Characterization of Condensed Organic Matter in Soils and Sediments

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Condensed organic matter (OM) such as nonhydrolyzable C (NHC) is important in C cycling and the sorption and fate of hydrophobic organic contaminants in soils and sediments, but its structural components are rarely known. Nonhydrolyzable C in three contaminated soils and 22 bulk and size-fractionated sediments from the Pearl River delta and estuary in China were measured following treatment with an HCl–HF–trifluoroacetic acid method. It was characterized using elemental analysis, radiocarbon accelerated mass spectroscopy, and Raman microspectrometry. The results show that NHC is an important or even dominating component of the organic C (OC) in the investigated soils and sediments. The NHC contents in this study are highly correlated with the OC contents, with a slope of 0.647 for the 25 soil and sediment samples, which is higher than previously reported NHC–OC correlations in the soils. The radiocarbon analysis demonstrates the importance of ancient OM in the NHC samples. The NHC fractions are chemically and structurally different from the biopolymer and humic substances in the soils and sediments, and originated from different thermally matured bitumen or kerogens, polymethylene C (algaenan, cutan, cutin, cuticle, and lipid), aged terrigenous OM (lignin and humin), and black carbon.

Abbreviations: BC, black carbon; HA, humic acid; NHC, nonhydrolyzable carbon; NMR, nuclear magnetic resonance; NR, North River; OC, organic carbon; OM, organic matter; PRD, Pearl River Delta; SOM, soil and sediment organic matter; TFA, trifluoroacetic acid; WR, West River.

Soil and sediment organic matter (SOM) comprises a major reservoir of organic C on Earth and makes an intimate link between the terrestrial, freshwater, and marine environments. It is also a dominating factor in the sorption, distribution, transport, bioavailability, and fate of hydrophobic organic contaminants (McGinley et al., 1993; Pignatello and Xing, 1996; Farenhorst, 2006). It often contains a range of physically and chemically different organic materials consisting of biopolymers such as lignin, polysaccharides, lipids, and proteins; humic substances derived from biopolymers; and diagenetically matured kerogen and black carbon (BC) (Stevenson, 1994; Huang and Weber, 1997; Ran et al., 2002). Soil and sediment organic matter is generally grouped into a dual-phase model or a three-pool model(McGinley et al., 1993; Pignatello and Xing, 1996; Paustian et al., 1992). Condensed, glassy, and resistant SOM is less polar and considered more aromatic than the amorphous SOM domains based on elemental molar ratios (e.g., [O + N]/C, C/H) (Huang and Weber, 1997; Kleineidam et al., 1999; Cuypers et al., 2002; Kang and Xing, 2005). Fractionation schemes have been used to (i) isolate meaningful pools that provide information on C and nutrient cycling; (ii) test hypotheses on soil formation and ecosystem functioning; (iii) relate SOM characteristics to soil management and global change; and (iv) aid in developing models describing SOM dynamics (Paul et al., 1997, 2006). Fractionation according to size shows that SOM among the size fractions differs in chemical composition and function (Dickens et al., 2006; Sun et al., 2008). The SOM in the sand fraction may consist

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mainly of fresh or slightly decomposed plant material or debris with a high concentration of carbohydrates and is easily degradable (Bergamaschi et al., 1997). In contrast, SOM in the clay- and silt-sized fractions represents a more advanced stage of decomposition, consists mainly of aromatic and aliphatic structures (Megens et al., 2002; Dickens et al., 2006), and is in general more resistant to microbial degradation (Preston, 1996). Moreover, finer soil OM particles are easily eroded and transported for a long distance to fresh water and oceans (Eisma, 1993). Despite many investigations previously conducted, there is still much to be revealed regarding what structural components make up this complex, heterogeneous OM in terrestrial and marine environments and how they are related to the transport of OC between the terrestrial and marine environments.

Various physical and chemical methods have been used to quantify condensed OC such as kerogen C (KC). The current protocols are mainly restricted to organic-petrographic analyses, chemical treatment, and nuclear magnetic resonance (NMR) spectroscopy (Kleineidam et al., 1999; Gélinas et al., 2001a; Song et al., 2002; Ran et al., 2002, 2003; Cornelissen et al., 2005). Kerogen is the most abundant OM in the Earth's crust (Tissot and Welte, 1984). The major input of kerogen to soils and sediments is from the natural weathering processes of sedimentary rocks and from coal, since the latter is comprised mainly of kerogen and is dispersed during mining operations. Kerogen typically has a three-dimensional structure with aromatic nuclei cross-linked by aliphatic chain-like bridges. The nuclei consist of aromatic sheets separated by voids with an average width of 30 to 40 nm. The aliphatic bridges contain linear or branched chains and S- or O-containing functional groups (Engel and Macko, 1993). Although most kerogens are distributed in deeply buried reservoirs (Tissot and Welte, 1984), they can be present in significant amounts in soils and sediments. For example, Ran et al. (2003) found that Borden aquifer OC with a content of 0.21 g kg^{-1} consisted of at least 186 g KC kg^{-1} OC. Song et al. (2002) reported 240 to 480 g KC kg^{-1} of total OC in one soil and three sediments. All existing KC quantification methods may suffer from operational shortcomings, however, such as fine SOM particle loss and incomplete amorphous OC removal (Gélinas et al., 2001b; Song et al., 2002; Ran et al., 2003).

Radiocarbon isotope geochemistry can provide constraints on the quantity of kerogen in soils and sediments (Blair et al., 2003; Raymond et al., 2004; Goñi et al., 2005; Komada et al., 2005). As the average KC concentration of the worldwide suspended load is about 5 g kg^{-1}, it was estimated that KC flux could be 80 Tg C yr^{-1}, accounting for about 30 to 50% of the OC output of rivers to the world's oceans (Meybeck et al., 1993; Blair et al., 2003). The radiocarbon method, however, cannot directly isolate KC for property characterization (Blair et al., 2003; Raymond et al., 2004; Goñi et al., 2005; Komada et al., 2005).

Chemical separation and characterization methods have been developed to differentiate various fractions of SOM. Soils and sediments have been treated with trifluoroacetic acid (TFA) and HCl to remove easily hydrolyzable organic matter (Paul et al., 1997, 2006; Gélinas et al., 2001a). Gélinas et al. (2001a) confirmed that hydrolyzable OM (mostly proteins and carbohydrates) was effectively removed with O_2–free TFA and HCl to minimize the potential for condensation reactions. The ^{13}C NMR spectrum of NHC was similar to that of kerogen or the slow relaxation fraction of SOM distinguished by proton spin relaxation editing techniques (Gélinas et al., 2001a). Hence, they could be applied to the isolation of condensed SOM fractions in soils and sediments.

