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Relationships between pesticides and organic carbon fractions in sediments of the Danshui River estuary and adjacent coastal areas of Taiwan

Chin-Chang Hung [a,*], Gwo-Ching Gong [a], Hung-Yu Chen [b], Hwey-Lian Hsieh [c], Peter H. Santschi [d], Terry L. Wade [e], Jose L. Sericano [e]

[a] *Institute of Marine Environmental Chemistry and Ecology, National Taiwan Ocean University, 2 Pei-Ning Road, Keelung 202, Taiwan, ROC*
[b] *Department of Marine Environmental Informatics, National Taiwan Ocean University, Keelung 20224, Taiwan, ROC*
[c] *Research Center for Biodiversity, Academia Sinica, 128 Sec. 2, Academia Road, Nankang, Taipei 115, Taiwan, ROC*
[d] *Laboratory for Oceanography and Environmental Research (LOER), Texas A&M University at Galveston, 5007 Avenue U, Galveston, TX 77551, USA*
[e] *Texas A&M University, Geochemical and Environmental Research Group (GERG), College Station, TX 77845, USA*

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Total organic carbon and black carbon regulate the distribution of trace organic pollutants in sediments of the Danshui River estuary and adjacent coastal areas of Taiwan.

Abstract

In order to understand the fate of pesticides in marine environments, concentrations of pesticides and different carbonaceous fractions were determined for surface sediments in the Danshui River and nearby coastal areas of Taiwan. The major compounds detected were tetrachlorobenzene, HCHs, chlordane, aldrin, DDDs, DDEs and DDTs. Total concentrations of pesticides in the sediments ranged from not detectable to 23 ng g^{-1}, with the maximum value detected near the discharge point of the marine outfall from the Pali sewage treatment plant. These results confirm that pesticides persist in estuarine and nearby coastal environments of the Danshui River well after their ban. Concentrations of total pesticides significantly correlate with concentrations of total organic carbon and black carbon in these sediments, suggesting that total organic carbon and black carbon regulate the distribution of trace organic pollutants in fluvial and coastal marine sediments.

Keywords: Pesticide; Sediments; POC; Black carbon; Danshui River; Taiwan

1. Introduction

Anthropogenic contaminants, such as persistent organic pollutants (POPs), are produced, and temporarily deposited in riverine drainage basins, and subsequently transported down-river over time, to end up, in ports, in estuarine and coastal sediments. The danger is that lipophilic POPs bioaccumulate in marine organisms and are transferred up the food chain. Thus, many of these POPs have been banned for two decades because of concern about detrimental effects on ecosystem and human health. However, their residues still persist in the environment due to their long half-life, about 20–30 years (Woodwell et al., 1971; Sericano et al., 1990).

Taiwan is located in a subtropical region of the world that has remarkably distinct dry and wet seasons. In the dry seasons, most of the pollutants (from point sources or non-point

* Corresponding author. Tel.: +886 2 2462 0330.
E-mail address: cchung@mail.ntou.edu.tw (C.-C. Hung).

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sources) are temporarily deposited in fluvial sediments (e.g., Jiann et al., 2005). During the wet season (often caused by winter monsoon or summer/fall typhoons), both inorganic and organic pollutants are further transported down-river to the coastal marine environment, which can be defined as a secondary transport process. As a consequence, secondary transport processes of fluvial pollutants often result in pollution of coastal ecosystems and marine organisms. For example, "green oysters" have been documented to have been caused by secondary copper pollution on the Taiwan coast (Han and Hung, 1990; Lee et al., 1996; Lin and Hsieh, 1999).

The Danshui River is the largest river in northern Taiwan, with a watershed area of 2726 km^2. The Danshui River includes three branches: the Da-han River, providing fresh water for agricultural crops, the Shin-dan River, containing numerous tea farms in its upper watershed and providing drinking water for citizens in Taipei and neighboring counties, and the Keelung River, containing numerous industrial plants in its drainage basin. Consequently, the Danshui River receives different amounts of POPs and pollutants from these three branches (Jiann et al., 2005), in addition to fallout from atmospheric pollution. According to a recent investigation, Doong et al. (2002a) reported that a variety of organochlorine pesticide (OCP) residues still exist in the fluvial sediments of the Da-han River, suggesting that these river sediments have been contaminated for decades. However, the distribution and fate of organochlorine pesticides in estuarine and coastal marine environments in northern Taiwan is still poorly understood. Previous studies have shown that POPs are strongly bound to organic matter, and recent laboratory experiments have demonstrated that one of the organic carbon fractions, in particular black carbon (BC), can adsorb POPs to a larger extent than expected from total organic matter concentrations (Jonker and Koelmans, 2002). Analogous field investigations have been conducted for PAHs and PCBs, but not for assessing the influence of BC on the distribution of pesticides.

This research investigated the sedimentary distribution of pesticides, including OCPs, as well as carbonaceous materials, including total organic carbon (OC), black carbon and total carbohydrates (TCHO, as a major hydrophilic component of OC), in order to evaluate the sources of POPs and potential contamination of the Danshui River estuary and nearby coastal areas of Taiwan. It is expected that the results of this study will increase our understanding of how organic matter in general, and BC in particular, influence the distribution and sedimentary distribution of organic contaminants.

2. Materials and methods

2.1. Sample collection

Surface sediment samples were collected in the lower Danshui River and nearby coastal areas with a grab sediment sampler (Shiptex; Wildco Inc.) on March 16, 2001 and November 5, 2004. The details of the sampling locations are given in Fig. 1 and Table 1.

2.2. Sample analysis

The grain size in the sediments was measured by wet sieving and pipette analysis as described by Hsieh (1995). The collected samples were transferred to the laboratory and frozen (~−20 °C) until analysis. Freeze-dried sediment samples were first heated at a relatively low temperature (60 °C), after 2–3 treatments with 2 N HCl to remove inorganic carbon. Total organic carbon (TOC) concentrations were determined using a Perkin–Elmer Series II CHNS/O analyzer, Model 2400. Total carbohydrate (TCHO) content was measured based on the method of Hung et al. (2003) and the analytical uncertainty of TCHO method ranged from 5% to 9%. Black carbon (BC) content in the sediment samples was determined by first treating the finely ground sediments three times with 2 N HCl. A 10–15 mg of each sample was then heated at 375 °C in an oxygenated atmosphere for 18 h using a Barnstead Thermolyne Furnace (Model 6000) (Gustafsson et al., 2001). An NIST diesel soot standard (SRM-2975, purchased in 2005) was combusted under identical conditions as the sediment samples, and measured by two different laboratories at Texas A&M University ($79.1 \pm 2.1\%$, $n = 6$) and at National Taiwan Ocean University (78.3 ± 1.3, $n = 6$). The BC content of the SRM-2975 was somewhat higher (i.e., 79%) than the value of 68% reported by Gustafsson et al. (2001), suggesting that our BC values may slightly (by about 10%) overestimate the BC content of our sediment samples, if the BC contents in both batches of NIST SRM-2975 reference materials are similar. However, it is also possible that the two batches of NIST SRM-2975 standards contained somewhat different black carbon contents, as NIST does not certify their SRM-2975 standard for its black carbon content. In addition, the SRM-2975 standard was processed by the CTO-375 method in two different labs and the BC content was measured by two different elemental analyzers. Thus, our measured BC content of the SRM-2975 standard should be reliable. It is thus worthwhile to test the carbon content of individual SRM-2975 batches in the future.

