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Relationship between carbonaceous materials and polychlorinated biphenyls (PCBs) in the sediments of the Danshui River and adjacent coastal areas, Taiwan

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Abstract

Persistent organic pollutants, POPs (e.g., polychlorinated biphenyls) can seriously and deleteriously affect environmental quality and human health. These organic pollutants are exhibiting high affinities to solid phases and thus, quickly end up in sediments. To better understand the role of carbonaceous materials in the transport and distributions of POPs in terrestrial and near-shore environments, concentrations of PCBs and carbonaceous materials (including total organic carbon, black carbon and total carbohydrates), were determined in surface sediments of the Danshui River and nearby coastal areas, Taiwan. Total concentrations of PCBs in the sediments ranged from non-detectable to 83.9 ng g^{-1}, dry weight, with the maximum value detected near the discharge point of the marine outfall from the Pali Sewage Treatment Plant. These results suggest that the sewage treatment plant has discharged PCBs in the past and the concentrations are still high due to their persistence; alternatively, PCBs are still being discharged in the estuarine and near-shore environment of the Danshui River. Organic carbon and black carbon concentrations correlated well with those of total PCBs in the sediments, suggesting that both organic carbon and black carbon significantly affect the distribution of trace organic pollutants through either post-depositional adsorption, or by co-transport of similar source materials. The field results demonstrate that black carbon and plays an important role in the general distribution of PCBs, while concentrations of some specific PCBs are affected by both black carbon and organic carbon concentrations.

Keywords: PCBs; Carbonaceous materials; Sediments; POC; Black carbon; Danshui River; Taiwan

1. Introduction

Polychlorinated biphenyls (PCBs), potentially toxic and persistent organic pollutants (POPs), are ubiquitous in terrestrial and coastal marine environments (Ghosh et al., 2003; King et al., 2004; Barra et al., 2005; Wurl and Obbard, 2005) and originate mainly from their use as insulators in transformers, capacitors, and similar equipment. They are hydrophobic and have the potential to be bioaccumulated and biomagnified in the food chain. They also partition to suspended particles in proportion to organic carbon (Xing, 1997; Gustafsson et al., 1997; Accardi-Dey and Gschwend, 2002) and black carbon contents (Gustafsson and Gschwend, 1997; Accardi-Dey and Gschwend, 2002; Jonker and Koelmans, 2002). Recent studies have

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shown that black carbon, e.g., soot from combustion engines or charcoal from wood burning, are able to adsorb PCBs and polycyclic aromatic hydrocarbons (PAHs) much stronger than bulk organic carbon (Jonker and Koelmans, 2002). As a result, equilibrium partitioning models for organic contaminants require both organic carbon and black carbon contents for optimal prediction (Gustafsson et al., 1997; Jonker and Smedes, 2000; Cornelissen et al., 2004, 2005).

Air pollution has become a serious health concern in many urban areas due in large part to various combustion processes (motorcycles, automobiles, industrial incineration and coal fired power plants). Primary by-products of these combustion processes include black carbon. Although black carbon is "weathered" (i.e., partly oxidized) in the environment, it is relatively resistant to decomposition as compared to other organic carbon compounds. Therefore, it is important to understand how black carbon produced in big cities with less pollution controls affects the fate and distribution of PCBs in sediments.

The Danshui River is the largest river in northern Taiwan, with a watershed area of 2726 km^2. Taipei and neighboring industrial counties have a total population of over five million, and are located along 5–70 km up the Danshui River. Consequently, the river receives liquid effluents and atmospheric fallout resulting from industrial and municipal emissions which include multiple forms of black carbon. Pollutants associated with these emissions (including PCBs and heavy metals) are transported down-river in association with particulates and deposited in riverine sediments, as well as those in nearby coastal areas.

This research investigated the sedimentary distribution of PCBs in the Danshui River Estuary and nearby coastal areas, as well as their associations with carbonaceous materials, including total organic carbon (TOC), black carbon (BC) and total carbohydrates (as major hydrophilic components of OC, Buffle, 1990), to investigate sources and potential carrier phases of PCBs. It is expected that these results will increase our knowledge of how OC and BC influence the supply, distribution and sedimentary accumulation of organic contaminants.

2. Materials and methods

Surface sediment samples were collected from 25 stations with a sediment sampler (Shiptex; Wildco Inc.) in the lower Danshui River and nearby coastal areas on March 16, 2001 and November 5, 2004 (Fig. 1). The grain size, ratio of clay/silt and sorting coefficient in the sediments were measured as described by Hsieh (1995). The collected samples were transferred to the lab and frozen (~−20 °C) until analysis. Freeze-dried sediment samples were first ground and then 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