This study investigated the contents and geochemical properties of condensed SOM such as NHC in soils, sediments, and their size fractions from the Pearl River delta and estuary. Our recent research showed that NHC was important to the distribution, extraction, and sorption of polycyclic aromatic hydrocarbons (Ran et al., 2007a,b; Sun et al., 2008). In this study, a much larger sample set was used for the quantification of NHC and detailed characterization by elementary analysis, ^{14}C accelerated mass spectroscopy, and Raman microspectrometry.

MATERIALS AND METHODS

Site Description and Sample Collection

The Zhujiang (Pearl) River is one of the major rivers in China, with a length of 2214 km and a drainage area of 453,690 km^2. It flows to the South China Sea and consists of three main rivers: the Xijiang (West) River, the Beijing (North) River, and the Dongjiang (East) River (Fig. 1). The lower reaches of the three rivers form the Pearl River Delta. The West River basin is dominated by limestone, while in the East River basin, granite and shale are the main rock types. The upper reaches of the West River drain the world-famous karstic limestone areas in South China, whereas the East River drains the South China granite area. The North River basin is composed of different rock types, including limestone, shales, clastic rocks, and granite (Zhang and Wang, 2001). The climate of the Pearl River Delta is subtropical monsoon and humid, with an annual average temperature of about 22°C. In summer, it is around 28°C and, in winter, about 14°C. The annual precipitation is >1500 mm. Biogeochemical processes and mechanical erosion are very intense in the Pearl River basin. Limited studies have indicated that the total suspended particulate matter is 445 Tg yr^{-1} for the Pearl River system, and transported particulate OC is 2.93 and 0.3 Tg C yr^{-1} in the West River and North River, respectively (Gao et al., 2002).

Three surface soil samples (HP04, HP05, and HP06) were collected at a depth of 0 to 20 cm in July 2002 from the Hangpu district of Guangzhou, China, which has a population of more than 7 million, a total area of >7000 km^2, and is one of the fastest developing cities in China. Six surface sediment samples (0–20 cm) were collected from the Pearl River estuary using a box sampler in August 2002. The water depth was 25 m for C01, 16 m for C02, 25 m for C03, 29 m for C04, 39 m for C05, and 69 m for C08. Two surface river sediments (West and North rivers) at water depths of 10 and 15 m were collected, using a box sampler, from the surface layer (0–10 cm) of the West River (WR) and North River (NR) of the Pearl River Delta in November 2003. The NR sample was collected from a busy harbor. The sample locations are presented in Fig. 1. After collection, the samples were quickly transported to the laboratory and kept at −18°C in a refrigerator. An aliquot of each soil and sediment was freeze-dried and passed through a stainless steel sieve with 0.177-mm openings.

Size Separations of Sediments

To compare the difference in the distribution and properties of NHC among particle-size fractions between the estuary of the Pearl River and the river sediment of the Pearl River Delta, three sediments (C08, WR, and NR) were selected for size fractionation (Dickens et al., 2006). Suspensions of 500 g of sediment in 2.5 L of deionized (DI) water were sonicated for 30 min in a standard laboratory cleaner and then wet washed to separate the three largest size fractions: >180 µm (Fraction 1), 180 to 61 µm (Fraction 2), and 61 to 30 µm (Fraction 3). The clay-sized particles were isolated by standard settling techniques. The <30-µm suspension was dispersed in an aqueous solution of 0.1 mol L^{-1} sodium pyrophosphate to prevent flocculation and was settled in several cylinders (1 L) for 24 h to get the fraction 2 to 30 µm (Fraction 4). The clay fraction (<2 µm, Fraction 5) was collected by centrifugation at 4500 rpm for 30 min. The colored supernatants were acidified to pH 2 and used to collect the colloidal SOM (humic acid, HA). A portion of the WR samples was also treated with 0.1 mol L^{-1} NaOH for three times in a N_2 atmosphere and the HA and the HA-free residue (Sample WR-A) were isolated by an HA extraction procedure (Li et al., 2002). After treatment, the fractionated samples were freeze-dried, finely pulverized with a mortar and pestle, and passed through a 0.18-mm sieve. They were stored in glass bottles for the elemental analysis and NHC isolation. The ^{13}C NMR spectra and size distributions of the size fractions for C08 and NR have been reported (Sun et al., 2008).

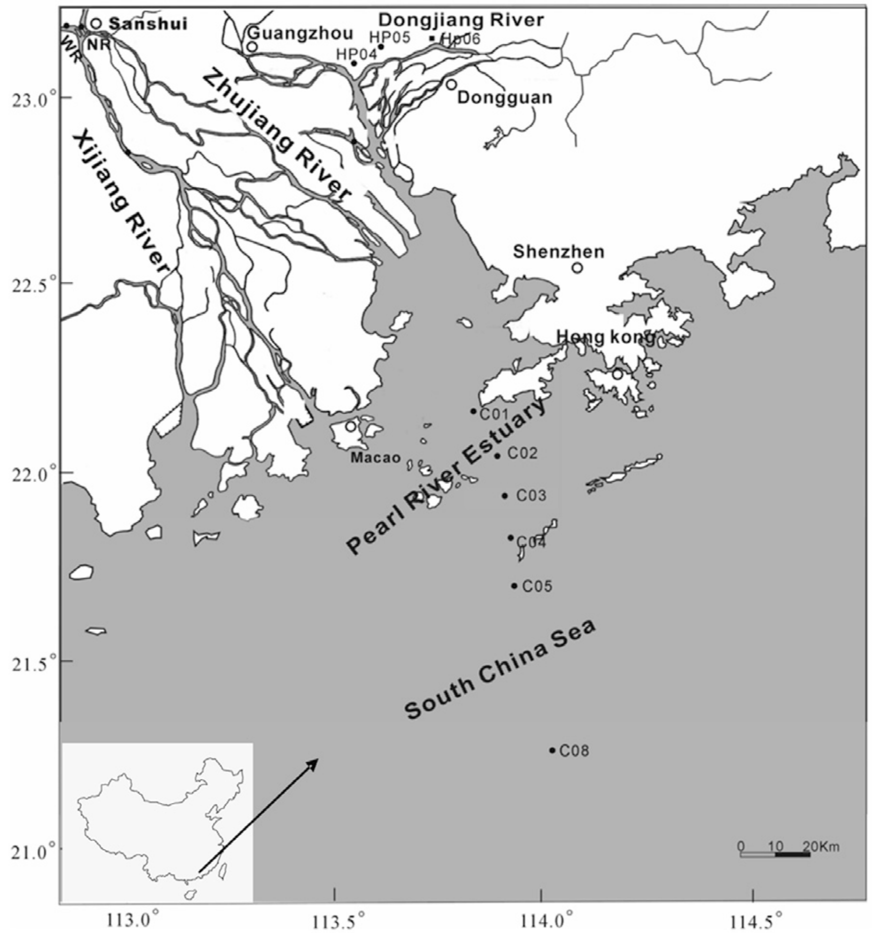

Fig. 1. The sampling locations for the three soils and eight sediments in the Pearl River Delta region, China.

