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# Seasonal variation of the distribution of PCBs in sediments and biota in a PCB-contaminated estuary

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**Abstract**

To elucidate the effects of seasonal variation of precipitation on the distribution of polychlorinated biphenyls (PCBs) in estuarine sediments and benthic feeders, PCB concentrations of river surface sediments and mullet fish (*Liza macrolepis*) were investigated in the estuary of Er-Jen River near former PCB contamination sites before and after each wet season from 2002 to 2004. Analyses of grain size distribution and organic matter revealed that the pre-existing surface sediments were covered by and mixed with the soil particulates brought by surface runoff after each wet season. Obvious increment of PCB content and significantly elevated fraction ($p < 0.005$) of light PCBs of the river mouth's sediments after each wet season indicated that the invading particles were rich in unweathered PCBs. PCBs previously buried in the surface soil of heavily contaminated sites were flushed into this estuary through surface runoff. The precipitation altered the PCB patterns in sediment organic matter, the dietary source of mullet, and consequently changed that of mullets accordingly, which all possessed significant greater fraction of light PCBs. In this study, it was demonstrated that seasonal summer precipitation affected the distribution of PCBs on surface sediments and the mullets of this estuary. PCB residuals retained in this region still pose potential threats to biota resided here.


*Keywords:* Estuary; Mullet fish; Sediments; Precipitation

## 1. Introduction

Seasonal variations of patterns or concentrations of polychlorinated biphenyls (PCBs) have been observed in various environmental media. The dominating factors of seasonal variation include temperature difference, precipitation, congener-specific properties, physiological behaviors of biota, etc. Temperature-dependent variations were observed in water (Bremle and Larsson, 1997; Bruhn and McLachlan, 2002), atmosphere (Manchester-Neesvig and Andren, 1989; Haugen et al., 1999; Kiss et al., 2001), soil (Wilcke and Amelung, 2000) and atmospheric deposition (Carrera et al., 2002). In which higher PCBs level is commonly observed in warmer season than in colder season was attributed to the higher water temperature, air/gas exchange rate and desorbing rate of PCBs from sediment to water. Meanwhile, higher PCB body burden in aquatic biota was found in spring than in autumn. This was mainly attributed to the

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consumption of lipid of biota in winter, which resulted in a concentration effect seen in spring (Huhnerfuss et al., 1995; Harding et al., 1997; Stapleton et al., 2002; Wiklund et al., 2003). Additionally, precipitations, either seasonal or episodic, are important factors on the distribution of PCBs. Seasonal precipitation not only scavenged the airborne PCBs down to ground water bodies, but also changed the concentration and patterns of PCBs in the river water (Bremle and Larsson, 1997). On the other hands, short-term episodic precipitation brought intense surface runoff to the watershed. Original bed sediments were diluted or buried by sediments with different organic compound compositions flushed in from the river catchment (Barber and Writer, 1998). However, aforementioned investigations on the variations were mostly concentrated on the temperate or around the arctic/sub arctic regions. Only few attempts have been made to investigate the seasonal variations of PCBs in previously contaminated sites of tropical areas where terrestrial sources of PCBs exist, and temperature difference varies slightly and intense precipitation occurs just in limited seasons.

Temperature difference in tropical areas is not as great as in temperate regions, insomuch it seems not to be a dominating factor for the distribution of PCBs. Instead, surface runoff brought in by intense summer precipitation might change the composition and distribution of PCBs of original sediments. An increased PCB level was observed in the river water, sediments, (Barber and Writer, 1998; Bergqvist et al., 1998; Kowalewska et al., 2003) and in the fish that resided in a lake (Stewart et al., 2003) after a flooding event. Therefore, the seasonal precipitation happened in mid-summer, rather than the temperature difference, was more likely the governing role for the seasonal variation of PCBs in tropical area. Additionally, surface sediments are the primary food sources for benthic feeders so that the change in sediment might have also altered the body burden and pattern of PCBs in their predators through food chains. Though Stewart and coworkers (2003) did observe the accumulation of PCBs in fish after an episodic flooding event, little attention has been given to the precipitation induced seasonal variation of PCBs found in sediments and fish of tropical areas.

