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Diagenetic alterations of amino acids and organic matter in the upper Pearl River Estuary surface sediments

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Abstract

The objective of this study was to investigate the sources, diagenetic alterations of, and bacterial contributions to sediment organic matter (OM) in the upper Pearl River Estuary. Sediment analyses were conducted for three size fractions of OM, including coarse particulate OM (CPOM), fine particulate OM (FPOM), and ultrafiltered dissolved OM (UDOM). Results showed that the highest and lowest carbon (C): nitrogen (N) ratios were in CPOM and UDOM, respectively, indicating CPOM was relatively enriched in organic C, whereas FPOM was enriched in N-containing molecules. Distributions of amino acids and their D-isomers among the sediment fractions indicated that the percentage of total N represented by total hydrolysable amino acids, C- and N-normalized yields of total D-amino acids, and C- and N-normalized yields of D-alanine, D-glutamic acid, D-serine could be used as diagenetic indicators of sediment OM. Correlations between the N yields in total D-amino acids and total hydrolysable amino acids, and total N yields suggested that the bacterial N in general reflected the bulk N changes in CPOM, FPOM, and UDOM. Our results demonstrate the crucial role of bacteria as a N source in the terrestrial (soil and vascular plant debris) OM transported by the river.

1 Introduction

Bio-molecules undergo major transformations in the natural environment following the disintegration of bacterial cell materials through death (Tremblay and Benner, 2009), viral lysis (Riemann and Middelboe, 2002), and protist grazing of source organisms (Nagata and Kirchman, 2000). Heterotrophic microorganisms are the primary agent of decomposition, and exhibit a significant impact on preserved organic matter (OM) abundance and biochemical composition (Tremblay and Benner, 2009). Over half of the nonliving (or detrital) OM in aquatic environments still remains unidentified at the molecular level (Hedges et al., 2000), although extensive effort has been taken to determine its origins, productions, and diagenetic alterations.

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Several studies have confirmed the occurrence and origin of bacterial biomarkers in the detrital OM from water columns and sediments (Davis et al., 2009; Jørgensen and Middelboe, 2006; Lomstein et al., 2006, 2009; Pedersen et al., 2001). Among these biomarkers are bacteria-derived amino acids and the respective D-enantiomers. Pure culture investigations in the laboratory have demonstrated that D-amino acids (DAAs), commonly found in peptidoglycan, are released during bacterial growth (Kawasaki and Benner, 2006; Jørgensen and Middelboe, 2006), suggesting a bacterial origin of these amino acids. Amino acid-related parameters have been shown to be useful as source indicators of OM in particulate OM and dissolved OM in sediments through the comparison of the yields and compositions of amino acids and the associated D-enantiomers between OM samples and source materials (Cowie and Hedges, 1992; Lomestein et al., 2006; Pedersen et al., 2001).

The yields and compositions of amino acids have been used successfully as diagenetic indicators because they are selectively decomposed or preferentially preserved during different stages of diagenesis, and seem uncompromised to source variations (Amon et al., 2001; Dauwe and Middelburg, 1998; Davis et al., 2009; Tremblay and Benner, 2009). Davis et al. (2009) reported that carbon (C)-normalized amino acid yields were the most effective indicator for early dissovled OM diagenesis, relative abundances of amino acid yields for intermediate stages of diagenesis, and the mole percent composition of the non-protein amino acid (γ-aminobytyric acid) for advanced diagenesis during microbial decomposition of marine dissolved OM on a short time scale. Dauwe et al. (1999) revealed systematic compositional changes upon progressive particulate OM degradation and derived a quantitative degradation index based on amino acid compositions of particulate OM samples from various marine environments. Also, the amino acid-related degradation index has been successfully used to characterize the diagenetic status of OM in marine and coastal sediments (Dauwe and Middelburg, 1998; Lomstein et al., 2006). However, there is little information on the diagenetic alteration and degradation status of OM with different sizes. Tremblay and Benner (2009) found a consistent trend of increasing proportions of DAAs among

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Amazon River detrital size fractions and suggested the portion of DAAs as a useful diagenetic indicator. Nevertheless, few studies are available on the diagenetic state of sediment OM of different sizes, especially in estuary sediments.

The abundance and composition of amino acids in total hydrolysable amino acids (THAA) have been used to quantify bacterial contributions to OM (Kaiser and Benner, 2008; Lomstein et al., 2009). Pedersen et al. (2001) showed that the percentages of four DAAs in the THAA pool increased with the sediment depth and that bacterial peptidoglycan contributed to the pool of organic nitrogen (N). Measuring the DAA composition in THAA, Kaiser and Benner (2008) found that bacterial detritus was the major component of particulate OM and an important source of submicron size particle and colloids in the ocean. These amino acid-based estimators are affected by many factors, such as sediment depth (Pedersen et al., 2001), diagenetic status (Lomstein et al., 2009), and OM size (Kaiser and Benner, 2008; Tremblay and Benner, 2009), suggesting different contributions of bacteria to OM under different conditions. However, the bacterial contributions to sediment OM of different size fractions and the respective diagenetic status are still poorly understood.

Therefore, the aim of this study was to assess the sources of and bacterial contributions to sediment OM of different size fractions through measurements of compositions and concentrations of sediment particulate and dissolved amino acids. Moreover, the diagenetic status of sediment OM of different size fractions was also investigated.

2 Materials and methods

2.1 Site description

The Guangzhou reach of the Pearl River Estuary (GZPR) was selected as the study site (Fig. 1). The Pearl River crosses Guangdong Province, China in the subtropical region, and opens to the northern part of the South China Sea (Yin and Harrison, 2008). The GZPR is in the upper Pearl River estuary (PRE). The tidal range at the GZPR is

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nearly 1.2 m, affected by the Guangdong micro-tidal coast (irregular semi-diurnal tide) and the inverted funnel-shape topography of the PRE (Harrison et al., 2008). The GZPR is quite shallow with a water depth less than 10 m. The fresh water from the GZPR discharges into the PRE and adjacent South China Sea through the Humen Gate, locating at the northeast of the PRE with a yearly sediment load of 658×10^4 t (Dong et al., 2006). The yearly freshwater discharge from the Guangzhou channel is 3.8×10^{10} m^3. Suspended sediment in the GZPR is composed mainly of clay and silt with a high percentage of organic particles because of urban sewage (Dong et al., 2006). The sedimentation rate in the GZPR varies from 0.42 to 4.26 cm a^{-1} with an average of 1.17 cm a^{-1}. The sedimentation flux in the GZPR ranges from 337 to 5140 mg cm^{-2} a^{-1} (Zhang et al., 2002). The bottom sediment in the GZPR is sandy in texture. The GZPR system is strongly affected by the combination of seasonal monsoon winds, tidal dynamics, complex topography, and large seasonal variations in both the runoff and coastal circulation (Dong et al., 2006). The terrestrial organic C contribution to the surface sediments in the GZPR is ca. 78%, suggesting that a pronounced portion of sediment OM derives from soils and much of it has undergone substantial diagenetic alterations. On the other hand, evidences of bacterial contributions to Pearl River OM have been reported, including relatively lower C:N ratios than those in local plants and enriched concentrations of deoxy sugars in the surface sediments (fucose and rhamnose) (He et al., 2010).