Nonhydrolyzable Carbon Fractions

The separation protocol for NHC is a revised procedure based on that of Gélinas et al. (2001b). The preliminary test showed that the treatment with 1 mol L^{-1} HCl and 100 g kg^{-1} HF two times was not enough to isolate adequate OC concentrate for the ^{13}C NMR analysis, so each of the samples was demineralized with HCl and HF four times with an extended treatment duration. Specifically, carbonates were first dissolved in 1 mol L^{-1} HCl for 24 h at room temperature, and then the residue was separated from the supernatant by centrifugation at 4500 rpm for 30 min. The residual fraction was treated with 1 mol L^{-1} HCl and 100 mL L^{-1} HF at a 1:5 solid/liquid ratio and put on a shaker at 30°C for 5 d. Finally the supernatant was removed by centrifugation at 4500 rpm for 30 min. The same treatment was repeated four times. After removing the fourth supernatant, the residue was washed three times with DI water and dried in an oven at 60°C.

Hydrolyzable OM was then removed from the demineralized residues. First, polysaccharides were released by TFA hydrolysis according to Allard et al. (1998). Hydrolysis with 2 mol L^{-1} TFA was performed twice at 100°C for 3 h in Teflon centrifuge tubes, followed by twice more (4 and 6 mol L^{-1} TFA) at 100°C for 18 h. Finally, the residual hydrolyzable OM was removed with 6 mol L^{-1} HCl at 110°C for 24 h. Before heating, the solutions and headspaces were purged with N_2 for at least 1 min before sealing the vials with a Teflon-lined cap. The selective removal of polysaccharide and other forms of easily hydrolyzable OM with increasing TFA concentration and reaction time was shown to be an efficient approach to reduce the potential for the formation of melanoidin-like material during the 6 mol L^{-1} HCl hydrolysis (Allard et al., 1998). Following each hydrolysis, the supernatants were separated from the residues by centrifugation as described above. The samples were rinsed with DI water after the last HCl hydrolysis treatments. The NHC residues remaining after the 6 mol L^{-1} HCl hydrolysis were then freeze-dried and stored in glass vials for further study.

Elemental Concentrations and Radiocarbon Isotope Analyses

Carbon, H, O, and N contents of the original and NHC samples of the WR river sediments and their six fractions were measured using a Heraeus CHN-O-RAPID (Hanau, Germany) and Elementar Vario EL III elemental analyzer (Hanau, Germany). The other data for the six marine sediments, three soils, and nine sediment size fractions of C08 and NR were taken from Ran et al. (2007b) and Sun et al. (2008). Elemental measurements were performed immediately after the freeze-drying so that moisture interference to O and H would be minimal. The relative precision was better than 90 g kg^{-1} for C in the bulk samples, except for C02, WR-1 to WR-3, C08-4, and NR-3 (Table 1). The relative precision was better than 62.5 g kg^{-1} for C, 92.2 g kg^{-1} for H, and 100 g kg^{-1} for O in the duplicate determinations of the 25 NHC fractions, except for WR-1 to WR-3 and C08-3 (Table 2). The bulk and >30-μm size samples tended to be more heterogeneous and had much lower OC concentrations than the finer grained fractions, leading to the principal uncertainties in the OC measurements.

Five selected NHC samples (C01, C05, C08 and its clay fraction, and WR) for ^{14}C measurements were put into quartz tubes. They were combusted in an O_2 stream and the CO_2 produced was purified repeatedly in dry ice and a liquid N_2 trap and then converted to graphite via an Fe–H_2 catalytic reduction for ^{14}C analyses, which were made by accelerated mass spectroscopy at Peking University, Beijing, China. Radiocarbon results are reported as Δ^{14}C, which is the per-mil deviation of the ^{14}C/^{12}C ratio relative to a 19th-century wood standard. The ^{14}C results were corrected further for procedural blank contributions (Shen et al., 2004). The relative precision for ^{14}C age was 2 g kg^{-1} for the NBS-22 hydrocarbon standard.

Raman Spectroscopy

The Raman spectra were collected with a Renishaw Ramascope (RM 2000, Wotton-under-Edge, UK) equipped with two holographic filters and an electrically cooled charge-coupled device camera. The Raman microprobe was configured with a 514-nm Ar$^+$ laser (Newport Spectra-Physics, Mountain View, CA) with maximum output of 20 mW. The samples were analyzed with a 50× long working distance objective lens (Leica) using 3-mW laser power focused on a 2-μm surface of sample to prevent thermal degradation.

RESULTS AND DISCUSSION

Size Fractions of the River and Estuary Sediments

The grain size distribution and relative content of each fraction are illustrated in Fig. 2. From Fig. 2, it can be seen that the two river sediments, WR and NR, contain coarser sand particles (>180- and 180–61-μm fractions) than the estuary sediment C08. The silt (61–30-μm), fine silt (30–2-μm), and clay (<2-μm) fractions of the C08 estuary sediment are slightly higher than the corresponding fractions of the NR sediment and much higher than the WR river sediment. The OC contents of the bulk sample and the sum of the six fractions of WR, NR, and C08 are comparable. The OC recovery for the six fractions is 99.4% for NR, 100% for C08, and 49.7% for WR. The large percentage of coarse sand particles (75.2%), very low OC (0.97 and 1.70 g kg^{-1}), and relatively large CV of the duplicate analysis (13.5–30.3%) (Table 1) led to the low OC recovery in WR.