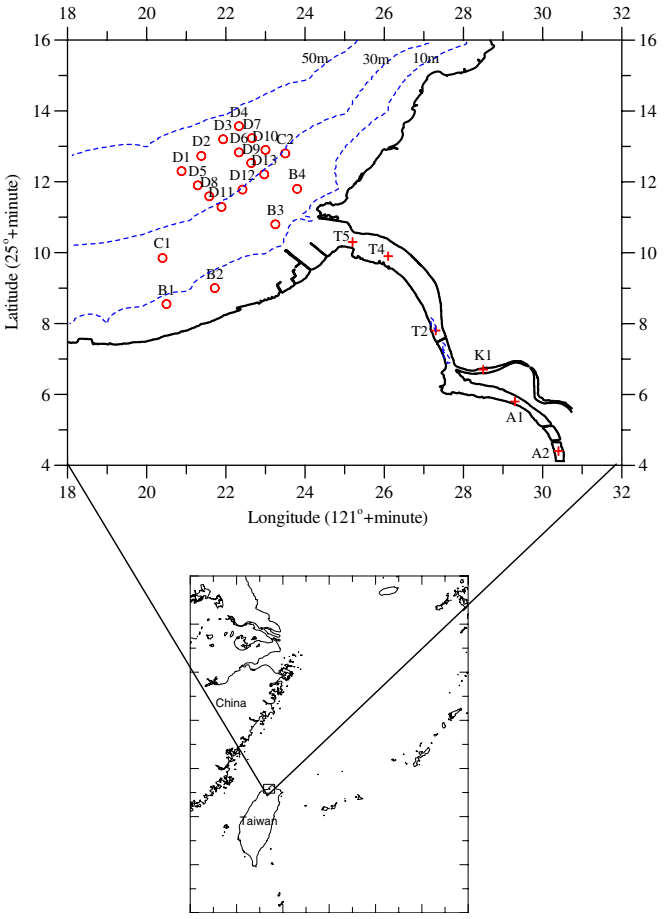

Fig. 1. Sediment sampling stations in the Danshui River and nearby coastal zone, Taiwan.

Series II CHNS/O analyzer, model 2400. Total carbohydrate (TCHO) content was measured based on the method of Hung et al. (2003). Black carbon (BC) contents in the sediment samples, treated by three times of 2 N HCl and then finely ground, 10–15 mg for each single run, were determined after heating at 375 °C for 18 h with air (Gustafsson et al., 2001). A NIST diesel soot standard (SRM-2975) was combusted under identical conditions as the sediment samples. The BC content of the SRM-2975 was slightly higher (i.e., 79%) than the value of 68% given by Gustafsson et al. (2001), suggesting that our BC values may slightly overestimate the BC content in our samples.

PCBs in the freeze-dried samples were extracted according to Wade et al. (1988) and Santschi et al. (2001). In summary, between 5 and 10 g of freeze-dried sediment were Soxhlet-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 hours 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 (aromatic-pesticide/PCB fraction) and 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 activated Cu pellets to remove any remaining sulfur before PCBs 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 and 1941b). Internal/surrogate standards 4,4′-dibromooctaflorobiphenyl (DBOFB), PCB 103 and PCB 198 were added to the samples prior to extraction and PCB 103 was used for quantitative analysis. PCB 103 is not found in aroclor mixtures.

PCBs were separated and quantified by gas chromatography mass spectrometry (GC-MS) (HP 5890-GC and HP 5970-MSD) following the method by Sericano (2002). A 30 m × 0.25 mm I.D. fused silica column with DB-5MS bonded phase (J & W Scientific or equivalent) was used. The chromatographic conditions for the PCB analysis were 75 °C for 3 min, then 15 °C/min to 150 °C, hold for 0 min., then heated at 2 °C /min to 260 °C, hold for 0 min, and then heated at 20 °C/min to 300 °C, and a final hold of 1 min. The method measures all 209 PCBs as 167 individual peaks, some of which contain two or more congeners. PCB retention times and elution order were established by analyses of all 209 individual congeners.

Precision and accuracy of the PCBs analytical method was established by analyses of SRMs from the National Institute of Standards and Technology (NIST). Concentration determined in the SRMs was generally within 2 standard deviations of the certified concentrations. Blanks contained no analytes above the detection limit. The matrix spike had acceptable recoveries of between 78% and 100%. The sum of all the PCBs congeners found, even those below the method detection limit of ~1 ng g^{-1}, was used to calculate total PCB concentration, as ng g^{-1} dry weight.

3. Results and discussion

3.1. Distributions of carbonaceous materials and PCBs

Summary data including total organic carbon (TOC), black carbon (BC), total carbohydrates (TCHO), and other auxiliary parameters (grain size, ratio of silt/clay and sorting coefficient) in surface sediments are shown in Table 1. The TOC content in these sediments ranged from 0.27% to 1.71%, and with a trend similar to that of PCBs, with

Table 1
Total organic carbon (TOC), black carbon (BC), total carbohydrates (TCHO), total PCBs and other ancillary data for sediments of the Danshui River and nearby coastal zone, Taiwan, na = not available, nd = non-detectable

Station	Grain Size (mm)	Silt/Clay (%)	Sorting Coeff.	TOC (%)	BC (%)	TCHO (%)	Total PCBs (ng g^{-1})
A1	na	na	na	0.97	0.08	0.061	10.2
A2	na	na	na	0.84	0.08	0.048	5.9
K1	na	na	na	1.48	0.12	0.117	19.9
T2	na	na	na	0.77	0.07	0.055	13.0
T4	na	na	na	0.73	0.06	0.036	5.1
T5	na	na	na	0.99	0.05	0.018	14.0
B1	0.11	15.8	0.78	0.29	0.05	0.009	2.6
B2	0.04	67.9	0.82	0.54	0.08	0.019	15.3
B3	0.20	0.7	0.48	0.27	0.05	0.003	nd
B4	0.15	21.0	1.61	0.59	0.07	0.014	5.3
C1	0.03	43.5	2.06	0.62	0.07	0.032	28.1
C2	0.27	0.3	2.71	0.37	0.05	0.021	0.2
D1	0.06	56.6	1.51	0.86	0.10	0.080	16.0
D2	0.06	63.6	1.64	0.53	0.09	0.049	11.9
D3	0.10	45.1	1.55	0.54	0.08	0.057	8.9
D4	0.05	69.0	1.61	0.78	0.11	0.060	23.2
D5	0.16	21.0	1.37	0.33	0.06	0.064	2.9
D6	0.05	71.3	1.68	0.75	0.09	0.061	20.9
D7	0.14	21.1	1.51	0.46	0.09	0.030	5.5
D8	0.03	80.9	1.22	1.20	0.11	0.077	27.4
D9	0.23	1.2	0.84	0.29	0.04	0.031	nd
D10	0.03	86.2	1.21	0.91	0.10	0.075	11.9
D11	0.03	90.1	1.00	0.80	0.09	0.061	19.0
D12	0.13	19.1	1.25	0.42	0.07	0.035	11.9
D13	0.07	50.8	1.55	1.71	0.19	0.100	83.9