2.2 Sediment sampling and sample processing

Thirteen sediment samples (namely S1, S2, ..., S13) were collected at the study site in January of 2010. The sampling area and stations are shown in Fig. 1. Topographical characteristics of the sampling stations and physicochemical properties of the respective water columns are summarized in Table 1. Water column samples were collected at a water depth of 0.5 m. Sediment samples were collected using a piston lead core equipped with a PVC tube of inner diameter 6 cm and 47 cm long. The length of sediment cores collected was 35 cm. The cores were immediately stored in ice and

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transported to the laboratory. In the present study, we only used the upper 8 cm of each sediment core for analyses. Samples were freeze-dried, homogenized by grinding in an agate mortar, and stored in polyethylene vials prior to analyses.

2.3 Sediment fractionation

Sediment samples were dispersed by sonication. Coarse particulate organic matter (CPOM) in the sediment was separated by sieving onto a 63-µm Nitex screen and oven-dried at 40 °C. The sand-free suspension was then passed through a Nalgene filter with a 0.2-µm cutoff size, to isolate fine particles to get fine particulate organic matter (FPOM). The FPOM fraction was oven-dried at 40 °C. The sediment fraction (The ultra-dissolved organic matter (UDOM) fraction) that permeated the 0.2-µm-pore filter was recovered with MSC300 cup type ultra-filter system with a nominal cutoff size of 1000 atomic mass units (Daltons), corresponding roughly to 0.001-µm. The UDOM fraction was freeze-dried prior to analysis. The detailed sediment fractionation procedure is shown in Fig. 2.

2.4 Elemental analysis

Total organic carbon (TOC) for CPOM and FPOM was determined using the wet oxidation method (Gaudette et al., 1974). Concentrations of total organic C and inorganic C for water column samples and UDOM were measured by high-temperature catalytic oxidation techniques using a Shimadzu TOC-V CPH TOC analyzer. Total N for CPOM and FPOM was determined using Kjeldahl digestion. Total N for water column samples and UDOM was determined using Persulfate digestion (D'Elia et al., 1977). Concentrations of NH_4^+ and NO_3^- of the water column samples were colorimetrically measured after filtering through 0.45 µm pore-size GF/F filters.

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2.5 Amino acid analysis

Approximately 500 mg of dried CPOM or FPOM particles and 5 to 10 mg of UDOM powders were hydrolyzed with 6 M HCl at 110 °C for 24 h in a sealed screw capped glass vial (Labco Exetainer, UK) under N_2. The hydrolysate was filtered to remove mineral particles, then the pH of the solution was adjusted with KOH to a range of 6.6 to 6.8. Thereafter, the hydrolysate was centrifuged and filtered before the chromatography analysis. Derivatization with OPA and N-isobutyryl-L-cysteine (IBLC) was performed in a borate buffer (pH 9.5). Separation and detection of D-enantiomers were performed on an Agilent 1100 system with a Agilent Zorbax Eclipse XDB-C18 reverse phase column (150 mm × 4.6 mm, 5 µm) and a guard column (4 × 4 mm, 5 ml). The flow rate was 0.8 ml min^{-1} and the elution temperature was 20 °C. A mobile phase linear gradient was applied, from 100% 23 mmol L^{-1} Sodium Acetate (pH 5.95–6.0) to 53.5% methanol/acetonitrile (600:50 v/v) after 75 min and 80% methanol/acetonitrile (600:50 v/v) after 85 min. The excitation wavelength was set at 230 nm (band width 25 nm). The emission length was set at 445 nm (cutoff filter 280 nm and band width 50 nm). DAA was quantified using four external DAA standard solutions containing a mix of D-serine (D-Ser), D-glutamic acid (D-Glu), D-alanine (D-Ala), and D-aspartic acid (D-Asp). The DAA measurements were corrected for chemical racemization occurring during hydrolysis. The correction was based on the average of measured racemization rates of free and protein amino acids (Kaiser and Benner, 2005). The concentration of THAA pools was analyzed by an ICS 3000 Dionex AAA-Direct System with an AminoPac PA10 analytical column (2 mm × 250 mm, 8.5 µm) with guard column (2 mm × 50 mm) and IPAD detector. The flow rate was 0.25 ml min^{-1} and the elution temperature was 30 °C. The gradient for amino acid analysis was listed in Table 2. Concentrations of the individual amino acids were calculated according to individual standard curves, produced from a mixture of the amino standard solution AA-S-18 (Sigma-Aldrich), which included ornithine (Orn), β-Ala, γ-Aba, and α-Aba. Twenty one amino acids were analyzed and the sum of them was used to represent the THAA concentration. In our study no corrections for acid-hydrolysis efficiency were conducted (Benner and Kaiser, 2003).

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3 Results

3.1 Bulk C and N for CPOM, FPOM, and UDOM

Sediment TOC content increased with the sediment size. Average TOC contents for UDOM, FPOM, and CPOM were 4.12, 8.95, and 10.95 mg C g^{-1} dry weight, respectively. The largest average total N content was observed in the FPOM fraction (2.1 mg N g^{-1} dry weight) and CPOM had the lowest average total N content of 1.1 mg N g^{-1} dry weight. The UDOM fraction had an intermediate total N value of 1.9 mg N g^{-1} dry weight. The results indicated that CPOM was relatively enriched in organic C and depleted in N compared to the FPOM and UDOM fractions, whereas FPOM was enriched in N-containing molecules. C:N ratios varied greatly from 1.2 to 40.9 among the fractions of the samples (Table 3). For each sampling location, the highest C:N ratio value was in CPOM among the three fractions, whereas the lowest C:N ratio was in UDOM except for S6 and S7 (Table 3). CPOM had a wide range of C:N ratios (5.3–40.9), whereas the C:N ratios in FPOM (3.7–8.1) and UDOM (1.2–5.6) were much narrower (Table 3). The highest average C:N value was found in CPOM, whereas UDOM had the lowest average C:N ratios (Fig. 3), also indicating that the CPOM fraction was N poor relative to the FPOM and UDOM fractions.

