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ORIGINAL PAPER

Constraining Sources of Organic Matter to Tropical Coastal Sediments: Consideration of Nontraditional End-members

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Abstract Molar organic carbon to total nitrogen to organic phosphorus (OC:TN:OP) ratios are used in tandem with carbon isotopic values to constrain sources of organic matter (OM) to marine sediments in a tropical coastal embayment. Analysis of end-members specific to the study site indicates that the bulk OM pool cannot be modeled as a simple mixture of two end-members (terrestrial vs. marine OM), but rather reflects a more complex, multicomponent mixture. Mangrove, coral reef ecosystems, and bacterial biomass contribute OM to tropical coastal marine sediments that is compositionally distinct from traditional marine and terrestrial end-members and thus preclude the application of a classical two end-member mixing model of the sort that has been used traditionally in sediments from temperate environments. A survey of elemental ratios and carbon isotopic values of potential OM end-members reported in the literature, as well as depth profiles before and after whole-core incubation experiments conducted as part of this study, were used to evaluate the strength of OC:TN versus OC:OP ratios as OM source indices. Our study suggests that OC:TN ratios are a weaker indicator of OM source than OC:OP ratios, because: (1) the more restricted dynamic range of OC:TN ratios prevents clear distinction of terrestrial-from marine-derived OM, and (2) post-depositional changes in OC:TN ratios occur during diagenesis, obscuring the source signature of initially deposited OM. The fidelity of OM indices during early diagenesis underscores the importance of quantifying OP in sediments to assess sedimentary OM source.

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1 Introduction

Organic matter (OM) in coastal aquatic sediments derives from marine sources, such as phytoplankton, microalgae, macroalgae, and seagrasses, as well as terrestrial sources that are principally delivered by rivers. The most commonly used tools for distinguishing marine versus terrestrial OM in sediments are elemental ratios and the isotopic composition of bulk sediment OM. This multitracer approach allows tighter constraints to be placed upon the source of OM to coastal sediments than either parameter alone (Gordon and Goñi 2003; Middelburg and Nieuwenhuize 1998; Ruttenberg and Goñi 1997a, b). The use of these tracers in determining OM source is dependent upon the assumption that elemental ratios and isotopic composition of OM are (1) unique to distinct OM end-members and (2) conservative during transport to coastal sediments and during diagenesis.

Marine phytoplankton have a mean molar organic carbon to total nitrogen to organic phosphorus ratio (OC:TN:OP) of 106:16:1 (Redfield et al. 1963), while terrestrial, vascular plants have characteristic OC:OP up to or exceeding 800, and OC:TN ratios ranging up to or exceeding 100 (Likens et al. 1981; Zhang et al. 2013). Bulk sediment stable isotope signatures of OM from marine and terrestrial systems are distinct because the carbon source utilized during primary production is isotopically different (e.g., Hedges and Parker 1976, as cited by Goñi et al. 1997). Organic compounds derived from marine OM are enriched in ^{15}N and ^{13}C relative to compounds originating as terrestrial OM (Gearing et al. 1977; Goñi et al. 1998; Ogrinc et al. 2005), and as a consequence have characteristically heavier isotopic ratios.

During transport to coastal sediments, OM undergoes degradation, driven by physical and biological processes (Arzayus and Canuel 2004; Hedges et al. 1997; Lehmann et al. 2002). It is well documented that both OC:TN and $\delta^{15}N$ are nonconservative tracers because the original OM source signature of these parameters is lost or overprinted during diagenesis (Cowie and Hedges 1994; Graham et al. 2001; Thornton and McManus 1994). However, $\delta^{13}C$ ratios of OM have been deemed a reliable provenance indicator because isotopic fractionation of $\delta^{13}C$ values during diagenesis of OM appears to be small, typically <2 ‰ (Meyers 1997). Despite being recognized as a nonconservative tracer, it is a regular practice to couple OC:TN ratios to $\delta^{13}C$ values to identify OM source signatures in coastal sediments (e.g., Hedges et al. 1986; Meyers 1994; Perdue and Koprivnjak 2007; Ramaswamy et al. 2008; Yu et al. 2010). When more specialized indices, such as sterol, lignin, and lipid composition are used in conjunction with isotopic signatures, more robust constraints can be placed on OM source (e.g., Volkman 1986; Meyers and Ishiwatari 1993; Goñi and Hedges 1995; Gordon and Goñi 2003, 2004). The highly specialized analyses required for quantification of biomarkers are, however, beyond the capacity of many interested researchers. The possibility that OC:OP ratios act as a more conservative tracer of OM source than OC:TN ratios was suggested by Ruttenberg and Goñi (1997b) and, when coupled with $\delta^{13}C$ values, provide a means for assessing the OM source to marine sediments that does not require specialized biomarker analysis.

The first objective of this study was to examine sources of OM to a protected tropical coastal marine embayment in Kane‘ohe Bay, Oahu, Hawai‘i. We utilized end-member OM

characterized during this study and from the literature to examine the contribution of mangrove, coral reef ecosystem components, and bacterial biomass to marine sediments from this study site, in addition to more traditional end-members (e.g., phytoplankton, terrestrial C3 plants). In order to sample a range of OM sources, sediment was collected along a transect that describes a terrestrial-to-marine gradient. Our second objective, to examine the effects of early diagenesis on the preservation of source signatures of terrestrial and marine OM, was addressed using down-core profiles of OM indices (elemental ratios and isotopic values) and the observed changes in these indices during laboratory whole-core incubations.

2 Study Site

He‘eia fishpond is an 88-acre coastal pond located on the eastern side of Oahu, adjacent to Kane‘ohe Bay, at the land–sea boundary of the He‘eia watershed (Fig. 1). The fishpond is a low-energy, shallow coastal system influenced by an influx of freshwater from terrestrial runoff and groundwater, and seawater from Kane‘ohe Bay. The pond is bounded by a mangrove forest along the terrestrial periphery and a coral reef on the bay side.

In order to study sediments characterized by distinct OM sources, sediment push cores were collected from four depositional environments sampled along a transect extending

