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Quantification, morphology and source of humic acid, kerogen and black carbon in offshore marine sediments from Xiamen Gulf, China

Yanting Chen^{1,4}, Jinping Zhao^{2,*}, Liqian Yin¹, Jinsheng Chen^{1,*}, Dongxing Yuan³

1. Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.

E-mail: ytchen@iue.ac.cn

2. Guangdong Environmental Monitoring Center, Guangzhou 510308, China

3. State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen 361005, China

4. Environmental Science and Engineering Department, Huaqiao University, Xiamen 361021, China

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Abstract

Three types of macromolecular organic matters (MOMs), i.e. humic acid (HA), kerogen+black carbon (KB), and black carbon (BC) were extracted from marine sediments of Xiamen Gulf, southeast of China. The chemical composition, morphological property and source of the three extractions were characterized by elemental analyzer/isotope ratio mass spectrometry (EA/IRMS) and scanning electron microscope (SEM). The results showed that KB was the predominant fraction in MOMs, which accounted for 61.79%–89.15% of the total organic content (TOC), while HA consisted less than 5%. The relative high contents of kerogen and BC, and low contents of HA in the samples indicated that anthropogenic input might be the major source of organic matter in marine sediments near the industrial regions. The characterization of SEM, not only revealed morphological properties of the three fractions, but also allowed a better understanding of the source of MOMs. The $\delta^{13}\text{C}$ values of the three fractions suggested that materials from terrestrial C_3 plants were predominant. Furthermore, the anthropogenic activities, such as the discharge of sewage, coal and biomass combustion from industry nearby and agricultural practices within drainage basin of the Jiulong River, were remarkably contributed to the variations in $\delta^{13}\text{C}$ values of MOMs in the offshore marine sediments.

Key words: macromolecular organic matters; elemental analyzer/isotope ratio mass spectrometry; scanning electron microscope; offshore marine sediment; Xiamen

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Introduction

Marine sediments, which had a strong ability to accumulate pollutants, were considered to be the ultimate sinks for different kinds of anthropogenic contaminants. With the rapid industrialization and economic development in coastal region, many organic and inorganic materials were introduced to estuarine and coastal environments (Garcette-Lepecq et al., 2000). The macromolecular organic matters (MOMs) with complex composition and structure, such as humic-like substances, humic acid (HA), kerogen (K), and black carbon (BC), represent quantitatively the main components of sedimentary organic matters. HA, K and BC had received increasing attentions from scientists. However, plenty of research works (e.g., Jansen et al., 1996; Middelburg et al., 1999; Muri et al.,

2002; Hiradate et al., 2004; Giani et al., 2010) had focused on methods applied to the structural characterization of these MOMs. Isolation of homogeneous MOMs, which were heterogeneous and macromolecular substances, from marine sediments, had always been a challenging work for researchers (Amir et al., 2005; Shirshova et al., 2006; Budinova et al., 2009). MOMs played an important role on the interaction and transportation of toxic organic, inorganic substances and nutrient cycling in the environment (Zech et al., 1997; Gustafsson et al., 2001; Xiao et al., 2004). Therefore, detailed chemical and physical characterization of MOMs was crucial in studying these reactions and processes.

Rapid urbanization of Xiamen City in the past two decades has made great environmental stress on its western bay and the adjacent area. Several investigations for contaminations in sediment had been conducted in Xiamen Gulf, which were mainly focused on organic pollutants, such as PAHs, HCHs, DDTs and PCBs, and heavy metals

* Corresponding author. E-mail: inyinh7935@sina.com (Jinping Zhao); jshchen@iue.ac.cn (Jinsheng Chen)

(e.g., Maskaoui et al., 2005; Jiang et al., 2007; Zhang et al., 2007). However, there was comparatively less investigation of MOMs in the offshore marine sediments in recent decade, due to their complexity of chemical composition and trace levels of presence in the coastal environment of Xiamen, China.

