). An alternative explanation for this is that a large-scale process of land transformation (i.e., transformation of agricultural land into residential, commercial, and industrial land uses) since the early 1980s may have liberated PCBs from environmental surfaces such as soil and vegetation to the sedimentary system. This process has been enhanced after 1992 due to even stronger economic growth in the region, leading to

accelerating urbanization (48). It was reported that the total loss of agricultural land within the Pearl River Delta amounted to about 292 000 hm^2 from 1980 to 1996, with 161 800 hm^2 loss during the economically "overheating" period in 1992$-$1993 (66).

To further elaborate the above explanation, the relationship among the time-dependent fluxes of ΣPCB, agricultural land area, and GDP per capita was examined for the period of 1980$-$1997. The increasing trend of ΣPCB fluxes in cores was consistently accompanied by an increasing profile of GDP and a decreasing profile of agricultural land area (Figure 3). The exponential rise in ΣPCB fluxes started at the depth corresponding to 1994 ($\pm$1 yr), fairly comparable to the initial stage of rapidly increasing GDP and a large-scale decline of agricultural land during 1991$-$1993. The small gap between the time frames for the rise of ΣPCB fluxes and decline of agricultural land probably reflected the kinetics factors, such as hydraulic residence times and particle settling velocities, controlling the transport and deposition of particle-bound contaminants. The increase of ΣPCB fluxes at ZJ-2 was sharper than those at ZJ-3 and ZJ-D (Figure 3), consistent with the fact that the watershed surrounding the city of Guangzhou has been more urbanized than other parts of the Pearl River Delta. Similarly, a recent study on reservoirs in Fort Worth, TX, and Boston, MA, showed that the contaminant trends in sediment cores were strongly influenced by the historical land use and urban development in the watersheds (67).

PCB Homologue Patterns. Fluxes of the individual homologue groups (Figure 4) generally mimicked those of ΣPCB at all three sampling sites (Figure 2). The tri- to hexa-PCBs accounted for more than 80% of the total PCBs. The homologue patterns at ZJ-2 and ZJ-3 were slightly different from that at ZJ-D. The fluxes of PCBs after 1940 decreased in the order of 4Cl > 5Cl > 3Cl > 6Cl homologue and 4Cl > 5Cl $\geq$ 3Cl > 6Cl homologue in core ZJ-2 and ZJ-3, respectively (Figure 4a,b). Conversely, two distinct patterns were observed throughout core ZJ-D. From 1930 to mid-1970s, 4Cl $\gg$ 3Cl $\gg$ 5Cl > 6Cl homologue was displayed, while 4Cl > 3Cl > 5Cl > 6Cl PCBs was observed after 1980 (Figure 4c). In addition, the homologue compositions in core ZJ-D were markedly different from those in cores ZJ-2 and ZJ-3 from 1940 to the late-1970s in terms of relative abundance. For example, the relative abundances of 4Cl and 3Cl (to a lesser degree) homologues at ZJ-D were considerably greater than those at ZJ-2 and ZJ-3 from 1940 to the mid-1970s (Figure 5). These are probably reflective of the differences between Guangzhou and Macao/Hong Kong in the timelines of using PCBs commercially and in the type of technical PCBs used. It appeared that sediments at ZJ-D captured a large amount of 3Cl and 4Cl PCB residues discharged from Macao and
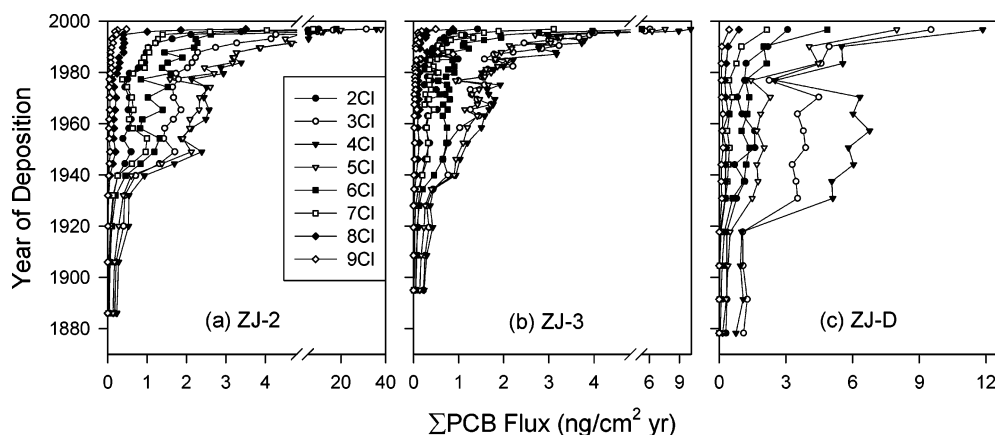
FIGURE 4. Temporal trends of PCB homologue fluxes at (a) ZJ-2, (b) ZJ-3, and (c)ZJ-D of Pearl River Delta, China.
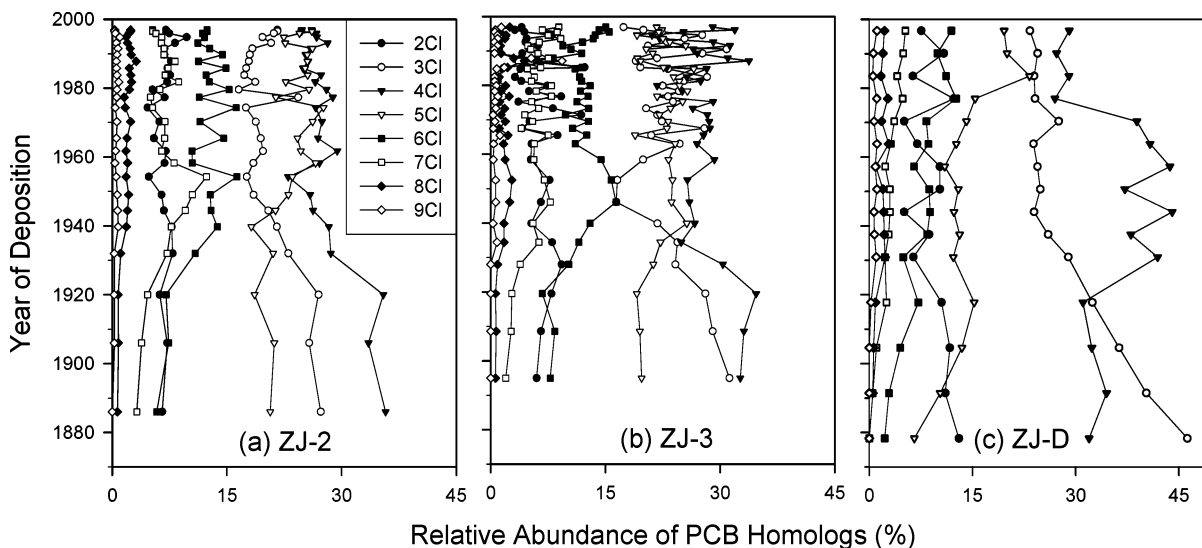
FIGURE 5. Temporal trends of the relative abundances of PCB homologues at (a) ZJ-2, (b) ZJ-3, and (c) ZJ-D of Pearl River Delta, China.