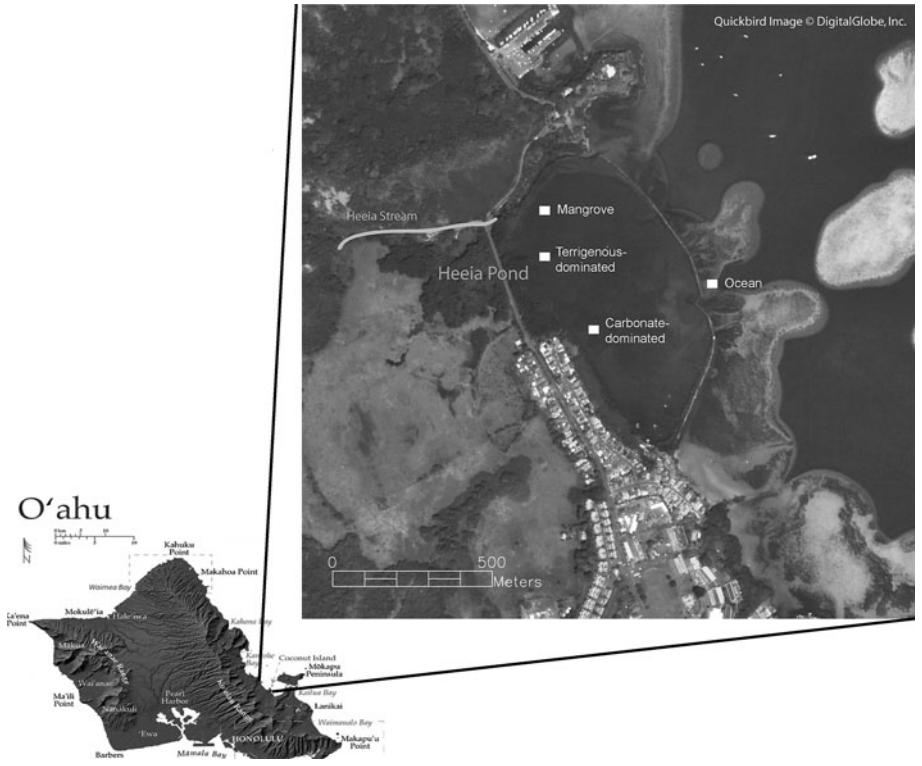

Fig. 1 Aerial photograph of He‘eia Fishpond with study sites marked as white boxes. Kane‘ohe Bay is seaward of the wall enclosing the pond

Table 1 Characteristics of sediment cores collected at each location within the study area. Porosity, salinity, elemental ratios, and isotopic values are averaged over the top 13 cm of the sediment core ($n = 18$ for each core) with standard error* reported in parentheses. Grain-size fractionation and carbon analyses were conducted on surface sediments at each site

Site	Mangrove	Terrestrial	Carbonate	Ocean
Porosity (%)	82.9 (1.2)	54.2 (2.1)	52.9 (1.0)	43.5 (0.3)
Porewater salinity (psu)	23.4 (1.3)	N/A	29.6 (0.6)	32.1 (0.1)
Molar OC:OP ratio	421 (42)	121 (17)	155 (16)	39.7 (2.8)
Molar OC:TN ratio	17.5 (0.3)	25.3 (1.5)	44.2 (4.2)	22.2 (1.2)
$\delta^{13}C$ value (‰)	−25.2 (0.2)	−22.9 (0.2)	−15.8 (0.6)	−17.7 (0.04)
Gravel (>2 mm) (wt%)	4.9	8.8	5.5	N/A
Sand (2 mm–63 μm) (wt%)	9.6	36.3	45.6	N/A
Silt (<63 μm) (wt%)	85.5	54.8	49.0	N/A
Surface inorganic carbon (wt%)	0.11	0.93	9.21	11.00
Surface organic carbon (wt%)	6.8	1.5	0.83	0.24

* *Standard error of the sample is an estimate of how close the sample mean is to the population mean*

N/A data unavailable

from the shoreline to progressively more marine-dominated sites (Fig. 1). These sites are hereafter defined as: (1) mangrove (collected under the mangrove canopy); (2) terrigenous-dominated (collected from a location proximal to stream input); (3) carbonate-dominated (collected from a location distal to stream input); and (4) ocean (collected outside He‘eia Fishpond, proximal to the fringing coral reef in Kane‘ohe bay; Fig. 1). Site characteristics are summarized in Table 1, highlighting the distinctive features of each depositional environment.

3 Methods

3.1 Sample Collection

Paired sediment push cores were taken at each site along the terrestrial-to-marine transect. To minimize heterogeneity between paired cores, sampling occurred within defined sampling grids (0.5 × 0.5 m), and care was taken to select areas at each site with visually uniform conditions that were devoid of macroalgae and appeared to be minimally affected by bioturbation. One core was collected for immediate sediment sectioning and porewater extraction and a second core for laboratory incubation experiments. The mangrove and terrigenous-dominated sites were sampled and incubations were initiated on April 17, 2008. Four days later, the experiment was repeated at the carbonate-dominated and ocean sites. Weather patterns remained constant during this 4-day sampling period, and all cores were collected within the same tidal regime. Immediately after collection, cores were placed on ice to reduce metabolic activity and covered to inhibit photosynthetic activity during transport to the laboratory.

Tissue samples were collected from terrestrial and aquatic plants that are likely sources of OM to He‘eia Fishpond, including mangroves and macroalgae. A surface-water plankton tow (100 μm mesh) was conducted from a small boat, both inside the fishpond and outside, in Kane‘ohe Bay. Plankton samples and plant tissues were freeze-dried and

analyzed for elemental and isotopic composition to characterize end-member sources of OM to the study site. Data for coral end-members are reported in Briggs et al. (2013).

3.2 Core Processing and Analysis

Cores from each site used to determine initial conditions were sectioned at 0.25–1 cm intervals under an inert (N_2) atmosphere to prevent oxidation artifacts (Bray et al. 1973). Porewater was separated from bulk sediment via centrifugation. In order to maximize porewater collection in sandy sediments, we adapted Whatman VectaSpin 20® centrifuge tubes that allow filtration during centrifugation by replacing the manufacturer installed polypropylene filter with a coarse (1.2 μm) GF/F filter. The coarse GF/F filter allowed maximum recovery of sediment porewater, which was subsequently filtered using a 0.4-μm Pall Life Sciences GHP acrodisc® filters. Filtered porewater was stored frozen until analyzed for dissolved ammonium (NH_4^+) using established colorimetric protocols (Grasshoff et al. 1983) on a BioTek Synergy HT Multimode Microplate Reader.

After removal of porewater, sectioned sediments were frozen under an inert atmosphere until freeze-dried under vacuum to prevent oxidation artifacts (Bray et al. 1973; Kraal et al. 2009). Sediments were ground with an agate mortar and pestle, sieved (<125 μm) and stored in sealed vessels prior to analysis. Inorganic sedimentary phosphorus (IP) was determined utilizing acid hydrolysis, and total sedimentary phosphorus (TP) was determined using the high-temperature ashing/hydrolysis method of Aspila et al. (1976). OP was estimated as the difference between TP and IP. Total carbon (TC), OC, inorganic carbon (IC), and TN, as well as carbon and nitrogen isotope values ($\delta^{13}C$ and $\delta^{15}N$, respectively) were determined on sediments using a combined coulometric (IC) elemental analyzer—mass spectrometry method, in which OC is quantified as the difference between TC and IC (OC = TC − IC). OC and $\delta^{13}C$ values of the OM were determined on acid-washed samples. Samples were analyzed for carbon and nitrogen at the Isotope Biogeochemistry Laboratory at the University of Hawai'i, Manoa. Carbon and nitrogen isotopic values are reported using conventional δ-notation with respect to VPDB and atmospheric N_2, respectively.

3.3 Incubation Setup

Sediment cores were incubated in the dark for 3 days with constant stirring of the overlying water (height of overlying water was approximately 20 cm). The core cap was left open, allowing for constant replenishment of O_2 in the overlying water. After day 3, sediment cores were processed according to the same procedures outlined for the pre-incubation cores (see Sect. 3.2).

4 Results

The four study sites represent distinct depositional environments as is clear from the contrasting physical and chemical parameters that characterize each site (Table 1). Sites range from terrigenous-dominated, silty sediments with a mean porosity of 82.9 to marine-dominated, sandy sediments with a mean porosity of 43.5. The mangrove site has lower salinity (mean = 23.4 psu) and higher concentrations of organic carbon (surface sediment OC = 6.8 wt%) compared with the ocean site (mean salinity = 32.1 psu and surface sediment OC = 0.24 wt%, respectively), with the terrestrial- and carbonate-dominated sites intermediate between the two.