Pesticides in the freeze-dried samples were extracted according to Wade et al. (1988). Briefly, about 10 g freeze-dried sediment were ASE (accelerated solvent extractor, DIONEX)-extracted with methylene chloride. The solvent was concentrated to approximately 20 ml in a flat-bottomed flask equipped with a three-ball Snyder column condenser. The extract was then transferred to Kuderna-Danish tubes, which were heated in a water bath (60 °C) to concentrate the extract to a final volume of 2 ml. During concentration of the solvent, dichloromethane was exchanged for hexane.

Extracts were then fractionated by alumina:silica (80–100 mesh) open column chromatography. Silica gel was activated at 170 °C for 12 h and partially deactivated with 5% (v/w) distilled water. Approximately 20 g of silica gel was slurry packed in dichloromethane over 10 g of alumina. Alumina was activated at 400 °C for 4 h and partially deactivated with 1% distilled water (v/w). Small activated Cu pellets were added to the top of the column to remove sulfur. The dichloromethane was replaced with pentane by elution, and the extract was applied to the top of the column. The extract was eluted from the column with 200 ml of 1:1 pentane–dichloromethane (pesticide/PCB fraction). The fractions were then concentrated to 1 ml using Kuderma-Danish tubes heated in a water bath at 60 °C. Finally, the solution was transferred to a vial, with addition of extra small activated Cu pellets to remove any remaining sulfur compounds before pesticides' analysis.

Quality assurance for each set of 20 samples included a procedural blank and a matrix spike, both of which were carried through the entire analytical scheme as samples and two appropriate standard reference materials (SRM-1939a, SRM-1941b). The determined and certified results are shown in Table 1, indicating that the analytical method in this study can accurately determine pesticides in estuarine and marine sediments. The duplicated measurements for blank, blank spike and matrix spike were conducted in this study and the sediment samples were only conducted as a single measurement. The standard deviation in blank spike and matrix spike for pesticides had an average value 7.8% and 5.2%, respectively. The surrogate 4,4′-dibromooctafluorobiphenyl (DBOFB) was added to the samples prior to extraction and used for quantitative analysis. The chlorinated pesticides were analyzed by gas chromatography in the splitless mode using an electron capture detector (ECD). A 30 m × 0.25 mm I.D. fused silica column with a 0.25 μm DB-5 bonded phase (JW Scientific,

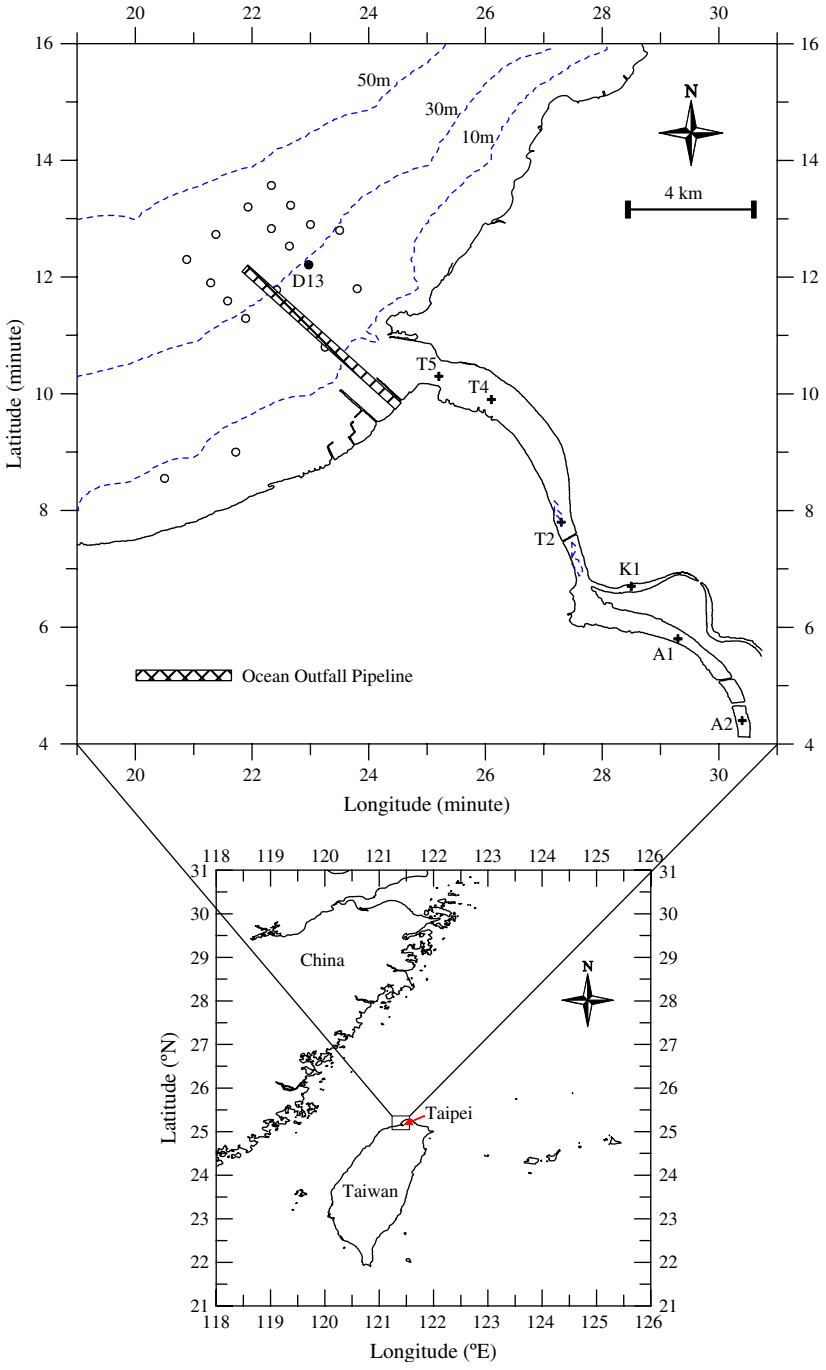

Fig. 1. Sediment sampling stations in the Danshui River and nearby coastal zone of Taiwan.