a maximum value (1.71%) at station D13. Concentrations of TCHO ranged from 0.003% to 0.11%, with an elevated value found in river sediment (K1), coinciding with a high value (19.9 ng g^{-1}) of total PCB. The BC content in these sediments accounted for 5%–19.5% (on average 14%) of TOC, with a maximum value also at station D13. Despite the fact that concentrations of BC in aerosols collected in Taipei are higher than typical values in other tropical urban areas (Chou et al., 2003), BC contents in sediments of the Danshui River and nearby areas are in agreement with those reported by others in similar settings (Gustafsson et al., 1997; Jonker and Smedes, 2000; Cornelissen et al., 2005). Fig. 2A–C shows the relationships between TOC, BC and TOC-TCHO, respectively, and grain size of sediments. This figure demonstrates that the contents of TOC, BC and TOC-TCHO, respectively, are inversely proportional to grain size, suggesting that smaller particles contain higher organic carbon and hydrophobic carbon (i.e., TOC-TCHO) contents than larger particles, because smaller particles have higher surface areas per unit weight. In addition, the inverse relationship between BC and grain size also suggests that BC (i.e., soot) is located in smaller particles transported to the sediments from the atmosphere.

Concentrations of total PCBs and individual PCB congeners are shown in Tables 1 and 2. Total PCB concentrations in these sediments ranged from non-detectable to 83.9 ng g^{-1} (dry weight), with an average value of 15.8 ng g^{-1}. Values of 10–30 ng g^{-1} are typical for river delta and coastal regions (e.g., Santschi et al., 2001). In comparison to previously reported data (Iwata et al., 1994, 4–200 ng g^{-1}, dry weight; Taiwan Environmental Protection Agency, 1997, non-detectable to 16 ng g^{-1}, mean value of 6.7 ng g^{-1}), concentrations of PCBs in sediments of the Danshui River showed little temporal change when compared to previous data, suggesting that PCBs continue to be discharged to the Danshui River and its watershed. It is not possible to evaluate if and to what extent the contamination of sediments with PCBs in the Danshui River Estuary and nearby coastal zone has increased during this time, due to very limited PCB data and sampling location differences between research conducted in 1994, 1997 and that reported herein. To accurately assess the input history of PCBs in the sedimentary environment, one should have vertical profiles of PCBs accompanied by an accurate geochronology of the host sediments (e.g., Santschi et al., 2001), which, however, is not currently available. Maximum PCB concentrations were found in the river sediments and the lowest PCB concentration (i.e., not detectable) was found in offshore sediments, demonstrating that inputs and sedimentary accumulation of PCBs are decreasing with distance away from the river mouth. However, it is difficult to explain the patchy distribution of PCBs in most of the study area, which could be due to irregular river discharge, high tidal amplitude or short residence times of the Danshui River water (Wang et al., 2004; Jiann et al., 2005). Interestingly,

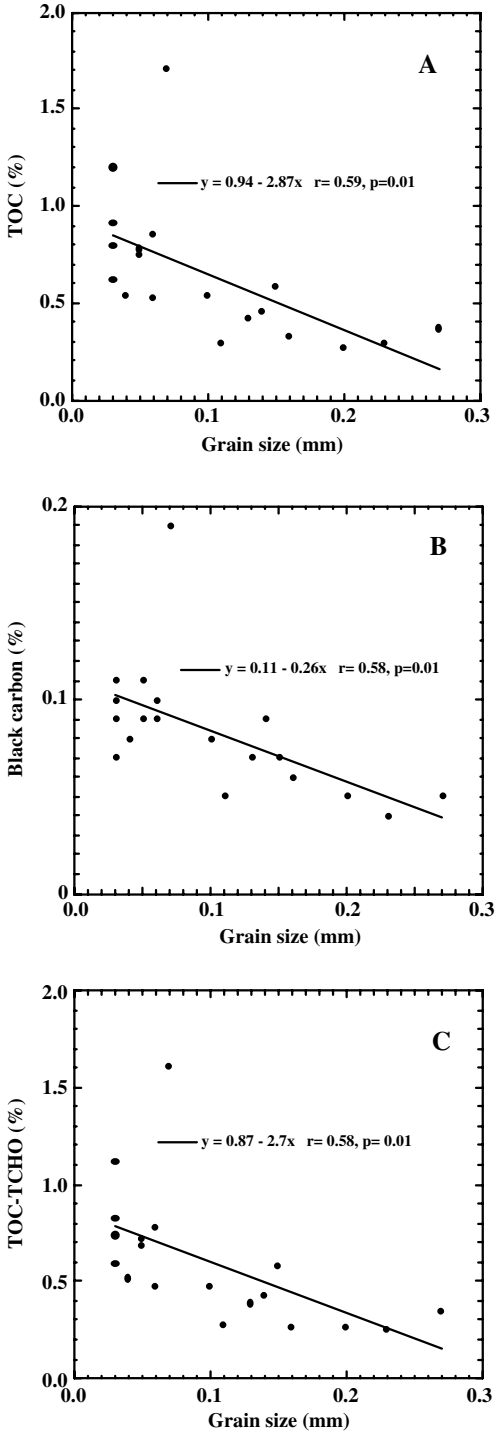

Fig. 2. Relationships between (A) grain size and TOC; (B) grain size and black carbon, BC (B); and (C) grain size and TOC-TCHO concentrations.