Er-Jen River, situated in southwestern part of Taiwan, is the most polluted river of the entire island due to its long-term receiving of untreated sewage and industrial wastewater (ROC EPA, 2004). In the 1980s, open burning and acid washing operations held along the riverside from the metal recovery industry led to large quantities of PCBs being discharged into the estuary and causing serious pollution. A PCB concentration as high as 77 $\mu g\ g^{-1}$ was found in the soil samples collected at the riverside in early 1990s (Huang et al., 1992). In addition, PCBs and dioxins were found in the fish residing in the estuary (Ling et al., 1995) and nearby fish farms (Lu et al., 1995). A PCB body burden of $3400 \pm 470\ ng\ g^{-1}$ was detected in the estuarine mullets (Chen et al., 1994). The contaminated sites were all found near the riverside where storm runoff has long been carrying the contaminated topsoil into the river and letting it settle at the bottom of the estuary water. Storm waters also conveyed large amounts of upstream sediments downward, which might dilute or cover the pre-existing sediments. The mid-summer storms that bring more than 90% of the yearly precipitation (ROC, CWB, 2005) might have great influences on the distribution of river sediment and probably to the sediment feeders. Therefore, to elucidate the precipitation effects on the seasonal variation of PCBs in sediment and bottom feeders in tropical regions, this study investigated the contents and patterns of PCBs in surface sediments and bottom feeders of Er-Jen River before and after the rainy seasons in year 2002–2004.

## 2. Materials and methods

### 2.1. Sample collection

Eleven sampling sites to collect surface sediments were situated along the estuary and were named EJ1–EJ11 in sequence from upstream to river mouth (Fig. 1). To avoid site deviations in each seasonal sampling, sampling sites were chosen based on their distinguishable locations and were positioned by a global positioning system (GPS) and terrestrial surrounding. EJ1 was located most upstream as the background reference. EJ2 was at the intersection of the mainstream and the heavily polluted main branch Sanyekon Creek, which contributes more than 60% of the total pollutant load in Er-Jen River (Wen, 2002). EJ4 was near the former metal recovery operation site, Nan-Din Bridge; EJ6 was in front of the sewer outlet that holds both the sewage and storm water, and EJ9, EJ10 and EJ11 were

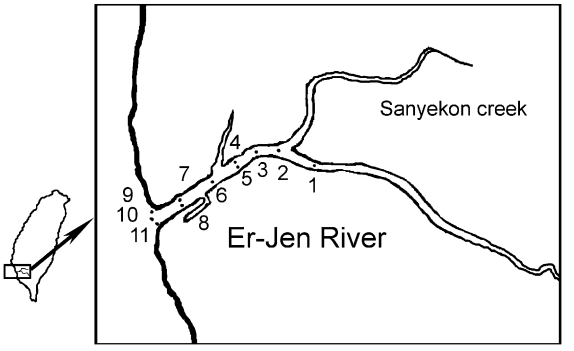


Fig. 1. The schematic diagram of the sampling sites in the Er-Jen Estuary.

situated at the river mouth. Among the eleven sites, EJ2, EJ4 and EJ6 were suspected contaminated sites which have either been near the former operation site of metal recovery (EJ4) or in front of the pollution plume (EJ2 and EJ6). Sediment samples were collected by a sediment grabber and each sample was a composite of three grabs to average the heterogeneity of sediments. Sediment samples were collected before and after the rainy season in May 2002, September 2002, September 2003 and May 2004, respectively. A total of sixty mullet fish, chosen as the target fish due to their abundance (Kuo and Shao, 1999) and high accumulation potential (Chen et al., 1994; Wang et al., 2000), were caught near site EJ6 in September 2002 ($n = 7$), May 2003 ($n = 35$) and September 2003 ($n = 18$), then froze and transported to the laboratory immediately. Water samples were collected simultaneously with the river surface sediment. Grain size distribution of sediment, total organic content of water, organic/lipid content and PCB content in sediment and fish were analyzed.

One might wonder why samples were not taken during the dry season in May 2003, but waited until May 2004, which interrupted the annual 'pre and post' rainy season samplings. In fact, this unforeseen change of date and plan was attributed to the outbreak of severe acute respiratory symptom (SARS) in spring 2003. All unnecessary meetings and long-distance traveling, including our scheduled sediment sampling in May 2003, were advised to cancel or postpone by authoritative regulations. The sampling of fish, unlike the sampling of sediment delayed by SARS until May 2004, was implemented in May 2003 by our cooperative fisherman alone. Fortunately, the defect of the experimental design was alleviated by the intrinsic characteristics of this study, the seasonal variation of sediment and biota. If the postulated periodic change did exist, then the similar seasonal variation before and after the rainy season should happen not only in the year 2002, but also in the succeeding years (2003 and 2004). Therefore, it was assumed that the variations due to precipitation might recur periodically and the distribution of PCBs in May 2003 was similar to May 2004. Thus, the original dataset before wet season in the second studied year (May 2003) was replaced by the dataset collected in May 2004.