Values of end-member OM indices compiled from the literature (Table 2) illustrate the extent to which different OM sources are distinguished by their elemental ratios and isotopic composition (Fig. 2). End-member OC:TN:OP and $\delta^{13}C$ values derived from OM collected at the He'eia Fishpond study site are consistent with previously published values of OM source materials (Table 2; Fig. 2). Terrestrial OM, such as C3 plant tissues, is characterized by elevated OC:OP and OC:TN ratios and more negative $\delta^{13}C$ values compared to marine sources, such as plankton, most macroalgae, benthic algae, and coral (Fig. 2). The elemental ratios for mangroves derived from the literature were distinct from other C3 plants and are therefore depicted separately in Fig. 2. Interestingly, elemental ratios of mangroves from our study site overlap with values for other (non-mangrove) C3 plants (Fig. 2). We cannot discern whether these disparate signatures are a consequence of the particular mangrove growth environment, or of the state of the material sampled (e.g., fresh or scenescent), but the overall characteristic of elevated OC:TN and OC:OP, and light $\delta^{13}C$ values characterizes all C3 plants surveyed in the present study.

Molar OC:TN:OP ratios and $\delta^{13}C$ values of bulk sediments from pre- and post-incubation cores (Fig. 3), plotted in the same format as the end-member property–property plots (Fig. 2), display a transition from lighter $\delta^{13}C$ values (−27 to −22 ‰) typical of terrestrial OM in mangrove and terrestrially dominated sites, to heavier marine-like $\delta^{13}C$ values (at or heaver than -20 ‰) in carbonate-dominated and ocean sites. OC:OP values drop from elevated ratios at sites dominated by terrestrial OM to low ratios in the sites dominated by marine OM (Fig. 3a). A similarly systematic trend along the transect is not evident for OC:TN ratios (Fig. 3b). In these plots, open symbols represent sediment samples from pre-incubation cores, while closed symbols represent post-incubation sediment cores. Post-incubation samples from the terrigenous-, carbonate-dominated, and ocean sites display lower OC:TN ratios relative to pre-incubation samples (Fig. 3b); no such systematic change in OC:OP ratios is observed (Fig. 3a). Bulk sediment OM from post-incubation samples from the terrigenous-dominated site displays a clear shift toward less negative $\delta^{13}C$ values. Ocean site sediments also display a shift to less negative values after the incubation, while mangrove site bulk sediment OM tends to shift to more negative values.

NH_4^+ concentrations from pre- and post-incubation sediment cores display lower concentrations in surface sediments building up to progressively higher concentrations at depth (Fig. 4a). Maximum concentrations in pre-incubation cores from all sites are *ca.* 80 μM NH_4^+, whereas post-incubation cores show increases in NH_4^+ concentrations above pre-incubation levels, particularly at the ocean site (up to ∼500 μM). OC:TN ratios fall within the same range for all sites (∼10–60), whereas OC:OP ratios are significantly higher at the mangrove site (∼400) compared with the other study sites (∼50–200). Post-incubation sediment OC:TN profiles (closed symbols) are nearly twofold lower than pre-incubation sediments at all sites, with the exception of the mangrove site (Fig. 4b). By contrast, OC:OP sediment profiles from post-incubation cores show no systematic shift from pre-incubation values (Fig. 4c).

5 Discussion

5.1 Signatures of OM End-members

Source is determined by the distinctive isotopic composition and elemental ratios of marine versus terrestrial OM (e.g., Hedges and Parker 1976; Perdue and Koprivnjak 2007; Ruttenberg and Goñi 1997a, b; Gordon and Goñi 2003, 2004; Yu et al. 2010; Ramaswamy et al. 2008). Sediments dominated by terrestrial sources generally contain less OP and TN

Table 2 Carbon, nitrogen, and phosphorus molar elemental ratios and isotopic composition of potential end-member contributors to marine sedimentary OM. The *n* values represent the number of distinct samples analyzed in each study, excluding replicates. Bold values are averages over reported data for each end-member type (excluding values from this study). Values from this study are averaged and listed in *italics*

	n	$\delta^{13}C$	$\delta^{15}N$	OC:TN	OC:OP	TN:OP	Source
Terrestrial end-members							
Mangrove C3 plants		**−27.4**	**2.7**	**87**	**9,983**	**66**	
Mangrove green leaf	3	–	–	50	3,298	66	Reviewed in Lee et al. (2008)
Mangrove green leaf	6	−26.7	–	41	–	–	Hemminga et al. (1994)
Mangrove senescent leaf	9	–	–	110	16,668	66	Reviewed in Lee et al. (2008)
Mangrove senescent leaf	5	–	–	152	–	–	Hemminga et al. (1994)
Mangrove coarse root	10	–	–	103	–	–	Reviewed in Lee et al. (2008)
Mangrove fine root	10	–	–	65	–	–	Reviewed in Lee et al. (2008)
Mangroves	2	−28.0	2.7	–	–	–	Loneragan et al. (1997)
Mangroves	*4*	*−28.1*	*1.1*	*53*	*1,583*	*40*	*This study*
Terrestrial and salt marsh C3 plants		**−27.6**	**5.2**	**49**	**1,826**	**27**	
C3 plants	4	−29.3	0.4	–	–	–	Reviewed in Peterson and Howarth (1987)
C3 plants		−28.5	–	100	1,000	8	Ruttenberg and Goñi (1997a, b), Likens et al. (1981)
C3 plants	6	−26.1	–	55	–	–	Reviewed in Meyers (1994)
C3 plants	2	−26.4	10.6	18	–	–	Decottignies et al. (2007)
C3 plants	4	−27.4	10.3	31	–	–	Cloern et al. (2002)
Terrestrial angiosperms	4	−28.1	1.5	–	–	–	Decottignies et al. (2007)
Terrestrial foliage	55	–	–	44	1,334	28	McGroddy et al. (2004)
Terrestrial litter	106	–	–	66	3,144	46	McGroddy et al. (2004)
Terrestrial plants	4	−27.6	3.0	26	-	-	Cloern et al. (2002)
Land based C4 plants and seagrass		**−12.2**	**5.8**	**51**	**1,137**	**60**	
C4 plant	2	−14.9	9.7	27	–	–	Cloern et al. (2002)
C4 Plants	4	−12.1	-	107	–	–	Reviewed in Meyers (1994)
C4 plants	1	−14.0	8.7	–	–	–	Decottignies et al. (2007)