the maximum PCB concentration (83.9 ng g^{-1}) was found in offshore sediments at station D13, approximately 7 km away from the Danshui River mouth. The discharge point of the ocean outfall pipeline from the Pali sewage treatment plant is located near this station (Sinotech, 1997). The plausible interpretation is that the Pali plant has discharged PCBs in the past and that the concentrations are still high because PCBs are so persistent. Alternately, it is possible

Table 2a
Concentrations of PCBs (ng g^{-1} dry wt.) in surface sediments of the Danshui River

Stations	A1	A2	K1	T2	T4	T5	B1	B2	B3	B4	C1	C2
PCB 8	0.31	nd	nd	nd	0.25	nd	0.23	0.66	nd	0.21	0.99	nd
PCB 15	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.46	nd
PCB 16	nd	nd	nd	nd	nd	0.38	nd	0.22	nd	nd	0.32	nd
PCB 17	0.16	0.18	0.47	0.36	0.09	0.32	0.08	0.27	nd	nd	0.5	nd
PCB 18	0.45	0.38	1.3	0.95	0.27	1.43	0.22	0.79	nd	0.28	1.39	nd
PCB 19	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.08	nd
PCB 20/33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.99	nd
PCB 28/31	1.57	1.27	4	2.25	1.22	2.72	0.83	2.64	nd	0.9	4.12	nd
PCB 32	nd	nd	nd	nd	nd	0.3	nd	0.31	nd	nd	0.5	nd
PCB 40	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.53	0.68	nd
PCB 41/64/71/72	nd	0.51	1.06	0.5	nd	0.4	0.15	0.57	nd	0.71	0.69	nd
PCB 42	nd	nd	0.56	0.27	nd	0.17	nd	0.53	nd	0.97	0.39	nd
PCB 43/52	0.59	0.56	1.06	0.66	0.39	0.72	nd	0.72	nd	nd	1.26	nd
PCB 44	0.68	nd	1.41	0.79	nd	0.67	nd	0.89	nd	0.64	1.15	nd
PCB 45	nd	nd	nd	nd	nd	0.09	nd	0.23	nd	nd	0.16	nd
PCB 47/48/62/65/75	nd	nd	nd	0.33	nd	0.24	nd	0.43	nd	nd	0.36	nd
PCB 49	nd	nd	nd	nd	nd	0.67	nd	nd	nd	nd	1.09	nd
PCB 50	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 51	nd	nd	nd	nd	nd	0.04	nd	nd	nd	nd	nd	nd
PCB 53	nd	nd	nd	nd	nd	0.1	nd	nd	nd	nd	0.17	nd
PCB 56/60	nd	nd	nd	0.58	0.35	0.39	nd	0.77	nd	nd	1.17	nd
PCB 66	0.51	0.39	1.12	0.73	0.31	0.43	0.18	0.71	nd	nd	1.19	nd
PCB 67	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 70	0.43	0.56	1.26	0.75	0.36	0.63	0.19	0.73	nd	nd	1.42	nd
PCB 74	nd	0.38	0.82	0.33	0.21	0.24	0.14	0.41	nd	nd	0.61	nd
PCB 84/92	0.13	0.11	0.24	0.14	nd	0.14	nd	0.17	nd	nd	0.35	nd
PCB 86/97	nd	nd	nd	nd	nd	nd	nd	0.14	nd	nd	0.2	nd
PCB 87	nd	nd	nd	0.23	nd	0.23	nd	0.17	nd	nd	0.37	nd
PCB 88/95	0.23	nd	0.56	0.26	0.13	0.21	0.06	0.28	nd	0.08	0.49	nd
PCB 91	nd	nd	nd	nd	nd	0	nd	nd	nd	nd	0.11	nd
PCB 99	0.11	0.14	0.35	0.2	0.08	0.16	0.07	0.16	nd	0.08	0.33	nd
PCB 100	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 101	0.37	0.23	0.6	0.35	0.16	0.28	0.08	0.31	nd	0.1	0.54	nd
PCB 105	nd	nd	0.34	nd	nd	0.32	nd	0.28	nd	nd	0.24	nd
PCB 106/118	0.47	nd	nd	0.62	0.3	0.45	0.08	0.3	nd	0.15	0.76	nd
PCB 110	0.36	0.4	0.95	0.45	0.23	0.45	0.11	0.52	nd	0.17	0.72	nd
PCB 132/153/168	0.73	0.5	0.86	0.64	0.24	0.37	0.08	0.31	nd	0.15	0.8	0.1
PCB 138/158/163/164	0.58	nd	nd	nd	nd	0.36	nd	0.33	nd	0.14	0.62	nd
PCB 139/149	0.37	0.27	0.61	0.33	0.16	0.19	0.08	0.25	nd	0.11	0.46	0.07
PCB 160	0.28	nd	nd	nd	nd	0.15	nd	0.18	nd	nd	0.29	nd
PCB 170/190	0.51	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.3	nd
PCB 174	0.28	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 175	nd	nd	nd	nd	nd	nd	nd	0.23	nd	nd	nd	nd
PCB 180/193	0.6	nd	0.91	0.52	0.32	0.3	nd	0.27	nd	0.11	0.4	nd
PCB 181	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 182/187	nd	nd	nd	0.25	nd	0.16	nd	0.1	nd	nd	nd	nd
PCB 183	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 184	0.5	nd	1.38	0.5	nd	0.31	nd	0.4	nd	nd	0.39	nd

that the sewage treatment plant is still discharging some PCBs, and thus, PCBs may bind to activated sludge/carbon and be accumulated in local sediment. The concentration of total suspended matter (SPM) from the ocean outfall (after treatment) can be as high as 70 mg/l, which is 10–20 times higher than that from adjacent areas (Department of Publics Sewerage Systems Report, 2001). Additionally, the PCBs distribution indicates that PCB pollution also persists in the watershed of the Danshui River, despite the use of PCBs having been prohibited by the Environmental Protection Agency of Taiwan, immediately following the 1979 outbreak of Yucheng or "oil disease" which afflicted more than two thousand people there (Yu et al., 2000). To make certain that the elevated PCB concentration is from the discharge point of the ocean outfall, one would need to compare fingerprints of individual PCB congeners in sediments with those from the original marine outfall and the sewage treatment plant, which, however, could not be done here.

