

# The carbon and nitrogen isotopic values of particulate organic material from the Florida Keys: a temporal and spatial study

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**Abstract** The  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values of particulate organic material (POM) were analyzed from 35 sites in the Florida Keys over the time interval 2000 to 2002. The sites within the study area were delineated into nine transects stretching from Key West to Key Largo. Each transect consisted of three to five sites extending from close to the Keys to the edge of the reef tract. The POM had mean  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  values of +3.6‰ ( $\sigma = \pm 3.2\%$ ) and  $-19.9\%$  ( $\sigma = \pm 0.6\%$ ) respectively. Over the study period there were no statistically significant changes in  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ , or C:N. For the majority of the sampling dates, the  $\delta^{13}\text{C}$  values showed a distinct inshore ( $\delta^{13}\text{C} = -18.3\%$ ,  $\sigma = \pm 1.0\%$ ) to off-shore gradient ( $\delta^{13}\text{C} = -21.4$ ,  $\sigma = \pm 0.9\%$ ). In contrast, the  $\delta^{15}\text{N}$  values showed no consistent patterns related to the distance from land. The more positive  $\delta^{13}\text{C}$  values of the nearshore samples suggest that the source of the carbon and the nitrogen in the POM in the nearshore was mainly derived from the degradation of seagrass detritus and not from the input of anthropogenically derived material from the Florida Keys. In contrast, the POM on the outer reef was dominated by marine plankton. As mineralization and nitrification of the organic nitrogen pool are major contributors to the dissolved inorganic nitrogen in the water column, it is unlikely that variations in the  $\delta^{15}\text{N}$  of the algae

and other benthic organisms reported in the Florida Keys are related to the input of sewage.

**Keywords** Carbon isotopes · Nitrogen isotopes · Nutrients · Sewage

## Introduction

Many reef systems worldwide have experienced a decrease in the sustainability and in their corals and related fauna. A striking example of this decline is seen in the Florida Keys (Porter 1992; Porter et al. 2001; Shinn et al. 2003; Lapointe et al. 2004), which over the past 50 years has seen a deterioration in the health of its reefs, coinciding with a large increase in human population and development of the adjacent islands. This decline, as well as others worldwide (Goreau 1992; Sebens 1994; Wilkinson and Buddemeier 1994; McCook 1999; White et al. 2000), manifests itself as a decrease in the percentage cover of corals and an increase in the number of diseases afflicting the coral communities (Porter 1992; Porter et al. 2001, 2002). There have been many suggested reasons for the change in coral abundance and health, but there has been growing speculation that coral reef ecosystems are being adversely affected by an increase in the macro-algal growth promoted both by the decrease in the number of natural predators and an increase in the loading of nutrients, such as nitrogen (Hughes et al. 1999; Szmant 2002).

Although nutrients, such as nitrogen, are critical in supporting coral reefs ecosystems, when supplied in excess they can be detrimental for these communities which typically thrive in oligotrophic waters. It has been shown that prolonged periods of high nutrient loads can severely impair the delicate balance of coral reefs, even

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at nutrient concentrations as low as 1  $\mu\text{M}$  dissolved inorganic nitrogen (DIN) (Bell 1992). One perceptible manifestation of elevated water column nutrients is an increase in fleshy benthic macroalgal growth on a reef. Algae can out-compete corals for viable substrate on a stressed reef and therefore jeopardize the success of coral repopulation and survival (Birkeland 1977; Connell et al. 1997; McCook et al. 2001). Following storm- or human-induced damage to a reef, macroalgae can utilize excess nutrients in the water column and establish themselves on hard bottom surfaces faster than coral polyps, essentially displacing them (Gabric and Bell 1993; McCook et al. 2001; Belliveau and Paul 2002). Several studies over the past 30 years have documented the adverse impact of macroalgae growth as a result of nutrient enrichment in areas such as Hawaii (Banner 1974), Bermuda (Lapointe and O'Connell 1989), Barbados (Tomascik and Sander 1985, 1987), the Seychelles (Littler et al. 1991), the Red Sea (Mergner and Schuhmacher 1981) and the Florida Keys (Lapointe et al. 1992, 1994). Furthermore, established macroalgae can act as a sediment trap and may smother surrounding corals (McCook et al. 2001). An increased nutrient load can also trigger phytoplankton blooms (Bode et al. 2003; Beman et al. 2005). These blooms not only reduce light penetration into the water column, but also increase the detrital deposition on a reef, often times smothering corals and encouraging the proliferation of other filter feeders, which compete with corals for substrate (Fabricius 2005).

