行政院國家科學委員會專題研究計畫　<u>成果報告</u>

河口生態系統持久性有機物暴露途徑之研究(I)-基本資料調查與模式架構建立

計畫類別：個別型計畫
計畫編號：NSC91-2211-E-002-029-
執行期間：91 年 08 月 01 日至 92 年 07 月 31 日
執行單位：國立臺灣大學環境工程學研究所

計畫主持人：吳先琪
共同主持人：張美玲
計畫參與人員：傅崇德、卓坤慶、楊高宏、謝明凱

報告類型：精簡報告

處理方式：本計畫可公開查詢

中　華　民　國 92 年 10 月 31 日

Exposure Pathway in Estuarine Ecosystems (1) – Baseline information investigation and Conceptual model development

Shian-Chee Wu*　Mei-lin Chang#　Chung-Te Fu#

**Graduate institute of Environmental Engineering, National Taiwan University, Taiwan, ROC*

#Department of Environmental Engineering, Van Nung Institute of Technology, Taiwan, ROC

摘要

本研究針對二仁溪口十一個採樣點之河川底泥進行多氯聯苯、有機物組成及粒徑分布之分析，以探討夏季降雨對河川底泥中多氯聯苯之分布濃度及型態之影響。研究結果顯示底泥中多氯聯苯及有機物組成分別由降雨前的 17.3 ng/g 及 1.5％降至降雨後的 12.6 ng/g 及 1.0％，此兩者間之線性相關係數由降雨前的 0.87 大幅降低至降雨後的 0.54。同時多氯聯苯在河海交接處及河口內兩處底泥之濃度及型態分布明顯不同，河海交接處之低氯數同源物在降雨後有明顯增加，推測是暴雨逕流造成之影響。河川集水區域內之表土具有較多低氯數之同源物，當表土被暴雨逕流沖刷至河川內，可能於河海交接處沉積，遂可能造成前述結果。

本研究同時對河口內魚體及底泥中多氯聯苯同源物進行分析，發現兩者間具有相近之濃度及型態分布，顯示了其間有密切的食物階層關係，並反應出多氯聯苯存在於底泥與魚體間之暴露途徑。

Abstract

The distribution of the concentration of PCBs in sediments and fishes of eleven sampling sites along the ErJen estuary were investigated. The sediment properties of this tropical estuary near a former PCB contamination hot spot were also investigated before and after wet season to evaluate the effects of storm events on the seasonal variation of them and the distribution pattern of PCBs. The results revealed that the averaged PCB concentration decreased from 17.3 to 12.6 ng/g and the organic content of sediments decreased from 1.5 to 1.0 % after the wet season. The strong correlation (r = 0.87) between the organic matter content and the PCB content observed before precipitation was disappeared after the rainy season (r = 0.54). The pattern of PCB concentration in the sediments in river mouth reflected the influences of surface runoff brought by high precipitation. The concentration of the light PCBs increased while the heavy PCBs decreased after precipitation in the sediment at the river mouth. Topsoil in the catchment with relatively higher concentration of light PCBs was proposed to contribute to the change of the PCB pattern in the sediments downward the combined sewer outlet. Comparison between the patterns of PCBs in the fishes and in the sediments within the estuary revealed that surface sediments are the stable food sources of these bottom feeders. Preliminary study on the exposure route of the bottom feeder, *mullet*, demonstrated a strong trophic relationship between sediments and fishes. Relatively similar fingerprints of PCBs in fishes and in sediments support the hypothesis of the sediment-to-fish exposure route suggested above.

Keyword : PCBs; estuary; fish, sediments, exposure route; seasonal variation;

Introduction

Polychlorinated biphenyls (PCBs) were highly stable chemicals that had been introduced to the environment from various industrial applications such as the production and uses of transformers and capacitors starting several decades ago.　PCBs were widespread in the world and were transported among different environmental media such as water bodies, atmosphere, soils and even biota. Bioconcentration and biomagnification of these persistent organic pollutants in biota have been considered as a global problem. A great number of researches have demonstrated the exposure routes how PCBs were uptaken into the biota. However, the climatic and seasonal variation as well as the physiological behavior and the environmental heterogeneity made the exposure routes more complicated.

Seasonal variations of the pattern of the concentration of PCBs in environmental media have been observed by researchers. The variations were attributed to the temperature difference (Agrell, *et al.* 2002; Bruhn and McLachlan, 2002), evaporation, precipitation (Bremle and Larsson, 1997; Kiss, *et al.* 2001) and biota physiological behavior (Huhnerfuss *et al*, 1995), etc. The observations on the variation were mostly concentrated on the temperate and arctic regions where temperature was most responsible for this variation, for temperature governs the evaporation rate of semivolatile substance. However, few observations have been reported on tropical region where the temperature variation is not as high as that in the temperate regions, and the precipitation is often concentrated within limited months. As for open estuary, unlike closed lakes, with fluctuating river flow and external sources, accumulation and erosion brought about by storm water may change the properties of the sediment. The surface sediments in tropical estuary are considered as the primary food source for bottom feeders. Elucidation on the variation of sediment is necessary prior to clarifying the bioaccumulation between sediment and bottom feeders. To elucidate the exposure route of PCBs towards fishes, and ultimately to the human bodies, seasonal variation of possible sources deserves further attentions.