The major congeners of PCBs in the sediments were PCBs 28/31, 43/52, 66, 110, and 132/153/168, respectively. Some congeners of PCBs 28/31 and 132/153/168 were

Table 2b
Concentrations of PCBs (ng g^{-1} dry wt.) in surface sediments of the Danshui River, nd = non-detectable

Stations	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13
PCB 8	0.48	0.35	0.31	0.80	0.15	0.71	0.21	0.91	nd	0.39	0.63	0.39	3.77
PCB 15	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.61
PCB 16	0.21	0.11	nd	0.25	nd	0.14	nd	0.40	nd	nd	0.25	nd	1.26
PCB 17	0.26	0.16	0.15	0.43	0.10	0.23	0.08	0.55	nd	0.22	0.28	0.13	1.29
PCB 18	0.66	0.45	0.36	0.98	0.16	0.69	0.24	1.27	nd	0.51	0.95	0.40	3.41
PCB 19	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.09	nd	0.28
PCB 20/33	nd	0.78	nd	1.60	nd	1.19	nd	2.64	nd	nd	1.59	nd	6.78
PCB 22	nd	nd	nd	nd	nd	0.60	nd	nd	nd	nd	nd	nd	2.87
PCB 25	nd	nd	nd	nd	nd	nd	0.19	nd	nd	nd	nd	nd	nd
PCB 26	nd	nd	nd	nd	nd	nd	0.26	nd	nd	nd	nd	nd	nd
PCB 28/31	2.54	1.69	1.28	3.52	0.77	2.49	1.04	4.26	nd	2.37	2.80	1.67	13.77
PCB 32	0.32	0.20	nd	0.43	nd	0.27	nd	0.64	nd	nd	0.40	0.35	1.66
PCB 37	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.29
PCB 39	nd	0.33	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
PCB 40	0.73	nd	nd	nd	nd	nd	nd	0.70	nd	nd	0.60	nd	0.38
PCB 41/64/71/72	0.72	0.27	0.33	0.57	nd	0.52	0.22	0.76	nd	0.57	0.62	nd	1.69
PCB 42	0.68	0.21	0.27	0.45	nd	0.50	nd	0.72	nd	nd	0.57	nd	1.05
PCB 43/52	0.80	0.53	0.49	0.85	0.17	0.73	0.31	0.99	nd	0.70	0.76	nd	2.45
PCB 44	0.87	0.54	0.41	0.91	nd	0.70	nd	1.36	nd	0.65	0.81	0.51	2.24
PCB 45	nd	nd	nd	nd	nd	0.13	nd	0.19	nd	nd	nd	nd	0.44
PCB 46	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.45
PCB 47/48/62/65/75	nd	0.26	0.17	0.58	nd	0.25	0.23	0.57	nd	nd	0.26	nd	1.04
PCB 49	nd	0.37	0.33	0.85	nd	0.55	nd	0.83	nd	nd	nd	nd	2.02
PCB 51	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.12
PCB 53	nd	0.07	nd	nd	nd	0.08	nd	0.16	nd	nd	0.11	nd	0.40
PCB 56/60	0.61	0.43	0.43	0.92	0.16	0.67	0.29	0.98	nd	0.70	0.76	nd	2.69
PCB 66	0.69	0.43	0.36	0.98	0.22	0.82	0.34	0.93	nd	0.74	0.77	0.44	2.75
PCB 70	0.69	0.54	0.45	1.11	0.21	0.98	0.35	1.12	nd	0.68	0.94	0.28	3.38
PCB 74	0.44	0.24	0.25	0.54	nd	0.54	nd	0.53	nd	0.53	0.55	nd	1.64
PCB 82	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.33
PCB 84/92	0.15	0.11	0.08	0.20	nd	0.18	0.04	0.23	nd	0.13	0.17	0.06	0.63
PCB 85	nd	0.18	nd	0.36	nd	0.45	nd	0.24	nd	nd	0.37	nd	0.54
PCB 86/97	nd	0.11	nd	0.16	nd	0.16	nd	0.19	nd	nd	nd	nd	0.63
PCB 87	nd	0.13	nd	0.29	nd	0.34	nd	0.23	nd	0.21	0.25	0.17	0.94
PCB 88/95	0.31	0.18	0.13	0.36	0.13	0.31	0.12	0.39	nd	0.22	0.24	0.11	1.00
PCB 89/90	nd	nd	0.04	nd	nd	0.02	nd	nd	nd	nd	nd	nd	0.15
PCB 91	nd	0.06	0.05	0.09	nd	0.08	nd	0.09	nd	nd	nd	nd	0.24
PCB 99	0.19	0.15	0.11	0.24	nd	0.26	0.09	0.23	nd	0.15	0.20	0.11	0.88
PCB 101	0.43	0.23	0.21	0.55	nd	0.51	0.15	0.48	nd	0.32	0.34	0.17	1.47
PCB 105	0.12	0.16	0.09	0.32	nd	0.36	0.10	0.26	nd	nd	0.24	0.11	1.31
PCB 106/118	0.31	0.31	0.25	0.63	0.14	0.67	0.14	0.73	nd	0.51	0.41	0.21	2.14
PCB 110	0.46	0.34	0.34	0.60	nd	0.69	0.22	0.70	nd	0.38	0.46	0.20	2.14
PCB 119	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.13
PCB 132/153/168	0.60	0.28	0.39	0.75	0.20	0.74	0.24	0.65	nd	0.57	0.44	0.23	2.01
PCB 135	nd	nd	nd	nd	nd	0.06	nd	nd	nd	nd	nd	nd	0.18
PCB 136	nd	0.04	0.09	0.12	nd	0.08	nd	nd	nd	nd	0.06	nd	0.26
PCB 138/158/163/164	0.45	0.20	0.24	0.45	0.11	0.52	0.19	0.54	nd	nd	0.35	0.16	1.43
PCB 139/149	0.34	0.19	0.17	0.38	0.14	0.38	0.13	0.32	nd	0.25	0.25	0.11	1.28
PCB 151	nd	nd	nd	0.06	nd	0.10	nd	nd	nd	nd	nd	nd	0.36
PCB 160	0.26	0.12	0.16	0.16	nd	0.26	0.07	0.25	nd	nd	0.11	0.11	0.68
PCB 170/190	0.35	0.17	0.19	0.27	nd	0.22	nd	nd	nd	0.21	0.18	nd	0.54
PCB 174	0.15	0.11	nd	0.17	nd	0.17	nd	nd	nd	0.22	0.16	0.09	0.00
PCB 175	nd	0.17	0.20	0.18	nd	0.19	nd	0.22	nd	0.19	nd	0.17	0.29
PCB 177	0.19	nd	nd	nd	nd	0.10	nd	nd	nd	nd	0.06	nd	0.32
PCB 179	nd	0.05	nd	nd	nd	0.09	nd	nd	nd	nd	0.08	nd	0.28
PCB 180/193	0.55	0.23	0.24	0.39	0.25	0.39	0.21	0.42	nd	0.35	0.30	0.15	0.88
PCB 181	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.59
PCB 182/187	nd	0.08	0.11	0.26	nd	0.15	nd	0.24	nd	0.10	0.14	0.07	0.55
PCB 183	nd	0.06	nd	nd	nd	0.12	nd	nd	nd	nd	0.07	nd	0.27
PCB 184	0.40	0.29	0.26	0.44	nd	0.39	nd	0.44	nd	nd	0.35	0.30	0.49