Despite the consensus amongst most scientists of the effects of elevated nutrient levels on reefs, there is still much debate over the origins of the nutrients reaching reef ecosystems. To this end, various studies have suggested that utilizing the stable isotopic composition of nitrogen ( $^{15}\text{N}/^{14}\text{N}$ ) and carbon ( $^{13}\text{C}/^{12}\text{C}$ ) could be beneficial in revealing the possible source of nutrient enrichment (Lapointe et al. 1990; Heikoop et al. 2000a; Risk and Erdmann 2000; Costanzo et al. 2001; Umezawa et al. 2002; Griggs et al. 2003).

Several researchers working in South Florida (Lapointe et al. 1990; Lapointe and Clark 1992; Lapointe 1995; Paul et al. 1995) have claimed to have unequivocally confirmed that anthropogenic wastes are the principal culprit for reef degradation in this area. Lapointe et al (1990) and Paul et al (1995) verified that domestic waste from septic tanks and shallow injection wells can enter nearby canals within hours, after finding dissolved organic nitrogen (DON) and soluble reactive phosphorous levels in affected groundwater to be 4,000 and 70 times greater, respectively, than in control areas. A study by Lapointe (1997), found DIN levels in the water column as high as 3.4  $\mu\text{M}$  during algal blooms of *Codium isthmocladium* on deep reefs, 3 km offshore Palm Beach County, Florida. In a separate study,

Lapointe and Clark (1992) claimed that anthropogenic wastes were responsible for algal blooms, seagrass epiphytation and die-offs, and the overall decline of coral cover on patch- and bank reefs, after finding elevated levels of dissolved and particulate nitrogen as far as 3 km offshore. Lapointe and Clark (1992) maintain that nutrients originate mainly from leaky septic tanks, sewage outfalls and injection wells and make their way out to the reef tract where they promote macroalgal dominance.

Combined with the concentration data, Lapointe also measured the  $\delta^{15}\text{N}$  of *C. isthmocladium* tissues, a fleshy macroalgae, from one site over a 5-month bloom in 1995 (Lapointe 1997). The tissues yielded  $\delta^{15}\text{N}$  values of  $\sim +10$  to  $+12\text{‰}$ , which Lapointe concluded were a direct result of anthropogenically-contaminated groundwater. In later work (Lapointe et al. 2004), algal tissue values as low as  $\sim +4\text{‰}$  were cited as being indicative of sewage enrichment. Other studies have recently documented an increase in the  $\delta^{15}\text{N}$  of benthic organisms in South Florida and concluded that the changes were the result of increased input of anthropogenic derived nitrogen (Ward-Paige et al. 2005a, b). These studies suggested that  $\delta^{15}\text{N}$  values of between  $+4$  and  $+5\text{‰}$  in sponges and gorgonians relative to values of  $+3\text{‰}$  at sites which were considered to be not influenced by anthropogenic sources, were indicative of contamination.