Table 1 lists the C and NHC contents of the five size fractions for each of the two fluvial sediments (NR and WR) and one marine sediment (C08). The C and NHC contents in the 14 size fractions ranged from 0.89 to 37.8 and from 0.60 to 28.5 g kg^{-1}, respectively. For the less contaminated and C-depleted river and estuary sediments (WR and C08), the C and NHC concentrations increased as particle size decreased. For the more contaminated and C-enriched river sediment (NR), the C and NHC concentrations were higher in both the coarser and the finest fractions, and they exhibit minima in the fine silt size fraction (2–30 μm). The coarse size fractions may contain larger amounts of coal and BC particles, which contribute to higher C concentrations. On the other hand, the higher C concentrations of the finer size fractions are often due to their large specific surface area and the high sorption for natural OM (Hedges and Keil, 1995; Mayer, 1994). Therefore, it is possible that anthropogenic activities and the clay mineral content influence the distribution of OC among the particle size fractions.

Table 1. Carbon, N, nonhydrolyzable C (NHC), and black carbon (BC) contents and C/N and NHC/organic C (OC) atomic ratios in the bulk or size-fractionated soils and sediments†.

Sample	Type or size fraction	C	N	C/N	NHC/OC	NHC	BC
		g kg^{-1}			g kg^{-1}		
C01	marine sediment	10.2 ± 0.79	0.70	16.4	354	3.61	1.33
C02	marine sediment	3.36 ± 0.31	0.30	12.7	314	1.06	0.32
C03	marine sediment	6.18 ± 0.20	1.00	7.50	343	2.12	0.49
C04	marine sediment	6.80 ± 0.36	0.80	9.40	349	2.37	0.12
C05	marine sediment	5.36 ± 0.27	0.50	12.0	256	1.37	0.32
C08	marine sediment	5.68 ± 0.17	0.90	7.70	454	2.58	ND‡
HP04	soil	17.7 ± 1.40	1.10	18.9	705	12.5	2.21
HP05	soil	33.5 ± 1.77	2.10	18.3	648	21.7	3.45
HP06	soil	24.7 ± 0.47	1.20	24.3	553	13.5	4.00
C08-2§	61–180 μm	3.80 ± 0.00	0.40 ± 0.00	12.8	250	0.95	ND
C08-3	30–61 μm	5.30 ± 0.10	0.60 ± 0.10	9.70	300	1.59	ND
C08-4	2–30 μm	2.70 ± 0.10	0.60 ± 0.10	5.60	619	1.67	ND
C08-5	<2 μm	17.0 ± 0.10	2.70 ± 0.10	7.50	600	10.2	ND
WR	river sediment	4.46 ± 0.26	ND	ND	482	2.15	ND
WR-A	humic acid free sediment	3.36 ± 0.16	ND	ND	282	0.95	ND
WR-1	>180 μm	0.89 ± 0.23	ND	ND	577	0.60	ND
WR-2	61–180 μm	1.60 ± 0.22	ND	ND	449	0.72	ND
WR-3	30–61 μm	4.22 ± 1.07	ND	ND	448	1.89	ND
WR-4	2–30 μm	5.20 ± 0.03	ND	ND	371	1.93	ND
WR-5	<2 μm	8.01 ± 0.13	ND	ND	289	2.31	ND
NR-1	>180 μm	37.8 ± 0.10	2.10 ± 0.10	21.4	754	28.5	ND
NR-2	61–180 μm	12.2 ± 0.10	0.70 ± 0.10	20.0	910	11.1	ND
NR-3	30–61 μm	10.7 ± 0.30	0.70 ± 0.00	18.0	765	8.19	ND
NR-4	2–30 μm	7.80 ± 0.30	0.70 ± 0.00	13.2	715	5.58	ND
NR-5	<2 μm	18.9 ± 0.20	2.20 ± 0.10	9.90	593	11.2	ND

† The C, NHC, and BC data for the marine sediments, soils, and size fractions of C08 and NR are from Ran et al. (2007b) and Sun et al. (2008).

‡ ND, not determined.

§ The suffixes 1, 2, 3, 4, 5 represent the five size fractions of the marine sediment C08 and the West River (WR) and North River (NR) sediments. Fraction 1 of C08 was not detected.

Organic Carbon, Nonhydrolyzable Carbon, and Black Carbon in the Bulk Soils and Sediments

Table 1 shows that the C contents of the seven bulk sediment samples (C01, C02, C03, C04, C05, C08, and WR) ranged from 3.36 to 10.2 g kg^{-1}. The three soils samples (HP04, HP05, and HP06) were collected from an industrial region and their C contents of 17.7 to

33.5 g kg^{-1} were higher than those of the bulk sediment samples.

The NHC contents with respect to sediment and soil weights in the seven bulk soil and sediment samples varied from 1.06 to 21.7 g kg^{-1}, accounting for 25.6 to 70.5% of the OC contents (Table 1). The three more contaminated soils exhibited NHC/OC ratios ranging from 553 to 705 g kg^{-1}. The other less contaminated sediment samples exhibited NHC/OC ratios ranging from 256 to 482 g kg^{-1}.

The NHC/OC ratio in the bulk sample WR (482 g kg^{-1}) was higher than in the HA-free sample WR-A (282 g kg^{-1}; Table 1). A possible reason is that some parts of the NHC were removed when the HA was extracted from the WR sample. As the fine size clay has a high percentage of the NHC/OC ratio, it could be suspended during the HA extraction process. Other studies have also shown that the sequentially extracted HA molecules have higher polymethylene and aliphatic C structure, and lower O/C and higher H/C ratios as the successive extraction steps increase from one to eight (Li et al., 2002; Kang and Xing, 2005); however, more samples are needed to test this observed phenomenon.

Black carbon is cited from a previous study for the three soils and five marine sediments in the range of 41.4 to 173 g kg^{-1} OC (Table 1). The BC content on average was 112 g kg^{-1} OC in the eight samples, with a standard deviation of 50.3 g kg^{-1}. This value is close to the median value of 90 g kg^{-1} (quartile range 50–180 g kg^{-1}) reviewed from around 300 global sediments (Cornelissen et al., 2005). The correlation analysis showed that the BC contents were well correlated with the OC contents, with a correlation coefficient $R = 0.929$ in the eight studied samples (Fig. 3b).

Table 2. Elemental compositions and atomic ratios of nonhydrolyzable C and black carbon†.

