Chemosphere, Vol. 64, No. 9, 2006, pp. 1545-1549

Persistent organic pollution characterization of sediments in Pearl River estuary

K.W. Chau
Department of Civil and Structural Engineering, Hong Kong Polytechnic University, Hong Kong
Email: cekwchau@polyu.edu.hk

Abstract

As a byproduct of rapid urbanization and industrial development in the Pearl River estuary of South China, excessive release of various types of persistent toxic substances were conveyed from agricultural, industrial and municipal discharges at upstream section down into the estuary largely via various river outlets. In this paper, a persistent organic pollution (POP) characterization of sediments in the estuary is undertaken. More than one bioavailable toxicants are detected to play active roles in causing toxicity of marine sediments in the estuary. POPs may be transported for long distances to the downstream end of the Pearl River Delta region. The data suggests that DDT might still be applied illegally within the region recently and that the prevalent levels of DDTs and HCHs in sediments are likely to pose detrimental biological effects on benthic organisms. The findings have significant implications in order to understand the environmental changes, to determine reasonable ways for future development, and to maintain a sustainable environment in the Pearl River estuary region.

Keywords: Pearl River estuary; Persistent organic pollution, contamination; South China; Toxicology characterization; sediment

1. Introduction

The rapid economic boom and growing agricultural, industrial and municipal development in the delta region of the Pearl River estuary, which is one of the largest river systems in China, leads to substantial accumulation of toxic organic compounds and a significant environmental impact has been imposed on the ambient conditions (Chau 2001; Mai et al. 2001; Chau and Jiang 2002). In estuarine ecosystems, settling or sedimentation on the seabed has been identified as an important fate of contaminants. Sediments act both as a pollutant sink and as a carrier and future source of contaminants. These pollutants are not necessarily fixed permanently to sediments, but may be recycled via chemical and biological processes. They may re-suspend to water column. Benthic organisms may also be affected through direct association with contaminated particles. Bioaccumulation and food chain effect may also be built up. The endocrine disruptors in the bottom sediments pose a potential environmental threat to ambient aquatic organisms with their chronic toxicity (Burgess 2000; Ho et al. 2002; Hosokawa et al. 2003). The identification of toxicants affecting aquatic benthic system is critical to sound assessment and management of water bodies. Knowledge of the causes of toxicity which shifted benthic community structure would be helpful in performing ecological risk assessments (Ho et al. 1997; Burgess et al. 2000; Stronkhorst et al. 2003).

In this paper, a toxicity characterization of sediments in the estuary is undertaken. The available data on persistent organic pollution (POP) in sediments within the Pearl River delta are gleaned and compiled. This study will serve as an assessment of the recent status, severity, distribution, and environmental consequence of detected contaminants in sediments. It could provide possible insight as well as future prospective for overall strategic environmental planning and management of the Pearl River delta. The findings may have significant implications in order to understand the environmental changes, to determine reasonable ways for future development, and to maintain a sustainable environment in the Pearl River estuary region.

2. Existing Conditions in Pearl River Estuary

During the past two decades, the Pearl River delta is a significant and quickly developing economic zone in China. The region includes eight major cities in Guangdong Province of China, namely, Dongguan; Foshan; Guangzhou; Huizhou; Jiangmen; Shenzhen; and, Zhongshan. There are many potential pollutant sources in the Pearl River delta, including contaminants derived from improper agriculture discharge, high shipping activities, heavy manufacturing effluent discharge, high volume of vehicular emissions, petrochemical industrial practices, municipal and industrial sewage disposal practices of low standard, and so on. The release is largely discharged to the downstream of the Pearl River estuary through five outlets, namely, Hu men, Jiao men, Hongqi men, Heng men, and Shenzhen River. Moreover, untreated sewage with enormous amount of various pollutants is discharged in an escalating volume. The water quality within the delta is found to be deteriorating (Jin et al. 1998; Hong et al. 1999; Chau and Jiang 2002).