Inc.) provided component separations. The chromatographic conditions for the pesticides' analysis were 100 °C for 1 min, then 5 °C/min to 250 °C, hold for 1 min, and then 10 °C/min to 300 °C and a final hold of 5 min. The internal standard, 2,4,5,6-tetrachloro-m-xylene (TCMX), was added prior to GC/ECD analysis to monitor the recovery of surrogates, which ranged from 87% to 96%. The QA/QC procedures included analysis of matrix spikes, duplicates, laboratory blanks and certified reference material (Wade and Cantillo, 1994). The method detection limits (Table 2) for each analyte was determined as the Student's t for 99% confidence level times the standard deviation of seven replicate measurements of the same low level sample or spiked sample following the EPA method detailed in 40 CFR Part 136, Appendix B.

3. Results and discussion

3.1. Distributions of organic carbon species and pesticides

Concentrations of total organic carbon (TOC), black carbon (BC), total carbohydrates (TCHO), and ancillary parameters (grain size and ratio of silt/clay) in surface sediments are given and discussed in Hung et al. (2006), and are shown in Table 1.

Concentrations of total and individual pesticides, including tetrachlorobenzene, HCHs, chlordane, aldrin, DDTs, in the

Table 1
Sampling locations, average grain size, organic carbon (TOC), black carbon (BC), total carbohydrates (TCHO) and total ($\sum$) Pesticides in sediments of the Danshui River and nearby coastal zone of Taiwan

Station	Longitude (°E)	Latitude (°N)	Grain size (mm)	TOC ($n=2$) %	BC ($n=2$) %	TCHO (%)	$\sum$Pesticides (ng g^{-1})
A1	121.4867	25.0950	n.a.	0.97 ± 0.08	0.08 ± 0.01	0.061	7.24
A2	121.4983	25.0733	n.a.	0.84 ± 0.06	0.08 ± 0.01	0.048	10.72
K1	121.4750	25.1150	n.a.	1.48 ± 0.07	0.12 ± 0.02	0.117	20.75
T2	121.4483	25.1300	n.a.	0.77 ± 0.04	0.07 ± 0.01	0.055	9.91
T4	121.4350	25.1633	n.a.	0.73 ± 0.07	0.06 ± 0.01	0.036	6.03
T5	121.4200	25.1700	n.a.	0.99 ± 0.09	0.05 ± 0.00	0.018	13.02
B1	121.3417	25.1425	0.11	0.29 ± 0.03	0.05 ± 0.00	0.009	3.21
B2	121.3620	25.1500	0.04	0.54 ± 0.07	0.08 ± 0.01	0.019	10.17
B3	121.3875	25.1800	0.20	0.27 ± 0.04	0.05 ± 0.01	0.003	3.52
B4	121.3967	25.1967	0.15	0.59 ± 0.03	0.07 ± 0.01	0.014	2.78
C2	121.3917	25.2133	0.27	0.37 ± 0.02	0.05 ± 0.00	0.021	2.95
D1	121.3480	25.2050	0.06	0.86 ± 0.06	0.10 ± 0.01	0.080	5.30
D2	121.3563	25.2122	0.06	0.53 ± 0.03	0.09 ± 0.01	0.049	4.49
D3	121.3655	25.2200	0.10	0.54 ± 0.03	0.08 ± 0.01	0.057	4.48
D4	121.3722	25.2262	0.05	0.78 ± 0.07	0.11 ± 0.01	0.060	5.87
D5	121.3548	25.1983	0.16	0.33 ± 0.05	0.06 ± 0.00	0.064	3.17
D6	121.3722	25.2138	0.05	0.75 ± 0.06	0.09 ± 0.01	0.061	5.46
D7	121.3777	25.2205	0.14	0.46 ± 0.04	0.09 ± 0.01	0.030	3.35
D8	121.3597	25.1932	0.03	1.20 ± 0.11	0.11 ± 0.02	0.077	9.44
D9	121.3773	25.2088	0.23	0.29 ± 0.03	0.04 ± 0.00	0.031	1.43
D10	121.3833	25.2150	0.03	0.91 ± 0.05	0.10 ± 0.01	0.075	7.49
D11	121.3648	25.1882	0.03	0.80 ± 0.04	0.09 ± 0.01	0.061	9.05
D12	121.3737	25.1963	0.13	0.42 ± 0.04	0.07 ± 0.01	0.035	3.64
D13	121.3828	25.2035	0.07	1.71 ± 0.10	0.19 ± 0.02	0.100	23.23

n.a., Not available.

Table 2
Recoveries, method detection limits (MDLs) and results from analysis of certified standard sediment reference materials (SRM-1939a, SRM-1941b)

Pesticides	Recovery (%)	MDLs (ng g^{-1})	SRM-1939a		SRM-1941b	
			Determined (ng g^{-1})	Certified (ng g^{-1})	Determined (ng g^{-1})	Certified (ng g^{-1})
Tetrachlorobenzene 1,2,4,5	94.5 ± 2.4	0.11				
Tetrachlorobenzene 1,2,3,4	86.3 ± 1.2	0.05				
Pentachlorobenzene	97.8 ± 0.8	0.05				
Hexachlorobenzene	98.8 ± 3.4	0.04			7.43 ± 0.40	5.83 ± 0.38
α HCH	88.4 ± 1.5	0.12				
β HCH	110.9 ± 5.4	0.04				
γ HCH	90.2 ± 2.7	0.09				
δ HCH	88.1 ± 1.1	0.04				
Heptachlor	110 ± 20	0.03				
Heptachlor epoxide	97.3 ± 1.2	0.02				
Oxychlordane	84.3 ± 1.2	0.05				
α chlordane	87.0 ± 2.4	0.03	4.12 ± 0.12	4.8 ± 1.3	0.51 ± 0.06	0.85 ± 0.11
γ chlordane	91.7 ± 0.9	0.03			0.45 ± 0.03	0.57 ± 0.09
cis-Nonachlor	93.7 ± 1.0	0.02			0.46 ± 0.04	0.38 ± 0.05
trans-Nonachlor	95.4 ± 2.9	0.02			0.29 ± 0.03	0.44 ± 0.07
Aldrin	88.0 ± 3.7	0.02				
Dieldrin	91.3 ± 2.7	0.02				
Endrin	92.2 ± 1.3	0.04				
Pentachloroanisole	94.9 ± 2.3	0.04				
Chlorpyrifos	94 ± 23	0.21				
Mirex	101.9 ± 2.4	0.05				
Endosulfan II	92.5 ± 1.2	0.04				
2,4′ DDE	92.2 ± 2.8	0.04			0.22 ± 0.06	0.38 ± 0.12
4,4′ DDE	86.7 ± 3.4	0.02			3.15 ± 0.10	3.22 ± 0.28
2,4′ DDD	110.9 ± 16.9	0.07				
4,4′ DDD	104.9 ± 11.6	0.03			2.78 ± 0.62	4.66 ± 0.46
2,4′ DDT	91.2 ± 14.5	0.06				
4,4′ DDT	87.3 ± 11.1	0.02	3.13 ± 0.57	2.72 ± 0.42	1.50 ± 0.12	1.12 ± 0.42