In the present study, we isolated HA, KB and BC from offshore marine sediments in Xiamen Gulf, and then characterized the chemical compositions, morphological properties and source of the extracted macromolecular organic matters using scanning electron microscopy (SEM) and elemental analyzer/isotope ratio mass spectrometry (EA/IRMS). The aim of this study is to provide new chemical information about organic macromolecules from the sediment in Xiamen.

1 Materials and methods

1.1 Sampling

The samples were collected from four different sites (XM1, XM2, XM3, XM4, Fig. 1) in July, 2010. A Van Veen grab sampler was used for collecting samples from the top 0–20 cm layer of surface sediments in Xiamen Gulf.

XM1 is closed to the uninhabited Jiyu Island, and is regarded as the background site. XM2 is near Songyu Port that is a commercial port situated in the Western Xiamen Bay. This bay is semi-enclosed, and has an excellent natural condition for navigation and shipping activities in southeast China. XM3 and XM4 are located at the estuary of Jiulong River, and are influenced by intense industrial activities nearby and diversified agricultural practices within drainage basin of the Jiulong River. These anthropogenic activities represent a potential major source of pollutants in Xiamen Gulf.

After the field work, sediment samples were carefully shipped and preserved in a refrigerator (-20°C). The sediment samples for extraction and purification were initially

dried at -85°C under vacuum, ground to powder with the agate mortar, sieved through a sieve of 0.15 mm, and kept in a pre-cleaned polyethylene bottle for further experiment.

1.2 Sequential extraction of MOMs

The isolation protocol of MOMs, including HA, KB and BC, was based on the methods of Song et al. (2002) and Zhao et al. (2011). HA, KB and BC were separated from the sediment by sequentially treatment with NaOH, HCl/HF and $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (Fig. 2).

For the isolation of HA, the sediment sample was extracted by 0.1 mol/L NaOH under a nitrogen atmosphere, and then treated in ultrasound bath. After extraction for 12 hr on a shaker, it was centrifuged and the supernatant was then transferred to another bottle. The extraction was repeated until the supernatant became colorless. The extracts from different batches were combined and acidified to $\text{pH} = 1.0\text{--}2.0$ by concentrated HCl acid (6 mol/L) to precipitate HA. The base-extracted residues of sediment were subjected to subsequent treatment for isolation of KB and BC.

After 24 hr stagnant precipitation, the acidified solution was centrifuged and the residue, i.e., the HA fraction, was purified by a dissolution and precipitation processes with 0.1 mol/L KOH/0.2 mol/L KCl and 0.1 mol/L HCl/0.3 mol/L HF, respectively. HA precipitate was dialyzed with distilled water until the Cl^- ion tested by silver nitrate (AgNO_3) disappeared. Finally, HA was dried under vacuum (-85°C) and stored in a refrigerator for further analysis.

For the isolation of KB, the residue following NaOH extraction was treated with 6 mol/L HCl to remove carbonates, mixed solution HCl/HF at 1 (6 mol/L):2 (22 mol/L) volumetric ratio to demineralize, and 6 mol/L HCl to remove the minerals, i.e., the fluorite, formed during the demineralization procedure. It was important to note that HF/HCl treatment, when applied to extraction, results in not only the elimination of most minerals, but also