However, increases in the concentration of DIN close to the Florida Keys are not supported by other published data (Szmant and Forrester 1996; Boyer and Jones 2002). Szmant and Forrester (1996), found only slightly elevated DIN levels ( $\sim 1 \mu\text{M NO}_3$ ) in waters near canals and marinas, but these levels returned to oligotrophic levels within 0.5 km of the shoreline. Szmant and Forrester, in fact, argue that most water column nutrients are consumed by nearshore algal and seagrass communities and do not directly impact the coral reef communities found further offshore. In a study on the  $\delta^{15}\text{N}$  of nitrate on the Florida Reef tract, Leichter et al (2007) measured mean values of between  $+5.26$  and  $+4.24\text{‰}$  with the elevated values being measured in deeper waters. As these waters upwell onto the reefs, the nitrate is rapidly utilized by benthic and planktonic algae. More positive  $\delta^{15}\text{N}$  values are produced through a series of processes including fractionation during assimilation and trophic enrichment. This results in organisms such as the zooxanthellae in corals from the Florida Keys having  $\delta^{15}\text{N}$  values of  $+4.82\text{‰}$  (similar to the nitrate). However the corals themselves are more positive ( $+6.55\text{‰}$ ; Swart et al. 2005) reflecting a trophic enrichment. Such  $\delta^{15}\text{N}$  values would place the Florida Reef corals in the group of reefs unaffected by anthropogenic sources (Heikoop et al. 2000b).

In this investigation, particulate organic matter (POM) was systematically sampled from stations throughout the

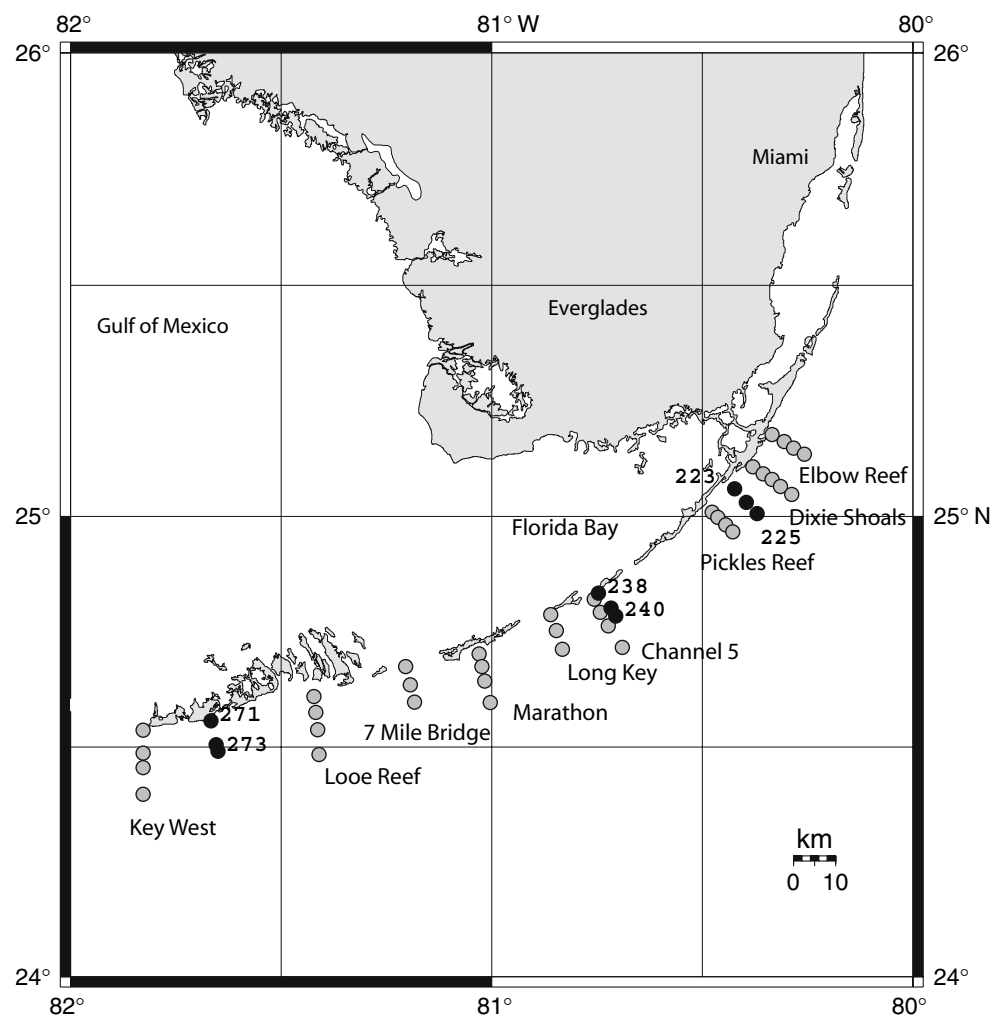
Florida Keys reef tract. The POM was chosen as the primary focus of this study because previous works (Altabet and Deuser 1985; Ostrom et al. 1997; Kendall et al. 2001; De Brabandere et al. 2002; Lehmann et al. 2004) have shown that seasonality can be detected in the  $\delta^{15}\text{N}$  values of POM and that the magnitude of  $\text{NO}_3^-$  flux into the euphotic zone and subsequent phytoplankton uptake, can be measured (Lathja and Michener 1994). In addition, the amount of nitrogen contained in the POM is approximately 10 to 50 times higher than all the pools of DIN and has a relatively short turnover rate (Cherrier et al. 1996; Loh and Bauer 2000). Mineralization and nitrification of the DON is therefore an important source of DIN and hence ultimately the  $\delta^{15}\text{N}$  of the organisms found in the community.