Table 3a
Concentrations (ng g^{-1} dry wt.) of individual pesticides in surface sediments of the Danshui River and delta region

Stations	A1	A2	K1	T2	T4	T5	B1	B2	B3	B4	C2
Tetrachlorobenzene 1,2,4,5	0.23	0.30	0.56	0.67	0.22	0.89	0.61	0.96	0.43	0.11	0.87
Tetrachlorobenzene 1,2,3,4	0.21	0.25	0.44	0.15	0.14	0.43	0.13	0.43	0.18	0.24	0.08
Pentachlorobenzene	0.06	n.d.	n.d.	0.20	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.
Hexachlorobenzene	0.29	0.33	0.23	0.24	0.13	0.17	n.d.	0.06	0.04	0.09	n.d.
α HCH	0.25	0.23	0.99	0.28	0.19	0.39	0.15	0.26	0.24	0.14	0.19
β HCH	n.d.	0.07	0.11	0.06	n.d.	0.17	0.34	n.d.	0.25	0.18	0.31
γ HCH	n.d.	n.d.	0.17	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
δ HCH	0.28	n.d.	0.37	0.17	0.08	0.13	0.04	n.d.	n.d.	n.d.	n.d.
Heptachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Heptachlor epoxide	0.14	0.29	0.28	0.51	0.05	0.45	n.d.	n.d.	n.d.	n.d.	n.d.
Oxychlordane	n.d.	n.d.	n.d.	n.d.	0.42	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
α chlordane	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
γ chlordane	n.d.	0.09	0.22	0.08	n.d.	0.14	0.10	0.10	n.d.	n.d.	0.18
cis-Nonachlor	0.05	0.05	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
trans-Nonachlor	n.d.	n.d.	0.26	0.04	0.04	0.23	n.d.	n.d.	n.d.	n.d.	n.d.
Aldrin	1.69	4.95	6.25	2.43	1.46	2.29	0.50	2.10	0.43	0.55	0.46
Dieldrin	0.11	0.42	0.73	0.60	0.77	3.01	n.d.	0.06	n.d.	n.d.	n.d.
Endrin	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	0.23	n.d.
Pentachloroanisole	n.d.	0.11	n.d.	0.38	n.d.	0.68	n.d.	0.06	0.22	0.44	0.06
Chlorpyrifos	n.d.	n.d.	n.d.	n.d.	n.d.	0.24	0.92	1.31	1.30	0.29	0.21
Mirex	0.09	0.11	0.22	0.10	0.05	0.11	n.d.	0.47	n.d.	n.d.	n.d.
Endosulfan II	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4′ DDE	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.
4,4′ DDE	1.01	1.04	2.38	1.06	0.64	0.69	n.d.	0.68	n.d.	n.d.	0.14
2,4′ DDD	0.93	1.23	3.70	1.41	0.84	1.70	0.12	1.65	0.22	0.21	0.24
4,4′ DDD	0.75	0.58	2.36	0.95	0.55	0.96	0.19	0.92	0.22	0.30	0.08
2,4′ DDT	0.25	0.28	0.74	0.38	0.13	0.29	n.d.	0.26	n.d.	n.d.	n.d.
4,4′ DDT	0.91	0.36	0.67	0.22	0.28	n.d.	0.08	0.74	n.d.	n.d.	0.13
Total pesticides (ng g^{-1})	7.24	10.72	20.75	9.91	6.03	13.02	3.21	10.17	3.52	2.78	2.95

n.d., Not detectable (i.e., <detection limit).

surface sediments were detected at most stations (Tables 3a and 3b). Total pesticide concentrations in these sediments ranged from 1.4 to 23 ng g^{-1} (dry wt.). The two highest values that appeared in the investigated area were from the Keelung River (Station K1, 20.8 ng g^{-1}) and a station in the offshore area (Station D13, 23.2 ng g^{-1}). In general, the pesticides in the fluvial sediments along the upper watershed were relatively constant (Fig. 2. Elevated pesticide concentration (13 ng g^{-1}) was found in the river outlet sediments (T5). The TOC distribution in the fluvial sediments appeared in a pattern that mirrored the pesticide distribution (Fig. 2). Work similar to that has been reported in previously, i.e., that fluvial pollutants might be accumulated in the estuary because fluvial colloids flocculate in the estuarine mixing zone (Simpson et al., 1996; Sanudo-Wilhelmy et al., 1996; Doong et al., 2002b). Values of total pesticides (sum of tetrachlorobenzene, HCHs, aldrin, dieldrin, chlorpyrifos, mirex, DDEs, DDDs, and DDTs) of 10–80 ng g^{-1} are typical values for river delta and coastal regions (e.g., Santschi et al., 2001; Lee et al., 2001; Yuan et al., 2001). In comparison, recently reported total pesticide data measured in sediments from the Da-han River, one of the branches of the Danshui River (Doong et al., 2002a), ranged from 0.2 to 14.8 ng g^{-1} dry wt., with an average value of 6.4 ng g^{-1}. These pesticides have thus been widely dispersed, have accumulated in river sediments and have found their way to the coastal environment at similar concentrations. This suggests that many of these pesticides can still enter the marine food chain in the coastal area of the Danshui River.

However, there are some notable exceptions from this pattern (e.g., tetrachlorobenzenes and aldrin), which are difficult to explain. It could be due to different sources of individual POPs in the three branches of the river (the Da-han River, the His-Dan River, and the Keelung River), as well as pollution sources from the atmosphere and a marine outfall of a treatment plant. Interestingly, the maximum pesticides' concentration (23.2 ng g^{-1}, the sum of pesticides, including tetrachlorobenzene, HCHs, aldrin, dieldrin, chlorpyrifos, mirex, DDEs, DDDs, and DDTs, was found in offshore sediments at station D13, approximately 6–7 km from the Danshui River mouth (Fig. 1). Coincidently, the discharge point, with several output pipelines connecting to the main pipeline, of the marine outfall pipeline from the Pali sewage treatment plant is located near this station (Sinotech, 1997).