Er-Jen River, situated in the southwestern part of Taiwan, is classified as the most polluted river of the whole island for her long-term receiving of untreated sewage and industrial wastewater. Moreover, open burning and acid washing operations held in early 1980s' along the riverside for metal recovery from transformers and capacitors led to large quantity of PCBs discharged into the estuary and caused serious soil and water pollution. PCB concentrations as high as 77 μg/g were found in the soil samples collected at the riverside in early 1990'(Huang *et al*, 1992). In addition, the significantly high body burden of PCBs in fishes collected in this estuary and nearby fish farms indicated the bioaccumulation attributed to the contamination of the river water, sediments and the atmosphere (Lin, *et al*, 1995; Lu, *et al*, 1995). The contamination hot spots were just near the riverside so that the storm runoff might have carried the contaminated topsoil into the river and let them settled in the bottom of the estuary water. On the other hand, storm waters also transport large mount of upstream sediments downward, which may dilute or cover the originally existing sediments. The effects of storm runoff on the sediment PCB distribution have not been studied. The seasonal variation of PCB in tropical region, where temperature deviation from the yearly average is usually within 15℃ and the precipitation happened in limited seasons deserves careful investigation.

The purpose of this study is trying to illustrate the effect of the precipitation on the seasonal variation of PCBs in the river sediments. Sampling and analyses on the sediment properties and PCB contents before and after wet season will be performed and will provide useful information for identifying the sources of the contaminants and establishing the seasonally varying source-fish-human exposure routes.

Material and Methods

Sample collection. Eleven sampling sites for surface sediments were situated along the estuary and were named EJ1 to EJ11 in the direction from upstream to the river mouth as shown in fig. 1. 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 to Er-Jen River. EJ6 was in front of the sewage and storm water combined sewer outlet. EJ4 was near the former metal recovery processing site, Nan-Din Bridge; and EJ9, EJ10and EJ11 were situated around the river mouth. Samples were collected in May and September 2002 before and after the rainy season, respectively. Surface sediments (0-7cm) were collected with a sediment grabber. Samples were refrigerated and sent to the laboratory within 5 hours. Grain size distribution, organic content and PCB content were analyzed. Fishes were caught in September 2002 in the estuary near the sites EJ6, frozen and transported to the laboratory immediately.

Sample preparation and analyses.
Sediments were freeze-dried for 100 hours and ground into fine powders using a stainless steel mortar and pestle. About 10 grams of the sediments were extracted, purified and concentrated to I mL for GC analysis.

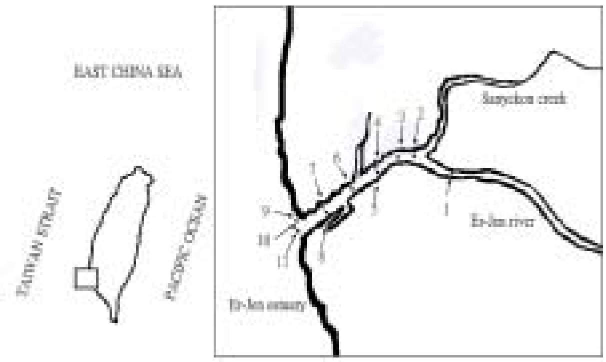

Fig. 1 The schematic figure of eleven sampling sites in the Er-Jen estuary.

PCB contents were quantitatively analyzed by a high resolution gas chromatograph (Hewlett Packard 6890N) equipped with a ^{63}Ni electron capture detector (ECD) and a 30 m×0.25 mm×0.25 μ m, 5% phenyl phase fused silica capillary column (RT-5mx, J&W). A mixing standard of twelve environmental significant congeners, IUPAC Nos. 18, 28/31, 52, 44, 101, 149, 118, 153, 138, 180, and 194, provided by Supelco was introduced as the quantification standard and summarized as ΣPCB_{12} . CB209 (Supelco) was spiked into the sample before the extraction as a surrogate of the target compounds. Only the peaks within the proper range (2%) of the retention time when compared to the standards were counted for the quantification of PCBs congeners.
Organic content of sediment was determined by sulfuric dichromate digestion, and grain size distribution analyses was performed through wet sieving and grain size analyser (CILAS, M175) with twelve sieves ranged from less than 2μm to larger than 710μm. Each sediment sample was analyzed triplicate to get the mean and standard deviation. The recovery of surrogate CB209 was $70 \pm 16\%$ for 66 sediment samples and $70 \pm 5\%$ for seven fish samples. All data were not corrected to the recovery.

Result

The effects of wet season runoff in Er-Jen estuary. The long term trend of the characteristics of the climate and the water quality of this estuary including the atmosphere temperature, precipitation, river flow rate, and the water concentration of ammonia nitrogen, biochemical oxygen demand and suspended solid were shown in fig.2. Those values were expressed as the ratio of the monthly mean to the yearly mean all averaged in the period of 1991 to 2000. The monthly averaged values of water quality parameters, except water pH, deviated from the yearly average during rainy season. The ammonium nitrogen (r = 0.91) and BOD (r = 0.81) were negatively correlated to the flow rate, while SS(r = 0.63) was positively correlated to the flow rate. Meanwhile the river flow rate was positive correlate to the precipitation (r = 0.93), which suggested that the precipitation might be attributed to as the main factor on the deviation of river water quality. The average TOC of May and September were 6.1±0.56 mg/l and 1.0±0.16 mg/l, respectively.
The precipitation in Er-Jen estuary is concentrated in a very short period of time, normally from June to August as shown in fig.2. Wet season precipitation comprises more than 80 % of the year's precipitation (yearly mean 1672mm); and that of the other month is quite low. In the period of the observation, the year