3.2 Amino acid yields and compositions

The ranges of percentage of total N as THAA were 20.1% to 57.3% in CPOM, 14.6% to 56.7% in FPOM, and 1.36% to 58.3% in UDOM. The percentages of total N as THAA generally overlapped over a broad range, exhibiting a relatively large variability among the sediment samples (Table 3). The average percentages of total N as THAA were 36.87%, 32.2%, and 25.5% in CPOM, FPOM, and UDOM, respectively (Fig. 4).

The D-enantiomers of Ala, Glu, Asp, and Ser were measured in some samples. C- and N-normalized yields of specific and total D-enantiomers (D-Ala, D-Glu, D-Asp and D-Ser) varied among the three fractions (Table 4). C-normalized yields of D-Ala

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for CPOM, FPOM and UDOM varied from 0.00 to 8.91, 0.00 to 104, and 0.00 to 708 nmol mg C^{-1}, respectively. N-normalized yields of D-Ala for CPOM, FPOM and UDOM varied from 0.00 to 227, 0.00 to 461, and 0.00 to 2243 nmol mg N^{-1}, respectively. C-normalized yields of D-Glu for CPOM, FPOM and UDOM varied from 0.00 to 57.3, 0.00 to 1009, and 0.00 to 1084 nmol mg C^{-1}, respectively. N-normalized yields of D-Glu for CPOM, FPOM and UDOM varied from 0.00 to 430, 0.00 to 2151, and 0.00 to 1176 nmol mg N^{-1}, respectively. C-normalized yields of D-Asp for CPOM, FPOM and UDOM varied from 0.00 to 165, 0.00 to 22.4, and 0.00 to 207 nmol mg C^{-1}, respectively. N-normalized yields of D-Asp for CPOM, FPOM and UDOM varied from 0.00 to 747, 0.00 to 76.6, and 0.00 to 328 nmol mg N^{-1}, respectively. C-normalized yields of D-Ser for CPOM, FPOM and UDOM varied from 0.00 to 10.2, 0.00 to 65.8, and 0.00 to 1481 nmol mg C^{-1}, respectively. N-normalized yields of D-Ser for CPOM, FPOM and UDOM varied from 0.00 to 122, 0.00 to 310, and 0.00 to 1903 nmol mg N^{-1}, respectively (Table 4). C-normalized yields of total DAA were between 0.00 and 165 nmol mg C^{-1} for CPOM with corresponding N-normalized yields of total DAA ranging from 0.00 to 747 nmol mg N^{-1}. C-normalized yields of total DAA for FPOM were in the range of 0.00 to 1157 nmol mg C^{-1} with respective N-normalized yields of total DAA from 0.00 to 2689 nmol mg N^{-1}. C- and N-normalized yields of total DAA in UDOM ranged from 0.00 to 1660 nmol mg C^{-1}, and 0.00 to 3170 nmol mg N^{-1}, respectively (Table 4). The highest average C- and N-normalized yields of total DAA were in UDOM, whereas the lowest ones were in CPOM (Fig. 5a, b).

Either the spatial-averaged C- or N-normalized yields of D-Ala, D-Glu, D-Ser increased with the sediment OM sizes (Fig. 6a, b). In contrast, the highest average C-normalized yield of D-Asp was found in UDOM and the lowest in CPOM, whereas the highest average N-normalized yield of D-Asp was found in CPOM and the lowest in UDOM (Fig. 6a, b).

The N yields (mg (100 mg C)$^{-1}$) in total DAA and THAA are plotted against total N yields measured in the three size fractions in Fig. 7a and b, respectively. The N yields in total DAA and total N were linearly correlated based on the data of all the three

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size fractions (Fig. 7a). Likewise, a linear relationship was also observed between the N yields in THAA and total N when combing data from all the three size fractions (Fig. 7b). These observations demonstrated that the N yields in total DAA and THAA reflected the changes in bulk N concentrations of sediment fractions. However, the non-zero y-intercept suggested that nitrogenous compounds other than amino acids still contributed to total N.

4 Discussion

4.1 Sources of CPOM, FPOM and UDOM

The weight percentages of C contents in CPOM were within the range of previously reported in Amazon River, whereas the C contents in FPOM and UDOM were relatively lower than those in Amazon River (Hedges et al., 1994). These differences indicated that the suspended sediments had undergone extensive decomposition before deposition, which was supported by the lower organic C contents relative to soil samples in the Pearl River Delta (Yu et al., 2010). The sediment OM in the GZPR sediments consists of a mixture of multiple sources, including the terrestrial OM, phytoplankton-derived OM, bacterial OM, and anthropogenic OM. The Pearl River system is mostly affected by C3 plants with an average δ^{13}C value about −27‰ (Zhang et al., 2009). The δ^{13}C value of bulk sediment OM in the GZPR ranges from −23.05 to −26.05 ‰ (He et al., 2010). The δ^{13}C values of phytoplankton-derived OM and sewage particulate OM vary from −31.2 to −25.8‰, and from −25.9 to −22.8‰, respectively (He et al., 2010), although the stable carbon isotope ratio has not been well documented (Andrews et al., 1998; Lee, 2000). Additionally, fatty acids profiles in sediment cores showed that bacterial biomass contributed to sediment OM besides phytoplankton and terrestrial OM (Fu et al., 2010). Based on the C:N ratios of sewage and planktonic materials, He et al. (2010) demonstrated that the terrestrial OM predominated in sediment OM with OM derived from sewage outfalls and local primary productivity extensively

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processed by microbes. However, the sewage was an insignificant contributor to the organic C in sediments in the PRE (Yu et al., 2010). Yu et al. (2010) proposed that the microbial degradation was likely to play a key role in changes in the bulk sediment organic δ^{13}C and C:N over time in the PRE. Overall, the results suggested that bacterial biomass or bacterial remnant was another source of sediment OM in the GZPR sediment as well as terrestrial OM (He et al., 2010).

As the OM sizes of plankton (e.g. diatoms) and sewage are usually smaller than 80 and 63 µm (Sophonsiri and Morgenroth, 2004), respectively, the sediment CPOM is mainly composed of the relatively coarse terrestrial OM. The coarse terrestrial OM primarily contains soil sand-associated terrestrial OM and floated vascular plant fragments. The above result was confirmed by the relatively high TOC content, comparatively low total N content, and high C:N ratio in the CPOM fraction in the present study (Fig. 3). However, as discussed by Cowie and Hedges (1992), with particularly low amino acid yields, woody vascular plant tissues are very unlikely to contribute significantly to the CPOM fractions in sediments. In addition, the C:N ratios in the CPOM fraction in our study were similar to those in soils (8.9–17.9) in the Pearl River Delta (Yu et al., 2010). These results indicated that soil sand-associated terrestrial OM made the most important contribution to sediment CPOM fractions in the GZPR. Nonetheless, the C:N ratios of local C3 and C4 plants in the Pearl River Delta are in the range from 13.7 to 31.0, suggesting that the vascular plant may also contributed significantly to CPOM in the GZPR. The FPOM fraction is derived from fine soil particle-associated terrestrial OM, sewage POM, bacterial POM (living bacterial cells and cellular debris), and phytoplankton POM (e.g., in situ plankton remains). However, it has been recently suggested that bacteria-derived bio-macro-polymers can represent dominant components of high molecular weight DOM in ocean waters (Nagata and Kirchman, 2000). Lomstein et al. (2006) and Pedersen et al. (2001) suggested the likely contribution of bacterial remnants (e.g., empty cell sacs and cell wall fragments) to sediment OM. The occurrence of muramic acid (a biomarker unique in bacterial peptidoglycan) in the UDOM fraction in our study confirmed the contribution of bacterial DOM to this