co-eluted in this investigation and were difficult to distinguish from each other. In general, river sediments (i.e., Stations A, B, K, and T series) were composed of fewer PCB congeners than marine sediments (i.e., Stations

D series). This may be explained by the contrasts in setting, i.e., river sediments can be repeatedly sub-aerially exposed and inundated while marine sediments are consistently sub-aqueous, Bushart et al. (1998) showed that significant and rapid losses of PCBs via volatilization can occur from sub-aerially exposed sediments following initial transformation of parent compounds by microbial reductive de-chlorination.

3.2. Relationships between total PCB concentration and carbonaceous materials

Statistically significant relationships between total PCB concentrations with TOC, BC and TOC-TCHO are shown in this study (Fig. 3A–C). Due to their hydrophobicity, POPs are adsorbed or absorbed by different organic phases, which are found as coatings on particle surfaces or inside aggregates (Xing, 1997; Pignatello, 1998). Significant relationships between total PCB and total organic carbon concentrations were also found for the sediments of Kyeonggi Bay, Korea, by Lee et al. (2001). It is important to note that this relationship does not solely indicate that organic carbon has a strong sorption capacity for PCBs, but also that such a relationship can result from both PCBs and OC having been derived from similar sources and having been subject to the same transport processes. Another interpretation for the significant correlations is that they are caused by an in situ partitioning process (i.e., organic matter partitioning model).

Fig. 3C shows a significant correlation between the concentrations of total PCBs and that of the hydrophobic fraction of TOC (i.e., TOC-TCHO), suggesting that hydrophobic components of organic matter other than BC may also play an important role in affecting PCB distributions (Accardi-Dey and Gschwend, 2002). Overall, good relationships between total PCBs and carbonaceous materials can result from either post-depositional sorption (i.e., PCBs are sorbed to the TOC, BC, or TOC-TCHO after being transported to the area), or co-emission (i.e., PCBs originate in association with TOC, BC or TOC-TCH).

If all samples are separated into two groups (deep water >30 m, $n = 10$ and shallow water <30 m, $n = 15$), one finds a higher slope of PCBs vs BC in the shallow water than in the deep water group (Fig. 4A), suggesting that BC in shallow water sediments contains more PCBs per unit BC weight than in deeper water sediments. According to recent laboratory experiments (Bucheli and Gustafsson, 2000; Jonker and Smedes, 2000; Jonker and Koelmans, 2002; Bucheli and Gustafsson, 2003), the extent of POP adsorption by BC is approximately two orders of magnitude higher than by bulk sedimentary organic matter, with the exact value dependent upon the type of BC. Jonker and Koelmans (2002) compared BC sorbent-water distribution coefficients for 11 PCB congeners on different types of soot and found that traffic soot has a distribution coefficient that is one order of magnitude higher than that for oil, wood and coal soot. Thus, it is probable that the ratio of