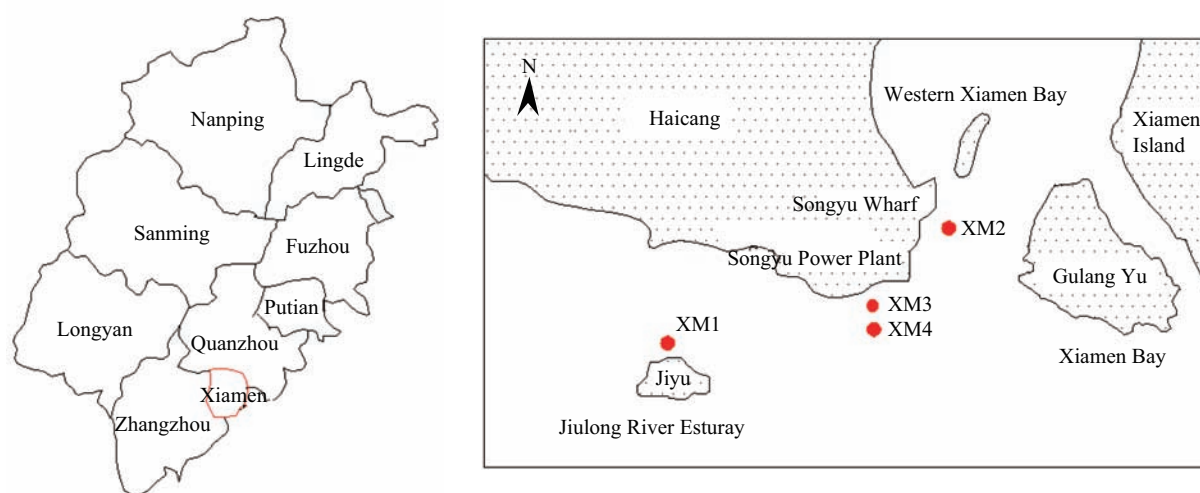


Fig. 1 Location of the four sampling sites in Xiamen, China.

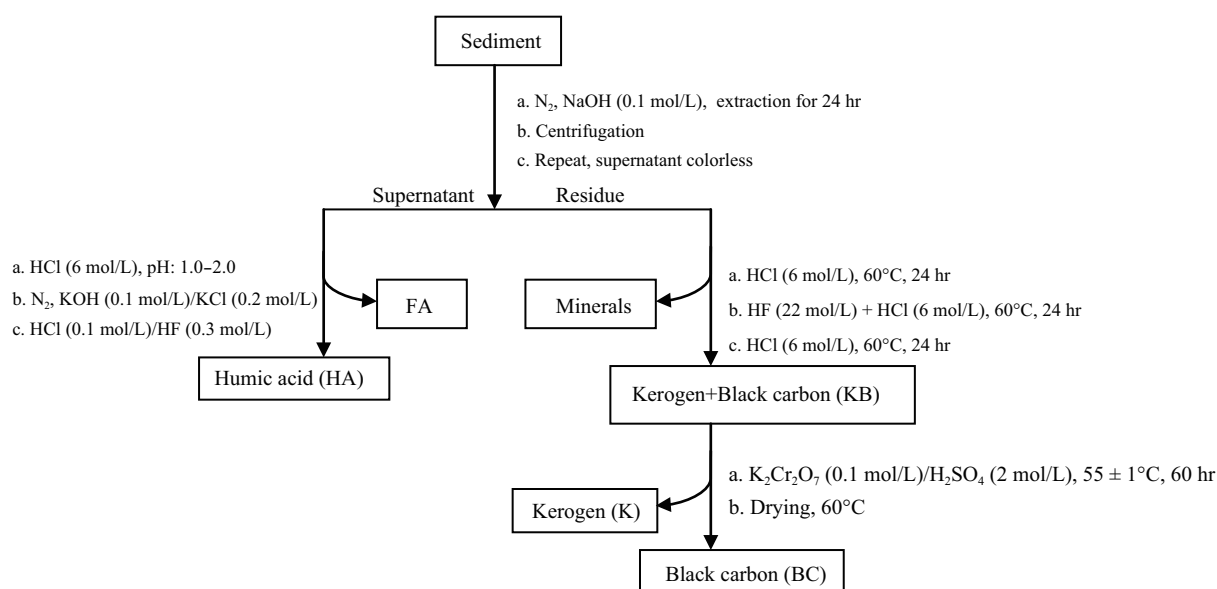


Fig. 2 Flow chart of extraction and quantification of the three MOM fractions.

the removal of some insoluble, macromolecular organic constituents (such as labile protein and polysaccharide-derived moieties) due to acid hydrolysis (Garcette-Lepecq et al., 2000).