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sediment fraction (unpublished data). As a result, the sediment UDOM class is primarily composed of organic C from bacterial remains (bacterial DOM) besides phytoplankton DOM (e.g., dissolved phytoplankton exudates) and terrestrial DOM (e.g., soil DOM). The low abundance of muramic acid and relative enrichment of D-enantiomers in the UDOM indicated the significant contribution of bacterial DOM to the UDOM isolates in our sediments (Kawasaki and Benner, 2006). The origin of the three sediment OM fractions suggest that the diagenesis of the sediment OM proceeds further as the sizes decrease, which is supported by the decreasing C:N ratios in this study (Amon and Benner, 1996).

4.2 Diagenetic trends for sediment OM of different size classes

Bacteria are important agents of degradation of sediment OM. As microbial decomposition progresses, the reactive components of sediment OM are selectively consumed, leading to an enrichment of less reactive sediment OM components (Wakeham et al., 1997). N-containing bio-molecules exhibit different dynamics during sediment OM diagenesis, thus these N-containing molecules can be used as good indicators of OM "freshness" and diagenetic state (Davis et al., 2009; Tremblay and Benner, 2009). Specifically, amino acids and the respective D-enantiomers have been reported to display different reactivities at different stages of OM diagenesis (Amon et al., 2001; Tremblay and Benner, 2009). Distribution patterns observed with amino acids and their D-isomers can be employed for the assessment of their relative reactivity. Knowledge about the diagenetic status of the samples can highlight new compositional trends or features that are indicative of the degradation state and diagenetic history (Tremblay and Benner, 2009). In the present study, compositional features that seemed sensitive to different stages of diagenesis were percentage of total N as THAA, C- and N-normalized yields of total DAA, and C- and N-normalized yields of D-Ala, D-Glu, D-Ser.

The C:N ratio was found to consistently decrease with declining particle size. CPOM was enriched in terrestrial organic C and depleted in N. The results were consistent

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with those from relatively unaltered vascular plant debris. Plants are rich in C and poor in N, resulting a large C:N ratio compared to other organisms, such as bacteria and phytoplankton. As shown by He et al. (2010), terrestrial OM made a large contribution to sediment OM in the PRE. However, the C:N ratios for sediment CPOM and FPOM in this study were relatively lower than those observed in Amazon River water columns (Hedges et al., 1994), probably attributable to the lower C:N ratios (13.7–21.7) of local plants in the Pearl River Delta (Yu et al., 2010) than those (25.2–484) in the Amazon River system (Cowie and Hedges, 1992). Furthermore, the C:N ratios of UDOM in our sediment samples were considerably lower than those in water column samples from the Amazon River, which were related to the general N depletion characteristic in the river water samples (Hedges et al., 1994). The lower C:N ratios in our study were attributable to the relative enrichment of inorganic N (e.g., ammonia) in several sediment samples (e.g., S3, S5, and S13 in Table 3). Microbial degradation of protein and amino acid-rich sewage outputs in the GZPR resulted in a significant inorganic N source to sediment pore water. Additionally, the regeneration of inorganic nutrients can also occur with undergoing diagenetic alteration after OM deposition.

The result of percentages of total N as THAA decrease with sediment particle sizes indicates that amino acids are more reactive than bulk TOC or N in the sediments. Percentage of total N as THAA is diagenetically sensitive and has generally been observed to fall with progressive degradation, for example with depths in marine sediment cores (e.g., Amon et al., 2001; Cowie and Hedges, 1992; Henrichs et al., 1987; Pedersen et al., 2001). Cowie and Hedges (1992) found a downcore decrease of percentage of total N as THAA in sediments and demonstrated the potential of this parameter as a valuable diagenetic indicator. It has been reported that percentages of total N as THAA for most living organisms and tree leaves are >50% but decrease as degradation progresses to near 10% for ancient sediments (Cowie and Hedges, 1994). The total N represented by amino acids in our CPOM samples was similar to that of CPOM in the water column samples in the Amazon River system (Hedges et al., 1994). In contrast, FPOM in the Amazon River water samples was enriched in protein amino

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acids relative to that of the GZPR sediment samples, which was possibly related to the reduced amount of adsorbed amino acids due to more coarse sediments in the GZPR. Hedges et al. (1994) reported a percentage of total N as THAA of 13.5% for the Amazon River water column UDOM, which was lower than our values, indicating a relative lability of the shallow water sediment UDOM isolates in GZPR. Although diagenetic alterations of amino acids are variable, observations on the general trend toward low percentages of total N as THAA with declining particle sizes supports the capability of the percentage of total N as THAA as a diagenetic indicator.

The observed C- and N-normalized yields of total DAA trends were in the order of CPOM < FPOM < UDOM, which agreed with the observed patterns of degradation alteration in the sediment samples, with CPOM being the least processed and UDOM the most. The trends confirmed the "size-reactivity continuum" model by Amon and Benner (1996). Similarly, the percentage of total dissolved organic C as total DAA was shown to increase during the decomposition of fresh, algal-derived DOM from an Arctic ice floe (Amon et al., 2001). Moreover, Tremblay and Benner (2009) found that %DAA (the ratio of summed mole of DAA to THAA) increased with OM in the Amazon River system. These studies indicate that C- and N-normalized yields of total DAA are useful diagenetic indicators. The increased N-normalized yields of total DAA and decreased percentages of total N as THAA with the ongoing diagensis suggests the relatively rapid use of L-amino acids and the preservation of DAAs in the process. A possible explanation for these observations is that most L-amino acids are found in "conventional" proteinaceous materials, whereas DAAs are components of more refractory, bacterial cell-wall macromolecules, like peptidoglycan (Schleifer and Kandler, 1972). C- and N-normalized yields of individual D-enantiomers other than those of D-Asp show consistent diagenetic trends towards the decreasing physical size of OM. Likewise, C-normalized yield of mole D-Ala was found to increase in particulate OM from surface to mesopelagic waters in the North Pacific and North Atlantic (Kaiser and Benner, 2008). However, there are still not enough data available to confirm the pattern based on C- and N-normalized yields of individual D-enantiomers during OM

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diagenesis. A likely reason to explain the discrepancy in the patterns of the four D-enantiomers is that other bacterial macromolecules with reactivity different from peptidoglycan may have contributed to D-Asp (Kaiser and Benner, 2008). Nevertheless, the size-specific trends in our study show the potential of individual D-enantiomers yields to be used as diagenetic indicators.