Hong Kong during the economically growing periods between the 1950s and the 1970s. After 1980, the homologue patterns at ZJ-D were converged with those at ZJ-2 and ZJ-3 (Figures 4 and 5). This, combined with the sharp increases of ΣPCB fluxes in the surface sediments of ZJ-2 and ZJ-3 (Figure 2), probably signaled a substantial change of the PCB input structure as a result of the rapid economic growth and urbanization in the Pearl River Delta in the last two decades.

Post-depositional Transformation and Mobility. Although PCBs are usually persistent in the environment, they could be subject to biological transformation, as well as physical/chemical weathering. Both aerobic and anaerobic degradation of certain PCB congers have been shown to take place in the environment (68−71). Experiments demonstrated that heavily chlorinated PCB congeners were preferentially dechlorinated in subsurface sediments (68, 71). Therefore change of the proportion between low- and high-chlorinated PCB congeners with depth in coastal sediments has been interpreted as in situ dechlorination (72, 73). Other processes that may significantly change the profiles of PCBs in sediment cores after deposition include physical mixing by currents and waves, sediment reworking due to bioturbation (27), and upward/downward diffusion/migration in the sediment column (19, 62).

To investigate the potentials for reductive dechlorination and postdepositional mobility of PCBs, we examined the percent composition of individual PCB homologues throughout the sediment cores (Figure 5). In sediments deposited after 1940, no apparent abundance increases for the lightly chlorinated PCBs (2Cl to 4Cl homologues) and decrease for the highly chlorinated PCBs (6Cl to 9Cl homologues) were observed with depth (except for a slight increase of 3Cl homologue during 1940−1950), suggesting that dechlorination was not significant in the Pearl River Delta sediments. The increase of 3Cl homologue abundances with increasing depth during 1940−1950 was attributed to percolation of less chlorinated PCBs that migrated downward to deep sediments, as discussed below.

The presence of PCBs in sediments predating the first commercial use of PCBs (Figure 2) suggested downward migration of PCB congeners in the sediment column and/or physical mixing of sediments. The relative abundances of tri-PCBs and tetra-PCBs in cores ZJ-2 and ZJ-3 increased with depth in sediments deposited before 1940 (Figure 5a,b), indicating that lightly chlorinated homologue groups were preferably subject to post-depositional mobilization. In core ZJ-D the trichloro-PCBs were also increasingly abundant with

increasing downward depth (Figure 5c). These results were consistent with results from two previous studies that investigated the post-depositional behavior of PCBs in a dated lake core from the U.K. (62) and a core from Tokyo Bay, Japan (21). Other possible sources for the presence of detectable PCBs in the pre-1940 sediments could be natural and/or anthropogenic combustion and natural production (62). PCBs from anthropogenic combustion and natural sources have been documented by other studies (4, 74, 75). However, contributions from these sources remain to be quantified in the Pearl River Delta sediments.

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