### 2.2. Sample preparation and analyses

Sediment samples were freeze-dried for 100 h and ground into fine powders using a stainless steel mortar and pestle. About 10 g of sediments were transferred into a soxhlet apparatus and extracted with 300 ml of a mixture of residue grade acetone and *n*-hexane (1:1, v/v) in a 70 °C water bath for 36 h. The sediment extracts were then concentrated to 1 ml in a rotary evaporator (Büchi) and cleaned with 5 ml of concentrated sulfuric acid (Merck). Afterwards, it was back extracted with hexane three times and concentrated to 1 ml by nitrogen stream. The 1 ml concentrate was then passed through a pipette (10 mm ID) packed with sulfuric-acid (Merck) treated silica gel (70–230 mesh, for column chromatography, Macherey-Nagel), silver-nitrate (J.T. Baker) coated silica gel and florisil (Merck). This extract was finally eluted with 70 ml *n*-hexane and rotary-evaporated to 1 ml for GC analysis. Each fish was sliced to fillets and was treated as an individual sample. The fish fillets were prepared with the same procedure as the sediment. Lipid content analyses were performed on the fish fillet by weighing them after rotary evaporation, but prior to the purification process with sulfuric acid.

PCB contents were analyzed with a high resolution gas chromatograph (Agilent 6890N) equipped with a $^{63}$Ni electron capture detector and a 30 m × 0.25 mm × 0.25 μm, 5% phenyl phase fused silica capillary column (RT-5mx, J&W). The column flow was set at 1 ml/min with a linear velocity of 27 cm/min. The oven temperature was programmed as follows: 80 °C for 4 min, increases to 160 °C at an increment of 20 °C per min, to 265 °C by increasing 2 °C per min, to 295 °C by increasing 25 °C per min and holding it at 295 °C for 5 min. The injector was set at 250 °C in splitless mode, and the detector was set at 295 °C. Twelve environmentally significant congeners, IUPAC Nos. 18, 28/31, 52, 44, 101, 149, 118, 153, 138, 180, and 194, provided by Supelco were introduced as a quantification standard for specific congeners and summarized as $PCB_{12}$. Decachlorobiphenyl (Supelco) was spiked into samples before extraction and served as a surrogate of target compounds. The internal standard of GC performance was 2,4,6-Trichlorobiphenyl (Supelco). Only the peaks within proper range (2%) of the retention time when compared to the standards were counted for the quantification of PCBs congeners. A standard reference material (NIST 1939a) was applied to verify the feasibility of the measuring method. The average recovery of the congeners in the SRM is 82 ± 6% with the range of 73% (CB118) to 90% (CB138/163). Every batch of eight samples was accompanied with one duplicate sample, one QC sample and one blank sample. Method detection levels (MDLs) were in the range of 0.032 (CB44) to 0.088 (CB18) ng $g^{-1}$ with recovery of 96 ± 23% from spiked $PCB_{12}$ standards. The recovery of surrogate CB209 was 70 ± 16% of sediment samples and 73 ± 7% of fish samples. All data was presented without correction to the recovery.

Organic content of sediment was determined by sulfuric-dichromate digestion and back titration with standard ferrous ammonium sulfate solution. Grain size distribution analysis was performed through wet sieving and grain size analyzer (CILAS, M175) with 12 sieves ranged from less than 2 μm to larger than 710 μm. Total organic matter of river water was determined by the

persulfate oxidation method and analyzed by an O.I. Analytical Type 1010 TOC Analyzer.

## 3. Results and discussion

### 3.1. Seasonal change of the water quality in the Er-Jen Estuary

Unlike temperate estuarine regions where high river flow is brought about by snow melting in spring, the high flow of river water in this studied region was resulted from the intense precipitation brought in by typhoons from the Pacific Ocean in a short period, normally from June to August. The precipitation is so intensive that a huge amount of surface runoff and serious erosion of surface soils in the river catchment are commonly observed. Solid content as high as 5000 mg $l^{-1}$ and resultant solid loading of $5 \times 10^5$ ton $d^{-1}$ were observed in the upstream of the river during a summer storm in 2002, which contributed more than 85% of the annual solid loading. (ROC, WRA, 2005).