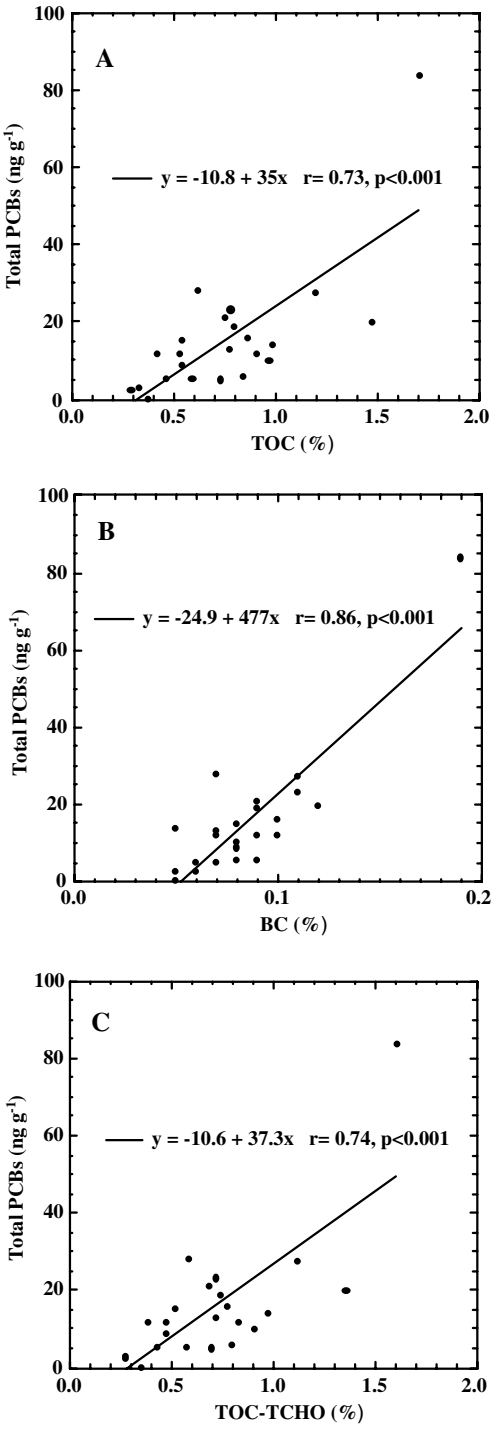

Fig. 3. Relationships between (A) total PCBs and TOC; (B) total PCBs and black carbon; and (C) total PCBs and TOC-TCHO concentrations.

total PCBs to BC in shallow water sediments is higher than that in deeper water sediments because there is more traffic soot in shallow water than deeper water sediments. Fig. 4B shows a higher fraction of TCHO in TOC from deep water sediments, suggesting that total carbohydrates in deeper water sediments are more refractory than those from shallow water environments. These results support the notion that BC in deeper water sediments could be older than that in shallower water environments.

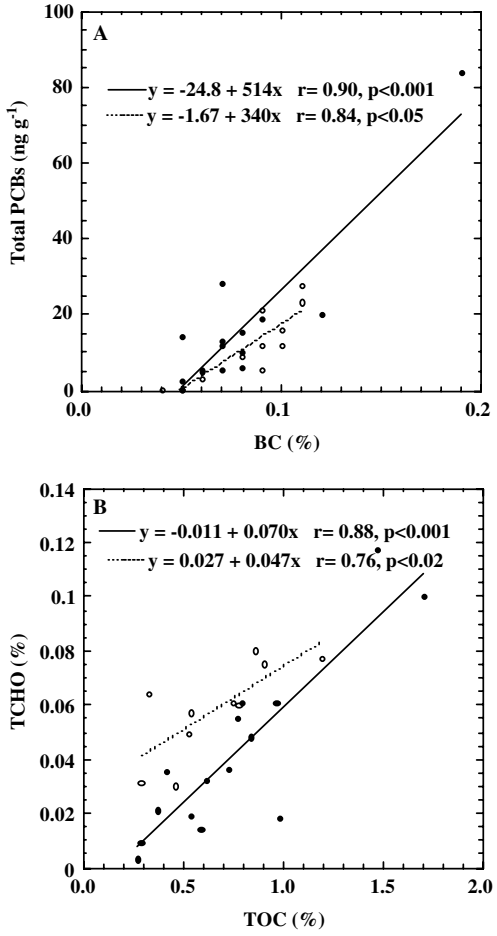

Fig. 4. Relationships between concentrations of (A) total PCBs and BC; (B) TCHO and TOC. Solid symbols denote shallow water group (<30 m) and open symbols denote deep water group (>30 m).

3.3. Relationship between carbonaceous materials and PCB congeners

Recent laboratory experiments have demonstrated that soot, mainly from fresh water sediments, is capable of sorbing PAH and PCB compounds two orders of magnitude more strongly than natural organic matter (NOM) does (Bucheli and Gustafsson, 2000; Jonker and Smedes, 2000; Bucheli and Gustafsson, 2003). For marine environments, there is little data on the relationships between individual sedimentary PCB congeners and BC or soot. The relationships between individual PCB congeners (PCB 28/31) and different carbonaceous materials, e.g., TOC, BC and the hydrophobic fraction of TOC, i.e., TOC-TCHO, are shown in Fig. 5A, B and C, with the highest correlation coefficient ($r = 0.86$, $p < 0.001$) in Fig. 5B (PCB 28/31 vs. BC). If the highest PCB concentration (at D13) is removed from the correlation, the re-processed correlations between PCB 28/31 vs. carbonaceous materials are still highly significant (Table 3), based on very low p values. Additionally, significant relationships between PCBs 43/52, 66, 70, 88/95, 110, 132/153/168, 139/149, 180/193, as well as 184, and carbonaceous materials (TOC, BC and TOC-TCHO, respectively) were also observed in our study (Table 4). It appears that light PCBs ($r = 0.86$ to 0.87), as compared to heavy PCBs 180/193 and 184 ($r = 0.32$ to 0.48), show a better correlation with BC. This suggests that post-emission sorption processes are dominating the sedimentary distribution of PCBs rather than co-emission processes. This is because for sorption processes, one might expect