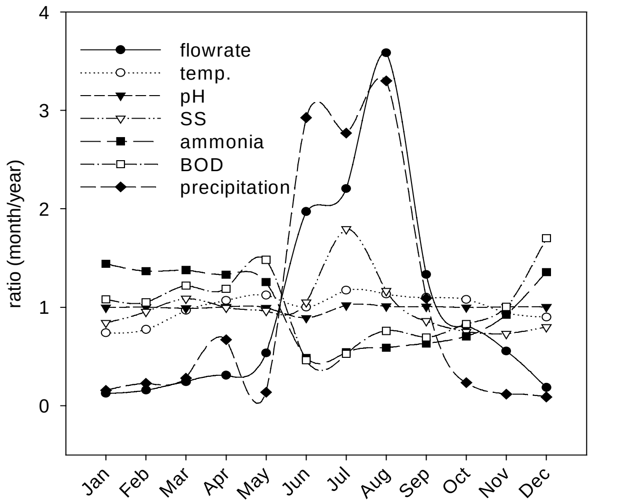

Fig. 2. the ratio of month mean to decade mean (1991-2000) show fluctuations in summer, SS and flow rate reach yearly peak while BOD and ammonia low down to yearly valley, at the meantime temperature and pH remain near yearly mean.

2002, there was almost no precipitation at all in other than the studying season. Unlike in thetemperate estuaries with snow melting in spring, in this region the high flow rate of river water brought by storm from the Pacific Ocean are concentrated in summer. The precipitations by summer storms were so intensive that huge quantity of surface runoff and the erosion of surface soils in the river catchment can be expected. The precipitation is responsible simultaneously for both the dilution of the water concentrations of BOD and ammonium nitrogen through the storm runoff, and the thickening of water solid content by the surface soil erosion.

PCBs concentration of the surface sediment. Dried sediment-based PCB concentrations of twelve selected congeners (ΣPCB_{12DS}) of the samples along the estuary collected in May were in the range of 2.2 to 37.1 ng/g, and in the range of 3.2 to 25.5 ng/g of in September (Table1). The higher concentrations were observed in EJ2, EJ4, and EJ6 which were located near the suspected pollution hot spots (Fig. 3a) The Sanyekon Creek, The Nan-Din Bridge, and the sewage outlet. ΣPCB_{12DS} of the upstream site EJ1 and the river mouth site EJ9, EJ10, and EJ11 were low and down to 2.2 ng/g, which indicated that the major pollution region was within the estuary from EJ2 to EJ8.

The PCB_{12DS} concentrations of the samples collected in May were slightly higher than that of September at site EJ2 to EJ 8. However, the PCB_{12} of the September's sample were higher than that of the May when normalized to the organic carbon content (Fig. 3b). The ΣPCB_{12OC} in May and September's sediment sample were in the range of 213 to 1533 ng/g and 684 to 2324 ng/g respectively. Unlike the ΣPCB_{12DS}, the highest concentration of PCB_{12OC} were observed at EJ4, EJ6, EJ7 and EJ8 instead of the suspected hot spot EJ2, and EJ4.

Organic content and grain size of sediment. The organic content of sediments collected on

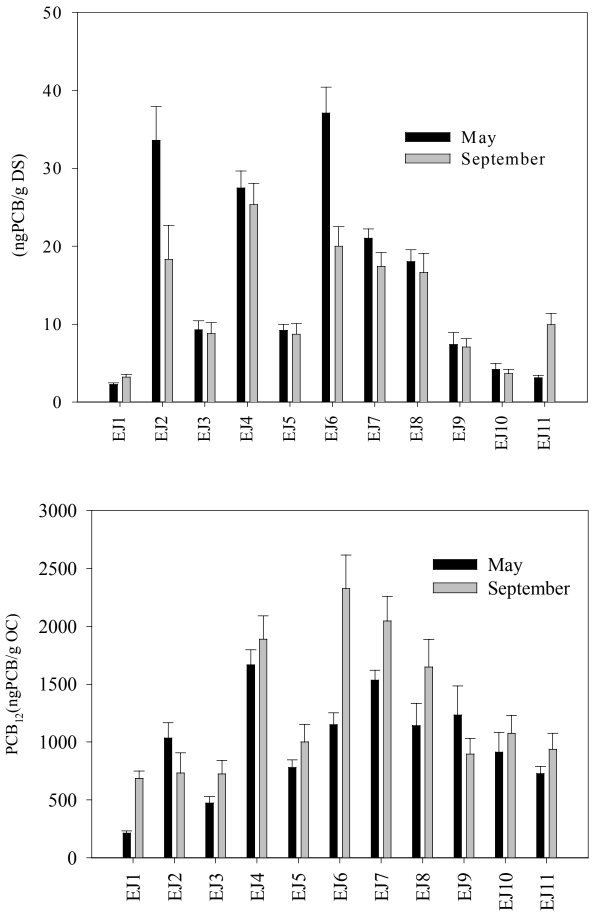

Fig. 3a. & 3b. PCB contents of sediments based on dry weight (a) or organic matter (b), respectively.