For the isolation of BC, a predetermined amount of KB was placed in a bottle containing aqueous dichromate/sulfuric acid solution (0.1 mol/L $K_2Cr_2O_7$ + 2 mol/L H_2SO_4), and disaggregated by ultrasonic bath. The bottle was then placed in a water bath at $55 \pm 1^\circ C$ for 60 hr. At last, the bottle was centrifuged and dried in an oven at $60^\circ C$. The advantage of wet chemical oxidation could avoid charring non-BC fractions, while the disadvantage was possible loss of BC phases during the oxidation by 0.1 mol/L $K_2Cr_2O_7$ /2 mol/L H_2SO_4 (Skjemstad and Taylor, 1999).

After dried, the HA, KB and BC samples were thoroughly ground in an agate mortar and homogenized, to reduce variability between replicates and potential charring during thermal treatments (Middelburg et al., 1999).

1.3 Characterization of MOMs

Carbon contents and isotope ratios of the three fractions of MOMs were determined by elemental analyzer/isotope ratio mass spectrometry (EA/IRMS). The elemental analyzer (Flash HT 2000, Thermo Fisher Scientific) was interfaced in continuous flow mode, through a gas chromatography (GC) column, to an isotope ratio mass spectrometry (DELTA V Advantage, Thermo Fisher Scientific). About 1 mg MOMs in tin capsules was introduced into a high-temperature combustion unit at $960^\circ C$ in an O_2 atmosphere, where MOMs were converted to CO_2 . Combustion gases were purified through a reduction column by a stream of inert He gas and passed into a GC column at $40^\circ C$, where CO_2 , still in the He stream was separated from other gases. Then CO_2 was carried into the elemental

analyzer/isotope ratio mass spectrometry, where the carbon contents and $\delta^{13}C$ values were determined. The complete analysis time for C was about 4.5 min. The laboratory standard was urea, with carbon content of 20% and $\delta^{13}C$ values of 40.81‰. The results of the carbon isotopic ratios ($\delta^{13}C$) were reported in per mil (‰) relative to PDB, and were calculated according to the following Eq. (1):

$$\delta^{13}C_{\text{value}} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000\text{‰} \quad (1)$$

where, $R = {}^{13}C/{}^{12}C$. The precision for the analysis of $\delta^{13}C$ of the urea was $\pm 0.2\text{‰}$.

The morphologies (shapes, sizes) of HAs, KBs and BCs were examined using a scanning electron microscope (Hitachi S-4800, Japan) with an energy-dispersive X-ray spectrometer (Oxford Link INCA 300). Samples were coated with Au for 180 sec and analyzed at 5 kV with a working distance in the range 6–8 mm.

2 Results

2.1 Relative contents and carbon contents of MOMs

The relative contents of HA, KB and BC of TOC were calculated based on the organic carbon contents (Song et al., 2002; Zhao et al., 2011) (Eq. (2)):

$$G_i = \frac{TOC_{G_i} \times M_{G_i}}{TOC_{G_0} \times M_{G_0}} \times 100\% \quad (2)$$

where, G_i (wt.%) is the relative content of HA, KB and BC of TOC, M_{G_i} (g) is the mass of HA, KB and BC, TOC_{G_i} (%) is the carbon content of the isolated fraction, M_{G_0} (g) is the mass of the original sample from which the MOMs were isolated, TOC_{G_0} (%) is the TOC contents of the original sample.

The average value of M_{G_i} was calculated based on six replicates and the relative standard deviations were less than 6%. The final results of the relative contents of different MOM fractions are summarized in **Table 1** for the four sediment samples.

The data listed in **Table 1** show that: (1) TOC contents for marine sediments in Xiamen Gulf varied in a range of 0.27%–0.48%, while the carbon contents fluctuated from 17.06% to 20.31% for HA, from 17.37% to 29.55% for KB, and from 24.02% to 38.84% for BC. (2) KB constitutes 61.79%–89.15% of the TOC, of which BC and K samples account for 10.37%–64.39% and 24.76%–67.04% of the TOC, respectively, while HA less than 5%.

2.2 Scanning electron microscopy analysis

Figure 3a1 represent a large aggregate of amorphous HAs with a foamed appearance and **Fig. 3a2** has a chunky morphology of solids. In addition, globular BCs covering with some HAs are observed (**Fig. 3a3**).