Sample	C	H	N	O	H/C	O/C	C/N
	g kg^{-1}						
			Nonhydrolyzable C				
C01	369 ± 2.10	24.9 ± 0.40	3.80 ± 0.00	92.6 ± 6.70	0.81	0.19	113
C02	307 ± 1.40	24.1 ± 1.90	3.40 ± 1.30	108 ± 7.20	0.94	0.27	105
C03	232 ± 4.90	18.2 ± 0.40	2.30 ± 0.20	74.9 ± 0.60	0.94	0.24	118
C04	49.7 ± 0.20	3.78 ± 0.20	1.30 ± 0.40	22.4 ± 0.10	0.91	0.34	45
C05	236 ± 5.70	18.0 ± 0.40	2.80 ± 0.20	87.9 ± 6.60	0.92	0.28	98
C08	344 ± 4.90	27.1 ± 2.50	4.60 ± 1.50	88.0 ± 3.50	0.94	0.19	87
HP04	507 ± 1.40	24.5 ± 0.70	3.20 ± 0.50	136 ± 1.00	0.58	0.20	185
HP05	523 ± 4.20	37.2 ± 0.50	5.60 ± 0.80	167 ± 13.0	0.85	0.24	109
HP06	559 ± 4.90	26.3 ± 0.10	3.60 ± 0.30	125 ± 0.70	0.56	0.17	181
WR	273 ± 0.00	24.2 ± 0.20	7.80 ± 0.30	112 ± 0.90	1.06	0.31	41
WR-A	3.28 ± 0.20	0.46 ± 0.00	1.80 ± 0.20	1.00 ± 0.10	1.69	0.22	2
WR-1	1.4 ± 0.10	1.17 ± 0.20	1.60 ± 0.00	0.30 ± 0.10	8.60	0.14	1
WR-2	2.0 ± 0.10	0.28 ± 0.10	3.40 ± 0.60	0.50 ± 0.00	1.71	0.18	1
WR-3	47.4 ± 0.90	1.58 ± 0.20	7.50 ± 2.40	ND‡	0.4	ND	7
WR-4	255 ± 3.50	17.6 ± 0.40	14.0 ± 0.90	54.1 ± 0.60	0.83	0.16	21
WR-5	285 ± 2.80	22.2 ± 0.40	11.5 ± 1.20	ND	0.94	ND	29
C08–2	21.9 ± 0.30	11.9 ± 0.10	0.80 ± 0.00	ND	6.55	ND	32
C08–3	225 ± 5.70	14.6 ± 0.40	3.80 ± 1.40	51.1 ± 0.20	0.78	0.17	69
C08–4	17.4 ± 1.00	1.45 ± 0.20	0.40 ± 0.00	2.50 ± 0.30	1.00	0.11	51
C08–5	252 ± 7.80	20.2 ± 1.70	5.90 ± 3.20	49.0 ± 2.40	0.96	0.15	50
NR-1	598 ± 2.80	42.4 ± 2.70	4.30 ± 0.90	133 ± 3.60	0.85	0.17	162
NR-2	295 ± 6.40	14.4 ± 0.10	2.00 ± 0.10	38.3 ± 2.30	0.58	0.10	172
NR-3	428 ± 9.90	22.4 ± 0.6	2.40 ± 0.50	88.7 ± 3.50	0.63	0.16	208
NR-4	174 ± 9.20	10.1 ± 0.50	1.20 ± 0.20	52.0 ± 3.50	0.70	0.22	169
NR-5	453 ± 2.10	41.6 ± 3.80	3.50 ± 0.40	126 ± 4.70	1.10	0.21	151
			Black carbon				
HP04	164 ± 3.50	5.28 ± 0.60	1.18 ± 0.20	17.2 ± 0.80	0.09	0.078	162
HP05	173 ± 4.90	7.72 ± 1.90	1.77 ± 0.40	30.9 ± 0.90	0.12	0.13	114
HP06	341 ± 7.10	8.25 ± 0.90	2.62 ± 0.020	53.3 ± 5.50	0.09	0.12	152

† The C, H, and O data for the marine sediments, soils, and size fractions of C08 and NR are from Ran et al., (2007b) and Sun et al. (2008).

‡ ND, not determined.

Correlation of Nonhydrolyzable Carbon with Organic Carbon in All the Samples

The NHC contents in the investigated 25 soil and sediment samples varied from 0.60 to 28.5 g kg^{-1}, accounting for 25.6 to 84.7% of the OC contents (Table 1). Statistical analysis showed that the NHC contents were highly correlated with the OC contents in the investigated 25 soils, sediments, and their size fractions (Fig. 3a). The correlation coefficient is highly significant. Its slope (0.647) represents the NHC average in the investigated soils and sediments. Our result is interestingly similar to other investigations on NHC in soils and sediments (reviewed by Paul et al., 2006; Komada et al., 2005; Wang et al., 1998). Analysis of 1100 data points in soils showed that the NHC measured after hydrolysis with 6 mol L^{-1} HCl ranged from 30 to 80% of the total OC (Paul et al., 2006). The amount of NHC was strongly correlated to the amount of total OC. The most frequently used method (6 mol L^{-1} HCl at 116°C for 16 h) had a regression slope of 0.51, while the use of 6 mol L^{-1} HCl at 96 and 100°C resulted in a regression slope of 0.58, and the use of 2 mol L^{-1} H_2SO_4 at 116°C resulted in a regression slope of 0.75 between NHC and OC (Paul et al., 2006). The NHC percentages are also close to values of the acid

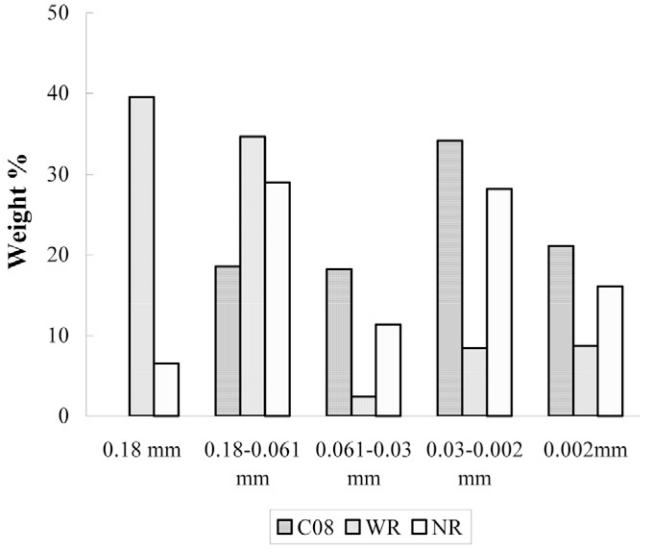

Fig. 2. Distribution of size fractions in the North River (NR), West River (WR), and C08 sediments.