Whilst many different types of pollutants exist in the Pearl River estuary, POPs are exceptionally hazardous due to their toxicity to human beings by nature, their impact on non-target organisms, their bioaccumulation capability in the tissues of animals and humans via the food chain, and their long-term persistence in the environment. For other contaminants, harmful environmental impacts are correlated with high concentrations in vicinity to input sources. On the contrary, POPs may be transported for long distances via air, rivers, and ocean currents without diminishing in effect. Through the interaction of tidal effects as well as runoff discharge, these pollutants may be transported from these outlets towards the entrance of the estuary.

The Hong Kong and Macau Special Administrative Regions are located at the downstream end of the estuary. The impact due to transboundary pollution from the inner Pearl River delta may potentially add complication to the environmental protection tasks in these Special Administrative Regions. Whilst discrete information is available in the estuary with regard to the prevalent conditions of the POP that were reported to have detrimental effects elsewhere, a necessity arises to determine the fates of these pollutants from the Pearl River delta in the ambient sediments in both quantitative and qualitative terms. In particular, increasing interactions as well as number of projects are undertaken which in turn lead to more attention to the region (Chau 2001 & 2002). In fact, two dimensional and three-dimensional models have been developed and employed in the Pearl River estuary region (Chau and Jiang 2001 & 2002) in order to simulate the environmental hydraulics and to make predictions on possible pollution scenarios.

3. POP Characterization of Sediments

The significance of sediment phase in the fate and transport of contaminants is well recognized. Isolated research efforts have been performed on surficial sediments in assessing the pollution of water bodies. Current concentrations of various POPs in sediments of Pearl River delta can be gleaned from the literature (Fu et al. 2001; Hong et al. 1999; Kang et al. 2000; Mai et al. 2001; Wu et al. 1999; Yuan et al. 2001; Zheng et al. 2001).

3.1 Polycyclic aromatic hydrocarbons (PAHs)

It is observed that PAHs are prevalent contaminants as a result of the heavy anthropogenic and industrial activities, such as incomplete combustion of fuel, petrochemical industrial practices, vehicular emissions and power plant emissions, in the Pearl River delta. Concentrations of total PAHs in sediment samples ranging from 156 to 10811 ng/g have been recorded (Fu et al. 2001; Mai et al. 2001). Moreover, the alkylated/non-alkylated ratio is found to be about 2 and the ratio between high molecular weight (HMW)/low molecular weight (LMW), denoting four to six-ring PAHs and two to three-ring PAHs, respectively is 1 or so. Whilst it is generally acknowledged that refined petroleum products comprises primarily LMW PAHs and alkylated PAHs, the relatively high alkylated/non-alkylated ratio and relatively low HMW/LMW indicate that the PAH pollution was mainly contributed by petroleum input. The explanation of this phenomenon might be justified by the heavy commercial as well as industrial shipping activities, including ship discharges and accidental oil spills in the estuary, over a long period.

3.2 Organochlorine pesticides (DDT & HCH)

Various organochlorine pesticides and related compounds were applied extensively in agricultural practices and might lead to accumulation in marine sediments via various runoff and watercourses. It should be noted that many types of organochlorine pesticides including Dichloro diphenyl trichloroethane (DDT) and hexachlorocyclohexanes (HCH) have been officially banned in China since 1983. A current high pesticide residue value might indicate their illegal uses after the banning. It is revealed from the sampled results that certain organochlorine pesticides, including DDT and related compounds, dichloro chlorophenyl chlorophenylethane (DDD) and dichloro chlorophenyl chlorophenylethylene (DDE), and HCH, exist extensively, whilst other commonly detected chlorinated pesticides are only trivial. It is noted that the concentrations of DDT and HCH range from 3 to 1629 ng/g and from 1 to 101 ng/g, respectively (Wu et al. 1999). Whilst HCH exhibits a relatively high composition of β-HCH, the ratios of DDT/(DDD+DDE) and DDT/DDE are about 6 and 26, respectively. It should be noted that DDT undergoes natural and dehydrochlorinated degradation to DDD and DDE under anaerobic and aerobic conditions, respectively. Thus, the relatively high ratio of DDT/(DDD+DDE) may be brought about by slow degradation of DDT or fresh illegal input of DDT compounds in this zone. These are signs that the estuary sediments have accumulated a considerable amount of DDTs from surface runoff and/or river discharge recently. Moreover, aerobic degradation may be deterred by high concentration of adjacent DDT source (Pereira et al. 1996). This deduction is further reinforced by the relatively high ratio of DDT/DDE.