Table 2 continued

	n	$\delta^{13}C$	$\delta^{15}N$	OC:TN	OC:OP	TN:OP	Source
Seagrass	1	–	–	19	1,137	60	Fourqurean et al. (1992)
Seagrass	1	−8.8	1.7	–	–	–	Anderson and Fourqurean (2003)
Seagrass	48	−11.5	–	–	–	–	Hemminga and Mateo (1996)
Seagrass	6	−12.0	3.2	–	–	–	Loneragan et al. (1997)
Freshwater algae		**−28.5**	**5.0**	**7**			
Freshwater plankton	30	−28.6	5.0	7	–	–	Cloern et al. (2002)
Lake algae	3	−28.3	–	7	–	–	Reviewed in Meyers (1994)
Marine end-members							
Macroalgae		**−17.3**	**4.2**	**21**	**482**	**37**	
Macroalgae	9	–	–	–	–	66	Larned (1998)
Macroalgae	92	–	–	20	700	35	Atkinson and Smith (1983)
Macroalgae	41	–	–	22	263	10	Lapointe et al. (1992)
Macroalgae	3	−14.9	8.4	21	–	–	Decottignies et al. (2007)
Macroalgae	1	−22.0	1.2	–	–	–	Loneragan et al. (1997)
Macroalgae	1	−15.0	3	-	-	-	Cornelisen et al. (2007)
Macroalgae	*3*	*−17.0*	*3.9*	*29*	*3,054*[a]	*109*	*This study*
Benthic algae		**−18.6**	**3.7**	**8**	**464**	**43**	
Benthic microalgae	11	–	–	7	119	17	Hillebrand and Sommer (1999)
Benthic diatoms	2	−22	7.0	8	–	–	Cloern et al. (2002)
Benthic diatoms	1	−12.9	5.3	7	–	–	Decottignies et al. (2007)
Microbial mat	20	–	–	12	809	68	Reviewed in Lee et al. (2008)
Marine algae	4	−21.6	–	5	–	–	Reviewed in Meyers (1994)
Marine Algae	1	−17.8	−1.2	7	–	–	Wild et al. (2008a, b)
Marine plankton		**−22.9**	**7.5**	**7**	**106**	**16**	
Estuarine plankton	31	−21.5	8.0	6	–	–	Cloern et al. (2002)
Marine plankton	56	−21.3	8.6	–	–	–	Reviewed in Peterson and Howarth (1987)

Table 2 continued

	n	$\delta^{13}C$	$\delta^{15}N$	OC:TN	OC:OP	TN:OP	Source
Marine plankton	–	−28.5	–	7	106	16	Ruttenberg and Goñi (1997a, b); Redfield (19XX)
Marine plankton	9	−20.4	5.8	–	–	–	Loneragan et al. (1997)
Marine plankton	*2*	*−16.3*	*5.7*	*6*	*223*	*38*	*This study*
Coral		**−13.8**	**5.3**	**12**	**362**	**25**	
Coral tissue	2	−16.0	5.0	–	–	–	Grottoli et al. (2004)
Coral tissue	2	−11.4	3.8	7	–	–	Hoegh-Guldberg et al. (2004)
Coral tissue	26	−13.8	4.4	–	–	–	Muscatine et al. (2004)
Coral tissue	1	–	–	6	172	27	Muller-Parker et al. (1994)
Coral tissue	6	−12.8	–	11	364	33	Briggs et al. (2013)
Coral symbiont	2	−16.0	5.0	–	–	–	Grottoli et al. (2004)
Coral symbiont	2	−11.7	3.1	6	–	–	Hoegh-Guldberg et al. (2004)
Coral symbiont	26	−18.4	6.3	–	–	–	Muscatine et al. (2004)
Coral tissue and symbiont	7	−13.9	5.0	–	–	–	Yamamuro et al. (1995)
Coral symbiont	1	–	–	20	365	21	Muller-Parker et al. (1994)
Coral eggs	1	−9.5	4.8	17	–	–	Wild et al. (2008a, b)
Coral eggs	15	−14.5	–	21	838	39	Briggs et al. (2013)
Coral sperm	1	−11.2	5.6	7	–	–	Wild et al. (2008a, b)
Coral sperm	4	−13.0	–	5	–		Briggs et al. (2013)
Coral bundles	10	−12.1	4.6	19	–	–	Briggs et al. (2013)
Coral mucus	1	−18.2	10	12	72	6	Wild et al. (2004a, b, 2005, 2008a, b)

[a] The large values for these macroalgae samples are driven by the high concentrations of structural carbon that characterizes *Kappaphycus* spp.

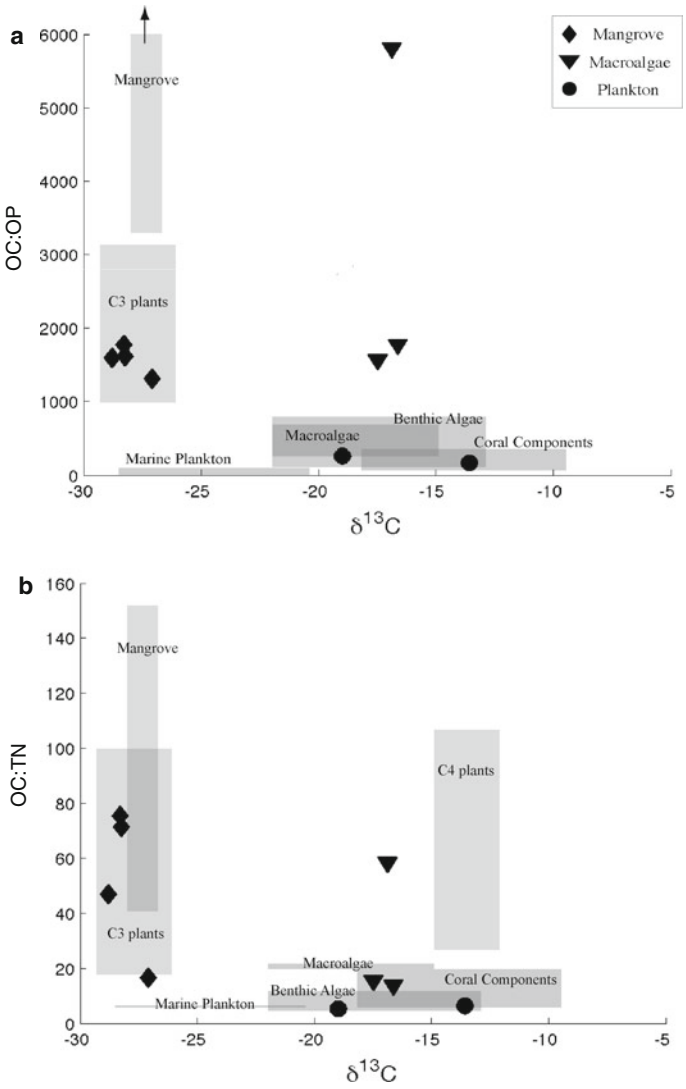

Fig. 2 End-member plot of (**a**) molar OC:OP ratios versus $\delta^{13}C$ and (**b**) molar OC:TN ratios versus $\delta^{13}C$. Mangrove end-members analyzed in this study are represented by *diamonds*, macroalgae by *triangles*, and plankton by *circles*. *Boxes* represent the range of (a) OC:OP and $\delta^{13}C$ and (b) OC:TN and $\delta^{13}C$ values for each end-member source are based on the literature review summarized in Table 2. The elemental ratios of mangroves derived from the literature are distinct from other C3 plants, whereas at our study site, they overlap with values for other (non-mangrove) C3 plants. These disparate signatures could be a consequence of the state of the material sampled (e.g., fresh or scenescent), or of site specific growth characteristics, but all C3 plants (including all mangroves) display elevated OC:TN and OC:OP values relative to marine OM sources. *Note* The high OC:OP value for macroalgae from this study is a consequence of the high structural carbon content characteristic of *Kappaphycus* spp. No published OC:OP data for C4 plants is available

relative to OC and are characterized by lighter $\delta^{13}C$ values than sediments dominated by marine sources (Perdue and Koprivnjak 2007; Ruttenberg and Goñi 1997a, b; Gordon and Goñi 2003, 2004) (Table 2). A closer inspection of published and new end-member data,