According to recent studies, surface sediment concentrations in the estuarine area of the Danshui River should reflect recent pollutant inputs to the area, due to the short residence time (i.e., 1–2 days during average river flow conditions) of the Danshui River water and high sedimentation rates (~1 cm/yr) (Wang et al., 2004; Jiann et al., 2005; Chen et al., submitted for publication). Therefore, the fact that individual pesticide concentrations that are found at the station near the marine outfall pipe are high or highest suggests that

Table 3b
Concentrations (ng g^{-1} dry wt.) of individual pesticides in surface sediments offshore from the Danshui River delta region

Stations	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13
Tetrachlorobenzene 1,2,4,5	1.08	0.64	1.00	1.28	0.74	1.30	0.79	1.76	0.09	0.12	1.31	0.14	1.89
Tetrachlorobenzene 1,2,3,4	0.36	0.13	0.12	0.21	0.57	0.08	0.12	0.27	0.11	0.17	0.44	0.14	1.38
Pentachlorobenzene	n.d.	n.d.	n.d.	0.07	n.d.	n.d.	n.d.	n.d.	n.d.	0.06	0.05	n.d.	0.06
Hexachlorobenzene	0.06	0.05	0.06	0.08	n.d.	0.10	n.d.	0.14	0.09	0.25	0.09	0.04	0.17
α HCH	0.21	0.15	0.22	0.18	0.28	0.20	0.18	0.34	0.16	0.27	0.17	0.14	0.37
β HCH	0.11	0.16	0.20	0.22	n.d.	0.21	0.24	0.09	0.36	0.40	0.22	0.17	0.19
γ HCH	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.
δ HCH	0.07	n.d.	0.09	0.12	n.d.	0.13	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Heptachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.
Heptachlor epoxide	n.d.	n.d.	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Oxychlordane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.15
α chlordane	n.d.	n.d.	n.d.	n.d.	n.d.	0.04	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	0.46
γ chlordane	n.d.	0.08	0.04	0.05	0.10	0.04	0.13	0.05	n.d.	0.21	n.d.	n.d.	0.07
cis-Nonachlor	0.04	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.14
trans-Nonachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.12	n.d.	n.d.	n.d.	n.d.	0.30
Aldrin	1.11	0.56	0.81	1.00	0.53	1.26	0.70	1.27	0.56	1.13	1.54	0.83	3.12
Dieldrin	0.07	0.04	0.11	0.13	0.40	0.09	0.05	0.18	n.d.	0.11	0.12	0.05	3.51
Endrin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.
Pentachloroanisole	0.05	n.d.	0.04	0.05	n.d.	0.07	0.04	0.08	0.06	0.32	0.07	0.05	0.08
Chlorpyrifos	0.32	0.55	0.16	0.37	0.09	0.34	0.12	0.83	n.d.	1.41	1.55	0.53	2.42
Mirex	n.d.	0.24	0.05	0.11	n.d.	0.08	n.d.	0.13	n.d.	n.d.	n.d.	n.d.	0.45
Endosulfan II	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2,4′ DDE	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.27
4,4′ DDE	0.46	0.41	0.45	0.65	0.08	0.44	0.25	0.72	n.d.	0.47	0.55	0.19	1.61
2,4′ DDD	0.62	0.61	0.45	0.55	0.22	0.56	0.20	1.69	n.d.	0.79	1.41	0.52	3.57
4,4′ DDD	0.44	0.51	0.26	0.40	0.07	0.31	0.14	0.83	n.d.	0.73	0.74	0.45	1.77
2,4′ DDT	0.15	0.16	0.07	0.18	n.d.	0.13	0.02	0.28	n.d.	0.21	0.24	0.12	0.80
4,4′ DDT	0.16	0.22	0.33	0.22	0.10	0.09	0.31	0.49	n.d.	0.85	0.54	0.26	0.45
Total pesticides (ng g^{-1})	5.30	4.49	4.48	5.87	3.17	5.46	3.35	9.44	1.43	7.49	9.05	3.64	23.23

n.d., Not detectable (i.e., <detection limit).

the sewage treatment plant is still discharging pesticides from residual activated sludges and/or fine particles (Fig. 3). For example, the average cyclodiene concentration (*A*, as the sum of aldrin, dieldrin and endrin) decreased along the river to its mouth, and also with water depth from the marine outfall region to the offshore station, suggesting that these pollutants are still being dispersed to surface sediments from points near the outfall. Another indication of recent discharges is the observation of total suspended matter (TSM) concentrations near the marine outfall of up to 70 mg/L (Department of Public Sewerage Systems Report, 2001). Therefore, the elevated pesticide concentration at this station is likely from the marine outfall discharge point that contains pesticides from present and past agricultural practices. Based on recently reported data about the quality of sewage discharge (Gong et al., unpublished data), the Pali sewage treatment plant has not operated properly due to budget deficits and/or technical problems in their waste processing system. Additionally, irregular hydrography, extreme discharge events resulting from rainfall during tropical depressions or typhoons, may have also affected the distributions of POPs in sediments from coastal areas adjacent to the Danshui River mouth. In other words, the pollutants sorbed onto deposited fluvial sediments during the dry season will be transported further by floods during the wet season. The famous ‘‘green oysters’’ that have been reported on the Taiwan coast are a good case study for this kind of phenomenon (Han and Hung, 1990; Lee et al., 1996; Lin and Hsieh, 1999).

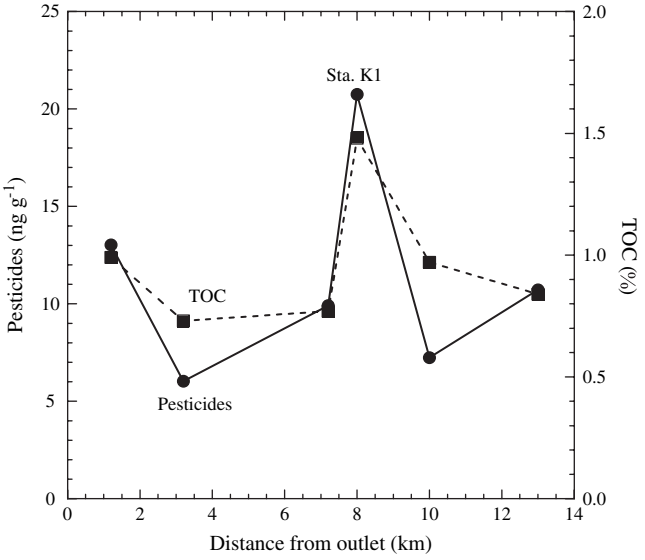

Fig. 2. Concentrations of total pesticides vs. distance from river mouth.