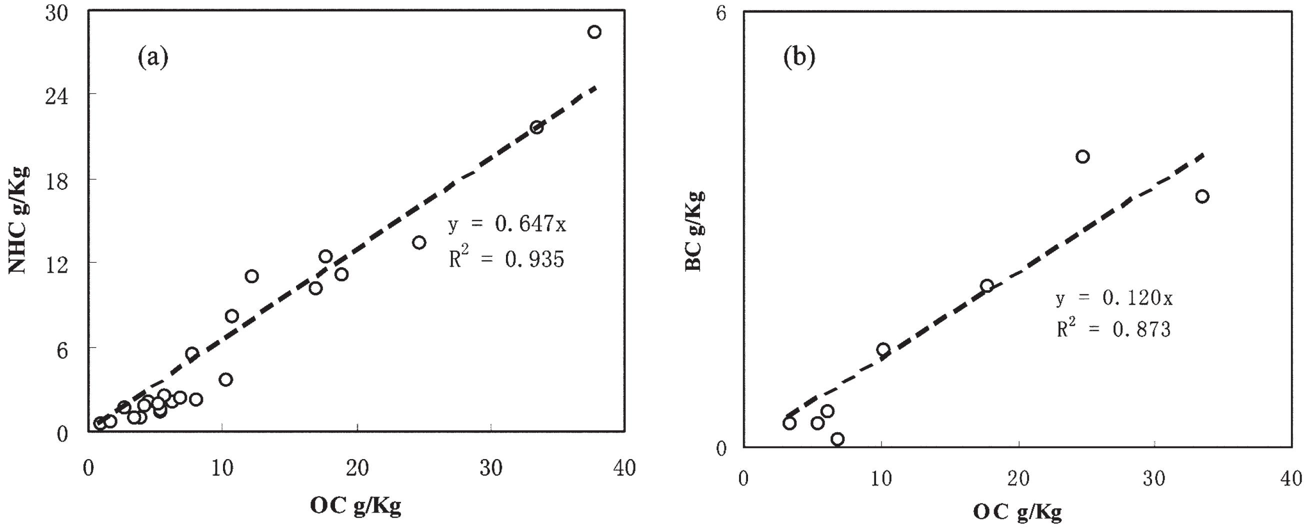

Fig. 3. Correlation of (a) nonhydrolyzable C (NHC) with organic C (OC) for the bulk soils and sediments and the size-fractionated sediments, and (b) of black carbon (BC) with OC in the eight BC samples in Table 1.

(6 mol L^{-1} HCl) insoluble C (43–69%) reported for other coastal and marine sediments (Komada et al., 2005; Wang et al., 1998).

Elemental Ratios of Nonhydrolyzable Carbon and Black Carbon

The H/C and O/C atomic ratios for the 25 NHC fractions and the three BC fractions are presented in Table 2. The O/C atomic ratios in the NHC samples ranged from 0.11 to 0.34, and the H/C atomic ratios ranged from 0.56 to 1.06. As the higher H/C ratios (1.69–8.6) in WR-A, WR-1, WR-2, and C08-2 may result from the relative precision for the H measurement, low OC, and mineral-bound water (Table 2), they are not considered in the following discussion. The O/C and H/C atomic ratios, when plotted on a van Krevelen diagram (Fig. 4), are similar to the Type III kerogen derived mainly from higher plant materials, which are rich in lignin with an aromatic structure. The degree of OM maturation increased as the H/C and O/C ratios decreased (Fig. 4). The O/C ratios for NHC were much higher than the average O/C ratios (0.53) for typical HAs extracted from soils and sediments (Gunasekara and Xing, 2003; Kang and Xing, 2005). The BC samples combusted at 375°C from the three soil samples had atomic O/C and H/C ratios of 0.078 to 0.13 and 0.09 to 0.12, respectively, suggesting that BC has a higher degree of maturation than NHC.

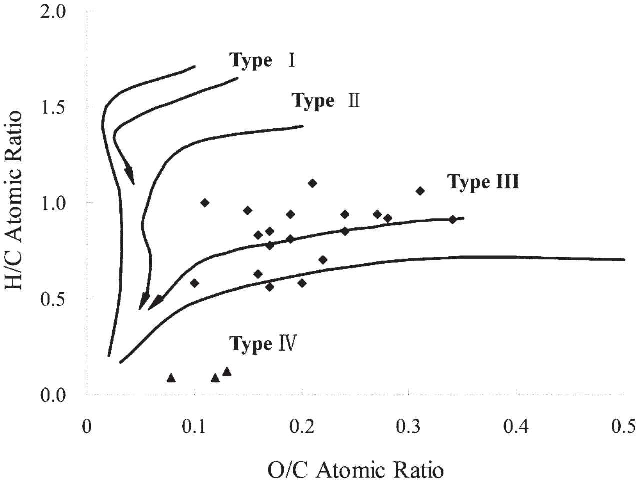

Fig. 4. The van Krevelen diagram for the isolated nonhydrolyzable C (NHC) (diamonds) and black carbon (BC) (triangles) fractions in Table 1. The arrow lines represent the evolution of chemical composition as diagenetic alteration advances for four types of kerogen: I, II, III, and IV.

The C/N atomic ratios in all the NHC samples, except four samples, ranged from 21 to 208 (Table 2), and in the three BC samples ranged from 114 to 162, suggesting that the NHC and BC fractions contained very low protein and other N compounds. For the surface sediments in the fresh and sea water, the C/N ratios generally ranged from 5 to 10 (Wang et al., 1998); however, the C/N ratios in the three untreated soils, three estuary sediments (C01, C02, and C05), and large-size sediment fractions were >10 (Table 2). This observation is consistent with the previous investigation. The terrestrial and ancient SOM have much higher C/N ratios (Hedges and Keil, 1995). Based on the C/N ratios, it is concluded from this investigation that the acid hydrolysis method can efficiently removed protein-like components such as proteins, peptides, and nucleic acids from the fresh, less humified SOM.