The SEM photographs of KB samples show various morphological properties of K and BC simultaneously. **Figure 3b1** is recognized as the ligneous debris and **Fig. 3b2** is presented as the morphological properties of irregular macroporous organic network. The kerogen samples contained a substantial amount of pyrites are found (**Fig. 3b3**), while such pyrite is not observed in BC samples. BC particles are also observed in KB samples, which represent unique porous and smooth surface (**Fig. 3b4**), a few spherical structure with rough surface (**Fig. 3b5**) and irregular structure with random pores locating on the surface (**Fig. 3b6**).

Except for the structures of BC particles observed in KB samples (**Fig. 3b4, 3b5, 3b6**), the images of BC fractions reveal the appearances of irregular shape and macroporous structure (**Fig. 3c1**), cylindrical structure with smooth, porous surface (**Fig. 3c2**), and plant cell structures with irregular shape (**Fig. 3c3**).

2.3 $\delta^{13}\text{C}$ values of MOMs

The $\delta^{13}\text{C}$ values of isolated fractions range from -21.9‰ to -23.0‰ for HAs, from -23.4‰ to -23.8‰ for KBs and from -23.2‰ to -23.3‰ for BCs. The highest $\delta^{13}\text{C}$ value of HA (-21.6‰) occurs at site XM4, whereas the lowest value (-23.0‰) is recorded at site XM3. The $\delta^{13}\text{C}$ values of KB and BC change slightly from site to site, 0.4‰ for KB and 0.1‰ for BC (**Table 2**).

3 Discussion

3.1 Relative contents and carbon contents of HA, KB and BC

The values of TOC content for sediments in Xiamen Gulf shown in **Table 1** were similar with those of TOC content for surface sediments in East China Sea (0.26%–0.62%), and were less than those of TOC content for surface sediments in north Yellow Sea (0.73%) and south China Sea (1.22%) (Kang et al., 2009). Previous studies had shown that carbon content of HA could reached 64.1% extracted from marine sediment in Tyrrhenian Sea (Paolis and Kukkonen, 1997) and 43.7%–53.8% extracted from river and lakes sediments (He et al., 2008), which were obviously higher than those observed in Xiamen Gulf. The formation of HA normally was associated with animal and plant decomposition in a process called humification. The different carbon contents of HAs observed from different sites in Xiamen Gulf may indicate the different degrees of humification. The greatest carbon contents for KB and BC were all found at site XM4, located near the dredging channel between Western Xiamen Bay and estuary of Jiulong River, remarkably affected by the transportation of the river and the coal dust left from the shipping. Compared with the results of Song et al. (2002), it was evident that the carbon contents for KB and BC in Xiamen Gulf were generally higher than those of the marine sediment (17.5% and 29.7%) collected from Wanshan Archipelagos in Zhuhai City, Guangdong Province, south of China, however, which were still less than those for KB and BC of river sediments (50.0% and 61.0%) and pond sediments (57.5% and 57.4%). Carbon contents of the fractions in all sampling sites decreased in the order: BC > KB > HA, indicating considerable differences stability between the three MOMs extracted from the sediments in Xiamen Gulf. Generally, the relative contents of HAs in the sediment of Xiamen Gulf were similar to those of the marine

Table 2 $\delta^{13}\text{C}$ values of HA, KB and BC extracted from marine surface sediments

Sampling site	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)		
	HA	KB	BC
XM1	-21.9	-23.7	-23.3
XM2	-21.9	-23.8	-23.2
XM3	-23.0	-23.4	-23.2
XM4	-21.6	-23.5	-23.2

Table 1 Relative contents and carbon contents of macromolecular organic matters

Samples	TOC and relative contents					Carbon contents		
	TOC ^a	G_{HA}	G_{KB}	G_{BC}	G_{K}^{b}	C_{HA}	C_{KB}	C_{BC}
XM1	0.44%	3.30%	81.26%	35.74%	45.52%	17.06%	24.87%	28.68%
XM2	0.27%	4.21%	89.15%	64.39%	24.76%	16.98%	17.37%	24.87%
XM3	0.37%	2.38%	77.41%	10.37%	67.04%	20.31%	23.14%	24.02%
XM4	0.48%	1.40%	61.79%	16.39%	45.40%	19.26%	29.55%	38.84%

^a Percentage weight of TOC means organic carbon content in the sediments; ^b relative contents of K were calculated based on KB and BC data.