May were higher than that of September except those from the sampling sites EJ9, EJ10, and EJ11, which were located around the river mouth zone. The precipitation seemed having diluted the organic content of the sediments as well as the water quality. The increasing of the organic content in the sediments around the river mouth must be the conveying of upstream material and re-deposition there. If the particles can be grouped in to fine (0-38μm), medium (38-250μm), and coarse (250-710μm) particulates the grain size of May's sediments increased along the river from fine particulate (upstream site EJ1) to medium ones (EJ2 to EJ8) and finally to the coarse ones (river mouth sites EJ9 to EJ11). The weight percentage of fine particulates decreased from 90% (EJ1) to 0% (EJ10), while that of coarse increase from 1% to more than 90%. However, the grain size of September's sediment showed apparently less difference. There seems that new materials have been deposited evenly in the whole estuary (Fig. 4). The change of the organic carbon content and the grain size distribution along the river indicates that the fine and organic-rich particulates were transported from upstream to river mouth.

PCB pattern deviation. PCB pattern is a useful information to identify the sources of the contaminants. Pattern expressed as the concentration ratio of selected congener to specific congener, for example (CBn/CB153), is one of the most popular approaches. The deviation of PCB pattern of each sample on the same site before and after the rainy season was expressed as the relative deviation, i.e. $((CBn/CB153)_{SEP} - (CBn/CB153)_{MAY}) / (CBn/CB153)_{SEP}$. Fig. 5 shows the spatial distribution of the relative deviation of eleven sites for twelve selected congeners. The relative deviation value above the reference line $(((CBn/CB153)_{SEP} - (CBn/CB153)_{MAY}) / (CBn/CB153)_{SEP} = 0)$ means higher congener ratio after the rainy season for this specific congener, while that beneath the reference line represents lower congener ratio. These values, though scattered along the whole estuary, still revealed slightly increasing spreading approaching the river mouth. To elucidate the deviation, CB18, CB101, and CB138 were chosen to represent the light, medium and heavy chlorinated compounds, respectively. The ratios were similar before and after the rainy season within the estuary (EJ2 to EJ8) with the exception of the river mouth, where CB18 and CB138 deviated considerably and revealed converse trend. For light PCBs, CB18, the ratio of CBn/CB153 increased after the rainy season at river mouth sites, i.e. EJ9, EJ10, and EJ11. The ratio of heavy PCBs such as CB138, on the other hand, decreased after rainy season at same sites mentioned above. The spread of the relative deviation near the river mouth suggests that there are new sources after the storms.

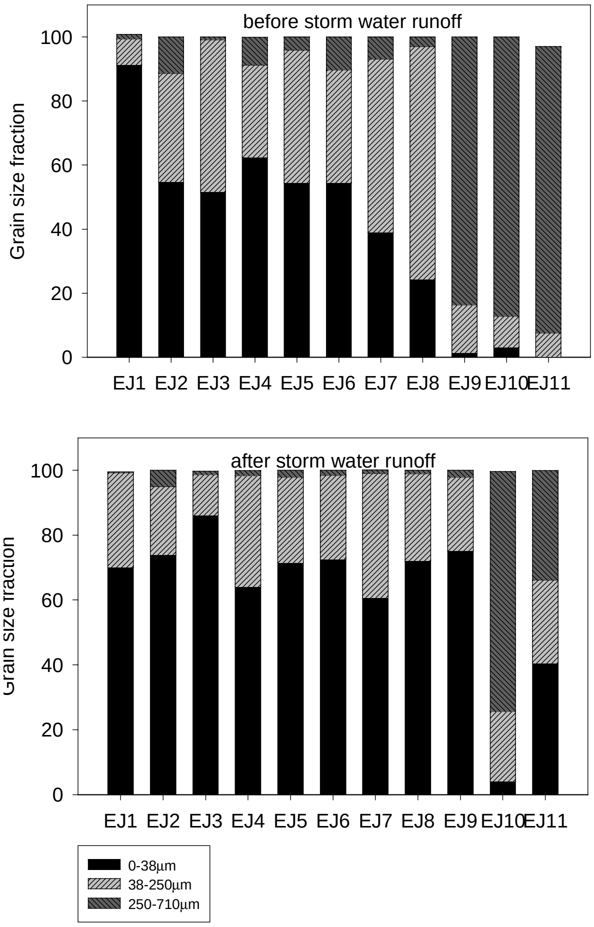

Fig. 4a and 4b. The effect of precipitation on grain size fraction of sediment, grain size shift from gradually coarser to evenly finer distribution.

The average relative deviations of estuary (EJ2 to EJ8) and river mouth only (EJ9 to EJ11) were shown in fig.6a and 6b. Obviously, the relative ratio deviations on river mouth sites could be grouped as two compartments, light PCBs and heavy PCBs. Light PCBs such as CB18, CB28&31, CB52 and CB44 increased from 20 % (CB28&31) to 71 % (CB18) after rainy season, while heavy PCBs, CB101, CB118, CB149, CB180, and CB194, decreased 28 % (CB101) to 114 % (CB180) after that period. Unlike the river mouth sites, the deviations of estuarine sites were slight.

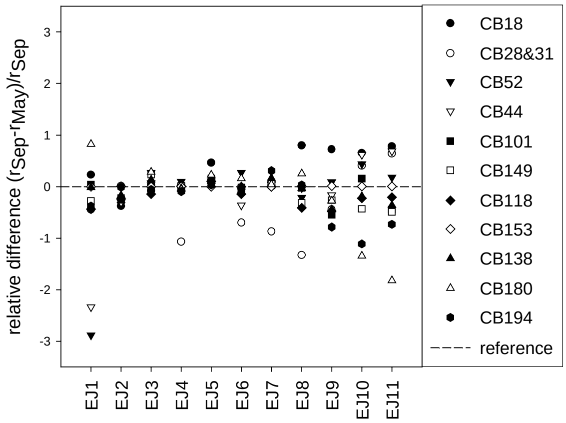

Fig. 5. Relative deviation of CBn/CB153 between May and September, those downstream sites of EJ6 showed gradually spread pattern that revealed the influence from the combined sewage outlet after precipitation.