3.3 Butyltins

It is noted that, for a long duration, organotin and other butyltin compounds, such as tributyltin (TBT), are often employed as an important ingredient of the antifouling agent in paints of ships in the estuary. Hence, the leaching from ship paint is in general considered the major sources of TBT in coastal sediments. However, the degree of pollution will vary depending on the frequency of shipping activities at the concerned location. Within the Pearl River estuary delta region, the recorded concentrations of TBT in the sediment samples range from 2 to 380 ng/g (Yuan et al. 2001). At the same time, concentrations of dibutyltin (DBT) and monobutyltin (MBT), which are the naturally degraded forms of TBT, are also quite abundant. High values of butyltins illustrate heavy shipping activities, in accommodating both large domestic and foreign vessels, in this major navigation channel in southern China.

3.4 Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF)

The primary sources of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) include waste incineration, combustion of PVC in landfill fires, production processes of PVC, vehicular emissions with leaded petrol, and so on. These activities in the Pearl River delta are very common. The concentrations of PCDD and PCDF in the surface sediment of the area are found to be between 472 to 2502 pg/g of dry weight (Zheng et al. 2001), which may be attributable to the extensive use of sodium pentachlorophenate (Na-PCP) in the upper reaches of the Pearl River in previous times. Nowadays, though Na-PCP has already been abandoned for quite some time and is no longer used recently, the persistent PCDD/Fs have been accumulated and remained in sediments. This justifies why high values of concentration remain.

3.5 Polychlorinated biphenyls (PCBs)

Possible sources of Polychlorinated biphenyls (PCBs) include insulation product in electrical equipments, combustion of chlorine-containing waste, processes involving organochlorines, vehicular emissions, and so on. From the measured data, the observed concentrations of PCB in the sediment samples, ranging from 10 to 486 ng/g, are not excessively high (Hong et al. 1999; Kang et al. 2000). It might be easily concluded that PCBs are neither major contaminants nor a major environmental threat in most of the Pearl River delta area. The high assimilative and self-purification capabilities of the estuary against anthropogenic activities and pollution impact via large runoff discharge during wet season and enormous sediment loads might be the major abating factors. Moreover, this may also be supplemented by various biogeochemical processes including volatilization, biodegradation, and so on. However, the situation might still be adverse at certain highly industrialized and urbanized areas such as Huangpujiang in Guangzhou.

4. Discussions

As far as of PAHs is concerned, environments in the Pearl River delta are considered moderately contaminated. Although its concentration is in general low compared with other highly polluted industrialized countries, such as Boston Harbor

(Shiaris and Jambard-Sweet 1986), Chespeake Bay (Foster and Wright 1988), and New Bedfor Harbor (Pruell et al. 1990) as shown in Table 1, the bioavailability of PAHs and bioaccumulation of PAHs by organisms can still be significant. Further studies on the impact of PAHs to different types of marine organisms in the Pearl River delta are to be undertaken.