4.3 Qualitative bacterial contribution to sediment OM of different sizes

Accurate estimations of bacterial contributions to sediment OM appear challenging since the bacterial community is highly diversified in the GZPR. Therefore, quantification of bacterial contribution to sediment OM requires information on spatial and temporal distributions of the bacterial community compositions. The observed correlations between the N yields in total DAA and THAA, and total N yields indicate that bacterial N in general reflected bulk N changes in CPOM, FPOM, and UDOM. Our results demonstrate that the crucial role of bacteria as a N source in terrestrial OM (soils and vascular debris) transported by the Pearl River. Tremblay and Benner (2009) reported consistent findings on the bacterial N contribution to the Amazon River water column OM of different size classes. However, their results showed that bacteria may not contribute to N in FPOM and the sorption of N-containing compounds to fine particles may have an important influence on total N content in FPOM (Hedges et al., 2000; Tremblay and Benner, 2009). It appears that OM in the Pearl River is more reactive and undergoes extensive microbial degradation in the water, and then deposits into the sediments. Thus, the interactions between the reactive transport pathways and particle sorption of OM may have significant influence on the quantification of bacteria-derived contribution to organic C and N. Further studies on the relative role of bacteria and sorption onto fine river particles are needed to accurate quantification of bacterial C or N contributions to OM in the Pearl River system.

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5 Concluding remarks

Based on the elemental compositions of sedimentary OM fractions, soil sand-associated terrestrial OM made the most important contribution to sediment CPOM fractions in the GZPR. The sediment FPOM fraction is derived from fine soil particle-associated terrestrial OM, sewage POM, bacterial POM and phytoplankton POM. The sediment UDOM class is primarily composed of organic C from bacterial remains besides phytoplankton DOM and terrestrial DOM. Distribution patterns observed with amino acids and their D-isomers among sediment fractions demonstrated that percent of total N as THAA, C- and N-normalized yields of total DAA, and C- and N-normalized yields of D-Ala, D-Glu, D-Ser can be used as diagenetic indicators. Besides, the observed correlations between the N yields in total DAA and THAA, and total N indicate that bacterial N in general reflected bulk N changes in CPOM, FPOM, and UDOM. Our results demonstrate that the crucial role of bacteria as a N source in terrestrial OM (soils and vascular plant debris) transported by the Pearl River in South China.

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Table 1. Topographical characteristic of the sampling stations and physical and chemical properties of the water columns.

Station No.	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
Latitude (°) N	23°06′679″	23°06′323″	23°04′482″	23°03′052″	23°02′958″	23°02′366″	23°02′115″	23°04′061″	23°05′487″	23°06′129″	23°06′289″	23°06′585″	23°06′201″
Longitude (°) E	113°17′365″	113°14′588″	113°15′512″	113°16′556″	113°18′111″	113°21′224″	113°21′948″	113°21′947″	113°24′610″	113°23′710″	113°21′722″	113°21′022″	113°18′880″
H (m)	540	540	541	542	542	541	541	541	541	541	541	541	541
Water depth (m)	3.8	1.9	2.6	2.2	2.4	1.8	1.0	1.7	2.7	2.4	3.4	2.7	0.5
Cond (mS cm^{-1})*	0.726	0.807	0.765	0.531	0.561	0.651	0.685	0.791	1.327	1.155	0.976	1.012	0.615
O_2 (mg L^{-1})	0.60	0.52	0.45	2.04	0.66	1.18	1.99	1.87	0.89	0.72	0.42	0.28	1.20
T (°C)	16.6	17.2	17.9	16.6	16.9	17.1	17.5	17.8	17.1	17.1	17.4	17.9	17.1
Chl a** (μg L^{-1})	49.39	6.9	50.37	5.92	12.77	11.69	na	62.73	na	49.34	56.19	88.02	15.3
pH	7.28	7.24	7.09	7.12	7.23	7.16	8.17	7.28	7.41	7.20	7.18	7.05	7.07
TOC (mg C L^{-1})	21.64	14.16	1.42	3.24	3.23	1.18	na	1.31	na	19.19	25.65	6.05	5.83
IC (mg C L^{-1})	44.90	44.53	62.01	36.11	37.00	39.56	na	58.72	na	40.85	32.71	50.44	40.72
Total N (mg N L^{-1})	23.32	30.74	32.49	14.73	23.32	24.79	na	na	na	35.23	27.03	22.54	15.03
C:N	1.08	0.54	0.05	0.26	0.16	0.06	na	na	na	0.64	1.11	0.31	0.45
NO_3^- (mg N L^{-1})	0.08	0.09	0.05	0.04	0.05	0.01	na	0.04	0.02	0.01	0.01	0.04	1.87
NH_4^+ (mg N L^{-1})	7.15	8.93	10.00	5.14	5.00	7.26	na	8.36	na	7.46	8.16	10.11	5.65

H, elevation; Cond, conductivity; O_2, dissolved oxygen; T, temperature; Chl-a, chlorophyll-a; TOC, total organic carbon; IC, inorganic carbon; Total N, total nitrogen; * Determined by conductivity meter; na, not available. ** Measured by spectrometry of acetone extracts of particulate matter in 20-ml water and collected on GF/C filters, according to Jespersen and Christoffersen (1987).

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Table 2. Gradient condition for 21 amino acids analysis.

Time (min)	%Deionized water	%250 mM NaOH	%1 M Sodium acetate	Flow rate (ml min^{-1})
Init	0	50	50	0.25
0	0	50	50	0.25
10	0	50	50	0.25
10.1	80	20	0	0.25
40	80	20	0	0.25
40.1	80	20	0	0.25
42	80	20	0	0.25
52	80	20	0	0.25
56	68	32	0	0.25
64	36	24	40	0.25
80	36	24	40	0.25

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Table 3. Total organic carbon (TOC) and total nitrogen (Total N) contents, C:N ratios (mole TOC:Total N), percentages of TOC and total N as total hydrolysable amino acids (THAA) in sediment samples of different size fractions. Abbreviations: CPOM, coarse particulate organic matter; FPOM, fine particulate organic matter; UDOM, ultrafiltered dissolved organic matter.