The characteristics of climate and water quality of this estuary, including atmosphere temperature, precipitation, river flow rate, and aqueous concentrations of ammonia nitrogen, biochemical oxygen demand and suspended solid, are expressed as the average of the ratio of the monthly average to the annual average in the period from 1991 to 2000 (Fig. 2). The monthly averaged values of water quality parameters, except water pH, deviated significantly from the annual mean during rainy seasons. Ammonium nitrogen ($r = 0.91$) and BOD ($r = 0.81$) were negatively correlated with the flow rate, while the variation of SS ($r = 0.63$) was synchronized with the variation of flow rate. Meanwhile, river flow rate was positively correlated to the precipitation ($r = 0.93$). Therefore, precipitation was considered the main factor on the fluctuation of river water quality. The average TOC found in river water for May and September were $6.1 \pm 0.56$ mg/l and $1.0 \pm 0.16$ mg/l, respectively. This significant reduction of TOC ($p < 0.0001$) in September revealed the dilution effect of runoff water on the water constituents within the studied period.

Consequently, precipitation is simultaneously responsible for both the dilution of water concentrations of BOD and ammonium nitrogen through the storm runoff, and the thickening of water solid content by upstream erosion.

### 3.2. Seasonal variations of organic content and grain size of sediment

The organic matter content of sediments collected in alternative seasons was shown in Fig. 3. Higher organic content of surface sediment was observed in mid-estuarine sector where industrial effluents were discharged into this region from Sanyekon creek. In comparison, organic contents were found lower in the upstream and river mouth sectors. After summer storms, the average organic content declined along the river (from 1.52% in May to 1.18% in September of 2002 and 2.10–1.66% during 2003–2004). An exception was found in the river mouth sites where organic contents increased significantly after summer and even exceeded the values of dry season.

A deposition of eroded material from the catchment was discovered in the river, especially at the river mouth site EJ9, EJ10 and EJ11. Precipitation might have been the cause in diluting or moving the organic-rich sediments down the river. An increase of organic content in the sediments around the river mouth was attributed to the conveying and re-deposition of materials from

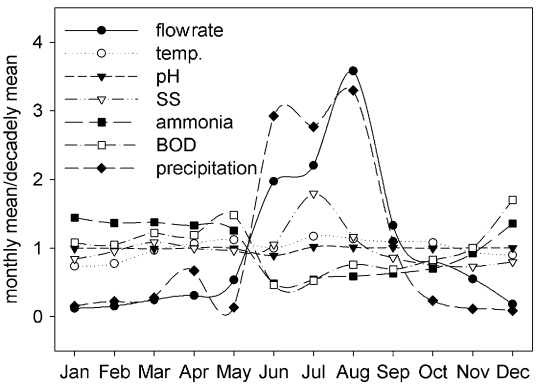


Fig. 2. The seasonal variations of some physical and chemical parameters (water temperature, pH, SS, BOD, ammonia, precipitation and flow rate) of Er-Jen River. The variations were expressed as the average of the ratios of monthly average to annual average in the year 1991–2000.

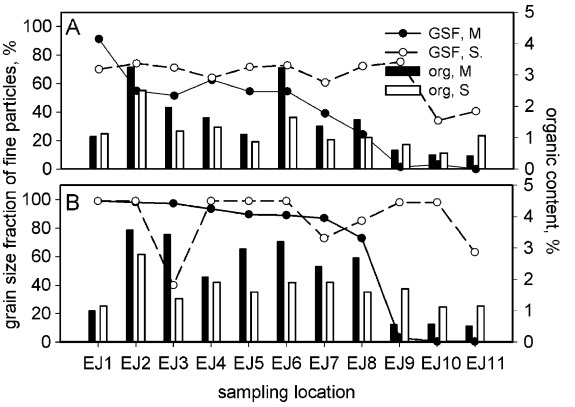


Fig. 3. The effects of precipitation on the fine grain fraction and organic matter content of the river sediments in year 2002 (A) and 2003–2004 (B). GSF denotes the fine grain size fraction of sediment particles, while M and S denote the sampling periods in May and September, respectively.

surface runoff and original sediments in the mid-sector of the estuary.

Grain size distribution of the river sediment, before and after the wet season of 2002 and during 2003–2004, is also shown in Fig. 3. By grouping sediment particles into fine (0–38 μm), medium (38–250 μm) and coarse (250–710 μm) fractions, the grain size of sediments increased gradually along the river from fine (upstream site EJ1) to medium (EJ2–EJ8) and eventually to coarse (river mouth sites EJ9–EJ11) in May. The weight percentage of fine particles decreased from more than 90% at EJ1 to 0% at EJ10, while that of coarse particulates increased from 1% to more than 90%. However, grain sizes of September's sediments were uniformly distributed along the whole estuary, which indicated that new materials had been deposited evenly after precipitations. In the dry seasons, from September to May of next year, tidal current would selectively remove fine particles in the sediment at the river mouth sites EJ9–EJ11, which resulted in the declining of fine particle fraction along the river.

