Black carbon and polycyclic aromatic hydrocarbons (PAHs) in surface sediments of China's marginal seas*

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Abstract   This study investigates the distribution of black carbon (BC) and its correlation with total polycyclic aromatic hydrocarbons (ΣPAH) in the surface sediments of China's marginal seas. BC content ranges from <0.10 to 2.45 mg/g dw (grams dry weight) in the sediments studied, and varied among the different coastal regions. The Bohai Bay sediments had the highest BC contents (average 2.18 mg/g dw), which comprises a significant fraction (27%–41%) of the total organic carbon (TOC) preserved in the sediments. In comparison, BC in the surface sediments of the North Yellow Sea, Jiaozhou Bay, East China Sea and the South China Sea is less abundant and accounted for an average of 6%, 8%, 14% and 5%, respectively, of the sedimentary organic carbon pool. The concentration of ΣPAH in the surface sediments ranges from 41 to 3 667 ng/g dw and showed large spatial variations among the sampling sites of different costal regions. The Bohai Bay has the highest ΣPAH values, ranging from 79 to 3 667 ng/g dw. This reflects the high anthropogenically contaminated nature of the sediments in the bay. BC is positively correlated to TOC but a strong correlation is not found between BC and ΣPAH in the surface sediments studied, suggesting that BC and PAHs preserved in the sediments are derived from different sources and controlled by different biogeochemical processes. Our study suggests that the abundance of BC preserved in the sediments could represent a significant sink pool of carbon cycling in China's marginal seas.

Keyword: Black carbon; PAH; marine sediment; carbon cycle; China's marginal seas

1 INTRODUCTION

Black carbon (BC) and polycyclic aromatic hydrocarbons (PAHs) are both combustion-derived organic pollutants that are widely dispersed in soils and marine sediments (LaFlamme and Hites, 1978; Goldberg, 1985; Schmidt and Noack, 2000). It is estimated that fossil fuel combustion and biomass burning produce about 12×10^6–24×10^6 and 50×10^6–270×10^6 tons of BC, respectively, each year worldwide (Penner et al., 1993; Kuhlbusch and Crutzen, 1995). The increased production and wide dispersal of BC in the natural environments have raised serious environmental concerns since it has been documented that BC produced in the atmosphere absorbs solar radiation, thus contributing to global warming (Charlock and Sellers, 1980; Jacobson, 2001; Koelmans et al., 2005). Additionally, BC

could carry carcinogenic compounds such as PAHs, polychlorinated biphenyls (PCBs) and pesticides into the environment and cause destruction of natural ecosystems as well as serious health risks to human beings (Rust et al., 2004; Lohmann et al., 2005).

Among the various organic contaminants being introduced into the coastal environment, PAHs form one of the most persistent classes of anthropogenic pollutants and have received considerable attention due to their mutagenic and carcinogenic impact on marine organisms (Grimmer, 1983; White, 1986). A significant fraction of PAHs preserved in natural environments is derived from the combustion of

biomass and fossil fuels (Laflamme and Hites, 1978), suggesting that a very strong correlation exists between PAH and BC in many soils and marine sediments due to the efficient sorption capacity of PAHs to BC (Gustaffsson and Gschwend, 1997; Dachs and Eisenreich, 2000; Bucheli et al., 2004; Cornelissen and Gustafsson, 2005; Koelmans et al., 2005). For example, Oen et al. (2006) examined the distribution and correlations of TOC, PAHs and BC in different size fractions of Norwegian harbor sediments. They found that the distributions of PAHs were well related to the presence of BC rather than TOC. A strong correlation between PAHs and BC was also found in the sediments of the Eastern Mediterranean Sea where atmospheric transport has been the main input source of both PAHs and BC to the sediments (Tsapakis et al., 2003). However, in their recent study of PAH and BC in soil samples from some background locations in the UK and in Norway, Nam et al. (2008) reported that positive (non linear) correlations between PAHs and BC were only found in one soil group but not in the other three soil group samples. They explained the difference as related to the variable degradation rates of PAHs in the different soils. The strong association of PAHs with BC in sediments could affect the solubility of PAHs (Oen et al., 2006) and reduce the bioavailability of the compounds in the environment (Koelmans et al., 2005).

The majority of the BC produced each year is stored in soils and only a small fraction (10×10^6 tons C/a) is buried in marine sediments through river discharge and aerosol deposition (Masiello, 2004). In addition to its environmental concern, in recent years BC preserved in marine sediments has attracted considerable attention from geochemists (Masiello and Druffel, 1998; Masiello et al., 2002; Dickens et al., 2004a; Wang and Li, 2007). Due to its stable chemical nature, BC deposited in soil and sediment is very persistent to microbial decomposition and chemical reactions, and thus could be preserved for geological time periods in the natural environment (Masiello et al., 2002). Although the amount of BC preserved in marine sediments is a small fraction compared with that in major global carbon reservoirs (Druffel, 2004), it accounts for a significant fraction (15%–50%) of total organic carbon (TOC) preserved in many marine sediments (Lim and Cachier, 1996; Verardo and Ruddiman, 1996; Masiello and Druffel, 1998; Wang and Li, 2007). Since BC preserved in marine sediments is indicative of long-term carbon storage, this "slow-cycling" BC pool could represent

a significant fraction of the missing carbon in the global carbon balance (Kuhlbusch and Crutzen, 1995; Kuhlbusch et al., 1996).