Station sampled	Size fraction	TOC (wt %)	Total N (wt %)	C:N	%C as THAA	%N as THAA
1#	CPOM	0.25	0.017	17.2	2.91	47.57
	FPOM	0.73	0.185	4.6	57.13	34.75
	UDOM	1.41	0.620	2.7	10.45	12.82
2#	CPOM	2.21	0.063	40.9	8.18	50.46
	FPOM	1.00	0.144	8.1	4.04	31.15
	UDOM	1.15	0.450	3.0	6.19	14.29
3#	CPOM	2.55	0.254	11.7	21.83	37.89
	FPOM	1.09	0.290	4.4	3.72	15.73
	UDOM	0.39	0.300	1.5	27.53	29.46
4#	CPOM	0.59	0.067	10.3	7.49	36.27
	FPOM	0.80	0.129	7.2	23.24	49.90
	UDOM	0.30	0.090	3.9	15.75	21.83
5#	CPOM	1.53	0.109	16.4	17.14	46.08
	FPOM	0.72	0.172	4.9	14.87	51.91
	UDOM	0.11	0.070	1.8	24.76	29.82
6#	CPOM	0.46	0.047	11.4	6.58	30.74
	FPOM	0.43	0.134	3.7	27.20	46.12
	UDOM	0.29	0.060	5.6	18.44	58.30
7#	CPOM	0.37	0.038	11.4	2.21	20.09
	FPOM	0.60	0.136	5.1	38.29	56.65
	UDOM	0.46	0.100	5.4	11.88	49.47
8#	CPOM	1.13	0.163	8.1	21.67	50.60
	FPOM	0.88	0.195	5.3	4.23	14.67
	UDOM	0.35	0.150	2.7	14.23	30.20
9#	CPOM	0.55	0.050	12.8	2.26	20.30
	FPOM	0.95	0.230	4.8	26.06	30.43
	UDOM	0.46	0.340	1.6	28.46	35.16
10#	CPOM	0.98	0.113	10.1	19.01	57.34
	FPOM	0.79	0.207	4.5	12.52	28.94
	UDOM	0.08	0.040	2.3	14.93	21.09
11#	CPOM	0.38	0.041	10.8	2.43	22.39
	FPOM	1.10	0.184	7.0	14.62	14.62
	UDOM	0.16	0.140	1.3	30.44	13.96
12#	CPOM	0.79	0.174	5.3	9.18	28.51
	FPOM	1.31	0.370	4.1	18.87	19.28
	UDOM	0.10	0.050	2.3	7.31	13.78
13#	CPOM	2.44	0.274	10.4	15.56	31.08
	FPOM	1.24	0.291	5.0	5.69	24.41
	UDOM	0.10	0.100	1.2	17.97	1.36

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Table 4. C- and N-normalized yields of individual (D-Ala, D-Glu, D-Asp and D-Ser) and total D-amino acids (total DAA, the sum of D-Ala, D-Glu, D-Asp and D-Ser) in sediment coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and ultra-filtered dissolved organic matter (UDOM) size fractions. D-Ala = D-alanine; D-Glu = D-glutamic acid; D-Asp = D-aspartic acid; D-Ser = D-serine.

Station sampled	Size fraction	D-Ala	D-Glu	D-Asp	D-Ser	D-Ala	D-Glu	D-Asp	D-Ser	Total DAA	Total DAA
		nmol mg C^{-1}				nmol mg N^{-1}				nmol mg C^{-1}	nmol mg N^{-1}
1#	CPOM	2.61	0.00	0.00	0.00	225	0.00	0.00	0.00	2.61	225
	FPOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	UDOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2#	CPOM	7.11	0.00	0.00	0.00	227	0.00	0.00	0.00	7.11	227
	FPOM	0.00	4.44	0.00	0.00	0.00	68.2	0.00	0.00	4.44	68.2
	UDOM	70.7	0.00	0.00	0.00	362	0.00	0.00	0.00	70.7	362
3#	CPOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	FPOM	11.6	0.00	0.00	13.9	203	0.00	0.00	122	25.4	325
	UDOM	0.00	130	49.4	1481	0.00	167	63.4	1903	1660	2134
4#	CPOM	0.00	0.00	0.00	10.2	0.00	0.00	0.00	122	10.2	122
	FPOM	0.00	40.4	0.00	0.00	0.00	184	0.00	0.00	40.4	184
	UDOM	0.00	0.00	0.00	441	0.00	0.00	0.00	1446	441	1446
5#	CPOM	8.78	0.00	0.00	0.00	117	0.00	0.00	0.00	8.78	117
	FPOM	25.8	18.5	4.83	0.00	461	165	43.1	0.00	49.1	669
	UDOM	708	378	207	0.00	2243	599	328	0.00	1294	3170
6#	CPOM	0.00	0.00	0.00	8.74	0.00	0.00	0.00	80.7	8.74	80.7
	FPOM	9.98	0.00	22.4	13.8	68.2	0.00	76.6	47.3	46.2	192
	UDOM	0.00	243	0.00	355	0.00	1176	0.00	1719	598	2894
7#	CPOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	FPOM	0.00	13.7	2.18	9.28	0.00	37.5	5.99	25.5	25.1	69.0
	UDOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
8#	CPOM	1.55	0.00	0.00	0.00	16.7	0.00	0.00	0.00	1.55	16.7
	FPOM	8.53	0.00	0.00	0.00	99.2	0.00	0.00	0.00	8.53	99.2
	UDOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
9#	CPOM	3.15	0.00	0.00	2.25	120	0.00	0.00	42.7	5.40	162
	FPOM	44.7	0.00	0.00	29.0	214	0.00	0.00	69.4	73.7	283
	UDOM	0.00	63.2	0.00	136	0.00	85.9	0.00	185	199	271
10#	CPOM	8.91	0.00	0.00	3.56	125	0.00	0.00	25.0	12.5	150
	FPOM	0.00	9.89	4.06	65.8	0.00	46.6	19.1	310	79.8	376
	UDOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
11#	CPOM	0.49	0.00	2.41	0.00	26.3	0.00	64.6	0.00	2.90	90.9
	FPOM	21.4	23.5	0.00	25.1	88.0	48.4	0.00	51.7	70.0	188
	UDOM	0.00	284	73.1	0.00	0.00	322	82.8	0.00	357	404
12#	CPOM	0.00	57.3	15.0	0.00	0.00	431	112	0.00	72.3	543
	FPOM	104	1009	0.00	43.6	445	2151	0.00	92.9	1157	2689
	UDOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
13#	CPOM	0.00	0.00	165	0.00	0.00	0.00	747	0.00	165	747
	FPOM	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	UDOM	328	1084	0.00	0.00	670	1107	0.00	0.00	1412	1777