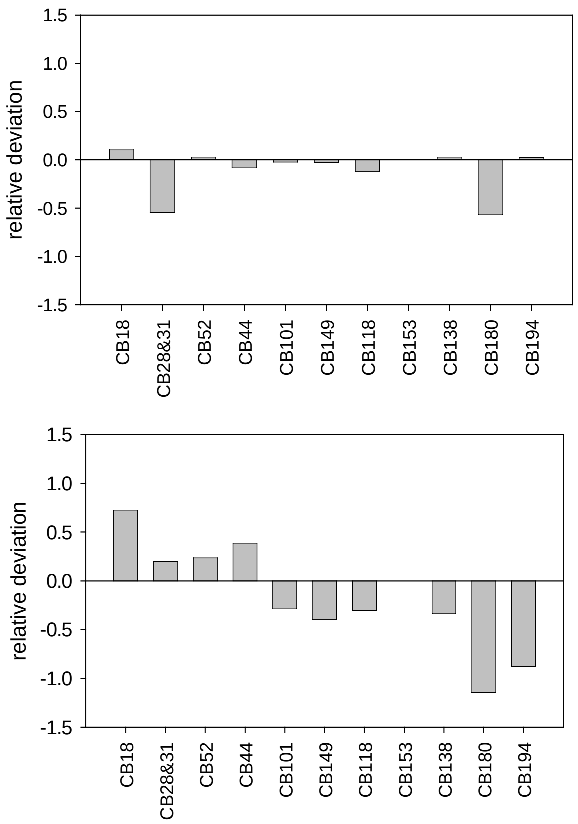

Fig.6. Relative deviation of CB/CB153 between May and September at the estuary (above) and the river mouth (down). Concentration of light PCB increased and that of heavy PCB decreased after precipitation at river mouth.

PCBs in fish. Fishes caught on September 2002 were analyzed for body burdens of PCBs. The average size and weight were 19.3 ± 0.55cm and 96.6 ± 11.6g, respectively. The dried-tissue-based body burden ΣPCB_{12DT} ranged from 204 ng/g to 489 ng/g and with the mean value of 356 ng/g. The lipid normalized body burden ΣPCB_{12LP} were in the range of 3023 ng/g to 9947 ng/g and with the mean value of 5747 ng/g. All fishes were *mullet*, which were bottom feeders and whose main food sources were detritus in the surface sediments. The ratios of PCB content of mullet tissue to that of sediments (C_B/C_S) represent the biomagnification factor (BMF). Considering the possible habitat of fishes, the mean value of the PCB contents of estuary sediments (EJ2 to EJ8) were chosen as the Cs. The dried tissue based $\log(C_B/C_S)$ of individual congeners were in the range of 0.45 to 2.01 and with the mean value of 1.10, while that of fish lipid and sediment organic matter adjusted ratios were in the range of –0.08 to 0.13 and with the mean value of 0.006. Fig.7 demonstrated the $\log(C_B/C_S)$ at different season and their mean value. No significant seasonal deviations observed, and all these lipid normalized log (C_B/C_S) approached zero. It means that PCB_s in the sediments and those in the fishes came from the same source(s).

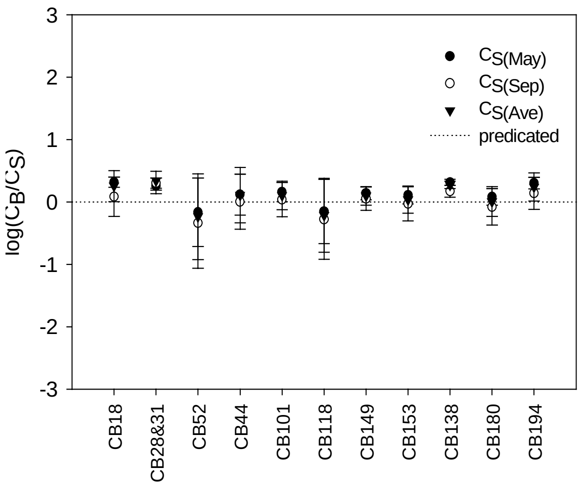

Fig. 7 lipid (organic) normalized log (C_B/C_S) approach zero both on May and September reveled the feasibility of partition equilibrium theorem in this estuary.

The PCB patterns of fishes were also applied as the identification tools for the food source and exposure route of fishes. As mentioned early that the surface sediments in this estuary were the possible food sources due to mullet's feeding behavior. Fig. 8 showed the lipid and organic carbon normalized average PCB_{12} of sediments and fishes. Both the sediments and the fish samples were collected in September. The PCB_{12} of fishes were the average of seven mullet fish samples and sediment values were the average of the estuarine sediments (EJ2-EJ8). The patterns of PCBs in fishes were similar to or slightly higher than those of the sediments for most of the selected congeners except CB52 and CB149, whose contents in the sediments were slightly higher than those in fishes when compared with other congeners.