Prior to 1983 when the usage of DDT has been banned, it was extensively used in China for many years. Since the current existence of any DDTs in the sediment should primarily be attributed to residue from the earlier usage, the expected trend is a gradual reduction of DDT concentrations over the years, which appears not to be the case in reality. Thus, in order to prevent further deterioration of the situation, more stringent controls have to be imposed on further disposal of DDTs and HCHs. This issue should be addressed with the highest priority and most urgent attention by the pertinent authorities.

Whilst it is delighted to note the relatively low TBT concentration, the high MBT concentration is observed in the sediment in the Pearl River delta. This shows that the butyltins have on the whole undergone chemical as well as microbial degradation. The generally short half-life of TBT may be due to the highly contaminated water. In this regard, Hattori et al. (1988) discovered that high contamination might facilitate the degradation process. In order to determine whether or not alarming level is already reached and whether or not new legislation should be enacted, continuous and more systematic monitoring of concentrations of various forms of organotin should be conducted in the Pearl River delta, particularly in areas with frequent shipping activities such as Victoria Harbor and Huangpu Harbor.

Recently, there is growing evidence that the organic micro-polluting PCDD/F compounds are awfully hazardous to aquatic ecosystems, particularly in view of their capability of bioaccumulation via the food chain (Loonen et al. 1996). It will be very helpful to perform an extensive monitoring program to gauge the temporal as well as spatial distribution and contamination levels of PCDD/Fs in sediments within the Pearl River delta region. Further research covering other media as well should also be undertaken.

The current condition for PCBs is quite similar to organochlorine pesticides. They were banned in 1983, yet a large proportion of PCBs still remain in use at present in older transformers and capacitors. Future research should be conducted to report infringement instances for prevention of further contamination to the environment. Rigorous surveillance and monitoring on the disposal of these organic chemicals is also entailed.

Table 2 shows the concentrations of POPs in surface sediments at different locations of the Pearl River delta. It is apparent that the concentrations of various POPs are in general higher at the upstream and decrease towards the downstream. Since there are almost no POP sources within the Hong Kong territories, all the concentrations would be derived through pollutant transport from the upstream locations of the estuary, with diminishing values following the dilution effect along the distance. It can be deduced that the impact due to transboundary pollution from the inner estuary is apparent in both HKSAR and Macau SAR located at the downstream end of the Pearl River Delta region. Long and Morgan (1990) has correlated the potential for biological effects of different concentrations of sediment-sorbed contaminants according to an extensive literature review. He ranked all these data from low to high degrees of adverse biological effects and termed the 10^{th} and 50^{th} percentiles as effects range low (ER-L) and effects range median (ER-M), respectively. The physical meanings of ER-L and ER-M values are possibility of toxic biological effects on benthic organism and high possibility of detrimental biological effects on benthic organisms, respectively. Figure 1 shows the concentrations of various contaminants in sediments of the Pearl River delta, which are based on Table 2 and represent average from different locations, in comparison with their corresponding ER-L and ER-M values. Since the concentration of DDT is above the ER-L value, it might have high possibility to pose detrimental biological effects on benthic organisms. On the other hand, the total PAH and PCB concentrations in the sediments are below the ER-L values, which indicate possible toxic biological effects for benthic organisms only. It can be deduced that, during the dry season when the runoff discharge may not be large enough to dilute and flush out the organochlorine compounds, the most crucial situation occurs.

In order to advocate sustainable management and to avoid further deterioration of the existing condition in the Pearl River delta, a more extensive as well as systematic research is required. For the ultimate formulation of effective strategic environmental management measures, there is a pressing necessity to make rigorous observations and measurements on both the temporal and spatial variations of all POPs in different carrying media as well.