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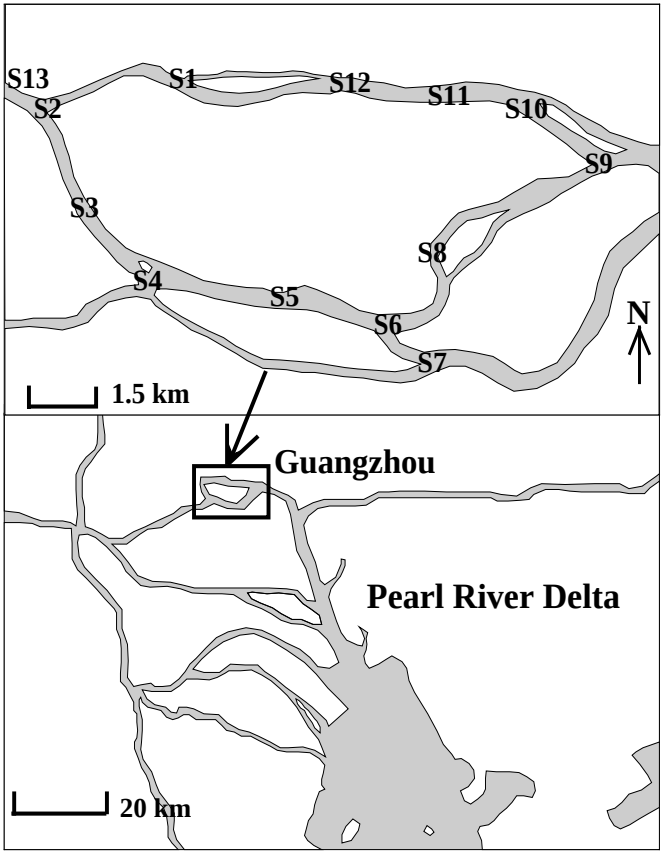

Fig. 1. Sampling stations along the Guangzhou reaches of the Pearl River Estuary, South China: S1 (Ersha Island), S2 (Baietan), S3 (Hedong Bridge), S4 (Yuxi Community), S5 (Luoxi Bridge), S6 (Xiaozhou Village), S7 (Nansha Express), S8 (Luntouhai), S9 (Emei Zhou), S10 (Xinchong Kou), S11 (Linjiang Road), S12 (Liede Village), S13 (Huadi Chong).

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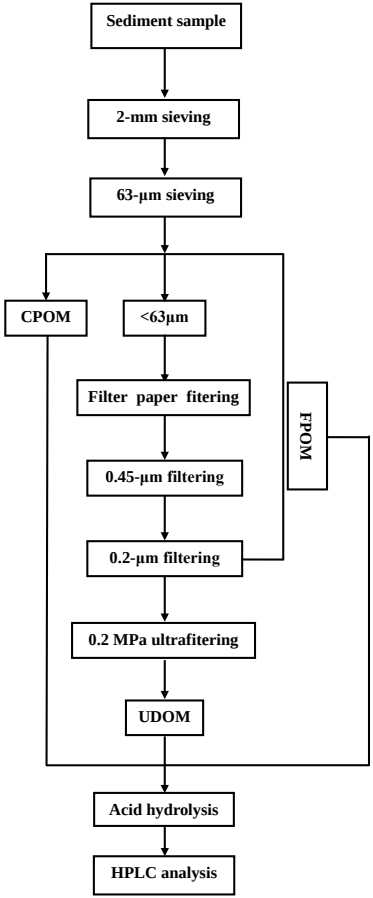

Fig. 2. Schematic graph for sediment fractionation procedure. CPOM, coarse particulate organic matter; FPOM, fine particulate organic matter; UDOM, ultrafiltered dissolved organic matter. TOC, total organic carbon; Total N, total nitrogen.

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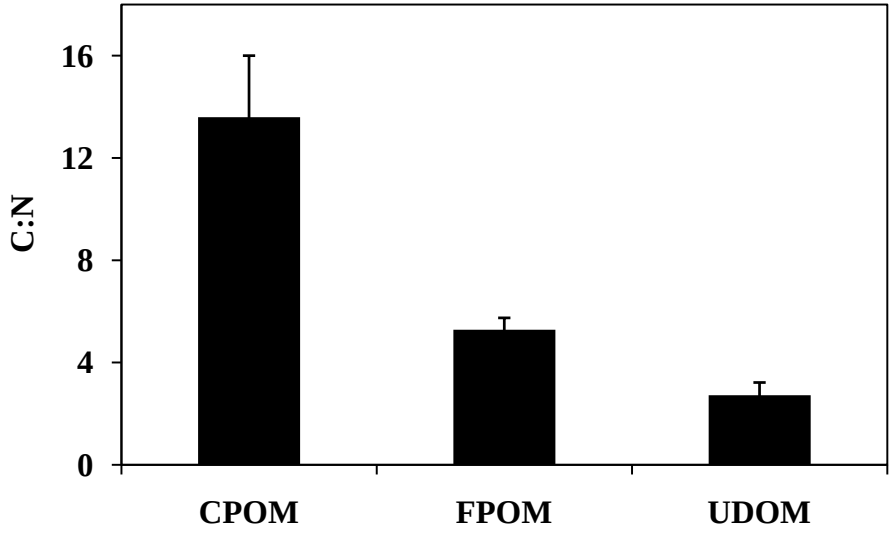

Fig. 3. Spatial-averaged mole C:N ratios for sediment coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and ultra-filtered dissolved organic matter (UDOM) size fractions based on values at the 13 sampling stations. Bars represent standard deviations.

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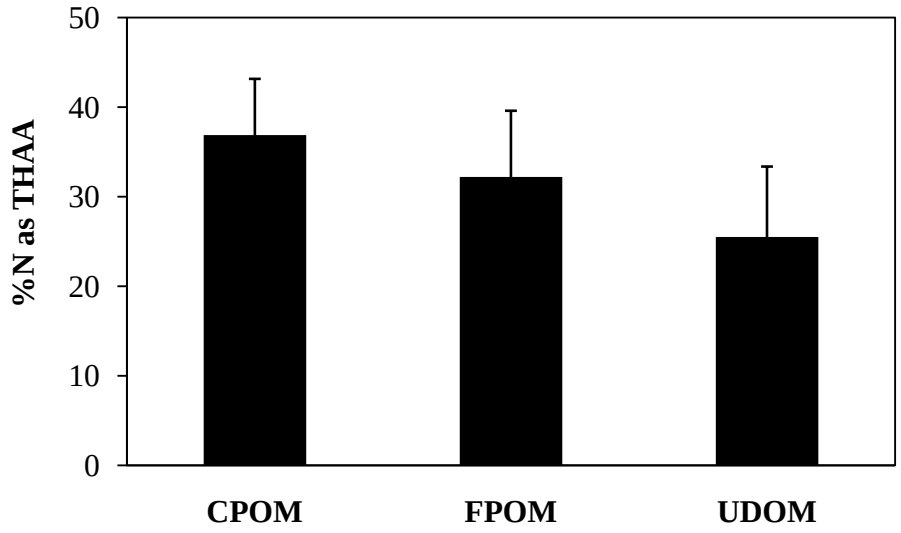

Fig. 4. Spatial-averaged percentages of total nitrogen (N) as total hydrolysable amino acids (THAA) for sediment coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and ultra-filtered dissolved organic matter (UDOM) size fractions based on values at the 13 sampling stations. Bars represent standard deviations.