## Materials and methods

Samples were collected from 13 cruises between 2000 and 2002 in the Florida Keys, utilizing the R/V Walton Smith

(University of Miami). On these cruises, nine transects were chosen, each having three to five stations positioned from nearshore to offshore (Fig. 1). Designated transects were named after local area landmarks, such as reefs, proximal islands or nearby passes or cuts through the barrier islands. Inshore stations were delineated as the most nearshore station along a particular transect, midshore stations were so-named for stations with water depths from 3 to 10 m that were not already established as an inshore station, offshore stations had water depths of 31–50 m, while stations with water depths exceeding 51 m were designated as deep stations. Transects were also categorized as either “Upper”, “Middle”, or “Lower” Keys. For this study, the Upper Keys consisted of Elbow Reef, Dixie Shoals and Pickles Reef transects; the Middle Keys was composed of transects Channel 5 (Ch5), Long Key and Marathon Key; transects 7 Mile Bridge (7 MI), Looe Reef and Key West comprised the Lower Keys (Table 1 and Fig. 1). Sampling occurred during both the wet and dry seasons of 2000 to 2002; for this study, the wet season

**Fig. 1** Map of Florida Keys showing individual station locations (circles with light shaded centers) at which particulate organic material (POM) was sampled from 2000 to 2002. Each of the nine transect lines were composed of three to five stations and were arranged perpendicular to the shoreline and named after local landmarks. Discrete transect lines are ER Elbow Reef, DS Dixie Shoals, PR Pickles Reef, Ch5 Channel 5, LK Long Key, MK Marathon Key, 7MI 7 Mile Bridge, LR Looe Reef and KW Key West. Also shown on the map in the solid dark circles are the locations of the stations sampled for  $\text{NO}_x$  and  $\text{NH}_4^+$  on a quarterly basis



**Table 1** Mean  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ , and C:N values ( $\pm$ SD) for the entire study, and then further subdivided based on temporal and spatial variations

	$\delta^{15}\text{N}(\text{‰})$	<i>n</i>	$\delta^{13}\text{C}(\text{‰})$	<i>n</i>	C:N	<i>n</i>
Entire study	+3.64 ( $\pm$ 3.17)	275	-20.00 ( $\pm$ 1.97)	293	8.59 ( $\pm$ 2.56)	293
<i>Temporal variations</i>						
Wet season	+3.07 ( $\pm$ 2.78)	148	-20.03 ( $\pm$ 1.80)	151	9.47 ( $\pm$ 2.57)	151
Dry season	+4.30 ( $\pm$ 3.47)	127	-19.96 ( $\pm$ 2.15)	142	7.66 ( $\pm$ 2.20)	142
	<i>p</i> < 0.05		ns		<i>p</i> < 0.05	
<i>Spatial variations</i>						
Upper keys	+3.57 ( $\pm$ 3.67)	100	-19.53 ( $\pm$ 1.84)	110	8.41 ( $\pm$ 2.64)	110
Middle keys	+3.53 ( $\pm$ 2.86)	96	-20.26 ( $\pm$ 1.98)	98	8.54 ( $\pm$ 2.31)	98
Lower keys	+3.87 ( $\pm$ 2.87)	79	-20.31 ( $\pm$ 2.04)	85	8.88 ( $\pm$ 2.37)	85
	ns		<i>p</i> < 0.05		ns	

A *t*-test was performed to determine the statistical difference between the wet and dry season and the upper and lower keys

included the months between May and October, while the dry season comprised the months of November through April of the following year.