3.2. Relationship between concentrations of pesticides and those of carbonaceous materials

The distributions of POPs, including PAHs and PCBs, can be regulated by several factors, including their source

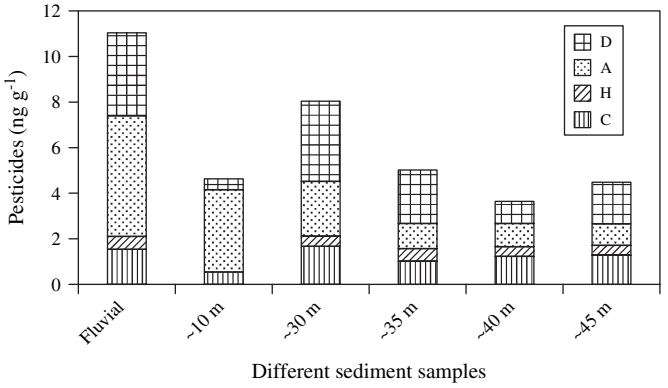

Fig. 3. Distribution of average major pesticide concentrations for the different sediment samples (across a transect from the river mouth to offshore regions based on the average water depth). Fluvial sediment including T5; ~10 m, including B3 and B4; ~30 m, including D11, D12, D13 and C2; ~35 m, including D8, D9 and D10; ~40 m, including D5, D6 and D7; ~45 m, including D1, D2, D3 and D4 (*D*, DDTs + DDDs + DDEs; *A*, aldrin + dieldrin + endrin; *H*, α + β + γ + δ HCH; *C*, 1,2,4,5-tetrachloroben zene + 1,2,3,4-tetrachlorobenzene + pentachlorobenzene + hexachlorobenzene.

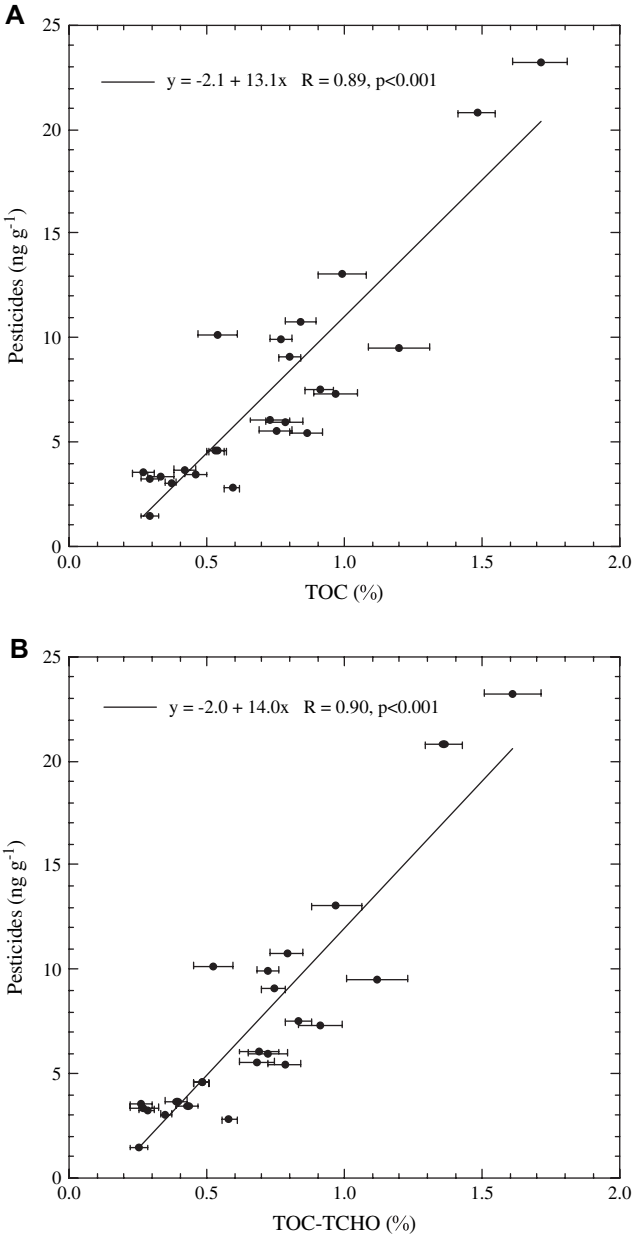

Fig. 4. (A) Relationship between concentrations of total pesticides and TOC. (B) Relationship between concentrations of total pesticides and hydrophobic carbon (TOC−TCHO).

contributions and relative concentrations as well as those of their carrier phases (TOC, BC) during transport, and partitioning rates to suspended particles (Xing, 1997; Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002; Jonker and Koelmans, 2002).

As shown in Fig. 4A and B, pesticides significantly correlate with both total organic carbon (TOC) and hydrophobic organic carbon (calculated as the difference between TOC and total carbohydrates, TCHO). This suggests that the distributions of these OCPs and other pesticides in the estuary are controlled by the distribution of organic matter, and more significantly, the hydrophobic fraction of the sediments. These relationships agree with previous studies that have shown that fate and distributions of OCPs in sediments are controlled by their organic matter content (McKenzie-Smith et al., 1994; Glynn et al., 1995). The significant correlations also suggest that OCPs and organic matter have similar sources prior to transport from the upper watersheds of the three riverine branches of the Danshui River to coastal areas. However, the correlation between BC and pesticides in all sediment samples (including six anoxic fluvial samples) is only slightly less significant than the other carbonaceous materials vs. pesticides (Fig. 5A and B). The correlation between BC and pesticides for the six anoxic fluvial samples (Table 4) is less significant, possibly due to the smaller number of samples, suggesting that BC might be less important for the distribution in the fluvial sediments. The results also reflect the fact that BC and pesticides likely have different sources. BC is from atmospheric sources, mainly from fossil fuel combustion and industrial emissions. BC concentrations in Taipei are higher than normal values from other tropical urban areas (Chou et al., 2003). Pesticides, on the other hand, are likely emitted in the upper watershed of the three branches of the Danshui River.

Subsequent to entering the aquatic environment at different rates, both BC and pesticides will partition to riverine particles. Moreover, when fluvial sediments are transported to the coastal areas, some labile organic carbon might be decomposed by bacteria or released as DOC, which may result in some pesticides' loss as well. We thus hypothesize that when fluvial sediments are re-distributed by flood water over wide areas during strong rain storms or Typhoons, the pesticides have again an opportunity to migrate to the most strongly binding carrier phase, i.e., to BC. In support of our contention, pesticides and BC in coastal sediments significantly correlate, as shown in Fig. 4B (with six anoxic river sediments excluded), as significantly as with TOC (Table 4).