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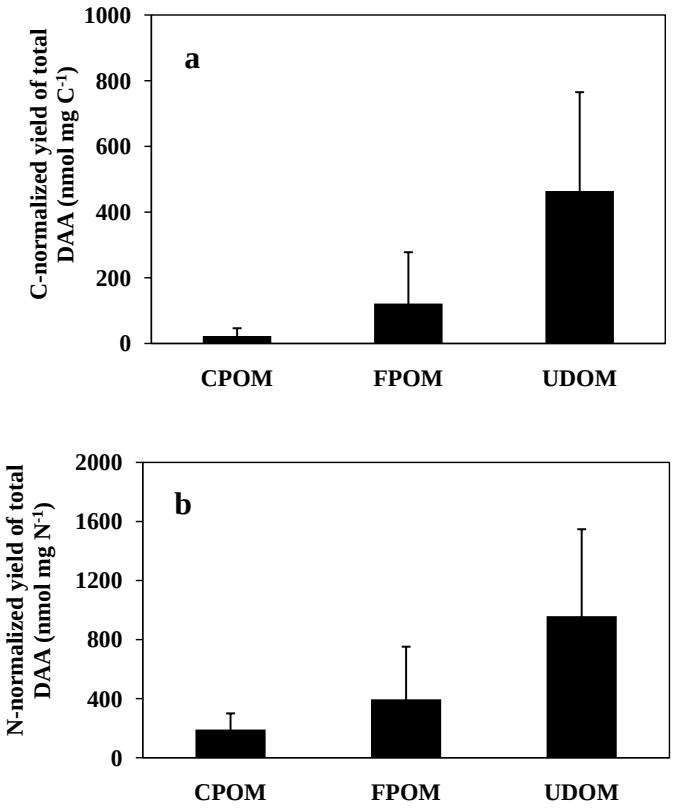

Fig. 5. Spatial-averaged C- **(A)** and N- **(B)** normalized yields of total D-amino acids (total DAA, the sum of D-Ala, D-Glu, D-Asp and D-Ser) in sediment coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and ultra-filtered dissolved organic matter (UDOM) size fractions based on values at the 13 sampling stations. Bars represent standard deviations.

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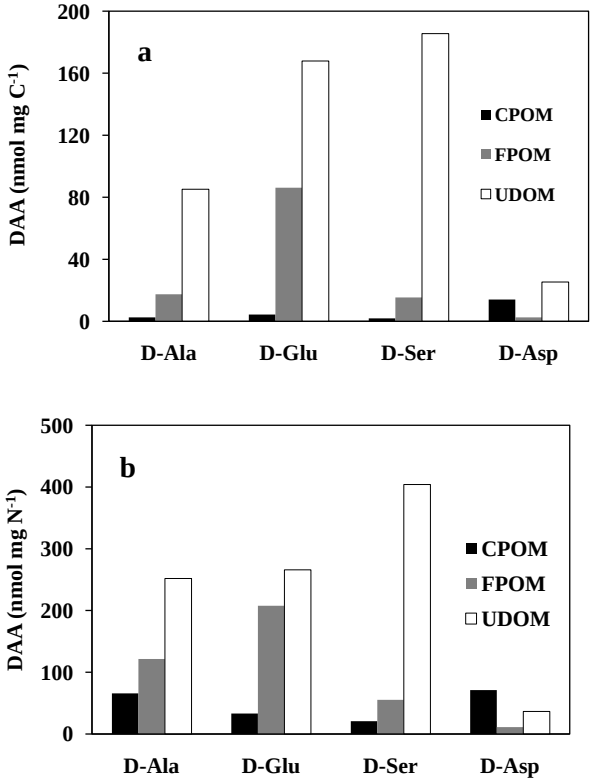

Fig. 6. Spatial-averaged C- **(A)** and N- **(B)** normalized yields of individual D-amino acids (DAAs, including D-Ala, D-Glu, D-Asp and D-Ser) in sediment coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and ultra-filtered dissolved organic matter (UDOM) size fractions. D-Ala = D-alanine; D-Glu = D-glutamic acid; D-Asp = D-aspartic acid; D-Ser = D-serine.

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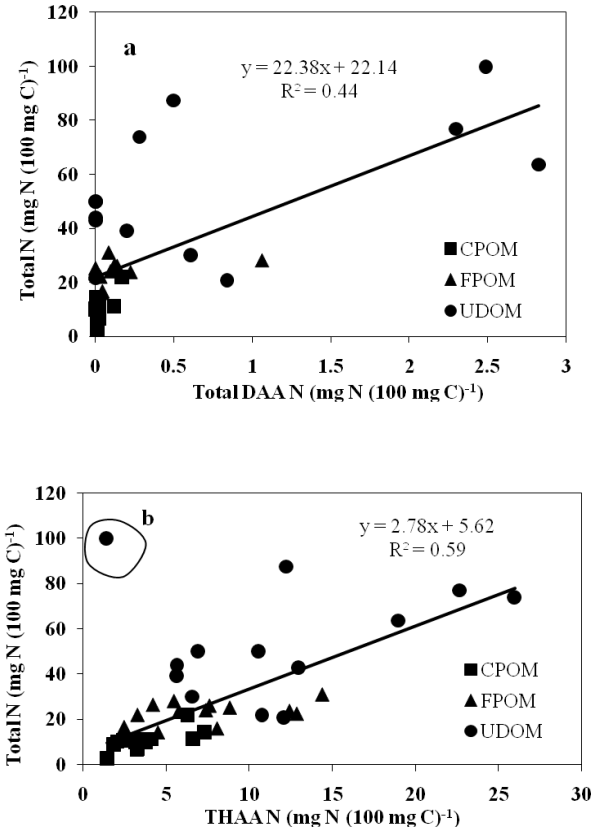

Fig. 7. N yields in **(A)** Total D-amino acids (total DAA, the sum of D-Ala, D-Glu, D-Asp and D-Ser); and **(B)** Total hydrolysable amino acids (THAA) vs. total N yields in sediment coarse particulate organic matter (CPOM), fine particulate organic matter (FPOM) and ultra-filtered dissolved organic matter (UDOM) size fractions. Circles indicate data points omitted from the linear regression.

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