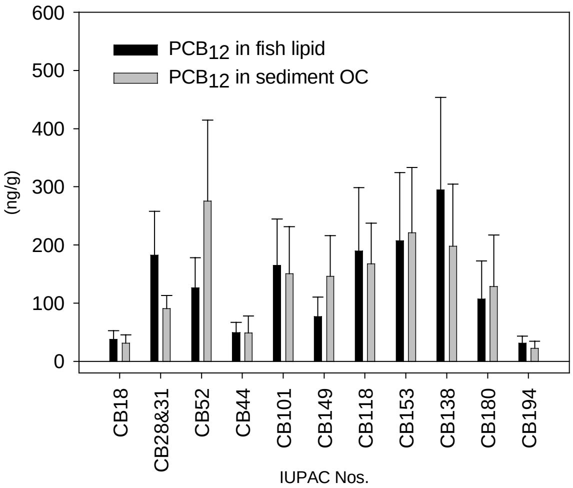

Fig. 8. PCB fingerprint in fish and sediment expressed as the fish lipid and sediment organic matter.

Discussion

Effects of Precipitation. The mean organic carbon contents of sediments collected on September (1.0%) were really less than that of May (1.5%) with the decrease of 33%. The decrease of organic content should not be directly analogized to that of river water as a sole dilution effect, but rather as a combined effect of dilution, erosion and re-deposition.

The gradually declined weight percentage of the fine particle fraction along the estuary shifted to an evenly distributed one suggesting that the surface sediments or the surface soils had been transported downward to river mouth by erosion during the precipitation. Size fraction at the river mouth indicated that the fine particles comprised the major part of the sediment after the rainy season. The source of the fine particles was not clearly identified in this study, nevertheless, erosion of the upstream sediment and the top soils were the possible ones. The atmospheric suspended particles washed down through wet deposition could also be another candidate. Considering the increased grain size fraction, limited in the range of 0-106 μm with the mode of 16-38 μm, were much higher than that of wet deposited atmospheric particulate. It has been reported that the dry deposition of atmospheric PCBs near the estuary, most of the PCBs were bounded on the fine particulate slightly larger than 2.5μm, or ranged in bimodal form (5.6 to 10.0 and 0.31 to 0.52 μm). (Chen *et al*, 1996, Lee *et al*, 1996, Fang, 1998). It was also demonstrated that wet and dry precipitation flux in urban and nonurban area were in the same order. Majority of the total atmospheric washout of PCBs resulted from particle scavenging. The fraction of atmospheric PCBs on particles was the best predictor of atmospheric washout in both urban and nonurban areas (Van et al, 2002). Which might suggest that the deviations of grain size in wet and dry deposition were not significant. It was proposed that wet deposited atmospheric particulates had the potential to increase the fine particulate weight percentage of sediment, but not the main contributor.

Compared with three possible sources mentioned above, the dilution of sediment organic matter was the consequence as the combined effect of the atmospheric wet deposition, the surface runoff and the upstream erosion rather than a sole effect. Particulates from different source with lower organic content mixed with or covered on the original sediments were referred to as a net result of dilution. Purely wet deposition from atmospheric particulates was not proposed because of whose dilution effect was not expected as the other two sources were. Considering the characteristics of grain size and organic content, surface runoff and upstream erosion of precipitation seemed as the main contributor on the variation of sediments.

PCBs in sediment. The average ΣPCB_{12} concentration of sediment were 17.3 ± 12.8 and 12.6 ± 7.2 ng/g-dw of May and September respectively. The mean values were much lower than that of the early 1990'. Since the sediments of the estuary has never been dredged for the past decade, the decrease of PCBs in the estuary suggests that above stated dilution effect might be one of the main mechanisms responsible for the sink of PCBs.

Before the wet season, the higher ΣPCB_{12DS} were found near the suspected hot spots of the Sanyekon Creek, the Nandin Bridge, and the combined sewer outlet, while that shifted to the lower estuary after summer storms. The ratio of summation of ΣPCB_{12DS} of upper estuary (EJ1 to EJ6) to that of whole estuary shifted from 0.72 to 0.60 just illustrating this phenomenon. The erosion of upstream sediments downward to lower estuary seemed the most probable reason for this shift. The fine particle fraction of EJ1 decreased from 90% to 70% of the total. On the contrary, particle sizes of the downstream sites all increased at significant amount. The increasing of the percentage of the fine particles highlighted the possibility of sediment transport from upstream. The average ΣPCB_{12DS} of river mouth increased slightly from 4.8 to 6.8 ng/g was the consequence of the accumulation of higher organic matter and higher sorbing capacity.

It has been found that the contents of hydrophobic substances in soils and sediments were proportional to the organic content of that media and such process was regarded as a partitioning process (Chiou *et al*, 1998). As proposed by Burgess et al (2001), organic content, among particles size, surface area, element composition, soot carbon, and polarity indices, is the most important controlling characteristics of PCBs and sediments. According to above concepts, a linear relationship should exist between ΣPCB_{12DS} and the organic carbon content when equilibrium had been achieved. In this study, correlation of ΣPCB_{12} and organic content of sediment varied significantly for May (r = 0.92) and September (r = 0.54) as shown in fig.9. A strong linear relationship in May suggested that equilibrium partitioning of PCBs in the sediment has been achieved, but this equilibrium was disappeared after summer storm events. Slope of the above correlation formulas, represent the average partitioning capacity of sediments toward PCBs, decreased from 1196 to 963 ng/gOC, which strengthen the hypothesis of equilibrium. The relocation of the sediments not only rearranged the composition of grain size, organic content, and PCB contents, but also destabilized the partitioning equilibrium.