Shift of organic matter content and grain size distribution along the river indicated that fine and organic-rich particulates had been transported from upstream sector and river catchment to the river mouth through surface runoff and strong river flow. Original surface sediments in the estuarine sector might have been mixed or masked by the particulates from external sources after precipitation. However, the original sediments in the estuarine sector and river mouth were exposed again in dry season owing to the tidal current. Thus, a periodical change in the organic content and grain size distribution occurred seasonally.

### 3.3. PCB concentrations of sediments

Dry solid based and organic matter adjusted PCB content ($PCB_{12}$), found in sediment samples that were collected along the estuary is shown in Fig. 4. Before the wet season, the spatial distribution of PCB concentration indicated high PCB contamination in the estuarine sector at points between EJ2 and EJ8, especially at EJ2, EJ4, and EJ6, which were near three suspected contaminated sites, Sanyekon Creek, Nan-Din Bridge and the sewage outlet, respectively. On the other hand, $PCB_{12}$ of upstream site EJ1 and river mouth site EJ9, EJ10, and EJ11 were lower than those found on other estuarine sites were. However, after the wet season, high concentrations of $PCB_{12}$ were observed at EJ4, EJ7 and the river mouth and not at EJ2 and EJ6.

For dry-solid-based PCB content (Fig. 4A), a dilution effect similar to what has found in the organic content was observed. Surface runoff brought in by precipitation demonstrated its masking and re-deposition effects on the PCB content of sediments in the estuary, where PCBs were reduced in the mid-estuarine

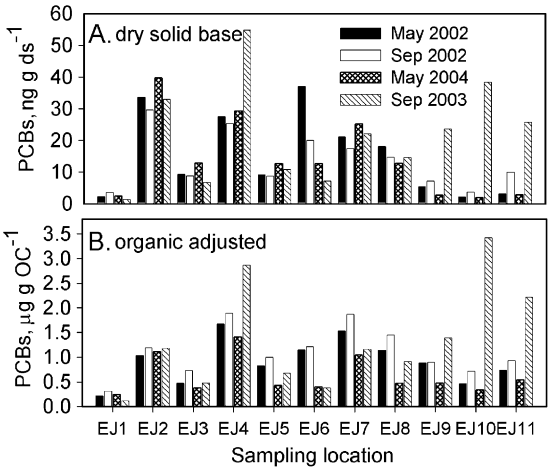


Fig. 4. The dry solid based (A) and organic adjusted (B) PCB content of the surface sediments in studied seasons and locations.

sector but increased in the river mouth. Before the wet season, higher $PCB_{12}$ were found near the suspected contaminated sites, but they were shifted to the lower estuarine sector after summer storms. Particles with low PCB content from upstream erosion were deposited evenly over the estuarine sector and resulted in dilution and masking effects on the original distribution pattern in sediments.

Contrary to the varied dry-solid-based PCB contents, organic-adjusted PCB content of the sediments along the estuary all increased after summer precipitation (Fig. 4B), which indicated that sediment enriched in PCBs were flushed into the estuary through surface runoff. The consequence of the re-deposition of high PCB content particles resulted in the average $PCB_{12}$ of river mouth to increase slightly in 2002 and significantly in 2003. An increase in sedimentary PCB content was observed at the river mouth in September 2003, to a level higher than the suspected hot spots, suggests that external contamination source other than upstream erosion dominated the distribution of the river mouth's surface sediment. Higher OM-normalized concentration denotes higher PCB activity and less aging material exported from PCB contaminated source during storm runoffs.

Similar to the periodic changes of grain size distribution, these new-deposited particles in the sediment were mostly fine particles that might be gradually lost to the sea by tidal current in the dry seasons. Therefore, PCB content found in the dry season following a wet one was similar to that of the previous dry seasons.

### 3.4. PCB pattern deviation in sediment

The change of PCB patterns on each site before and after the rainy season is expressed as the relative