Sediments of marginal seas usually receive a high input of both BC and PAHs from aerosol deposition, terrestrial input and river discharge. In our previous study (Wang and Li, 2007), we found that BC comprised 5% to 26% of the sedimentary TOC in the shelf sediments of the East China Sea. The discharge of Changjiang River represents a major factor in the deposition of BC in the sediments. By radiocarbon measurement and mass balance calculation, we estimated that fossil fuel (mainly coal) combustion contributed a major fraction (60%–80%) to the BC preserved in these sediments. China has the largest river-dominated marginal seas in the world, including Bohai Bay, Yellow Sea, East China Sea and the South China Sea (Fig.1). The land-sea interactions and anthropogenic influences are quite dynamic in these marginal seas. BC preserved in the surface sediments represents not only a major fraction of the sedimentary TOC but also a significant sink of anthropogenic CO_2, and thus could potentially influence the carbon cycling in the region. It would also be interesting to investigate the distributions and correlations of PAHs and BC in the sediments. However, no such study has been conducted in the region. It is thus the goal of this study to determine and compare the distributions of BC and PAHs in the surface sediments of the marginal seas along China's coast, and to examine the correlation between BC and PAHs as related to the input sources of these two pollutants to the coastal sediments.

2 METHODS

2.1 Study site and sample collection

A total of 49 surface sediments (0–10 cm) were collected from four coastal regions (Fig.1): 12 from Bohai Bay, 11 from the North Yellow Sea, 10 from Jiaozhou Bay and 16 from the northern region of the South China Sea (SCS) during several cruises from 2003–2007. Bohai Bay is a semi-enclosed shallow (mean water depth 10 m) coastal embayment located on the western side of the Bohai Sea (Fig.1a). Bohai Bay is surrounded by the most populated metropolitan area in China (Beijing, Tianjin and Hebei province) and thus is one of the most contaminated coastal regions along the east coast of China. We collected the sediment samples along the Yongding River and Haihe River estuaries and in the
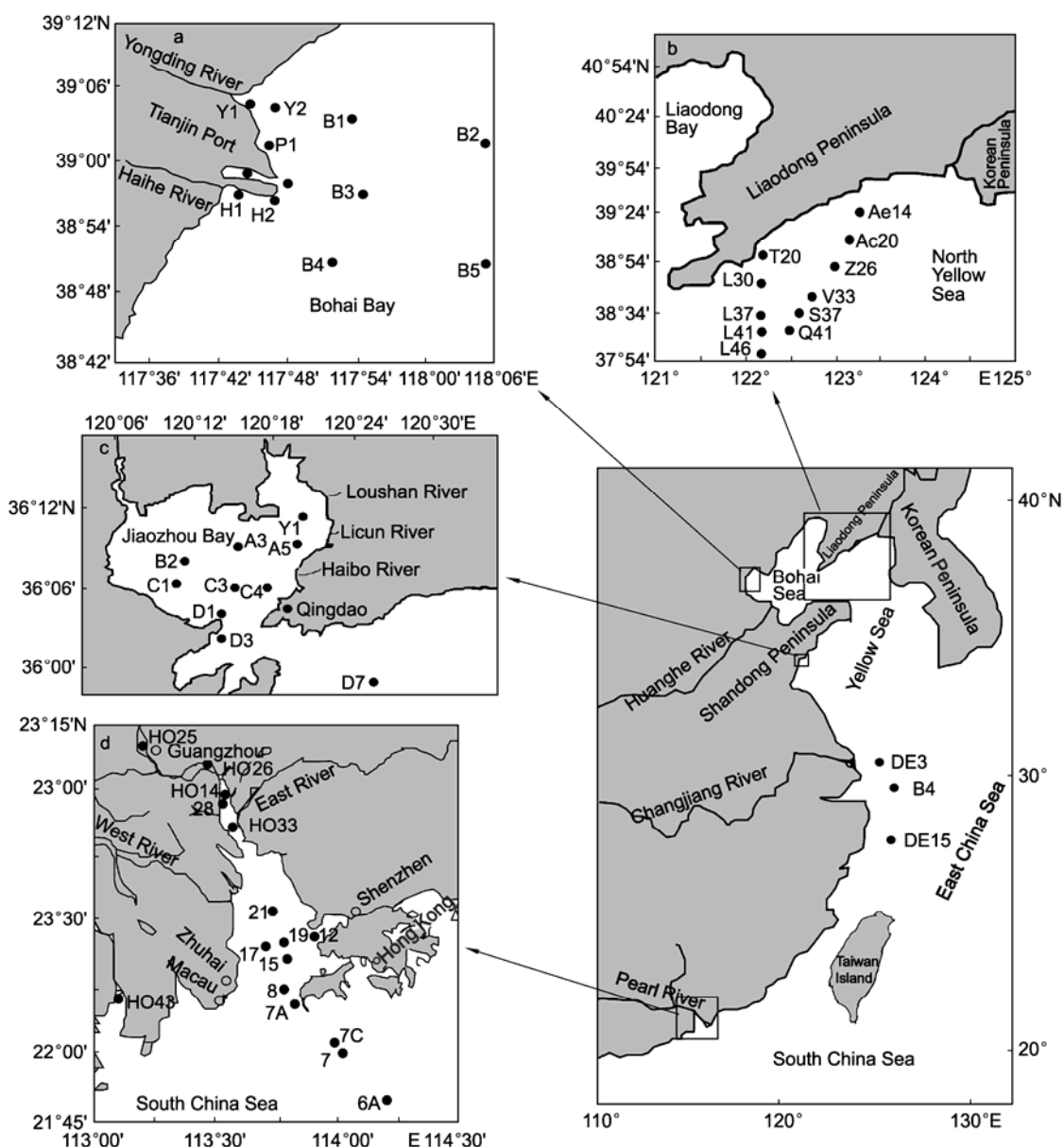
Fig.1 Map showing the four study areas and sampling locations in China's coastal regions

a. Bohai Bay; b. North Yellow Sea; c. Jiaozhou Bay d. northern South China Sea. It also shows the three sampling sites DE3, B4 and DE15 in the East China Sea studied previously by Wang and Li (2007)

Tianjin Port, which are the major channels of contaminant inputs to the bay, as well as western Bohai Bay.

The North Yellow Sea is also a semi-enclosed epicontinental sea with an area of about 1.5×10^4 km^2 and is bordered by China and the Korean peninsula (Fig.1b) (Liu et al., 2004). The North Yellow Sea has a relatively flat sea floor with water depths generally less than 50 m. Sediment deposition into the North Yellow Sea is largely influenced by the input of the Yellow River that has the highest sediment load in the world and transports about 1×10^9 tons/year into the Yellow Sea (Milliman et al., 1989; Liu et al., 2002). Eleven surface sediment samples were collected along two transect lines in the west side of the sea closer to the Bohai Bay mouth.