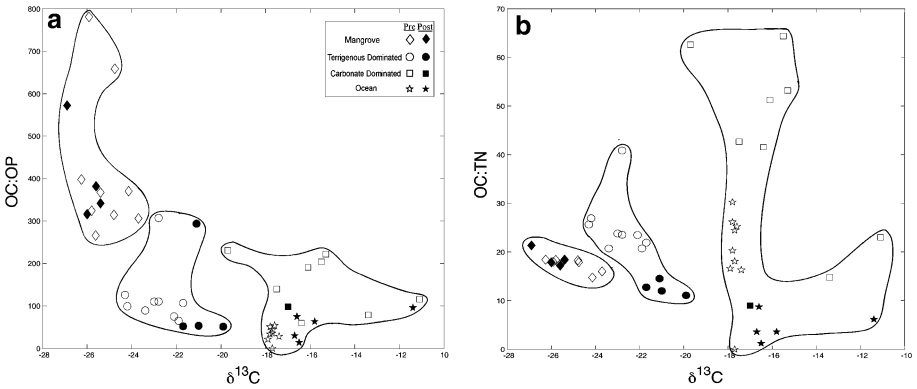

Fig. 3 Sediment (**a**) OC:OP ratios versus $\delta^{13}C$ and (**b**) OC:TN ratios versus $\delta^{13}C$. Sites are designated by different *symbols*: mangrove (*diamonds*), terrigenous-dominated (*circles*), carbonate-dominated (*squares*) and ocean (*stars*). *Open symbols* pre-incubation, *closed symbols* post-incubation; see text for further discussion of incubation parameters

however, reveals considerable heterogeneity in these signature parameters for both terrestrial and marine OM. In some cases, the elemental ratios and isotopic signatures of terrestrial and marine OM overlap (Fig. 2; Table 2). For instance, relatively high OC:TN and OC:OP in marine macroalgae (Table 2), as a consequence of high concentrations of structural carbon associated with some marine macroalgae (e.g., *Kappaphycus* spp.; Table 2), prevent a clear distinction between marine macroalgae and terrestrial vascular plants to be made solely on the basis of elemental ratios (Table 2; Fig. 2). However, the same two-end-members display distinctive $\delta^{13}C$ values, allowing marine macroalgae (mean $= -17.3$ ‰) to be distinguished from C3 plants (mean $= -27.6$ ‰) on the basis of their stable carbon isotopic compositions (Table 2; Fig. 2). Likewise, marine plankton can be characterized by light enough $\delta^{13}C$ values (as light as -28.5; Table 2; Fig. 2) to be indistinguishable from some terrestrial sources, such as C3 plants (including mangroves), on the basis of carbon isotopic composition, but have distinctively low, marine-like OC:TN and OC:OP ratios (mean $= 7$ and 106, respectively) relative to the higher ratios characteristic of terrestrial plants (Table 2). These two examples illustrate the importance of using a multitracer approach, including elemental ratios as well as $\delta^{13}C$ values, to evaluate sources of OM to marine sediments (Ruttenberg and Goñi 1997a, b; Gordon and Goñi 2003, 2004).

5.2 Evaluation of OM Sources to Sediments

The hyperbolic trend described in the end-member plots (Fig. 2a), which is characteristic of the mixing line between signature OC:OP ratios in terrestrial and marine sources of OM (Ruttenberg and Goñi 1997a, b), is also seen clearly when sediment OC:OP ratios are plotted versus $\delta^{13}C$ values (Fig. 3a). We observe a systematic progression from terrestrially derived material at the mangrove site (mean surface sediment values $\delta^{13}C = -25.2$ ‰; OC:OP $= 421$) to marine-derived material at the ocean site (mean surface sediment values $\delta^{13}C = -17.7$ ‰; OC:OP $= 39.7$); the terrigenous-dominated site is intermediate (Table 1; Fig. 3a).

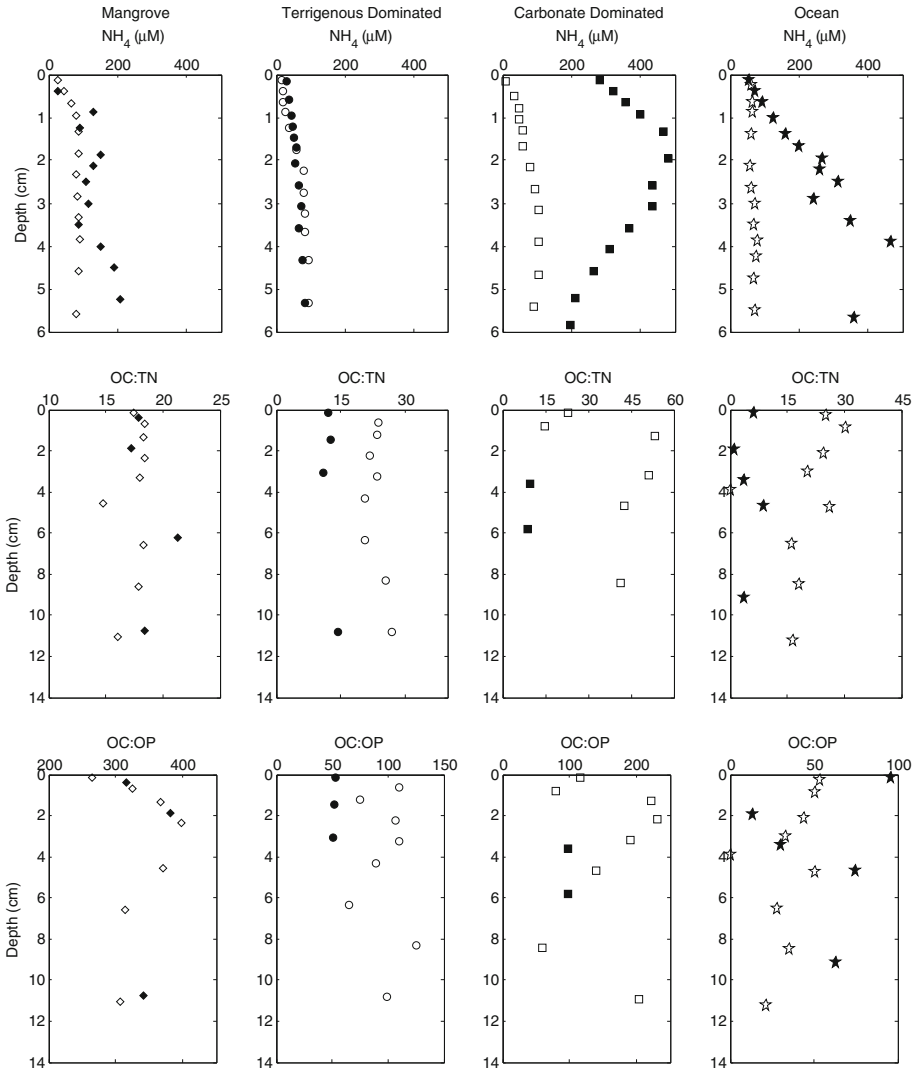

Fig. 4 Down-core sediment profiles of (**a**) NH_4^+, (**b**) OC:TN ratios, and (**c**) OC:OP ratios. Sites are designated by different *symbols*: mangrove (*diamonds*), terrigenous-dominated (*circles*), carbonate-dominated (*squares*) and ocean (*stars*). *Open symbols* pre-incubation, *closed symbols* post-incubation. *Note* different scales on *x*-axis. The observed reversals in porewater NH_4^+ may reflect a number of processes, including prior deep-irrigation events, anoxic nitrification, abiotic ammonium oxidation, annamox activity, and/or ammonium adsorption onto clays or humic material