deviation, i.e. $((CB_n/PCB_{12})_{Sep} - (CB_n/PCB_{12})_{May})/(CB_n/PCB_{12})_{Sep}$, where $CB_n$ is the organic adjusted concentration of $n$th congener. Principal component analysis (PCA) of the relative deviation of 12 selected congeners indicates that the main components of the first factor are CB138 and 149, and those of the second factor are CB52 and 44. These two factors explain more than 80% of the total variation. Since CB52 and CB44 are lightly chlorinated PCBs, and CB138 and CB149 are heavily chlorinated ones, degree of chlorination seems to be an appropriate indicator to characterize the relative deviations. Fraction of light PCBs to total $PCB_{12}$ was applied to interpret the PCB distribution along this estuary. The fraction of light PCBs, including tri- and tetra-chlorinated biphenyls such as CB18, CB28&31, CB52 and CB44, found at eleven sites for the months of May and September are shown in Fig. 5. The fraction of light PCB of the surface sediments collected in May within estuarine sector (EJ2–EJ8) were in the range of 30–40% and remained unchanged or varied insignificantly after the wet season ($p = 0.8$ of year 2002 and $p = 0.54$ of year 2003–2004). Contrarily, those collected from surface sediment of the river mouth zone (EJ9, EJ10 and EJ11) increased significantly from 30% to 50% ($p < 0.005$ of year 2002 and $p < 0.001$ of year 2003–2004). Based on the phenomenon of varying light PCB fractions, these sampling sites can be roughly grouped into three main clusters, the upstream background EJ1, the estuarine sector EJ2–EJ8, and the river mouth zone EJ9, EJ10 and EJ11. Based on their relative deviations of PCBs in 2002, a two-dimensional PCA plot of these sampling sites is displayed in Fig. 6. The plot also displayed three discrete clusters, which was similar to the findings from the light fractions in Fig. 5.

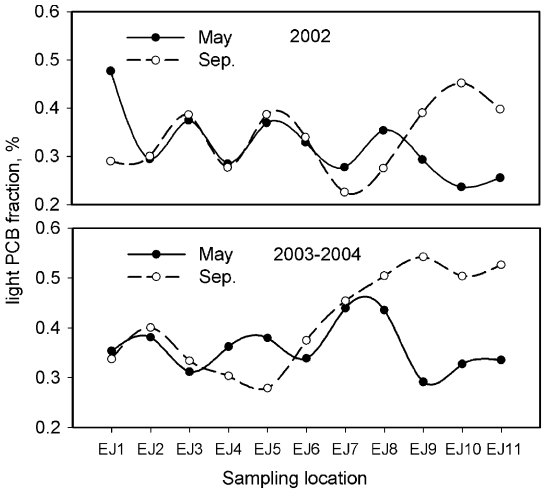


Fig. 5. The light PCB fractions of the eleven sampling sites in year 2002 and 2003–2004.

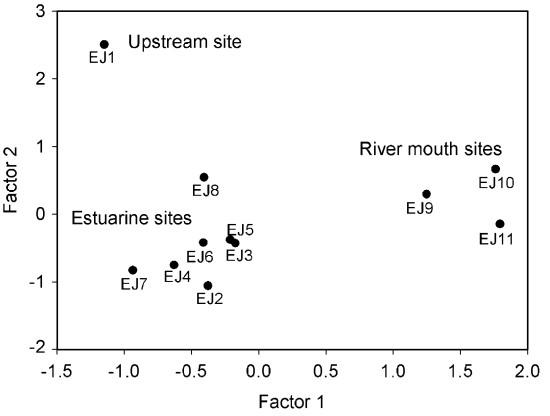


Fig. 6. The two-dimensional PCA plot of the sampling sites based on the relative deviation of PCB patterns before and after rainy season in 2002.

The seasonal variation of light PCB fraction in the river mouth sediments revealed that external sources had been introduced into this region. The most probable sources of invading mass were non-point sources flushed into the estuary during precipitation, including particles from atmospheric wet deposition, upstream erosion and surface runoff of river catchment. In addition, relatively high PCB content of the invading particles observed in the river mouth, as compared with upstream sectors, suggests that there was another major contributor of external contamination other than the re-suspended upstream sediments. Original surface sediments in the river mouth zone with coarser size, lower organic and lower PCB content were more susceptible to fine and organic-rich invading particles than those in the other estuarine sectors. Thus, a distinct PCB fingerprint indicating the terrestrial contribution of PCBs was observed clearly in the river mouth after the wet season. Furthermore, with the knowledge that sediments do not increase their light fraction spontaneously during precipitation, these elevated contents and light fractions found in the downstream of storm water outlet (EJ6) were resulted from the surface runoff of nearby catchment.

Previous studies (Wania and Mackay, 1993; Cousins and Jones, 1998; Ashley and Baker, 1999; Meijer et al., 2002) suggested that a heavy-PCB-dominated pattern is an indicator of near source emission of PCBs, while a light-PCB-dominated pattern reflects a more weathered pattern or one that is from air–water exchange. In other words, light PCBs were believed to possess higher potential than heavy ones to partition or evaporate into water column and atmosphere. Thus, PCB residuals retained near a contamination source exhibited a more heavily chlorinated fraction than remote ones did. Such effects are regarded as aging or weathering.