5. Conclusions

In this paper, a POP toxicity characterization of sediments in the Pearl River estuary is undertaken. There are many potential pollutant sources, including contaminants derived from improper agriculture discharge, high shipping activities, heavy manufacturing effluent discharge, high volume of vehicular emissions, petrochemical industrial practices, municipal and industrial sewage disposal practices of low standard, and so on. Whilst no single predominant cause of toxicity is found, more than one bioavailable toxicants are detected to play active roles in causing toxicity of marine sediments in the estuary. POPs may be transported for long distances to the downstream end of the Pearl River Delta region via different means. The data suggests that fresh DDT might still be applied illegally within the region and that the prevalent levels of DDTs and HCHs in sediments are likely to pose detrimental biological effects on benthic organisms. More stringent controls have to be imposed on their further disposal. The findings have significant implications in order to understand the environmental changes, to determine reasonable ways for future development, and to maintain a sustainable environment in the Pearl River estuary region. It may point to the necessity of the implementation of a more extensive as well as systematic research in both temporal and spatial dimensions in order to accomplish the goal of the formulation of an integrated environmental management and planning strategy in an efficient manner.

Acknowledgment

This research was supported by the Internal Competitive Research Grant of Hong Kong Polytechnic University (A-PE26).

References

Burgess, R.M.: 2000, Characterizing and identifying toxicants in marine waters: a review of marine toxicity identification evaluations (TESs). International Journal of Environment and Pollution 13(1-6), 2-33.

Burgess, R.M., Cantwell, M.G., Pelletier, M.C., Ho, K.T., Serbst, J.R., Cook, H.F., Kuhn, A.: 2000, Development of a toxicity identification evaluation procedure for characterizing metal toxicity in marine sediments. Environmental Toxicology and Chemistry 19(4), 982-991.

Chau, K.W.: 2001, Field studies of sediment nutrient fluxes and sediment oxygen demand in Hong Kong. Toxicology 164(1-3), 214-214.

Chau, K.W.: 2002, Field measurements of SOD and sediment nutrient fluxes in a land-locked embayment in Hong Kong. Advances in Environmental Research 6(2), 135-142.

Chau, K.W., Jiang, Y.W.: 2001, 3d numerical model for Pearl River estuary. Journal of Hydraulic Engineering, ASCE 127(1), 72-82.

Chau, K.W., Jiang, Y.W.: 2002, Three-dimensional pollutant transport model for the Pearl River estuary. Water Research 36(8), 2029-2039.

Foster, G.D., Wright, D.A.: 1988 Unsubstituted polynuclear aromatic hydrocarbons in sediments, clam, and clam worms from Chesapeake Bay. Marine Pollutant Bulletin 19(9), 459-465.

Fu, J.M., Sheng, G.Y., Chen, Y., Wang, X.M., Min, Y.S., Peng, P.A., Lee, S.C., Cheng, L.Y., Wang, Z.S.: 1997, Preliminary study of organic pollutants in air of Guangzhou, Hong Kong and Macao. In: Eganhouse, R.P. (ed.), Molecular Markers in Environmental Geochemistry. ACS Symposium Series 671, 164-176.

Fu, J., Wang, Z., Mai, B., Kang, Y.: 2001, Field monitoring of toxic organic pollution in the sediments of Pearl River Estuary and its tributaries. Water Science and Technology 43(2), 83-89.

Hattori, Y., Kobayashi, A., Nonaka, K., Sugimae, A., Nakamoto, M.: 1988, Degradation of tributyltin and dibutyltin compounds in environmental water. Water Science and Technology 20(6-7), 71-76.

Ho, K.T., McKinney, R.A., Kuhn, A., Pelletier, M.C., Burgess, R.M.: 1997, Identification of acute toxicants in New Bedford harbour sediments. Environmental Toxicology and Chemistry 16(3), 551-558.

Ho, K.T., Burgess, R.M., Pelletier, M.C., Serbst, J.R., Ryba, S.A., Cantwell, M.G., Kuhn, A., Raczelowski, P.: 2002, An overview of toxicant identification in sediments and dredged materials. Marine Pollutant Bulletin 44(4), 286-293.

Hong, H., Chen, W., Xu, L., Wang, X., Zhang, L.: 1999, Distribution and fate of organochlorine pollutants in the Pearl River Estuary. Marine Pollution Bulletin 39(1-12), 376-382.