The use of OC:TN is far more common than OC:OP in characterization of bulk sediment OM. This is largely due to analytical ease of measuring TN, which is quantified in tandem with OC via elemental analyzer; a separate analysis must be executed in order to quantify OP (see Sect. 3.2). However, consistent with other studies (e.g., Ruttenberg and Goñi 1997b), we find that OC:TN ratios are not as robust an indicator of OM source as OC:OP ratios (Figs. 2b, 3b). The lower fidelity of OC:TN ratios as indicators of OM source

is primarily a consequence of the low dynamic range of OC:TN ratios over terrestrial and marine sources. The literature compiled table of endmember OC:TN and OC:OP ratios (Table 1) lists ranges from 5 to 152 and 72 to 3298, respectively. Unlike the OC:OP versus $\delta^{13}C$ plots (Fig. 3a), the progression from terrestrially- to marine-dominated sources of OM is not evident in the plot of OC:TN versus $\delta^{13}C$ values for sediments from the four sites examined in this study (Fig. 3b). We note that our study examined bulk sediment only, and analysis of OC:TN versus $\delta^{13}C$ in size-fractionated sediments could improve the utility of OC:TN as an OM source indicator (Hedges and Keil 1995).

We expected $\delta^{13}C$ values from sediments at the ocean site to reflect dominantly, or even exclusively marine sources of OM, which is typically assumed to consist primarily of marine plankton. The heavy $\delta^{13}C$ values (as heavy as −11 ‰) observed in sediments from the carbonate-dominated and ocean sites, however, could not be reconciled with typical $\delta^{13}C$ values of marine plankton (mean value −22.9 ‰) (Table 2; Fig. 2). Heavy $\delta^{13}C$ values observed in sites dominated by marine sources of OM sometimes have been explained by contributions from seagrasses (−9 ‰ to −12 ‰, Table 2) (Goñi and Hedges 1995; Goñi et al. 1997), but seagrasses are absent from our study site. Recognizing that an additional end-member characterized by a heavy carbon isotopic signature must be contributing OM to sediments at the marine-dominated sites in our study area, we evaluated the OM derived from coral reef ecosystems. OM from adult tissue die-off in fragmented coral skeleton, coral symbionts, eggs/sperm material, and mucus derived from the coral reef ecosystem can contribute OM to sediments with $\delta^{13}C$ values ranging from −10 to −18 ‰ (Table 2), and thus is a likely candidate to explain the heavier than expected $\delta^{13}C$ values in OM from the marine-dominated study sites.

Several recent studies examine the impact of OM released from coral reef ecosystems on tropical food webs and diagenetic patterns in sediments that receive OM from coral reefs (Briggs et al. 2013; Glud et al. 2008; Wild et al. 2004b, 2008a, b). The relative importance of coral reef-derived material as a source of OM to sediments, as contrasted with more commonly identified OM sources such as marine plankton and terrestrial C3 plants, has not been explicitly evaluated. Corals produce significantly more particulate OM than benthic algae (Wild et al. 2008a), and fluvial sediment input to most coral reef ecosystems is typically minimal. Thus, coral reef-produced OM should be considered as a potentially important OM source to tropical sediments in proximity to coral reefs.

Given the overlap between end-member isotopic composition in some instances, and in elemental ratios in others, as well as the fact that some end-members fall outside the traditionally recognized fields for marine and terrestrial OM sources to marine sediments: marine plankton and terrestrial C3 plants (Table 2; Fig. 2), it is clear that conceptualizing the bulk sedimentary OM pool as a mixture of two distinct end-members, one terrestrial and one marine, is overly simplistic for most complex ecosystems. In the case of our study site, for example, the heavy $\delta^{13}C$ values observed at the marine-dominated sites suggested the need to explicitly consider coral as a potentially important source of OM to these sites.

In order to more quantitatively evaluate relative proportions of OM derived from different end-members that potentially could contribute to the bulk sediment OM at the study sites, we executed a series of linear-mixing calculations using measured $\delta^{13}C$ values and concentrations of OC, TN, and OP in likely end-members to calculate elemental ratios. Several studies have employed ternary-mixing models to account for more complex sedimentary OM sources (e.g., Gordon and Goñi 2003; Wu et al. 2003, as cited by Perdue and Koprivnjak 2007). To enable graphic representation of end-member mixtures to examine the fraction of OM from each of three-end-members, inverse ratios (e.g., TN:OC and

OP:OC) were utilized (see Perdue and Koprivnjak 2007, for discussion). We represent the results of these calculations in a series of ternary diagrams, in which inverse elemental ratios (OP:OC and TN:OC) are plotted against $\delta^{13}C$, with contour lines in increments of 10 ‰ (Fig. 5). By superimposing the mean elemental ratios and isotopic signatures averaged over the entire core from each study site (Table 1) on the ternary plots constructed from the end-member mixing calculations, we can evaluate which end-members are driving the source signatures observed in the bulk sediment OM at each site.

With respect to potential marine sources of OM, we initially considered plankton, algae (macro + micro), and mangrove, which we consider to fall into the category of more traditional marine and terrestrial end-members, respectively. However, we observed that mean sediment OM from our study sites is not adequately described when these three more traditional end-members are considered as dominant sources of OM to sediments, as the space spanned by the end-member OC:OP versus $\delta^{13}C$ values does not encompass any of the study sites (Fig. 5a). In particular, the carbonate-dominated site requires contribution from an end-member with heavier $\delta^{13}C$ values than is provided by mangrove, algae, and plankton, and all four sites require an end-member with more elevated OP:OC ratios. As previously discussed, because the coral component is characterized by relatively heavy $\delta^{13}C$ values, it may be a more reasonable marine end-member for OM source material in tropical environments such as those studied here. However, while the heavier $\delta^{13}C$ values observed at the marine-dominated sites are better represented by the coral end-member (Fig. 5b), its inclusion does not rectify the mismatch between OC:OP ratios in sediments versus those described by mixtures of mangrove, algae, and coral. In order to encompass all sites, another end-member is required, one that is more enriched in OP relative to OC.