In this study, although sediments in the river mouth exhibited elevated light PCB fraction after each wet

season in the succeeding years, significant increment of PCB content in this region suggested that its sources were not from remote weathered background contamination, but rather from a fresh local contamination source. Ling et al. (1995) reported that the major type of contamination in this estuary resembles light and medium chlorinated rich mixture Aroclor® 1242 and 1254. Meanwhile, PCB residues in the estuarine sector and nearby villages seemed not weathered enough to show an enhancement of heavy fraction within only one decade. Therefore, newly deposited river mouth sediments still exhibited an unweathered PCB pattern that resembled the original Aroclor's composition with prominent light PCB fraction. A similar pattern was observed by Ashley et al. (2000) in the Hudson River where light homologs dominated the near source emission.

Light PCB fraction is believed to be higher in the topsoils surrounding the estuary than in the river sediment due to the lower aging rate of PCBs in the topsoils. PCB residuals in the river sediments, especially the light ones, are presumed to partition easily into the aqueous phase by their intrinsically higher water solubility and by the external mixing effects from water current and sediment scouring. On the contrary, there is no strong disturbance to the topsoils as what the river sediment had experienced, most light PCBs were preserved in the topsoils in spite of minor losses mainly through evaporation. Meanwhile, tidal current also conveyed new-deposited particles to the sea. In accordance, as the consequence of continual partitioning, evaporation and tidal conveying, light PCB fractions of surface sediments declined from wet season's peak to dry season's valley, and increased again by fresh light PCB source from storm runoff. The alternation of PCB patterns observed in the river mouth was attributed to the periodic settlement of fresh PCBs, the aging of them and the tidal flushing.

Because settlement of eroded soil particles was minor within the estuary sector (EJ2–EJ8), as compared with what is at the river mouth, due to strong river flow. Invading sediments only comprised an insignificant portion of the upper part of sample cores. Therefore, the light PCBs fractions of the samples from the sites were nearly unchanged. Particles that lay beneath the newly deposited particles were aged particles with higher organic content and higher heavy PCB fraction that might buffer the influence of the invading particles and obscure the influence. However, the above consideration is not essential when applied to the river mouth, of which original PCBs and organic contents are much lower than those of the estuarine sector, and where the newly deposited particles are comprised of the majority of the increment of PCB content in the river mouth after precipitation. Therefore, surface sediment of the river mouth could better reflect the real characteristics of newly deposited surface sediments than the estuarine sediment.

### 3.5. PCBs in fish

The average size, weight and lipid content of mullet fish caught in May and September of year 2002 and 2003 are shown in Fig. 7. The average PCB burden of mullet varied insignificantly ($p = 0.79$) from May's 9012 to September's 8143 ng $g^{-1}$ (lipid adjusted). Interestingly it did not increase simultaneously with an increase in their presumed dietary source, the surface sediment (Horinouchi and Sano, 2000), which increased significantly ($p < 0.05$) from 769 to 1225 ng $g^{-1}$ (organic adjusted mean of all locations). One possible explanation is the larger partition capacity of fish caught in autumn, which were significantly larger in size ($p < 0.005$), heavier in weight ($p < 0.00001$) and richer in lipid ($p < 0.05$) than those caught in spring. The enrichment rate of fish lipid might be faster than the accumulation rate of PCBs and resulted in the dilution of PCBs. Therefore, the significant increase of lipid content in fish lowered their PCB concentration. This effect of dilution is similar to the findings in the temperate regions (Stapleton et al., 2002; Wiklund et al., 2003) that the change of lipid content of fish deviate their body burden. However, besides the lipid content (Wiklund et al., 2003), dietary preference (Loizeau et al., 2001), sediment burial rate (Berglund et al., 2001), habitat eutrophic status (Teil et al., 1996) and embryo development (Wiklund et al., 2003) were other possible governing factors. The mechanism behind the reduction of PCB level in fish is not fully understood. To better understand it, more researches are needed to focus on the enrichment of lipid content in fish.