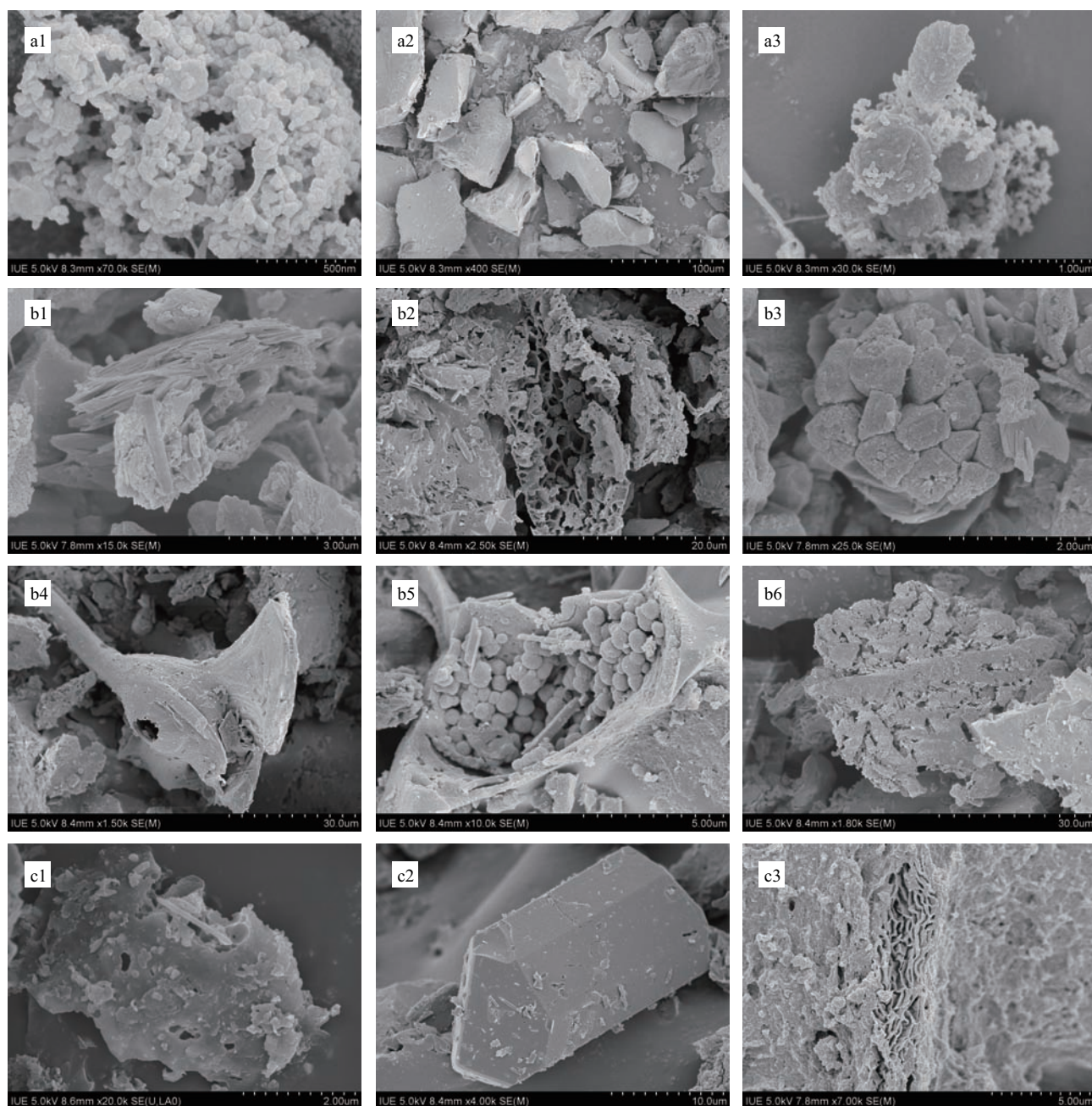


Fig. 3 SEM photographs of the isolated HAs (a), KBs (b) and BCs (c) in marine surface sediments. a1: amorphous HAs with spongy structure (XM1) ($\times 70.0$ k); a2: irregular HAs with chunky solids structure (XM1) ($\times 400$); a3: globular BC particles covered with HA (XM4) ($\times 30.0$ k); b1: KB, plant debris (XM1) ($\times 5.0$ k); b2: KB, irregular macroporous network (XM3) ($\times 2.50$ k); b3: framboidal pyrite (XM1) ($\times 25.0$ k); b4: BC particle with unique porous and smooth surface (XM2) ($\times 1.50$ k); b5: large spherical particles of BC particles (XM2) ($\times 10.0$ k); b6: BC, irregular shape and random pores (XM3) ($\times 1.80$ k); c1: BC, irregular shape and macroporous structures (XM1) ($\times 20.0$ k); c2: BC, cylindrical structure with smooth, porous surface (XM2) ($\times 4.00$ k); c3: BC, plant cell structures and irregular shape (XM1) ($\times 7.00$ k).

sediments collected from Wanshan Archipelagos in Zhuhai City (Song et al., 2002). The BC contents of TOC at site XM2 was the highest in this study, reaching 64.39%, which was also higher than those of TOC in previous studies that BC only covered about 15%–50% of the TOC in marine sediments (Lim and Cachier, 1996; Masiello et al., 2002; Druffel, 2004; Kang et al., 2009). The relative higher BC content at site XM2 might be ascribed to the anthropogenic sources (such as incomplete-combustion of fuels and coal)

or the coal dust from the shipping. The major errors of relative BC content of the TOC measured using this method were involved in the loss of fine particles during the process of base extraction, oxidation of BC particles and incomplete digestion of kerogen by dichromate (Song et al., 2002; Zhao et al., 2011). The relative high contents of BC and K and low contents of HA in the samples may indicate that anthropogenic input could be a major source of organic matter in sediments near the industrial