At each station, approximately 20 l of surface waters were collected in Nalgene carboys and filtered through a 47-mm Whatman GF/C pre-combusted glass fiber filter using a vacuum pump (particle retention > 1.2 mm). A portion of the filter was combusted using standard Dumas methods and the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of effluent analyzed using a continuous-flow isotope-ratio mass spectrometer (CFIRMS, Europa Scientific). Data are reported relative to Vienna Pee Dee Belemnite (V-PDB) and atmospheric  $\text{N}_2$  for carbon and nitrogen, respectively. Typical precisions of in-house organic standards are  $\pm 0.11\text{‰}$  for nitrogen and  $\pm 0.07\text{‰}$  for carbon.

Nutrient data were obtained from stations which are sampled at quarterly intervals by Florida International University. The locations of these stations and the methods used have been previously published (Boyer and Jones 2002).

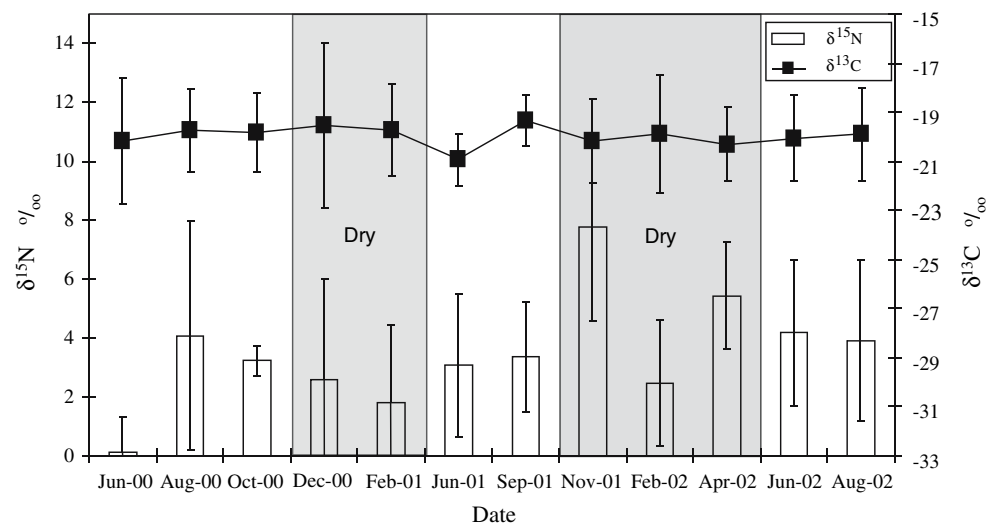
Prior to statistical analysis all data were tested for normality. Single-factor analysis of variance (ANOVA) was employed to test for significant site or seasonal differences.

For the cross reef transects, the inner sites were compared with the deeper sites using a two tailed *t*-test. Differences were considered significant at greater than the 95% confidence limits.

## Results

### Bulk isotopic composition

The mean  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and C/N values of the POM collected from all sites sampled during the oceanographic surveys are presented in Table 1 and Fig. 2. The mean  $\delta^{13}\text{C}$  of all the samples was  $-20.0\text{‰}$  ( $\sigma = 1.97\text{‰}$ ) and the  $\delta^{15}\text{N} = +3.64\text{‰}$  ( $\sigma = -3.17\text{‰}$ ) (the difference between the number of samples analyzed for C and N arises as a result of equipment malfunction). The  $\delta^{15}\text{N}$  data ranged from  $-5$  to  $+15\text{‰}$ . Only five samples exhibited values  $>+10\text{‰}$ , but based on the N yields of these samples, there was no valid rationale for excluding them from the data set and therefore they have been included. The  $\delta^{13}\text{C}$  data of the POM ranged from  $\sim -15$  to  $-25\text{‰}$ .