Hosokawa, Y., Yasui, M., Yoshikawa, K., Tanaka, Y., Suzuki, M.: 2003, The nationwide investigation of endocrine disruptors in sediment of harbours. Marine Pollution Bulletin 47(1-6), 132-138.

Jin, H., Egashira, S., Chau, K.W.: 1998, Carbon to chlorophyll-a ratio in modeling long-term eutrophication phenomena. Water Science and Technology 38(11), 227-235.

Kang, Y.H., Sheng, G.Y., Fu, J.M., Mai, B.X., Zhang, G., Lin, Z., Min, Y.S.: 2000, Polychlorinated biphenyls in surface sediments from the Pearl River delta and Macau. Marine Pollution Bulletin 40(9), 794-797.

Long, E.R., Morgan, L.G.: 1990, The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. NOAA Technical Memorandum NOS OMA 52. Seattle, Washington.

Loonen, H., Guchte, C., Parsons, J.R., Voogt, P., Govers, H.A.J.: 1996, Ecological hazard assessment of dioxins: hazards to organisms at different levels of aquatic food web. Science of Total Environment 182(1-3), 93-103.

Mai, B.X., Fu, J.M., Zhang, G., Lin, Z., Min, Y.S., Sheng, G.Y., Wang, X.M.: 2001, Polycyclic aromatic hydrocarbons in sediments from the Pearl River and Estuary, China: spatial and temporal distribution and sources. Applied Geochemistry 16(11-12), 1429-1445.

Pereira, W.E., Hostettler, F.D., Rapp, J.B.: 1996, Distributions and fate of chlorinated pesticides, biomarkers and polycyclic aromatic hydrocarbons in sediments along a contamination gradient from a point-source in San Francisco Bay, California. Marine Environmental Research 41(3), 299-314.

Pruell, R.J, Norwood, C.B., Bowen, R.D., Boothmas, W.S., Rogerson, P.F., Hackett, M., Butterworth, B.C.: 1990, Geochemical study of sediment concentration in New Bedford Harbor, Mass. Marine Environmental Research 29(2), 77-101.

Shiaris, M.P., Jambard-Sweet, D.: 1986, Polycyclic aromatic hydrocarbons in surficial sediments of Boston Harbor Mass, USA. Marine Pollution Bulletin 17(10), 469-472.

Stronkhorst, J., Schot, M.E., Dubbeldam, M.C., Ho, K.T.: 2003, A toxicity identification evaluation of silty marine harbor sediments to characterize persistent and non-persistent constituents. Marine Pollution Bulletin 46(1), 56-64.

Wu, Y., Zhang, J., Zhou, Q.: 1999, Persistent organochlorine residues in sediments from Chinese river/estuary systems. Environmental Pollution 105(1), 143-150.

Yuan, D., Yang, D., Wade, T.L., Qian, Y.: 2001, Status of persistent organic pollutants in the sediment from several estuaries in China. Environmental Pollution 114(1), 101-111.

Zheng, M.H., Chu, S.G., Sheng, G.Y., Min, Y.S., Bao, Z.C., Xu, X.B.: 2001, Polychlorinated dibenzo-p-dixins and dibenzofurans in surface sediments from Pearl River Delta in China. Bulletin of Environmental Contamination Toxicology 66(4), 504-507.