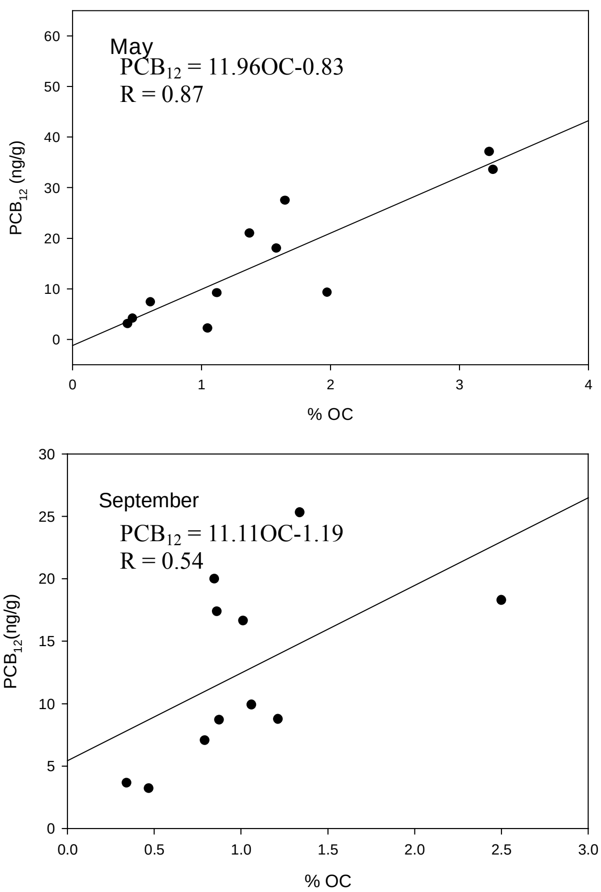

Fig. 8 Correlation of the PCB_{12} and the sediment organic carbon on May (above) and Sep. (down)

The obvious pattern rearrangement in river mouth was resulted from the different origins of the sediments. Higher portion of light PCBs in the river mouth revealed that additional source other than the original surface sediments had been introduced into this region. The most probable additional source was the non-point sources collected and transported by sewage, which was drained into the estuary. Investigation on the topsoils in the catchment of the sewer system near the estuary in year 2001 showed different PCB pattern from the sediment. The light PCBs comprised much higher portion in topsoil than that in sediment (Wang, 2001). It was proposed that particles in surface runoff with higher light PCB contents drained into the estuary might had mixed or masked the originally higher-heavy-PCB content sediments and resulted in the net increase on the fraction of light PCBs. However, downward the sewer outlet, the ratios of the light PCBs on EJ6, EJ7, and EJ8 were nearly unchanged and there was no significant influence observed. The originally higher organic content and finer grain size of these three sites buffered the invaded particles and obscured the influences.

PCB in Fish. The PCBs in fishes have been accumulated to an extremely high concentrations with amean of 356 ng/g for twelve selected congeners. It revealed that much higher body burden of fish could be expected if we summarized all the 209 congeners.

There were several models used to predict the fish body burden of hydrophobic substances, from simple partition theorem to complicated physiological based rate approach. The concept of partitioning was the one mostly applied in food chain system. Wang (Wang *et al*, 1999) used the equilibrium partitioning formula to predicate the relationship between the sediments and the periphytic biolayers. Both were based on the concept of fugacity and proposed by Karickhoff and Gobas, respectively. According to Karickhoff's concept (1984), fugacity within water, sediment and biota should equal when at equilibrium. Both models predict that hydrophobic substances such as PCBs will be retained in sediments or biota bodies following the partitioning rule, and these substances in the sediment organic matter and biota lipid should be similar.

In this study, the PCBs in the fishes were hypothesized originated from the surface sediments, the detritus on which comprised the majority food source of theses fishes. Thus, the contents and fingerprints of sediments' PCBs were expected to equal to that of fishes. The ratios of the organic- and lipid-normalized PCB contents, $(C_{\mathrm{b}} / C_{\mathrm{oc}})$, represent the biomagnification factor(BMF). The logarithm values of BMF of individual congener $log(C_{\mathrm{b}} / C_{\mathrm{oc}})$ are quite close to the reference line $log(C_{\mathrm{b}} / C_{\mathrm{oc}}) = 0$, which reveals that the partitioning equilibrium between sediments and fishes has been achieved, and suggests that the above partition theorem is feasible in Er-Jen estuary.

PCB patterns in fishes and sediments were similar, which was suggested by the exposure model. However, biomagnified heavy PCBs were not much higher than the light ones as reported by several studies, which indicated that light PCBs might be biotransformed outside their body and resulted in a different pattern between the feeders and their food (Teil *et al*, 1996; Willman, 1997). The deviations of the pattern for all selected congeners may be attributed to two reasons, age of the fishes and the short food chain. The fishes were all juvenile and were proposed at the low trophic level, which partitioning equilibrium had been achieved for all congeners between fish and sediments, and short food chain alleviated the possibility of biomagnification through another sublevel biota. On the other hand, biotransformation function of light PCBs may not be fully developed for the juveniles also lowered the function of biotransformation of the light PCBs. Nevertheless, the relatively similar fingerprints between sediments and fishes strengthened the hypothesis that we had proposed on the fish exposure routes.