In a study of OM sources to coastal sediments that included highly degraded OM from a temperate and a tropical system, Ruttenberg and Goñi (1997a) also observed unexpectedly low OC:OP ratios and proposed that the low ratios observed could be attributed to a bulk sediment OM pool dominated by bacterial biomass. Because it is not practical to isolate bacteria from sediments, bacterial end-members cannot be directly characterized with respect to their elemental ratios and carbon isotopic composition. We instead propose likely values based on literature reports of bacterial OC:OP ratios (range from 7 to 80: Luria 1960; Gächter and Meyer 1993; Cotner et al. 2006) and OC:ON ratios (range from 4 to 6: Luria 1960; Goñi and Hedges 1995; Cotner et al. 2006). In our mixing calculations, we initially adopted an intermediate value for bacterial elemental ratios, OC:OP = 45 and OC:TN = 5. Microbial $\delta^{13}C$ values reflect the source of carbon assimilated (Fry and Sherr 1984); so, for the purpose of the mixing calculations executed here, we used the average $\delta^{13}C$ value of bulk sedimentary OM from all study sites (−19.2 ‰) to represent sediment bacterial $\delta^{13}C$.

When the bulk sediment OM described by the mean over the cores at each site is overlain on the ternary diagram produced using mangrove, coral, and bacteria as end-members, it is clear that this mixture more successfully describes the bulk OM composition in sediments from these sites (Fig. 5b). The relative positions of the mean values for each site provide an indication of the relative importance of each end-member as a source of OM to that site. For example, the mangrove and terrigenous-dominated sites are positioned closer to the mangrove end-member, indicating that terrestrially derived OM dominates at these sites. The carbonate-dominated site falls closer the coral end-member, and the position of the ocean site indicates that bulk OM in these sediments is dominated by a mixture of coral-derived and bacterial OM. However, the ocean site is characterized by OP:OC ratios that exceed the mid-range value of 45 that we adopted for the bacterial end-member and requires an even higher OP:OC ratio to describe the bulk sediment OM than

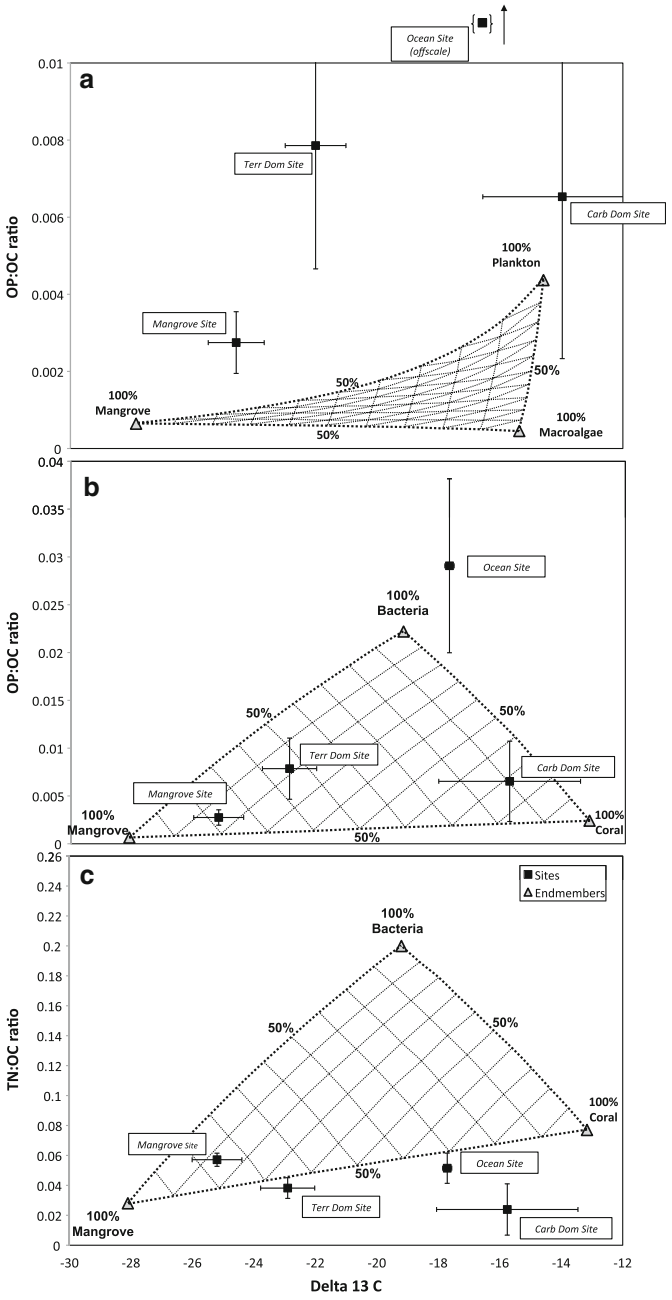

Fig. 5 Ternary diagram illustrating mixtures of organic matter sources with contour lines in 10 % increments. End-members are shown as *open triangles* at the apexes of the mixing *triangles*. Plots of (**a**) OP:OC versus $\delta^{13}C$ of mangrove/algae/plankton end-member mixture, (**b**) OP:OC versus $\delta^{13}C$ of mangrove/bacteria/coral end-member mixture, and (**c**) TN:OC versus $\delta^{13}C$ of mangrove/bacteria/coral end-member mixture. Elemental ratios for bacteria were chosen as the mid-range value from literature sources (OC:OP = 45; OC:TN = 6). Mean down-core values from each study site are superimposed (*filled squares*) with error bars representing the variance over all depths analyzed in each sediment core

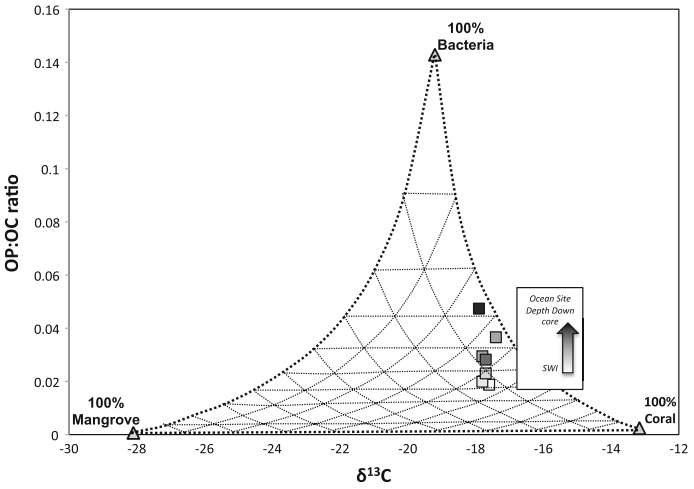

Fig. 6 Ternary diagram constructed in the same manner as Fig. 5b, but the lower end of the OC:OP range reported for bacteria was used (OC:OP = 7) in order to span a space that could include the elemental OC:OP ratios characteristic of the ocean site. In addition, rather than plotting the mean over the core, individual depth intervals were plotted to illustrate the down-core trend in OP:OC from less OP enriched near the surface (*lighter color symbols*) to more enriched at depth (*darker symbols*)

the mid-range values used to construct Fig. 5b. As was the case with the hyperbolic mixing trends (Fig. 3), OC:TN ratios also are unable to successfully describe the bulk OM at study sites using a three-end-member mixing model; only one of these sites fall within the defined TN:OC-$\delta^{13}C$ space (Fig. 5c).