The PCB patterns found in the mullet fish, unlike the content, exhibited a clear seasonal variation before

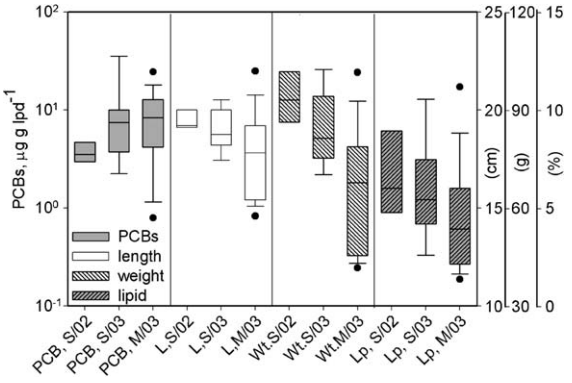


Fig. 7. The box plots of PCB content, length (denoted as L), weight (wt.) and lipid content (Lp.) of fish in May (M) and September (S). Bottom and top boundaries of box represent 25th and 75th percentiles. The line within the box marks the medians. Whiskers above and below the boxes indicate the 90th and 10th percentiles. Dots outside the whiskers represent the 95th and 5th percentiles.

and after each rainy season. Light PCB fraction increased significantly from dry season to wet season ($p < 0.00005$), while no significant change ($p = 0.75$) was observed for fish caught in September of the succeeding years 2002 and 2003, which denotes a periodic change of patterns in fish.

With congener patterns changing seasonally, the influence of surface sediments on the patterns of these mullets could be identified. Fig. 8 demonstrates the synchronous change of light PCB fraction of fish and sediment in May and September. It should note that the light fractions of mullets and river mouth's sediments lifted up significantly after precipitation. The simultaneous increase of the sediment and the fish revealed that PCB patterns of the fish body rapidly reflected those found in the sediments.

In actuality, the concept of the exposure route of hydrophobic chemicals to fish has been widely discussed in numerous studies and remains doubtful to many. The greater fraction of light PCB of mullets caught in September was owing to the elevated light PCB fraction in the surface sediment. Unfortunately, lack of information on the aqueous PCB content in this estuary weakens the aforementioned postulation, thus one may argue that the contribution of PCB body burden to these mullets, rather than the dietary source, was through gill exchange or so-called bioconcentration. Gray (2002) reviewed more than forty articles related to bioaccumulation and indicated that some of them, though more than half to two-thirds of these articles claimed that biomagnification was the dominant mechanism, lacked direct or appropriate evidences. Nevertheless, a commonly acceptable mechanism is that biomagnification occurs in highly hydrophobic chemicals, while bioconcentration dominates less hydrophobic chemicals, and the divide line is approximately in the $\log K_{ow}$ range of 5–6 (Clark et al., 1990; Thomann et al., 1992; Russell et al., 1999). The $\log K_{ow}$ of the light PCB congeners in current study is 5.24–5.84 ($K_{ow}$ value adopted from Hawker and Connell, 1988), which are just in the border region to support that both dietary uptake and gill exchange are possible mechanisms. However, a significant increase of PCB content in the surface sediment of the river mouth should not be attributed to the river water, because water might not carry such high PCB content to result in the lift of PCB in the sediment during the period of a summer storm. Conversely, it is more likely that intrinsically higher water solubility of light PCBs may partition from polluted sediment to water and increase aqueous PCB content according to an equilibrium concept. Therefore, successive lifts of light PCBs in the sediments and water may increase the light PCBs in these mullets due to simultaneous exposure from food and water. Although bioconcentration and biomagnification are all possible accumulation mechanisms to increase the light PCBs in fish, the exact PCB source was more likely to be from the newly deposited sediments rather than the water.

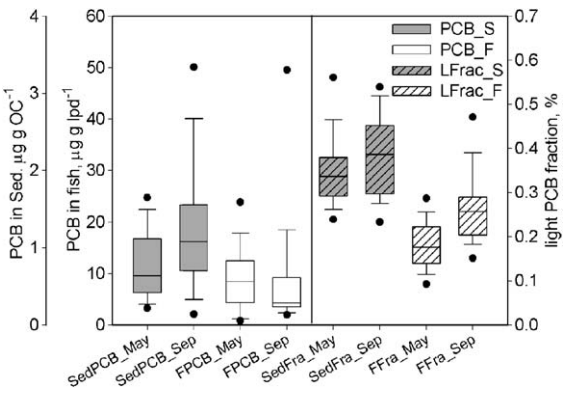


Fig. 8. The box plots of contents and light fractions of PCBs in the sediments and fish in May and September, in which S denotes sediments, F denotes fish, and LFrac means light PCB fraction.

In this study, through analyses of the precipitation induced seasonal variation of PCB distribution in the surface sediment and mullet fish, an exposure pathway from sediment to biota has been established. Congener pattern is a useful indicator to identify the origins and path of PCBs. PCB residues from early contamination retained in nearby areas could be brought into the estuarine ecosystem and concentrated in the bottom feeders, mullets.

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