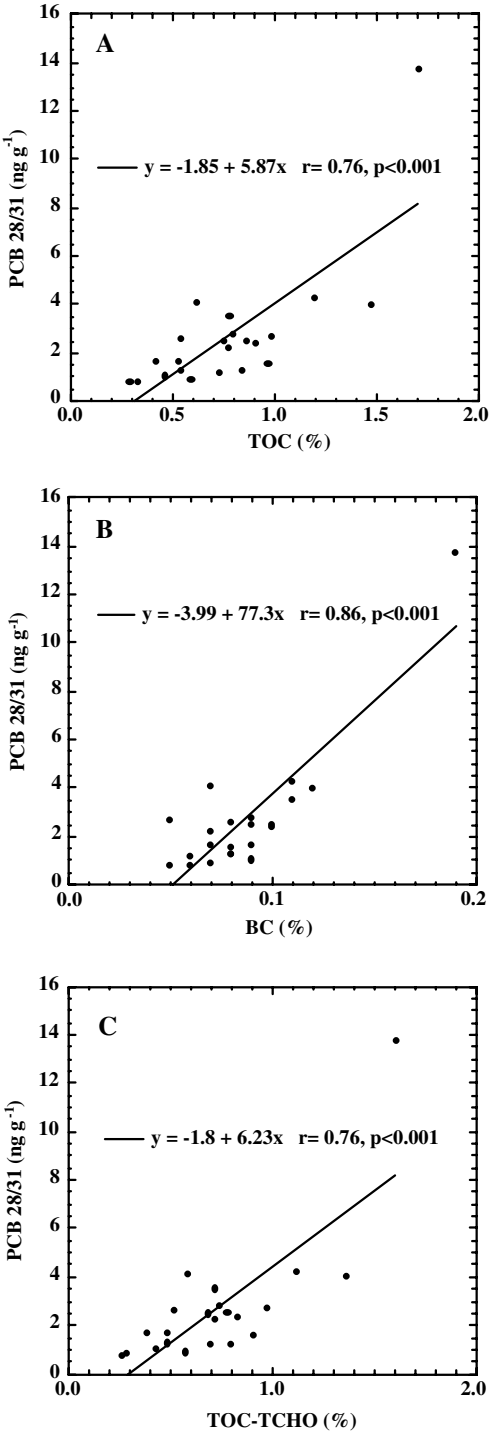

Fig. 5. Relationships between concentrations of (A) PCBs 28/31 and organic carbon (TOC); (B) PCBs 28/31 and BC; (C) PCBs 28/31 and TOC-TCHO in the sediments of the Danshui River.

Table 3
Correlations between PCB 28/31 and carbonaceous material concentrations

PCBs	C-species	*n*	*r*	*p*
28/31	TOC	22	0.76	<0.001
28/31	BC	22	0.86	<0.001
28/31	TOC-TCHO	22	0.76	<0.001
28/31	TOC	21	0.66	<0.002
28/31	BC	21	0.58	<0.01
28/31	TOC-TCHO	21	0.66	<0.002

Table 4
Correlations between concentrations of PCB congeners, and those of TOC, BC and TOC-TCHO, respectively

PCBs	C-species	*n*	*r*	*p*
28/31	TOC	21	0.76	<0.001
28/31	BC	21	0.86	<0.001
28/31	TOC-TCHO	21	0.76	<0.001
43/52	TOC	20	0.79	<0.001
43/52	BC	20	0.81	<0.001
43/52	TOC-TCHO	20	0.80	<0.001
66	TOC	21	0.76	<0.001
66	BC	21	0.87	<0.001
66	TOC-TCHO	21	0.76	<0.001
70	TOC	21	0.76	<0.001
70	BC	21	0.86	<0.001
70	TOC-TCHO	21	0.76	<0.001
88/95	TOC	21	0.82	<0.001
88/95	BC	21	0.85	<0.001
88/95	TOC-TCHO	21	0.82	<0.001
110	TOC	21	0.81	<0.001
110	BC	21	0.87	<0.001
110	TOC-TCHO	21	0.81	<0.001
132/153/168	TOC	23	0.83	<0.001
132/153/168	BC	23	0.87	<0.001
132/153/168	TOC-TCHO	23	0.82	<0.001
139/149	TOC	23	0.82	<0.001
139/149	BC	23	0.87	<0.001
139/149	TOC-TCHO	23	0.81	<0.001
180/193	TOC	20	0.75	<0.001
180/193	BC	20	0.48	<0.05
180/193	TOC-TCHO	20	0.72	<0.001
184	TOC	15	0.64	<0.02
184	BC	15	0.32	<0.5
184	TOC-TCHO	15	0.62	<0.02

that equilibrium is quickly reached for the lighter, but not for heavier PCBs, while associations derived by co-emission should not be restricted to lighter PCBs.

These significant relationships may also be explained by the fact that most types of BC preferentially sorb molecules that are planar, or as in our case, attain a near-planar structure (Jonker and Smedes, 2000; Jonker and Koelmans, 2002; Bucheli and Gustafsson, 2003). Thus, diverse carbonaceous materials may be good carriers and sorption phases for PCBs in natural sediments, as suggested by Accardi-Dey and Gschwend (2002).

4. Conclusions

The distributions of PCBs in the sediments of the Danshuei River, which flows through Taipei, a large tropical city, are significantly influenced by both TOC and BC fractions. The highest total PCB concentration in surface sediments was located near the discharge point of an ocean outfall pipeline, suggesting that the sewage treatment plant has discharged PCBs in the past and the concentrations are still high due to their persistence; alternatively, PCBs are still being discharged despite their ban in Taiwan. However, more measurements are needed to unequivocally identify the source of these PCBs. Some specific PCBs (e.g. PCBs 28/31, 43/52, 66, 70, 88/95, 110 and 132/153/168) showed more significant correlations with BC than with total organic carbon, suggesting that BC plays a major role in the distribution of some PCBs. Moreover, significant correlations between the hydrophobic fraction of organic carbon (TOC-TCHO) and total PCBs were found, suggesting that other hydrophobic natural organic matter compounds may also play an important role affecting the distribution of PCBs in the sediments.

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