The conceptual model that we envisage for the alteration of OM as it is buried below the sediment–water interface is that, in the extreme, the bulk of the OM originally deposited will eventually be converted to bacterial biomass or its residua (e.g., Ruttenberg and Goñi 1997a, b). We can evaluate this model explicitly by plotting the discrete data points for each depth within a core on the mangrove-coral-bacteria ternary plot, and examining the trend in source signature of the bulk OM as a function of depth below the sediment–water interface. For this model experiment, we assumed that bacterial OC:OP ratios fall at the low end of the range of reported bacterial OC:OP ratios (7–80, see previous discussion) and adopt an OC:OP ratio of 7 for bacteria, which results in a ternary plot that successfully captures the ocean site data (Fig. 6). Furthermore, consistent with the conceptual model just described, we observe a general shift toward OM with more bacteria-like OC:OP ratios with depth in the sediment column (Fig. 6). Similar depth trends are not as obvious for the other three sites (data not shown), which we attribute to the higher OC concentrations (Table 1) at these more shore-ward sites, such that conversion from primary OM sources to a bulk pool dominated by bacterially derived OM is not achieved over the timescale represented by the depth of the cores.

5.3 Impact of Diagenetic Degradation of Sedimentary OM on Source Signatures

One of the objectives of determining source signatures after controlled incubations in the laboratory was to evaluate the extent to which these signatures remain intact after OM degradation occurs during the earliest stages of diagenesis. To document the occurrence of OM decomposition during the laboratory incubations, the buildup of porewater of NH_4^+, a

product of OM remineralization, was examined in pre- and post-incubation sediment cores (Fig. 4). Higher concentrations of NH_4^+ were observed in post-incubation cores (filled symbols, Fig. 4), consistent with the occurrence of OM degradation during the 3-day incubation. The paired initial and incubation cores were carefully sited to minimize spatial heterogeneity, so that resulting data from pre- and post-incubations could be directly compared. However, we cannot rule out the possibility that some of the difference we observe between pre- and post-incubation cores may be due to natural heterogeneity.

We observe shifts of $\sim$2 ‰ when comparing the carbon isotopic composition of OM in pre- and post-incubated sediments. A shift of 2 ‰ in $\delta^{13}C$ of OM during diagenesis is not considered to represent a significant isotopic fractionation of the source organic material (Meyers 1997). Thus, the impact of diagenesis on $\delta^{13}C$ values in sediments from our sites can be considered minimal (Fig. 3a).

Post-incubation sediment cores did not display significant changes in OC:OP ratios at any of the four sites compared to pre-incubation sediments (Fig. 3a). Thus, despite the early diagenetic transformations that occurred throughout the 3-day incubation, OC:OP values from all depths within the sediment cores retain the signature of OM source material. This observation suggests that OC:OP ratios remain a robust indicator of organic source material during early diagenesis. In contrast, OC:TN ratios display post-incubation decreases from initial (pre-incubation) values (Fig. 3b). We consider two possible scenarios that could drive accumulation of solid phase N during diagenesis in excess of that present in source tissues. First, an increase in bacterial biomass during the incubation could result in progressively lower OC:TN ratios because bacteria have been observed to accumulate excess nitrogen during diagenesis (Rice and Tenore 1981; Rice and Hanson 1984). Alternatively, recognizing that the TN reservoir includes both organic nitrogen (ON) and inorganic nitrogen (IN), the potential exists for fixation of IN by clays (Freudenthal et al. 2001; Ruttenberg and Goñi 1997b), which would result in a decrease in OC:TN ratios during diagenesis. This latter scenario is most likely to be important at the ocean site, which is characterized by low OM (<0.3 %), and where the IN component may thus be an important fraction of the TN (e.g., Ruttenberg and Goñi 1997a). This complication is less likely to occur in sediments with higher OM (reviewed in Meyers 1997). Therefore, OC:TN ratios will be a more robust indicator of OM source in high OM sediments than in low OM sediments.

Contrasting down-core variations in OC:TN and OC:OP in post-incubation cores (filled symbols) to pre-incubation cores (open symbols) (Figs. 3, 4) permits us to examine the effect of short-term remineralization, occurring during the 3-day incubation, on sediments at different depths below the SWI that have experienced different extents of diagenetic transformation. Post-incubation OC:TN and OC:OP ratios are indistinguishable from pre-incubation ratios in sediment profiles from the mangrove site, indicating minimal fractionation of TN and OP from OC in OM source material due to diagenetic transformations which occurred during the incubation. However, post-incubation sediments from the terrigenous-dominated, carbonate-dominated and ocean sediment cores are characterized by OC:TN values that are systematically lower than OC:TN in pre-incubation cores. We attribute the greater susceptibility of OC:TN to short-term diagenetic modification at the latter three sites to the low quantities of OC at these sites (ranging from <0.1 to 1 %) relative to the mangrove site (4–8 % OC, Table 1). The magnitude of the shift observed, up to a twofold increase in OC:TN ratios, will obscure the source signature OC:TN ratio these sites. The OC:OP ratios in the post-incubation cores from all sites were not significantly different from pre-incubation ratios, indicating that sedimentary OM more faithfully retains the OC:OP ratios of initially deposited OM, even after significant remineralization has occurred, and even in sediments with low wt% OC.

6 Conclusions

A survey of literature values for elemental ratios and carbon isotopic values of potential OM end-members indicates that the bulk OM pool cannot necessarily be modeled as a simple mixture of two sources (terrestrial vs. marine). Considerable heterogeneity in elemental ratios and isotopic signatures exists for both terrestrial and marine end-members and, in some cases, the signature parameters of terrestrial and marine OM overlap. In addition to the considerable range in signatures within each traditional end-member pool, our attempt to explain the mixture of OM in sediments from our study site required other OM sources that are not typically considered in studies that aim to partition OM as to source. In particular, coral-derived OM, which has a signature that is distinct from traditionally considered marine end-members, appears to be an important OM source for our study site and may be important in other tropical environments with an abundance of coral reefs. Although inclusion of coral-derived OM in three-end-member mixing calculations enabled us to capture the range of $\delta^{13}C$ observed at all four coring sites along the transect, the exceedingly low OC:OP ratios led us to consider that bacterial biomass must be a quantitatively important component of the sedimentary OM pool, particularly in sites that are relatively impoverished in OM. In agreement with this model, we also observed systematic changes in OC:OP ratios with depth below the sediment–water interface that are consistent with increased bacterial biomass as a fraction of the total OM pool with depth in sediments.

The results of this study emphasize the importance of identifying and characterizing end-member sources specific to a particular environment, rather than applying published elemental ratios and isotopic signatures to describe a mixed-source sedimentary OM pool in a particular environment. Ternary diagrams derived from three-end-member mixing calculations can be used as an analytical tool for identifying end-member contributions to bulk sedimentary OM. In this study, the analysis of such ternary plots was instrumental in recognizing the important contributions of coral reef components and bacterial biomass to the bulk sedimentary OM pool in sediments across the transect in the coastal, tropical site studied here.

Finally, our study supports earlier suggestions that use of $\delta^{13}C$ of OC in conjunction with elemental ratios, the multitracer approach to OM source assessment, is more robust than use of elemental ratios or carbon isotope composition alone. Importantly, we present additional evidence that OC:OP ratios are substantially more robust than OC:TN ratios as indicators of OM source to marine sediments, principally for two reasons: (1) the more restricted dynamic range of OC:TN ratios prevents clear distinction of terrestrial- from marine-derived OM and (2) diagenetic changes in OC:TN ratios obscure the source signature of initially deposited OM. Sediment OC:OP ratios appear to be less vulnerable to diagenetic alteration than OC:TN ratios.

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