Jiaozhou Bay is another semi-enclosed coastal embayment located on the eastern coast of China and adjacent to the Yellow Sea (Fig.1c). The area of Jiaozhou Bay is about 400 km^2 with an average water depth of 7 m. Jiaozhou Bay is surrounded by the city of Qingdao. The east side of Jiaozhou Bay is the home of Qingdao Port, one of the largest trading ports in China. Due to its importance in resource for

Table 1 Concentrations of TOC and BC in the surface sediments of China's marginal seas

Station	Longitude (E)	Latitude (N)	TOC (mg/g dw)	BC (mg/g dw)	BC/TOC (%)	ΣPAH (ng/g dw)
Bohai Bay						
Y1	117°44'30"	39°04'26"	8.07	2.45 ± 0.05	30	818
Y2	117°46'44"	39°04'02"	6.13	2.07 ± 0.02	34	589
P1	117°46'12"	39°01'19"	5.95	2.30 ± 0.11	39	3674
P2	117°44'10"	38°58'41"	9.25	2.43 ± 0.06	26	1806
P3	117°47'54"	38°57'51"	5.94	2.16 ± 0.04	36	1514
B1	117°53'31"	39°03'36"	6.25	2.27 ± 0.04	36	324
B2	118°06'00"	39°01'48"	6.09	1.85 ± 0.02	30	364
B3	117°54'36"	38°56'46"	5.92	1.88 ± 0.01	32	83
B4	117°52'19"	38°49'06"	5.27	2.18 ± 0.08	41	1042
B5	118°06'00"	38°49'06"	5.56	2.25 ± 0.10	40	162
H1	117°43'52"	38°57'38"	7.15	2.40 ± 0.01	34	430
H2	117°46'48"	38°57'06"	7.17	1.92 ± 0.03	27	557
Mean			**6.56**	**2.18**	**34**	
North Yellow Sea						
V33	122°44'43″	38°33'33″	7.39	0.74 ± 0.01	10	202
L37	122°10'06″	38°22'43″	12.62	0.17 ± 0.01	1	314
Ac20	123°08'52″	39°08'35″	1.59	<0.10	6	216
T20	122°09'00″	38°59'58″	9.17	0.44 ± 0.06	5	114
L41	122°10'05″	38°12'00″	14.64	0.26 ± 0.06	2	1237
Q41	122°27'23″	38°11'56″	9.02	0.63 ± 0.10	7	87
L46	122°09'53″	38°58'29″	6.82	0.93 ± 0.12	14	48
S37	122°34'18″	38°22'43″	8.65	0.40 ± 0.05	5	81
Z26	122°58'35″	38°52'27″	3.05	<0.10	3	61
L30	122°10'11″	38°41'40″	3.38	0.17 ± 0.02	5	64
Ae14	123°15'52″	39°25'06″	3.75	0.18 ± 0.03	5	49
Mean			**7.28**	**0.37**	**6**	
Jiaozhou Bay						
A3	120°15'00″	36°09'30″	5.61	0.46 ± 0.07	8	n.d.
A5	120°19'48″	36°09'18″	9.57	0.84 ± 0.10	9	499
B2	120°11'12″	36°08'00″	3.40	0.26 ± 0.01	8	173
C1	120°10'31″	36°06'33″	4.73	0.54 ± 0.07	11	16
C3	120°15'00″	36°06'00″	6.00	0.40 ± 0.04	7	1481
C4	120°17'30″	36°06'00″	2.93	0.30 ± 0.01	10	52
D1	120°14'00″	36°04'00″	2.46	0.20 ± 0.09	8	244
D3	120°14'00″	36°02'12″	1.65	<0.10	6	379
D7	120°25'30″	35°59'00″	2.07	0.15 ± 0.02	7	669
Y1	120°20'12″	36°11'19″	9.27	0.97 ± 0.06	10	1482
Mean			**4.77**	**0.42**	**8**	
South China Sea						
sta6A	114º12'17"	21°47'54"	6.36	1.28 ± 0.05	20	358
sta7	113º59'46"	22°00'00"	7.50	0.33 ± 0.03	4	147
sta7A	113º48'20"	22°12'08"	8.63	<0.10	1	414
sta7C	113º58'05"	22°01'36"	3.01	0.35 ± 0.07	12	68
sta8	113º47'07"	22°16'31"	9.70	0.31 ± 0.03	3	751
sta12	113º53'00"	22°26'30"	8.32	0.30 ± 0.07	4	96
sta15	113º46'49"	22°21'32"	9.91	0.33 ± 0.02	3	3346

Continued

sta17	113°43'09"	22°24'16"	11.94	0.17 ± 0.02	1	758
sta19	113°45'03"	22°24'38"	7.29	0.25 ± 0.03	3	405
sta21	113°44'13"	22°30'36"	7.89	0.15 ± 0.03	1	446
sta28	113°33'29"	22°54'18"	15.66	0.40 ± 0.02	3	2169
HO14	113°36′51″	22°56′34″	14.32	0.35 ± 0.06	2	378
HO25	113°13′10″	23°06′56″	44.44	1.86 ± 0.02	4	1170
HO26	113°29′30″	23°03′30″	19.90	0.54 ± 0.04	3	577
HO33	113°37′26″	22°47′28″	10.56	0.55 ± 0.01	5	178
HO43	113°06′40″	22°12′41″	9.09	0.30 ± 0.08	3	107
Mean			**12.16**	**0.47**	**5**	
East China Sea						
DE3	122°74′	31°15′	2.6-5.4	0.64-1.38	17-26	
B4	122°01′	30°36′	2.7-5.4	0.59-1.18	17-25	
DE15	122°51′	28°07′	2.5-6.2	0.18-0.74	5-15	