These results suggest that the distribution of pesticides in fluvial sediments are controlled by their organic carbon concentrations, while the distribution of pesticides in coastal

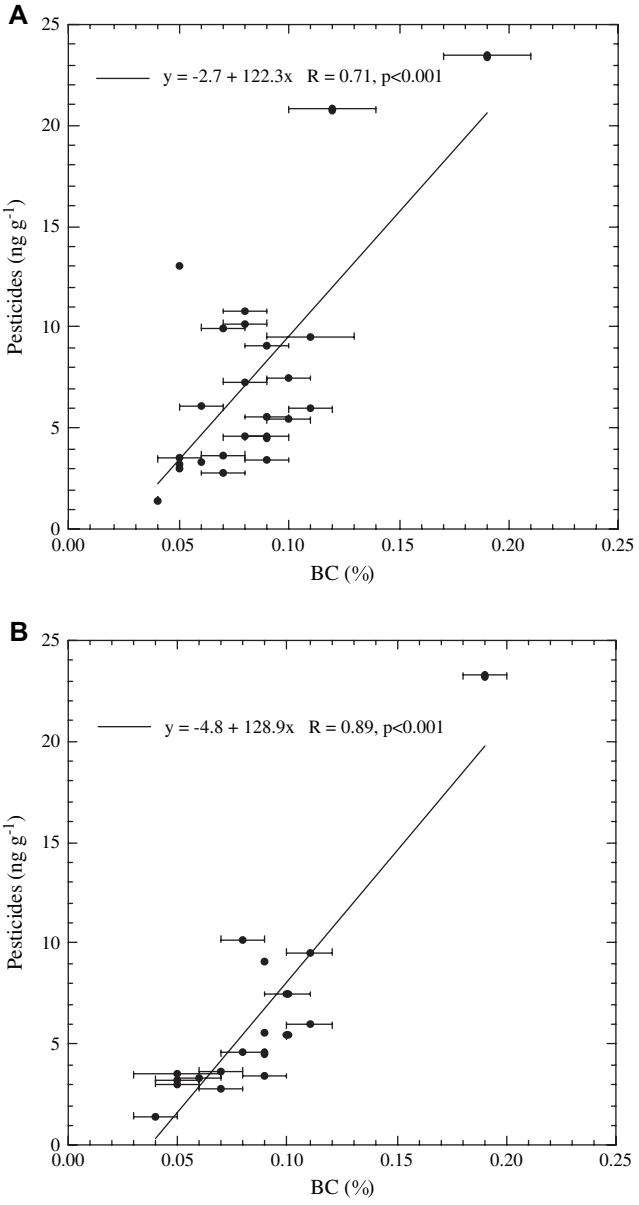

Fig. 5. (A) Relationship between concentrations of total pesticides and BC for all sampling stations. (B) Relationship between concentrations of total pesticides and BC in oxic environments only (excluding anoxic samples).

sediments (after secondary transport processes) is regulated by BC, besides total organic carbon, also because BC likely has a longer residence time as compared to that of total organic carbon. BC also plays an important role for the distribution of PCBs in the sediments of the Danshui River, as reported by Hung et al. (2006).

Table 4 gives the details of the different relationships between pesticides and carbonaceous materials in the sediments of the Danshui River and adjacent coastal areas. Based on the statistical information (i.e., *p*-values) given in Table 4, these results suggest that organic carbon, BC and hydrophobic organic matter (i.e., TOC−TCHO) all play key roles in the distribution and fate of pesticides. These relationships, however, cannot distinguish between pesticides absorbed by major

Table 4
Statistical details of correlations between pesticides and carbonaceous material concentrations

POPs	C-species	*n*	*r*	*p*
Pesticides	TOC	24	0.89	<0.001
Pesticides	BC	24	0.70	<0.001
Pesticides	TOC−TCHO	24	0.90	<0.001
Pesticides	TOC	18[a]	0.88	<0.001
Pesticides	BC	18[a]	0.88	<0.001
Pesticides	TOC−TCHO	18[a]	0.89	<0.001
Pesticides	TOC	6[b]	0.90	<0.02
Pesticides	BC	6[b]	0.70	<0.1
Pesticides	TOC−TCHO	6[b]	0.68	<0.1

C-species, carbonaceous materials.
[a] Excluding six anoxic sediment samples.
[b] Six anoxic sediment samples.

organic matter fractions and co-transport processes, e.g., absorption by BC after transport from the upper watershed. The linear correlation between BC and the pesticide concentration in oxic marine sediments is better than that in fluvial sediments. However, the average ratio of pesticides to BC in the whole study area is relatively constant, and ranges from 12 to 13 mg total pesticides/kg BC. The average ratio of pesticides to TOC for the whole study area is relatively constant as well, and ranges from 1.3 mg total pesticides/kg TOC for fluvial sediments to 1.2 mg total pesticides/kg TOC for coastal sediments. The same situation is also observed for the average ratio of pesticides to hydrophobic organic carbon, which ranges from 1.4 to 1.3 mg pesticides/kg (TOC−TCHO). These results suggest that both TOC and BC play an important role in the fate of pesticides in this subtropical region of Taiwan, which has distinct dry and wet seasons. Similar relationships of organic matter vs. different POPs were also found for other riverine sediments and/or estuarine environments (Wu et al., 1997; Lee et al., 2001; Accardi-Dey and Gschwend, 2002; Doong et al., 2002a; Oen et al., 2006).

4. Conclusions

The surface sediments of the Danshui River and adjacent areas are still contaminated by a variety of POP compounds. A positive correlation between the concentrations of total pesticides and those of total organic carbon was found in the sediments of the Danshui River and adjacent coastal areas, suggesting that the dispersal and distribution of total pesticides occur in proportion to that of natural organic matter. The highest total pesticide concentration was found at a station near the discharge point of a marine outfall pipeline, suggesting that pesticides are still being discharged. Moreover, the levels of significance of the correlations between black carbon and total pesticide concentration in oxic marine environments suggest that while organic matter may play an important role affecting the distribution of pesticides in both fluvial and estuarine sediments, black carbon plays an important role in the fate of pesticides in coastal marine sediments. Primary and secondary transport and dispersal processes in subtropical regions like Taiwan, which has distinct dry and wet seasons, will lead to

the wide dispersal of pesticides that tend to obliterate source-specific patterns in sediments.

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References

Accardi-Dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. Environmental Science and Technology 36, 21–29.

Chen, H.Y., Su, C.-C., Yeh, T.-C., Shen, Y.-H., Tsai, azaarenes C.-H., Chen, L.-D., Hung, C.-C., Gong, G.-C. Historical contamination of azaarenes in the Danshuei River sediments, Taiwan. Marine Pollution Bulletin, submitted for publication.

Chou, C.C.-K., Chen, T.-K., Huang, S.-H., Liu, S.C., 2003. Radiative absorption capability of Asian dust with black carbon contamination. Geophysical Research Letters 30, doi:10.1029/2003GL017076.