regions. Although MOMs content preserved in marine sediments was relative a small fraction compared with that in major global carbon reservoirs, their occurrence in marine sediments was an indicator of long-term carbon storage and might affect the global carbon cycle (Druffel, 2004).

3.2 Morphological properties of HA, KB and BC

HA with a foamed appearance (**Fig. 3a1**) was probably due to the effect of the extraction process and the sample with a chunky morphology of solids (**Fig. 3a2**) might be attributed to drying aqueous HA in a vacuum at -85°C .

The ligneous debris (**Fig. 3b1**) might source from the land plants (Garcette-Lepecq et al., 2000; Deniau et al., 2001), while the irregular macroporous organic network (**Fig. 3b2**) observed was similar to the fossilized colony of cells with the algaenan cell walls and degraded cells component (Nguyen, 2003). Pyrite, found in the kerogen samples (**Fig. 3b3**), while not observed in BC samples, was the mineral known to resist to HF/HCl attack, and could be digested by $\text{K}_2\text{CrO}_4/\text{H}_2\text{SO}_4$ oxidant. Framboidal pyrite mainly occurred as typically dominant texture (**Fig. 3b3**; Grice et al., 2003; Neumann et al., 2005), which could also be formed when oxygen was depleted by oxic degradation of benthic infauna (Lee et al., 2011).

BCs had unique pores situated and located on the surface, which were formed by the eruption of gas inside the particles. The cylindrical structure of BC particle (**Fig. 3c2**) and the BC particle with random pores locating on the surface (**Fig. 3b6**) might derive from the vegetation or coal incomplete-combustion (Stoffyn-Egli et al., 1997). **Figure 3b4** with unique porous and smooth surface seemed to be charcoal particle, which preserved wood structure (Jonker and Koelmans, 2002). Besides, a few spherical BC particles with rough surface and nonporous were observed in HA samples (**Fig. 3a3**) and KB samples (**Fig. 3b5**), which probably sourced from the oil and coal fly ash (Stoffyn-Egli et al., 1997; Fernandes et al., 2003).