Note: n.d.: not determined; ΣPAH data for Jiaozhou Bay are from Wang et al., 2006;

TOC and BC data for the three sediment cores in East China Sea are from Wang and Li, 2007.

civil, industrial and commercial development, Jiaozhou Bay has been selected as a long-term ecosystem station for studies of biological, chemical and ecosystem changes in response to the anthropogenic impact in the bay (Wang et al., 2006). Samples from the northern South China Sea (SCS) were collected from the Pearl River Estuary and adjacent shelf region (Fig.1d). The Pearl River is the second largest river in China in terms of water discharge and flows into the northern SCS. It discharges about $3.13×10^{11}$ m^3 of fresh water and $7.1×10^8$ tons of suspended particulate matter into the SCS annually (Hong et al., 1999；Zhang et al., 1999). Previous studies have shown that the sediments in the harbor and Pearl River estuarine region were highly contaminated by metals (Liu et al., 2003) and organic pollutants such as PAHs (Hong et al., 2000; Liu et al., 2005). Sixteen surface sediments were collected along the Pearl River Estuary. All surface sediments were collected using either stainless steel grab sampler or box corer. After collection, the sediments were kept frozen and transported back to the laboratory for further processing.

2.2 BC separation and analysis

Chemothermal oxidation (CTO) and chemical oxidation (CO) are the two most commonly used methods to separate BC in soils and marine sediments. Studies have shown that both methods are precise and reproducible for determining BC concentration (Gustafsson et al., 2002; Masiello et al., 2002). In our previous study (Wang and Li, 2007), we compared these two methods for measuring BC levels in the sediments collected from the East China Sea. We found that the two methods, in general,

yielded similar results but the CTO method gave slightly higher (<8%) BC concentrations than the CO method did. In this study, we applied the CTO method as described by Gustafsson and Gschwend (1998) and Gustafsson et al. (2002). The CTO method defines BC as the remaining organic carbon after the samples are thermally oxidized at high temperature. Applying this method, sediments were first oven dried at 60°C, then grounded to powder and acidified with 10% HCl solution to remove inorganic carbon. The acid-treated sediments were washed three times with Milli-Q water, centrifuged, and dried again. The dried sediments were placed in thin layers (3–5 mm) in an oven and heated at 375°C for 24 hours with continuous air supply. Organic carbon left after this oxidation step was operationally defined as BC and the concentrations of both BC and sedimentary TOC were measured in duplicate using a CHN elemental analyzer.

2.3 PAH extraction and analysis

For PAH extraction, 5.0 g of dried sediment was weighed into 50-ml centrifuge tubes and spiked with deuterated d_{10}-phenanthrene as an internal recovery standard. The sediment was extracted three times with a 30 ml mixed solvent of 70% dichloromethane (DCM) and 30% methanol by ultrasonication. After extraction, the samples were centrifuged (3 500 r/min, 10 min) and all extracts were combined and rotary evaporated to near dryness. The evaporated sample was re-dissolved in 2 ml hexane for further column separation.

PAHs were separated using a 1.0×20 cm glass chromatography column packed with pre-baked activated silica gel (100–200 mesh). PAHs were
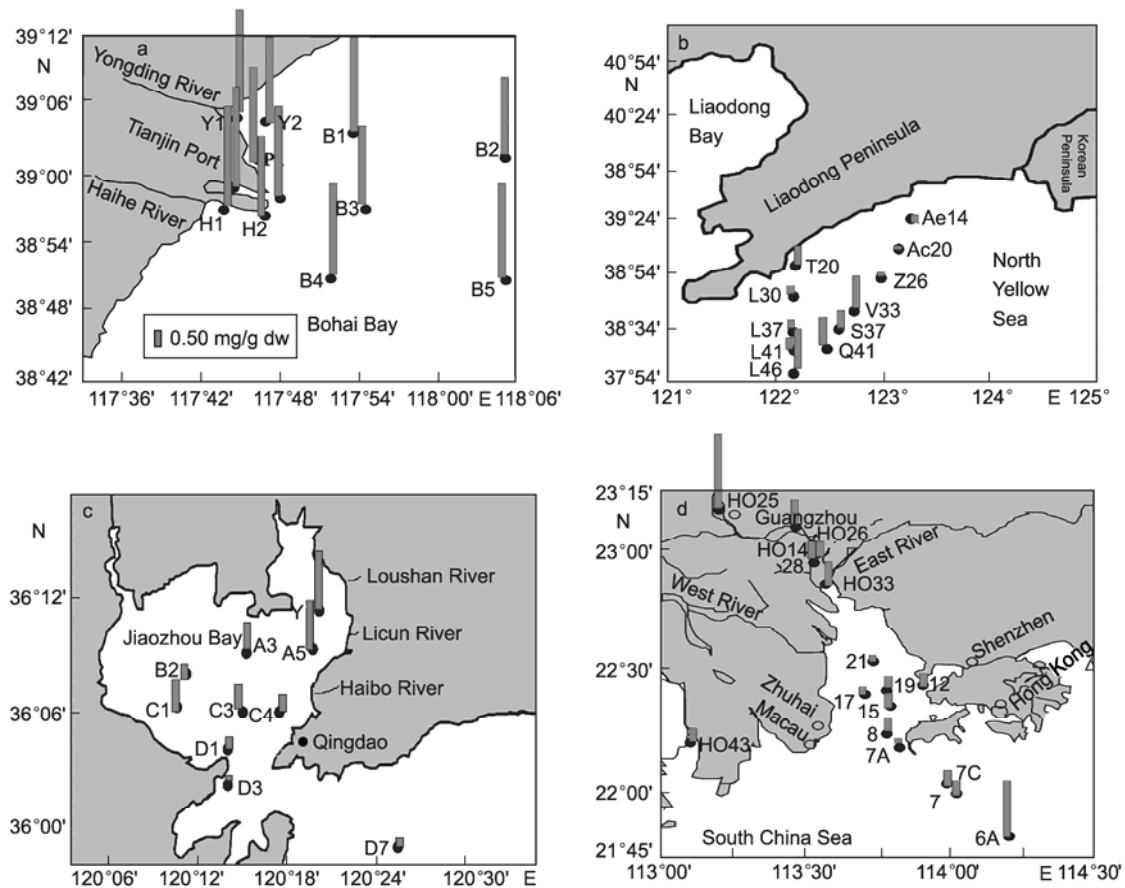
Fig.2 Distribution of black carbon (BC) in the surface sediments (0−10 cm) of the four marginal seas