Conclusion

The stream segments near the former suspected hot spots with external pollution source was studied in this paper. Identification of the seasonal variation on the characteristics of sediments suggests that the precipitation happened in the late summer was the main influencing factor for such variation. Averaged PCB contents in sediments decreased from 17.3 to 12.6 ng/g after the wet season. In addition, observed reduction of grain size and organic content of estuarine sediments revealed the influences of precipitation. Strong relation (r = 0.87) between organic and PCB contents observed before the wet season were disturbed afterwards (r = 0.54). The sediments of the sensitive river mouth with lower organic content and coarser grains made themselves easily effected by additional pollution.

Gradually spread of the relative deviation downward the sewage outlet and increased light PCB content in river mouth suggest that the surface runoff should be responsible for such phenomenon. Topsoils in the sewer collecting catchment with higher percentage of the light PCB was proposed to rearrange the PCB pattern in the sediment downward the outlet. Preliminary study on the exposure routes of PCBs toward the fishes revealed that the organic normalized PCB content and fingerprint between the fishes and the estuarine sediments are relatively close and similar. Logarithm values of the ratios of PCBs in the fish lipid to the PCBs in the sediment organic matter approached zero illustrated that the partitioning equilibrium has been achieved in these two compartments. Relatively similar fingerprints of PCBs in fishes and the sediments strengthened the hypothesis of the exposureroutes suggested above. It was found that the river sediments are the main sourcd of PCBS of fishes. Dredging of the estuarine sediment will efficiently reduced the PCB contents both in the s and the fishes

Reference

Agrell, Cecilia; Larsson, Per; Okla, Lennart; Agrell, Jep, 2002, "PCB congeners in precipitation, wash out ratios and depositional fluxes within the Baltic Sea region, Europe" 36(2), 371-383

Burgess R. M., Ryba S. A., and Cantwell M. G. 2001 "Exploratory analysis of the effects of particulate characteristics on the variation in partitioning of nonpolar organic contaminants to marine sediments" Wat. Res. 35(18) 4390-4404

Bremle G, Larsson P., 1997,"Long term variations of PCB in the water of a river in relation to precipitation and internal sources." *Environ Sci Technol,* 31 (11): 3232-3237

Bruhn R, and McLachlan M.S., 2002 "Seasonal variation of polychlorinated biphenyl concentrations in the southern part of the Baltic Sea." *Mar Pollut Bull*, 44 (2): 156-163

Chen S.J., Hsieh L.T., and Hwang P.S., 1996, "Concentration, phase distribution, and size distribution of atmospheric polychlorinated biphenyls measured in southern Taiwan." *Environ Int.* 22 (4): 411-423

Chiou C. T., McGroddy S. E. and Kile D. E., 1998 " Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments" *Environ Sci Technol* 32(2) 264-269

Fang G.C. 1998 "Dry deposition of atmospheric pollutants in Taiwan." *J. Environ Sci Heal A,* 33 (8): 1803-1823

Gobas F. A. P. C., BEDARD D. C., Ciborowski J. J. H. and Haffner G. D. J. 1989 " Bioaccumulation of chlorinated hydrocarbon by the mayfly (*Hexagenia limbata*) in Lake St. Clair." *J. Great Lakes Res.* V15 (4), 581-588

Huang C.W., Miyata H., and Lu Jr., 1992, "Levels of PCBS, PCDDS and PCDFS in soil samples from incineration sites for metal reclamation in Taiwan." *Chemosphere*, 24 (11): 1669-1676

Huhnerfuss H., Pfaffenber B., and Gehrcke B., 1995 "Stereochemical effects of PCBs in the Marine environment – Seasonal variation of coplanar and atropisomeric PCBs in blue mussels of the German bight." *Mar. Pollut Bull* 30 (5): 332-340

Karickhoff S. W. 1984, " Organic pollutant sorption in aquatic system." *J. Hydraul. Eng.* 110, 833-849

Kiss G, Varga-Puchony Z, and Tolnai B, 2001 "The seasonal changes in the concentration of polycyclic aromatic hydrocarbons in precipitation and aerosol near Lake Balaton, Hungary" *Environ Pollut* 114 (1): 55-61

Ling Y.C., Soong D.K., Lee M.K., 1995, "PCDD/DFS and Coplanar PCBs in sediment and fish sample from the ER-JEN River in Taiwan "*Chemosphere*, 31 (3): 2863-2872 AUG

Teil M. J., Blanchard M., Carru A. M., Chesterikoff A., and Chevreuil M. 1996 " Partition of metallic and organochlorinated pollutants and monoorthosubstituted PCB pattern in the trophic web from different areas of river Seine" *Sci Total Environ.* 181, 111-123

Van Ry DA, Gigliotti CL, and Glenn TR, 2002, "Wet deposition of polychlorinated Biphenyls in urban and background areas of the mid-Atlantic states." *Environ Sci Technol* 36 (15): 3201-3209

Wang, Hong; Kostel, Jill A.; St. Amand, Ann L.; Gray, Kimberly A , 1999, "The response of a laboratory stream system to PCB exposure: study of periphytic and sediment accumulation patterns", *Wat. Res.* 33(18), 3749-3761

Wang, S.M., 2001, "The spatial distribution and temporal trend of PCBs in the environment – Wan Li area for example. " Master thesis, Department of environmental engineering, National Taiwan University.

Willman E. J. Neesvig J. B. M., and Armstrong D. E. 1997 " Influence of ortho-substitution on patterns of PCBaccumulation in sediment, plankton, and fish in a fresh water estuary." *Environ Sci Technol* 31(12) 3712-37