Radiocarbon of Nonhydrolyzable Carbon and Importance of Ancient Organic Carbon

The Δ^{14}C values for the selected five NHC samples from the sediments (C01, C05, C08, C08-5, and WR) ranged from −321 to −431‰ (Table 3). Comparable ^{14}C values for acid (6 mol L^{-1} HCl) insoluble C were also reported for other coastal and marine sediments (Wang et al., 1998; Komada et al., 2005). These compositions translate to conventional ^{14}C ages of 3840, 4400, 4530, 3110, and 4120 yr before present in the samples C01, C05, C08, C08-5 and WR, respectively. The old ages suggest a significant contribution of ancient C sources to the sediments. This ancient OM includes bitumen or kerogens found in sedimentary rocks that have been thermally matured or the entrainment of terrigenous OM pre-aged as a result of long residence times within the drainage basin. The latter OM also contains chemically recognizable biochemicals, such as for example lignin, albeit in a more extensively degraded and altered state (Goñi et al., 2005). Quantitatively discriminating between the incorporation of fossil OC and the entrainment of terrigenous OM from old soils or paleosols is difficult, however, and needs further investigations. For the purpose of the following discussion, we assume that all of the ancient OC is fossil in origin (i.e., ^{14}C dead). Using isotopic mass balance, it is possible to quantitatively constrain ancient and modern C contributions in these samples (Blair et al., 2003; Goñi et al., 2005). Assuming simple two end-member mixing, the fraction of modern OC (f_m) and the fraction of ancient OC ($f_a = 1 - f_m$) in each sample can be estimated from the Δ^{14}C values presented in Table 3 using the following equation:

$$\Delta^{14}\mathrm{C} = f_m \Delta^{14}\mathrm{C}_m + f_a \Delta^{14}\mathrm{C}_a \qquad [1]$$

where $\Delta^{14}\mathrm{C}_m$ and $\Delta^{14}\mathrm{C}_a$ represent the Δ^{14}C signatures of the modern and ancient end members, respectively. Values of −1000 and 100‰ were used for $\Delta^{14}\mathrm{C}_a$ and $\Delta^{14}\mathrm{C}_m$, as suggested by Blair et al. (2003). The isotopic mass balance calculations quantitatively demonstrate the importance of ancient OM, which accounts for 390 to 490 g kg^{-1} OC in the NHC samples of this study (Table 3). The average value of f_a in the five NHC samples is 440 g kg^{-1} OC. This result is generally consistent with other recent investigations (Blair et al., 2003; Kao and Liu, 1996; Massiello and Druffel, 2001).

Ancient sedimentary OC is a significant component of the soil and the suspended load (Blair et al., 2003; Paul et al., 2006). In ^{14}C dating, NHC in soils is on average 1200 to 1400 yr older than the total OC in the surface soils, and even more so at depth (Paul et al., 2006). Kerogen may contribute as much as 50 to 70% of the suspended particulate OC from the Lanyang of Taiwan and the Santa Clara River of southern California (Kao and Liu, 1996; Massiello and Druffel, 2001). The nonprotein alkyl C comprised 204 to 358 g kg^{-1} of the OC when OC abundance was >10 g kg^{-1} in several ocean sediments (Gélinas et al., 2001a). Schmidt et al. (1996) reported the influence of brown coal emissions from a briquette factory on soil OM. They found that the content of OC originating from brown coal contamination in the bulk soil and size fractions contributed 510 to 970 g kg^{-1} of OC. Song et al. (2002) reported that the kerogen and BC fractions amounted to 578 to 806 g kg^{-1} of the OC contents in one soil and three sediments using a 0.1 mol L^{-1} NaOH extraction method. As these fractions had obvious O-containing peaks in the ^{13}C NMR spectra (Song et al., 2002), however, they were possibly overestimated. Another oxidation method using sodium persulfate to remove amorphous SOM also showed that condensed SOM had considerable O-alkyl C and carboxyl C and was likely to contain some amount of labile organic components (carbohydrates, peptides, and fatty acids) (Cuypers et al., 2002).

Functional Groups of Nonhydrolyzable Carbon

The ^{13}C NMR spectra for the NHC fractions of C02, C03, C08, HP04, and HP05, and for the silt and clay NHC fractions of C08 and NR are cited from previous studies (Ran et al., 2007b; Sun et al., 2008) and reveal a large contribution from alkyl (0–45 ppm) and aryl C (93–148 ppm), but a minor or negligible contribution from methoxyl (45–63 ppm), O-alkyl (63–93 ppm), O-aryl (148–165 ppm), and carboxyl (165–187 ppm) C, which are very similar to those of the kerogen isolate in the Borden aquifer (Ran et al., 2003). In contrast, the ^{13}C NMR spectra for the demineralized sample reveal a larger contribution from methoxyl C (45–63 ppm), carbohydrate (63–93 ppm), O-aryl (148–165 ppm), and carboxyl (165–187 ppm) C (Ran et al., 2007b). The aromaticity was calculated for each isolated NHC based on the peak areas for aromatic C (93–148 ppm) and total C (0–165 ppm), and ranged from 232 to 561 g kg^{-1}. The aliphatic C (0–93 ppm) was significantly higher in the sediments than in the soils, and higher in the <2-µm clay fraction than in the 30- to 61-µm size fraction for C08 and NR. The aromatic C (93–165 ppm) in the sediments, however, was lower than in the soils or decreased as the particle size decreased, which is comparable to two recent investigations on the SOM constituents in size-fractionated sediments (Dickens et al., 2006; Megens et al., 2002). It was noted that the clay NHC fractions were quite similar in terms of NMR spectra and elemental ratios between the river sediment NR and the estuary sediment C08, indicating that the terrestrial OC can transport for a long distance (Sun et al., 2008). Furthermore, the correlation analysis shows that aliphatic C is highly related to the H/C ratio (aliphatic C = 480 H/C + 5.01, $R^2 = 0.662$, $P < 0.01$) in the investigated nine NHC samples. Finally, considerable percentages of aromatic C in the bulk and NHC size fractions indicate that they may originate from different thermally matured bitumen or kerogen, aged terrigenous organic matter, BC, or lignin. So, NHC is very heterogeneous in terms of source, structure, and particle size, and is also important in the transport and land–ocean interaction of SOM.

The NHC fraction (Gélinas et al., 2001a) was reportedly rich in polymethylene C (cutan, cutin, cuticle, and lipid), and similar in abundance and chemical composition to nonprotein alkyl C, slow relaxing components, and kerogen from Type I oil shales in the OC-rich ocean sediment samples. Matured and unweathered kerogen often contains only alkyl and aromatic C, but less matured amorphous kerogen may have other functional groups indicative of its precursor materials such as humic substances. Humic substances, however, generally have relatively large contents of methoxyl, carbohydrate, alkyl-substituted aromatic, O-substituted aromatic–phenolic, and carboxylic C, as indicated in previous studies (Cuypers et al., 2002; Gunasekara and Xing, 2003; Kang and Xing, 2005; Ran et al., 2002). From the NMR spectra (Ran et al., 2007b; Sun et al., 2008), it is obvious that the isolation method was effective in removing fresh, less humified SOM materials such as lignin, carbohydrates, and humic substance.