a. Bohai Bay; b. North Yellow Sea; c. Jiaozhou Bay; d. northern South China Sea. The concentration of BC (in mg/g dry wt.) is indicated as the scale bar and the values are listed in Table 1

eluted with 25 ml of a mixture solvent containing 70% hexane and 30% DCM. After collection, the samples were rotary evaporated down to about 1 ml, transferred to a glass vial, and further concentrated down to 50–100 μl with high purity N_2. The samples were then capped and stored at -20°C until analysis. All glassware used in sample processing was pre-baked at 500°C for 6 h.

PAHs were analyzed using a Finnigan Trace DSQ Gas Chromatography/Mass Spectrometer (GC/MS). The GC was equipped with a split/splitless injector and an AS3000 auto-sampler. Sixteen US EPA priority PAHs were separated using a J&W DB-5 capillary column (30 m×0.25 mm) programmed from 50°C to 300°C at a rate of 6°C/min and held at 300°C for 10 min. Helium was used as a carrier gas, and the flow rate was set at 1 ml/min. The mass spectrum was scanned from 50 to 600 in the Electron Ionization (EI) mode (70 eV). Individual PAHs were quantified based on the retention time and m/z ratio of an authentic PAH mixed standard (Sigma), and concentrations of each PAH were calibrated based

on the standard calibration curve. A series of blanks were also analyzed following the procedures described above. Concentrations of PAHs associated with the blanks were undetectable.

3 RESULTS AND DISCUSSION

3.1 TOC and BC in sediment

Concentrations of TOC and BC measured in the sediments are summarized in Table 1. TOC values ranged from 5.27 to 9.25, 1.59 to 14.6, 1.65 to 9.57 and 3.01 to 44.4 mg/g dw (gram dry weight), for the sediments from Bohai Bay, North Yellow Sea, Jiaozhou Bay and South China Sea, respectively. Bohai Bay sediments had relatively constant TOC values compared with sediments from other coastal regions. For the North Yellow Sea, sediments collected from a nearshore site (T20) and sites outside of the Bohai Bay mouth (L37, L41, L46, V33, S37, Q41) had relatively higher TOC concentrations than sediments from other stations. Sediment deposition at these sites was likely affected directly by the coastal land
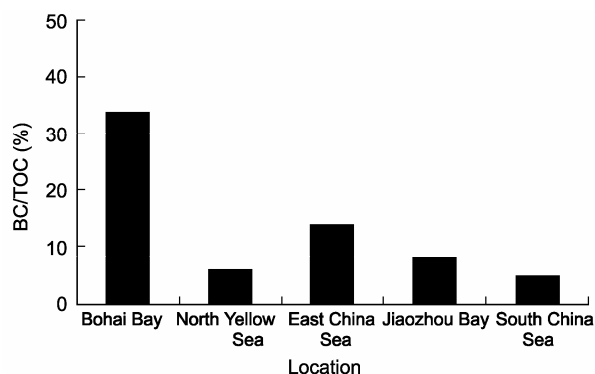
Fig.3 Comparison of the average BC/TOC ratios in surface sediments of China's five marginal seas
Data for the East China Sea is from Wang and Li (2007)

impact, water exchange between the Bohai Bay and the North Yellow Sea, and the discharge from the Yellow River. All these processes could transport significant amount of terrestrial organic matter into the North Yellow sea region. In Jiaozhou Bay, relatively high TOC values (9.27–9.57 mg/g dw) were measured for the sediments collected in the northeast region of the bay close to the Loushan River and Licun River estuaries which have been the major inputs of terrestrial material and contaminants to Jiaozhou Bay (Wang et al., 2006). TOC concentrations in the surface sediments of the Pearl River estuary in the South China Sea were higher and showed some spatial variations. Sediments from stations HO25 and HO26, which are located in the upper estuary and surrounded by a highly populated metropolitan area (Guangzhou city), had TOC values of 44.44 and 19.90 mg/g dw, respectively, much higher than the TOC values of sediments from other sites. The high TOC values of these sediments likely reflect a high degree of anthropogenic and industrial contamination of the sampled sites. A study by Li and Lee (1998) reported that anthropogenic organic carbon could make up 50% of the carbon pool in some coastal waters in the Pearl River Estuary due to growing urbanization and industrialization along the estuary. Sediment TOC values generally decreased from the upper estuary to the shelf of SCS. The spatial differences of the TOC values measured in the surface sediments from these marginal seas clearly reflect the influence of both terrestrial inputs and anthropogenic contamination in these coastal regions.

The BC contents measured in the surface sediments of the different marginal seas also showed large variations (Fig.2). The highest BC levels (1.85–2.45 mg/g dw) were found in the surface sediments

from Bohai Bay. These BC contents accounted for 27%–41% of the TOC pool in the sediments. In comparison, BC levels in the sediments from the North Yellow Sea (<0.10–0.93 mg/g dw), Jiaozhou Bay (<0.10–0.97 mg/g dw) and the South China Sea (<0.10–1.86 mg/g dw) were much lower and accounted for 1%–14%, 6%–11% and 1%–20%, respectively, of the sedimentary TOC in these coastal embayments. In Fig.3, we compared the average BC contents (BC/TOC) in the sediments for the five coastal regions in China. Bohai Bay has the highest BC contents (34%) in surface sediments, followed by the East China Sea (14%), Jiaozhou Bay (8%), the North Yellow Sea (6%) and the South China Sea (5%). These differences in BC contents of the surface sediments largely reflect the sources, inputs and deposition patterns of BC in different coastal regions. Bohai Bay is a semi-enclosed coastal embayment and the water exchange between the bay and the North Yellow Sea is relatively slow and poor (Tao, 2006). Furthermore, rivers and land inputs (e.g., runoffs, wastewater) could carry significant amounts of BC and contribute to the discharge of terrestrial materials into the bay. In addition, deposition from airborne particles that carry BC could also be a significant source of BC in the bay. This is substantiated by studies which report that coal combustion has been a major source of BC emission of airborne particles above Beijing and Tianjin (Liu and Shao, 2007; Cao et al., 2006). In the last 20 years, the consumption of coal in China has increased almost 200% from 0.82 billion tons in 1985 to 2.17 billion tons in 2005 (NBSC, 1987; NBSC, 2007).