Figure Captions

Figure 1. Concentrations of various contaminants in sediments of the Pearl River delta in comparison with their corresponding ER-L and ER-M values

Table 1. Comparison of concentrations of PAHs in surface sediments in Pearl River delta with other highly polluted industrialized countries

Location	PAHs (ng/g)	References
Pearl River delta	156-10,811	Fu et al. 2001; Mai et al. 2001
Boston Harbor	483-718,000	Shiaris and Jambard-Sweet 1986
Chespeake Bay	555-178,000	Foster and Wright 1988
New Bedfor Harbor	14,000-170,000	Pruell et al. 1990

Table 2. Concentrations of POPs in surface sediments at different locations (ng/g)

Type of POP	Macau Estuary, Macau (n=4)	Victoria Harbor, Hong Kong (n=3)	Lingding Bay, Shenzhen (n=6)	Shiziyang River (n=3)	Huangpu Jiang, Guangzhou (n=3)	Sampling method
PCB	11-22	3.2-16	10.2-11.9	16-30	52.1-486	surface sediment samples (10-20 cm depth) with Van Veen grab
PAH	922-996	330-733	156-1,570	408-854	1,434-10,800	
DDT	trace-79.0	1.4-25.4	2.6-115.6	22.9-40.4	35.1-91.1	
References	Zhang et al. 2001; Fu et al. 2001	Hong et al. 1999; Kang et al. 2000	Hong et al. 1999; Kang et al. 2000	Mai et al. 2001; Fu et al. 2001	Mai et al. 2001; Fu et al. 2001	

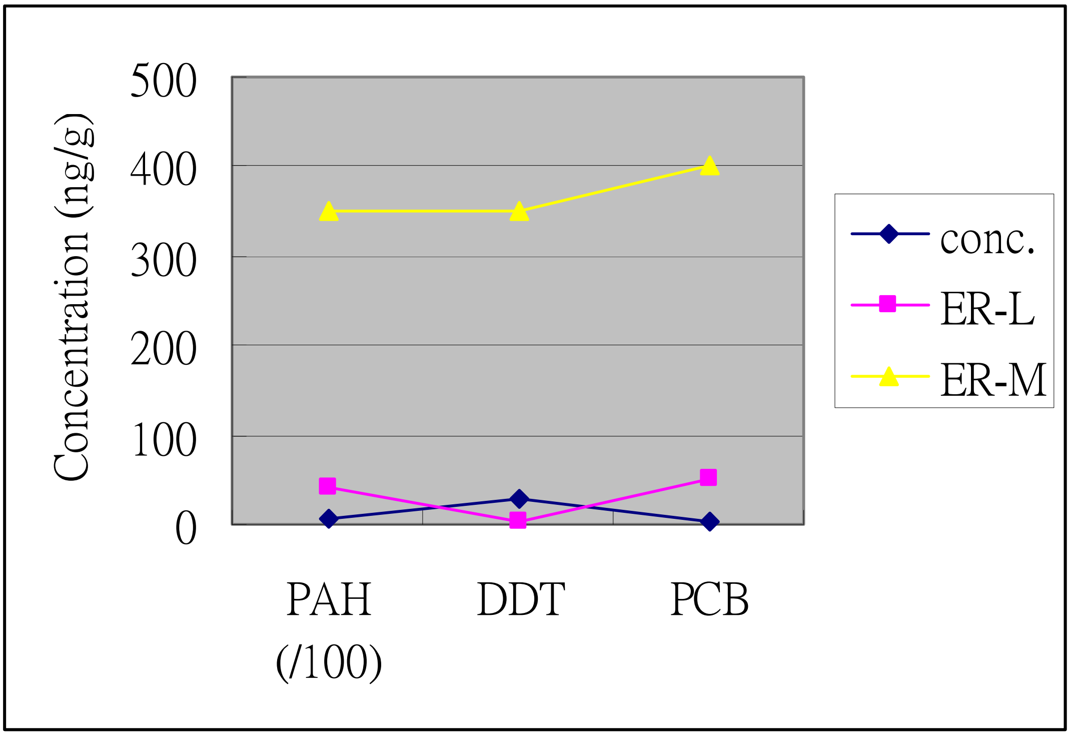
Concentration (ng/g)
500
400
300
200
100
0
PAH
(/100)
DDT
PCB
conc.
ER-L
ER-M

Figure 1.