3.3 Source of HA, KB and BC

The stable carbon isotopic composition of organic matter produced by photosynthetic organisms principally reflects the dynamics of carbon assimilation and the isotopic composition of the inorganic carbon source (Hayes, 1993). The difference of organic matters produced by land plants and marine algae had successfully been used to trace the sources and distribution of organic matters in coastal ocean sediments (Prahl et al., 1994).

Plants with a C_3 photosynthetic pathway had the $\delta^{13}\text{C}$ values in the range of -20‰ to -35‰ , while those with a C_4 pathway had higher $\delta^{13}\text{C}$ values ranging from -9‰ to -19‰ (Bernoux et al., 1998; Staddon, 2004). The $\delta^{13}\text{C}$ values of MOMs presented in **Table 2** were all in the range of $\delta^{13}\text{C}$ values of C_3 plants, whereas the information of C_4 plants was not obvious, even could be neglected

in this work. Besides, Xiamen was located in subtropical area and the dominant cultivated plant was C_3 plant (e.g., rice), which could also be explained for the fact that materials from terrestrial C_3 plants were the predominant compositions in MOMs.

The typical $\delta^{13}\text{C}$ value of marine organic matter was about -18‰ , while the terrestrial organic matter was about -26‰ (Middelburg et al., 1998). The $\delta^{13}\text{C}$ values of MOMs (**Table 2**) showed a bias towards terrestrial organic, indicating the terrestrial organic matter was the dominant contribution to the lower $\delta^{13}\text{C}$ values of MOMs in the offshore sediment from Xiamen Gulf.

Site XM3 with the relative low $\delta^{13}\text{C}$ value of HA (-23.0‰ , **Table 2**) is likely affected directly by the terrestrial organic matters. This is partly due to the drainage of desulfurization sewage of flue gas from coal-fired power plant through two pipes with 400 m length to sea. The previous study revealed that the typical $\delta^{13}\text{C}$ values of sewage ranged from -23.5‰ to -26.7‰ (Thornton and McManus, 1994; Rogers, 2003), whereas $\delta^{13}\text{C}$ value of HA at site XM3 was lower than that of other sites (**Table 2**) due to the influence of the sewage discharged. Previous studies (Gleason and Kyser, 1984; Widory, 2006) presented that $\delta^{13}\text{C}$ values of coal and coal products were between -21.0‰ and -24.9‰ . The $\delta^{13}\text{C}$ values for BCs and KBs (**Table 2**) were all in the range of $\delta^{13}\text{C}$ values of coal and coal products, indicating an obvious contribution of the coal and coal products to the lower $\delta^{13}\text{C}$ value of BCs and KBs. The coal and coal products contributed to BCs and KBs might be accounted for the coal and fly ash from the Songyu Power Plant, as well as the emissions of shipping transportation and the rural practices within drainage basin of the Jiulong River.

4 Conclusions

The information of chemical compositions, morphological properties and source of MOMs extracted from the offshore marine sediments were obtained from analyses by EA/IRMS and SEM. The results showed that KB was the main fraction in MOMs, which accounted for 61.79%–89.15% of the TOC, while HA consisted less than 5%, suggesting that anthropogenic input could be a major source of organic matter in sediments near the industrial regions. SEM analysis not only revealed the morphological properties of the three fractions, but also allowed a better understanding of the source of MOMs in combination with the stable carbon isotope analysis. The $\delta^{13}\text{C}$ values of the three fractions indicated that materials from terrestrial C_3 plants were predominant. Furthermore, the anthropogenic sources (such as the discharge of sewage, coal and biomass combustion from industry nearby and rural practices within drainage basin of the Jiulong River) were remarkably contributed to the variations of $\delta^{13}\text{C}$ values from site to site.

Acknowledgments

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