The BC contents in the surface sediments of China's marginal seas are comparable with the data reported for the other coastal regions in the world. In the United States, for example, studies reported that BC accounted for 1%–7%, 4%–7%, 3%–19% and 5%–11% of the TOC in the sediments from the Washington coast (Lim and Cachier, 1996), Pensacola Bay, Florida coast (Simpson and Hatcher, 2004), Gulf of Maine and New England Harbor (Gustafsson and Gschwend, 1998), and Santa Monica Basin in the northeast Pacific (Masiello et al., 2004), respectively. Oen et al. (2006) measured BC concentrations ranged from 0.10% to 1.7% and accounted for 1.3%–18.1% of the TOC in different size fractions in the Norwegian harbor sediments. Among the coastal regions investigated in this study, Bohai Bay had the highest BC abundance in the surface sediments and the sediments of North Yellow Sea, the East China Sea, Jiaozhou Bay and the South
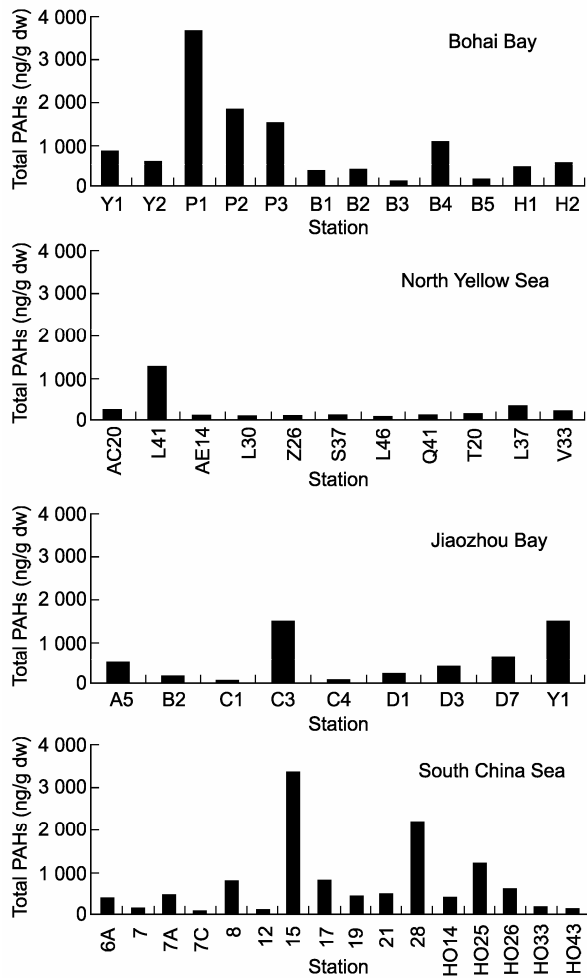
Fig.4 Distribution of total PAH in the surface sediments of Bohai Bay, North Yellow Sea, Jiaozhou Bay and South China Sea

Data for Jiaozhou Bay is from Wang et al. (2006)

China Sea had similar BC contents with reported data suggesting that the coastal sediments are important sink of BC worldwide.

3.2 PAH in sediments

In order to examine the correlation between BC and PAHs, we measured the 16 US EPA priorit PAHs (Naphthalene, Acenaphthylene, Acenanphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene,Benzo(a)anthracene, Chrysene, Benzo(b) fluoranthene, Benzo(k) fluoranthene, Benzo(a)pyrene, Indeno(1,2,3-c,d)pyrene, Dibenz(a,h)anthracene, and Benzo(g,h,i)perylene) for the sediments. The results of ΣPAH are summarized in Table 1. ΣPAH in the surface sediments ranged from 78 to 3 667 ng/g dw for Bohai Bay, 41 to 1 233 ng/g dw for the North Yellow Sea, 16 to 1 482 ng/g dw for Jiaozhou Bay and 64 to 3 341 ng/g dw for the northern SCS (Fig.4). Like BC, the concentration of ΣPAH also showed
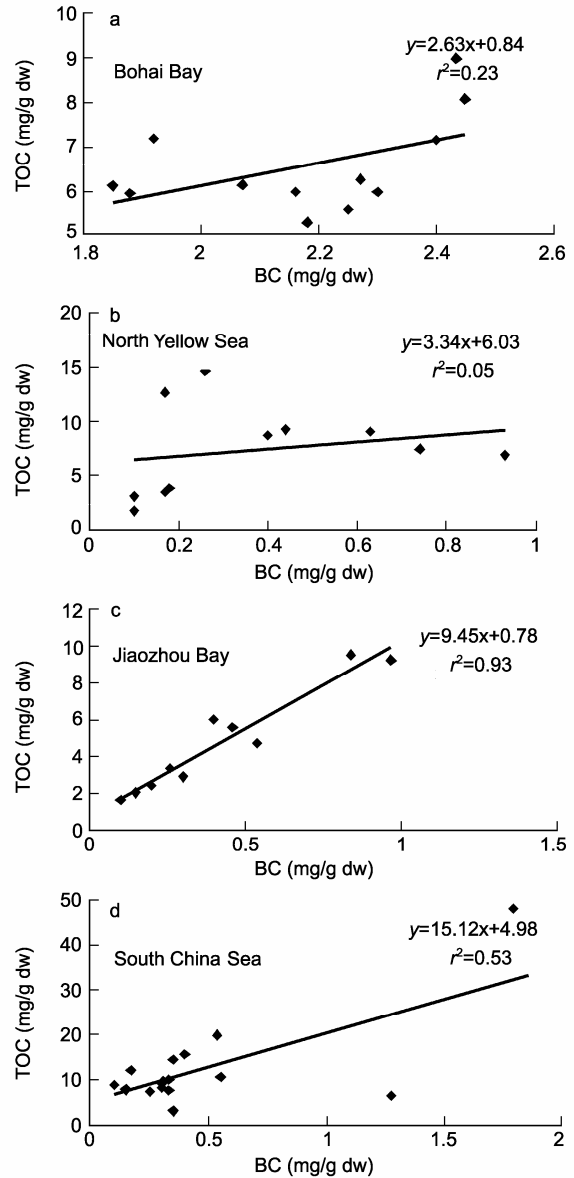