Department of Public Sewerage Systems Report, 2001. The Environmental Monitor Program of the Sewage Outfall in the Tanshui River System During 1998 and 1999. Taipei City Council, Taiwan (in Chinese).

Doong, R.-A., Sun, Y.-C., Liao, P.-L., Peng, C.-K., Wu, S.-C., 2002a. Distribution and fate of organochlorine pesticide residues in sediments from the selected rivers in Taiwan. Chemosphere 48, 237–246.

Doong, R.-A., Peng, C.-K., Sun, Y.-C., Liao, P.-L., 2002b. Composition and distribution of organochlorine pesticide residues in surface sediments from the Wu-Shi River estuary, Taiwan. Marine Pollution Bulletin 48, 237–246.

Glynn, P.W., Rumbold, D.G., Sendaker, S.C., 1995. Organochlorine pesticide residues in marine sediment and biota from the northern Florida reef tract. Marine Pollution Bulletin 30, 397–402.

Gustafsson, O., Haghseta, K., Chan, F., McFarlane, A., Gschwend, P.M., 1997. Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. Environmental Science and Technology 31, 203–209.

Gustafsson, O., Bucheli, T.D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J.-N., Reddy, C.M., Eglinton, T.I., 2001. Evaluation of a protocol for the quantification of black carbon in sediments. Global Biogeochemical Cycles 15, 881–890.

Hsieh, H.L., 1995. Spatial and temporal patterns of polychaete communities in a subtropical mangrove swamp: influences of sediment and microhabitat. Marine Ecology and Progress Series 127, 157–167.

Han, B.-C., Hung, T.-C., 1990. Green oysters caused by copper pollution on the Taiwan coast. Environmental Pollution 65, 347–362.

Hung, C.-C., Guo, L., Santschi, P.H., Alvarado-Quiroz, N., Haye, J.M., 2003. Distributions of carbohydrate species in the Gulf of Mexico. Marine Chemistry 81, 119–135.

Hung, C.-C., Gong, G.-C., Jiann, K.-T., Yeager, K.M., Santschi, P.H., Wade, T.L., Sericano, J.L., Hsieh, H.-L., 2006. Relationship between carbonaceous materials and polychlorinated biphenyls (PCBs) in the sediments of the Danshui River and adjacent coastal areas. Taiwan. Chemosphere 65, 1452–1461.

Jiann, K.-T., Wen, L.-S., Santschi, P.H., 2005. Trace metal (Cd, Cu, Ni and Pb) partitioning, affinities and removal in the Danshuei River estuary, a macro-tidal, temporally anoxic estuary in Taiwan. Marine Chemistry 96, 293–313.

Jonker, M.T.O., Koelmans, A.A., 2002. Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic considerations. Environmental Contamination and Toxicology 36, 3725–3734.

Lee, K.-T., Tanabe, S., Koh, C.H., 2001. Distribution of organochlorine pesticides in sediments from Kyeonggi Bay and nearby areas, Korea. Environmental Pollution 114, 207–213.

Lee, C.-L., Chen, H.-Y., Chuang, M.-Y., 1996. Use of oyster, *Crassostrea gigas*, and ambient water to assess metal pollution status of the charting coastal area, Taiwan, after the 1986 green oyster incident. Chemosphere 33, 2505–2532.

Lin, S., Hsieh, I.-I., 1999. Occurrences of green oyster and heavy metals contaminant levels in the Sien-San Area, Taiwan. Marine Pollution Bulletin 38, 960–965.

McKenzie-Smith, K., Tiller, D., Allen, D., 1994. Organochlorine pesticide residues in water and sediments from the Ovens and King rivers, North-East Victoria, Australia. Archives of Environmental Contamination and Toxicology 26, 390–483.

Oen, A.M.P., Cornelissen, G., Breedveld, G.D., 2006. Relation between PAH and black carbon contents in size fractions of Norwegian harbor sediments. Environmental Pollution 141, 370–380.

Sanudo-Wilhelmy, S.A., Rivera-Duarte, I., Flegal, A.R., 1996. Distribution of colloidal trace metals in the San Francisco Bay estuary. Geochimica et Cosmochimica Acta 60, 4933–4944.

Santschi, P.H., Presley, B.J., Wade, T.L., Garcia-Romero, B., Baskaran, M., 2001. Historical Contamination of PAHs, PCBs, DDTs, and heavy metals in Mississippi River Delta, Galveston Bay and Tampa Bay sediment cores. Marine Environmental Research 52, 51–79.

Sericano, J.L., Wade, T.L., Atlas, E.L., Brooks, J.M., 1990. Historical perspective on the environmental bioavailability of DDT and its derivatives to Gulf of Mexico oysters. Environmental Science and Technology 24, 1541–1548.

Simpson, C.D., Mosi, A.A., Cullen, W.R., Reimer, K.J., 1996. Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments form Kitimat Harbor, Canada. Science of the Total Environment 181, 265–278.

Sinotech Engineering Consultants, Ltd., 1997. Bali Ocean Outfall Project. Teipei county, Taiwan. <http://www.sinotech.com.tw/econtent/activity/activity01-1-1.asp?Acti01ID=7&Acti03ID=99>.

Wade, T.L., Atlas, E.L., Brooks, J.M., Kennicutt, M.C., Fox, R.G., Sericano, J., Garcia-Romero, B., DeFreitas, D., 1988. NOAA Gulf of Mexico Status and Trends Program: trace organic contaminant distribution in sediments and oysters. Estuaries 11, 171–179.

Wade, T.L., Cantillo, A.Y., 1994. Use of Standards and Reference Materials in the Measurement of Chlorinated Hydrocarbon Residues – Chemistry Workbook. NOAA Technical Memo NOS ORCA 77 (National Status and Trends Program for Marine Environmental Quality). NOAA, Silver Springs, MD.

Wang, C.-F., Hsu, M.-H., Kuo, A.Y., 2004. Residence time of the Danshuei River estuary, Taiwan. Estuarine, Coastal and Shelf Science 60, 381–393.

Woodwell, G.M., Craig, P.P., Horton, A.J., 1971. DDT in the biosphere: where does it go. Science 174, 1101–1107.

Wu, W.Z., Schramm, K.-W., Henkelmann, B., Xu, Y., Yediler, A., Kettrup, A., 1997. DCDD/Fs, PCBs, HCHs and HCB in sediments and soils of Ya-Er Lake area in China: results on residual levels and correlation to the organic carbon and the particles size. Chemosphere 34, 191–202.

Xing, B., 1997. The effect of the quality of soil organic matter on sorption of naphthalene. Chemosphere 35, 633–642.

Yuan, D., Yang, D., Wade, T.L., Qian, Y., 2001. Status of persistent organic pollutants in the sediments from several estuaries in China. Environmental Pollution 114, 101–111.