Table 3. Radiaocarbon measurements for the selected nonhydrolyzable C samples.

Sample	Organic C	Δ^{14}C	^{14}C apparent age	f_a†
	g kg^{-1}		yr	
C01	369	−390	3840 ± 40	0.45
C05	236	−422	4400 ± 40	0.48
C08	344	−431	4530 ± 40	0.49
C08–5	252	−321	3110 ± 40	0.39
WR	273	−401	4120 ± 40	0.46

† Fraction of ancient organic C.

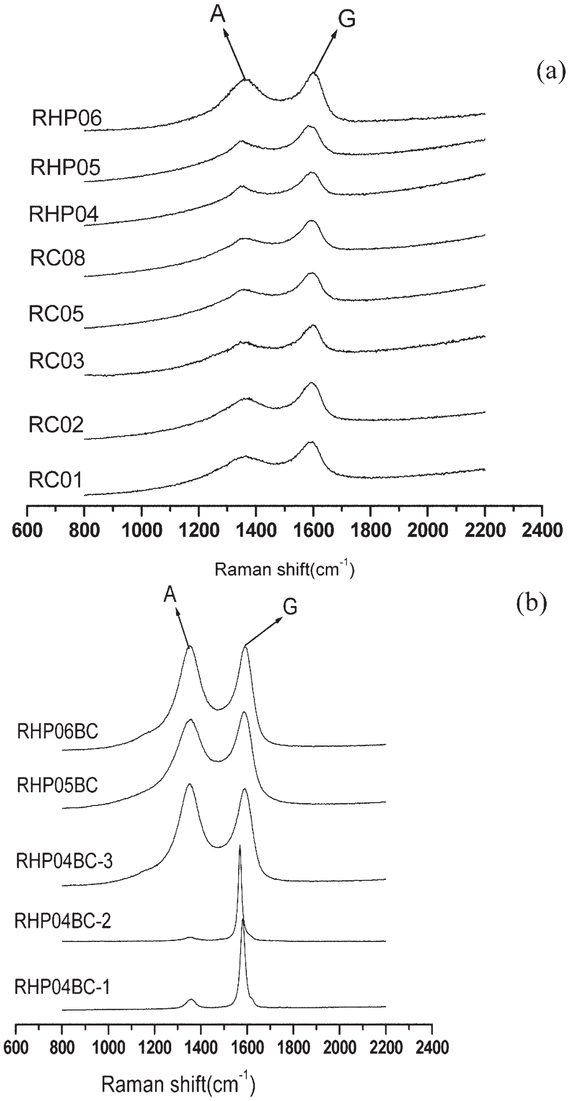

Fig. 5. Raman spectra of (a) the isolated nonhydrolyzable C (NHC) from the soils and sediments, and (b) the combusted black carbon (BC) from the three soils, showing the amorphous (A) and graphitic (G) peaks.

Raman Spectra

Raman spectra of the selected eight NHC and three BC samples are presented in Fig. 5 and Table 4. The NHC spectra are similar to the spectra of typical kerogens, as well as the isolated kerogens shown in previous studies (Sun, 2005). All of the spectra in Table 4 are dominated by two broad peaks, i.e., an amorphous (A) peak at 1340 cm^{-1} wavelength and a graphitic (G) peak at 1600 cm^{-1} wavelength (Sun, 2005). The ratio (*R*) of the A peak integral area to that of the G peak has been used as a measure of the microcrystalline size of kerogens and coals. The higher *R* is, the more disordered is the material. At the same time, the *R* value of a graphitic sample is <0.2 and lower than that of a kerogen. In general, graphitic samples contain a sharp and intense graphitic band at 1580 or <1580 cm^{-1}, while the disordered kerogen is from about 1590 cm^{-1} (Sun and Puttmann, 2001). As illustrated in Table 4, all G bands are at 1590 cm^{-1} and the *R* value is in the range of 0.97 to 1.38 for the nine NHC samples. The three BC fractions from the three soils have a degree of maturation similar to the NHC fraction, while BC from HP04 has microcrystalline graphite (Table 4). The observed graphite in the BC fraction from HP04 was probably derived from petrogenic rocks rather than from a combustion product, as suggested by a recent study (Pasteris and Wopenka, 2003), since BC from a combustion source could not reach as high maturation as that from petrogenic rocks. Therefore, it is concluded that the isolated NHC had similar structural organization to the isolated BC, and contained a considerable quantity of ordered graphitic structure as well as amorphous carbonaceous structure.

Table 4. Parameters of Raman spectra from the isolated samples.

Sample	Band A	Band G	*R* = A_a/G_a†
	cm^{-1}		
		Nonhydrolyzable C	
HP04	1346	1586	1.323
HP05	1340	1587	1.334
HP06	1355	1588	1.383
C01	1348	1585	1.191
C02	1344	1587	1.318
C03	1348	1587	1.217
C05	1348	1587	0.970
C08	1347	1584	1.357
		Black carbon	
HP04–1‡	1351	1589	1.588
HP04–2‡	1356	1581	0.352
HP04–3‡	1351	1570	0.162
HP05	1355	1587	1.476
HP06	1351	1590	1.444

† Ratio (*R*) of the amorphous (A) peak integral area to that of the graphitic (G) peak.

‡ Three determinations on three different points.

CONCLUSIONS

This study characterized the isolated NHC from the soils and sediments in the Pearl River Delta using a combination of advanced analytical and spectroscopic techniques. It is feasible that condensed OM (NHC and BC) can be effectively extracted from soil, sediment, and their size fractions with the revised hydrolysis procedure. The results showed that NHC accounted for 256 to 847 g kg^{-1} of total OC, with an average of 519 g kg^{-1}, indicating that NHC is an important or even dominant component of the OC in the investigated soils and sediments. The NHC contents in this study are highly correlated with the OC contents, with a slope of 0.647 for the 25 soil and sediment samples, which is higher than previously reported NHC–OC correlations in soils. Radiocarbon analysis for the NHC fractions indicated that ancient OC accounted for 390 to 490 g kg^{-1} OC, with an average value of 440 g kg^{-1}, demonstrating the importance of ancient OM in the soils and sediments, which was often overlooked in previous investigations. Systematic characterization of NHC showed that it consisted of a mixed source originating from different thermally matured bitumen or kerogens, polymethelene C (algaenan, cutan, cutin, cuticle, and lipid), aged terrigenous OM (lignin and humin), and BC.

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