Fig.5 Relationship between BC (mg/g dw) and TOC (mg/g dw) in the surface sediments of China's marginal seas

a. Bohai Bay; b. North Yellow Sea; c. Jiaozhou Bay; d. northern South China Sea. The lines are linear fits to the data

large variations among the different sampling sites and regions. In the Bohai Bay, high PAH concentrations were found in the sediments collected near the Tianjin Port (P1, P2 and P3) (Fig.1a), a highly contaminated industrial and commercial harbor. In the North Yellow Sea, ΣPAH concentrations were much lower, less than 320 ng/g dw for all the sediments except for station L41 where the ΣPAH concentration was several times higher than that of the other stations. In Jiaozhou Bay, ΣPAH concentrations in the surface sediments were also lower for most of the stations compared with the values in Bohai Bay but relatively high

concentrations were measured for the sediments at the C3 and Y1 sites. The distribution and sources of PAHs in the sediments of Jiaozhou Bay were investigated in our previous study. River discharge and point-source contamination were likely the causes of the observed distribution patterns of PAHs in the bay (Wang et al. 2006). In the northern SCS, concentrations of ΣPAH also showed large spatial variations, with high values determined for the sediments (HO25, 15, 28) inside the estuary. The observed variations of PAHs in the surface sediments were clearly related to the local contamination and point-source inputs to these different coastal regions.

3.2 Correlations of BC vs. TOC and PAH

Previous studies have suggested that a strong correlation exists between BC and TOC, and BC and PAHs in sediments due to the efficient adsorption of PAHs to BC (Muri et al., 2003; Thorson et al., 2004; Lohmann et al., 2005; Koelmans et al., 2006). We examined the correlations between BC and TOC, and BC and ΣPAH in the surface sediments of the China's marginal seas. As shown in Fig.5, it appeared that the distributions of BC in the surface sediments of the four coastal regions were all positively related to the sedimentary TOC but strong linear correlations were only found for Jiaozhou Bay and the Pearl River Estuary in SCS. These differences are likely related to the variations of input sources of both TOC and BC to the sediments of the different coastal regions. The poor correlation in the North Yellow Sea is likely related to the fine sandy sediment nature. In coastal sediments, organic matter in the sediments was from different sources including marine, terrestrial and anthropogenic introduced materials, while BC was mainly derived from combustion processes and weathering (Goldberg, 1985; Dickens et al., 2004b). High concentration of BC is therefore not necessarily associated with organic carbon rich materials when deposited into sediments. After being deposited, sedimentary geochemical processes will also affect the preservation of TOC and BC. Fresh organic matter will undergo rapid decomposition at the sediment-water interface whereas BC, due to its far more stable chemical nature, will be preserved in the sediment for a much longer time (Masiello and Druffel, 1998; Dickens et al., 2004b). To further support our explanations, we also examined the correlation of BC and TOC for the sediments studied worldwide (Fig.6). By comparing the five different regions, a strong liner correlation between BC and TOC existed only for the

Mediterranean Sea sediments and not for the Arctic coast and the coastal regions in the US, further suggesting that the different input sources and geochemical factors could affect the distribution of TOC and BC in coastal sediments.
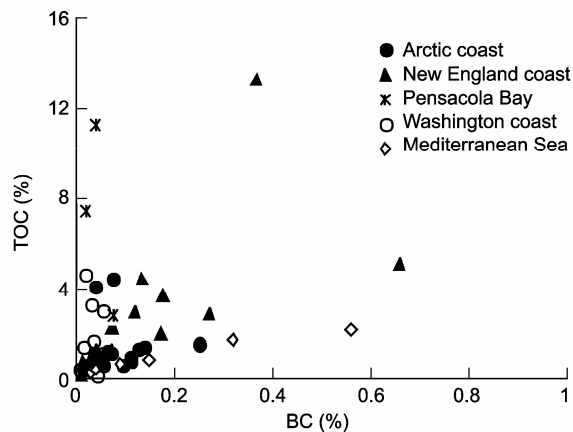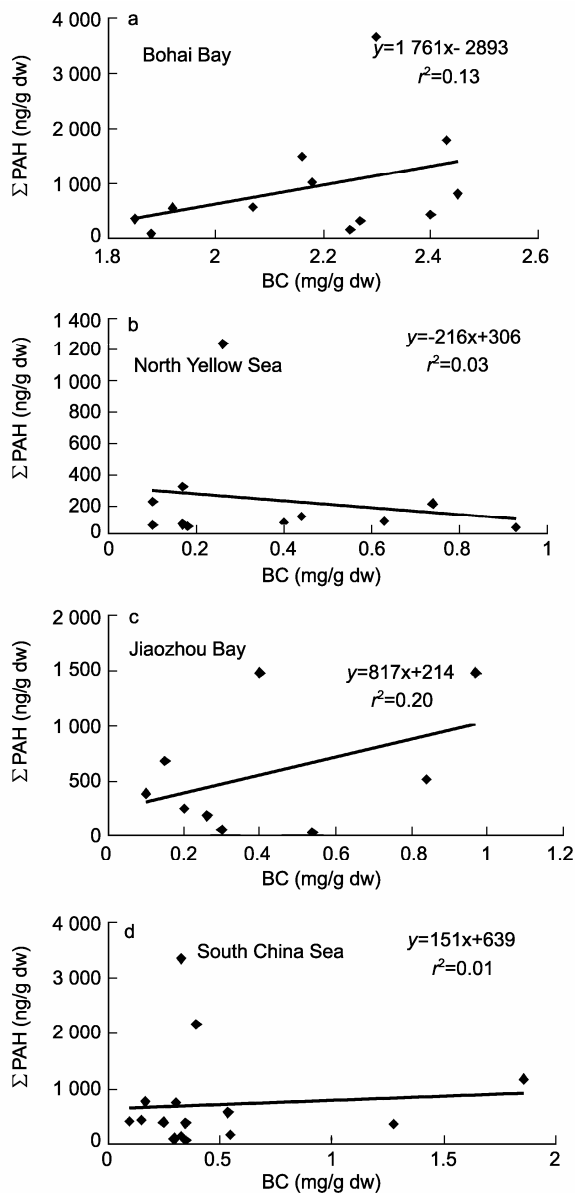

Fig.6 Relationship between BC (%) and TOC (%) in the surface sediments of other marine environments in the world

Arctic coast (Guo et al., 2004), New England coast (Gustafsson and Gschwend, 1998), Pensacola Bay (Simpson and Hatcher, 2004), Washington coast (Dickens et al., 2004b), and Mediterranean Sea (Taspakis et al., 2003)

In Fig.7, we examined the correlation between BC and ΣPAH in the surface sediments. Clearly, a strong positive linear relationship was not found in the sediments of any regions. Although concentrations of ΣPAH generally increased with high BC contents in the sediments in Bohai Bay, Jiaozhou Bay and the South China Sea, the correlations were rather weak (r^2=0.13, 0.20 and 0.01). In the sediments of North Yellow Sea, concentrations of ΣPAH even decreased slightly with increasing BC contents. This suggests that although BC has strong adsorption capacity for PAHs, the present of BC and PAHs in the surface sediments of these coastal regions was likely derived from different sources. We have also examined the correlation between BC and some 5 and 6 ring PAHs and no strong correlation was found either (Kang, 2008). If both BC and PAHs were from the same combustion-derived sources and both deposited into the sediment from airborne and river discharged particles, a strong correlation between BC and PAH would be expected. This has been well demonstrated in the remote alpine Lake Planina (Slovenia) sediment core in which BC and ΣPAH were well-correlated below the 8 cm depth, especially during a huge forest fire which occurred in 1948 and surrounded the lake, resulting in changes in the sediment core (Muri et al., 2003). In the surface layer

Fig.7 Relationship between total PAH and BC in the surface sediments of China's marginal seas

a. Bohai Bay; b. North Yellow Sea; c. Jiaozhou Bay; d. northern South China Sea. PAH data for Jiaozhou Bay is from Wang et al. (2006). The lines are linear fits to the data.

(0–7 cm) of the core, however, BC and ΣPAH was not found to be positively correlated at all (Muri et al., 2003). In their study of PAHs and BC in the surface sediments of the Eastern Mediterranean Sea, Tsapakis et al. (2003) found very strong correlations (r^2=0.95) between PAHs and BC. They contributed this to the importance of atmospheric transport as the major input of PAHs and BC to sediments of remote regions. This is certainly not the case for most coastal regions close to the urban areas. In our study, we could expect that the input sources of BC and PAHs to the surface sediments in China's coastal regions

were different. BC could be derived from both fossil fuel combustion and biomass burning. In our previous study using radiocarbon (^{14}C) measurement, we found that most of BC (60%–80%) preserved in the Changjiang River Estuarine and East China Sea shelf sediments was much older than sedimentary TOC and was derived mainly from fossil fuel (mainly coal) combustion (Wang and Li, 2007), consistent with the airborne BC studies conducted in China (Streets et al., 2001; Liu and Shao, 2007). As suggested by Dickens et al. (2004a, b), fossil weathering could also contribute to a significant fraction of old BC carried by rivers to the coastal sediments. Fossil fuel combustion will contribute to an increase in both BC and PAHs in the sediments whereas fossil weathering could only contribute to an increase in BC in coastal sediments (Dickens et al., 2004b). BC resulting from fossil weathering in coastal sediments could constitute a significant fraction of the determined BC pool (Dickens et al., 2004b). For PAHs, however, we have found that petrogenic sources (oil spill and contamination from petroleum products) have been the major inputs to the surface sediments in China's coastal regions, especially in the highly contaminated harbors, bays and metropolitan-surrounded estuaries (Wang et al., 2006). The petrogenic sources would not likely contribute BC to the surface sediment. A strong correlation between BC and ΣPAH in these surface sediments is therefore not expected. Our study also suggests that BC as an indicator of biomass fire could not be properly applied to the recent sediments of coastal environment.

4 SUMMARY

Our study demonstrates that BC and PAHs as common pollutants are widely dispersed in the surface sediments of China's marginal seas. Our results indicate that Bohai Bay has the highest BC and PAH contents and BC accounted for 27%–41% of the TOC preserved in the surface sediments. BC contents in the surface sediments of the other coastal regions in China are relatively lower but comparable with the values reported for the other coastal sediments in the world. BC preserved in these sediments represents a significant pool of "slow-cycling" carbon that will not only affect the carbon cycling in the region but also provides long-term carbon storage, possibly for the missing carbon in the global carbon balance.

BC was positively correlated with TOC in the surface sediments studied. BC and ΣPAH in these

sediments, however, was not strongly correlated, suggesting different input sources of BC and PAHs to the coastal sediments and also different biogeochemical processes that affect and control the distribution and preservation of BC and PAHs in the coastal sediments.

5 ACKNOWLEDGEMENT

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