**Fig. 2** Mean values  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  from all sites between January 2000 and August 2002. The shaded area represents the dry season in South Florida. Error bars represent SD

**Table 2** Mean  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ , and C:N values ( $\pm$ SD) of all particulate organic material (POM) samples taken during each monthly cruise

	$\delta^{15}\text{N}$ (‰)	<i>n</i>	$\delta^{13}\text{C}$ (‰)	<i>n</i>	C:N	<i>n</i>
Monthly averages						
June 2000	+0.13 ( $\pm$ 1.18)	25	-20.19 ( $\pm$ 2.57)	25	8.54 ( $\pm$ 1.45)	25
August 2000	+4.09 ( $\pm$ 3.88)	23	-19.75 ( $\pm$ 1.70)	23	10.14 ( $\pm$ 1.61)	23
October 2000	+3.23 ( $\pm$ 0.52)	14	-19.83 ( $\pm$ 1.64)	14	9.02 ( $\pm$ 0.69)	14
December 2000	+2.60 ( $\pm$ 3.41)	20	-19.53 ( $\pm$ 3.35)	20	6.86 ( $\pm$ 1.49)	20
February 2001	+1.81 ( $\pm$ 2.65)	18	-19.74 ( $\pm$ 1.88)	29	6.95 ( $\pm$ 0.78)	29
June 2001	+3.07 ( $\pm$ 2.41)	23	-20.93 ( $\pm$ 1.06)	24	7.14 ( $\pm$ 0.50)	24
September 2001	+3.35 ( $\pm$ 1.89)	18	-19.33 ( $\pm$ 1.03)	18	6.77 ( $\pm$ 1.00)	18
November 2001	+7.77 ( $\pm$ 3.20)	29	-20.18 ( $\pm$ 1.72)	33	5.02 ( $\pm$ 0.44)	33
February 2002	+2.45 ( $\pm$ 2.14)	30	-19.88 ( $\pm$ 2.40)	30	9.41 ( $\pm$ 0.72)	30
April 2002	+5.45 ( $\pm$ 1.83)	30	-20.32 ( $\pm$ 1.51)	30	10.02 ( $\pm$ 1.70)	30
June 2002	+4.17 ( $\pm$ 2.49)	19	-20.06 ( $\pm$ 1.76)	21	11.47 ( $\pm$ 1.49)	21
August 2002	+3.92 ( $\pm$ 2.73)	26	-19.90 ( $\pm$ 1.91)	26	12.41 ( $\pm$ 2.90)	26
	ns		ns		ns	

The statistical significance of the result of a regression analysis with respect to sampling time is indicated at the bottom of the table

### Temporal variations

The mean values for  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  data, or C:N are shown in Tables 1 and 2. There were no seasonal patterns in the  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  data, or C:N data at any particular station, although overall the  $\delta^{15}\text{N}$  of the samples collected during the dry season had a slightly more positive value than those collected in the wet season (+4.3 vs. +3.07‰ Table 1). The C:N ratio was slightly higher in the wet season than in the dry season (9.47 vs. 7.66 Table 1). There was no statistically significant change in the  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$  data, or C:N over the study period (Table 2).

### Spatial variations

The  $\delta^{13}\text{C}$  values of the POM throughout the entire length of the Florida Keys were normally more positive at the inshore stations and become more negative moving from mid-shore, to offshore and finally to the deep stations (samples from August 2000, September 2001, and June 2002 being the exceptions to this) (Figs. 3, 4 and Table 3). Overall, the mean  $\delta^{15}\text{N}$  and C:N values along a given transect did not show any statistically significant spatial trends, either nearshore to offshore (Table 3), or from Upper Keys to Lower Keys (Table 1), although during some months inconsistent spatial patterns were observed.

### Nutrient concentrations

The concentrations of  $\text{NO}_x$  ( $\text{NO}_2 + \text{NO}_3$ ) and  $\text{NH}_4^+$  have been measured at quarterly intervals at a large number of sites in the Florida Keys by Florida International University (Boyer and Jones 2002).

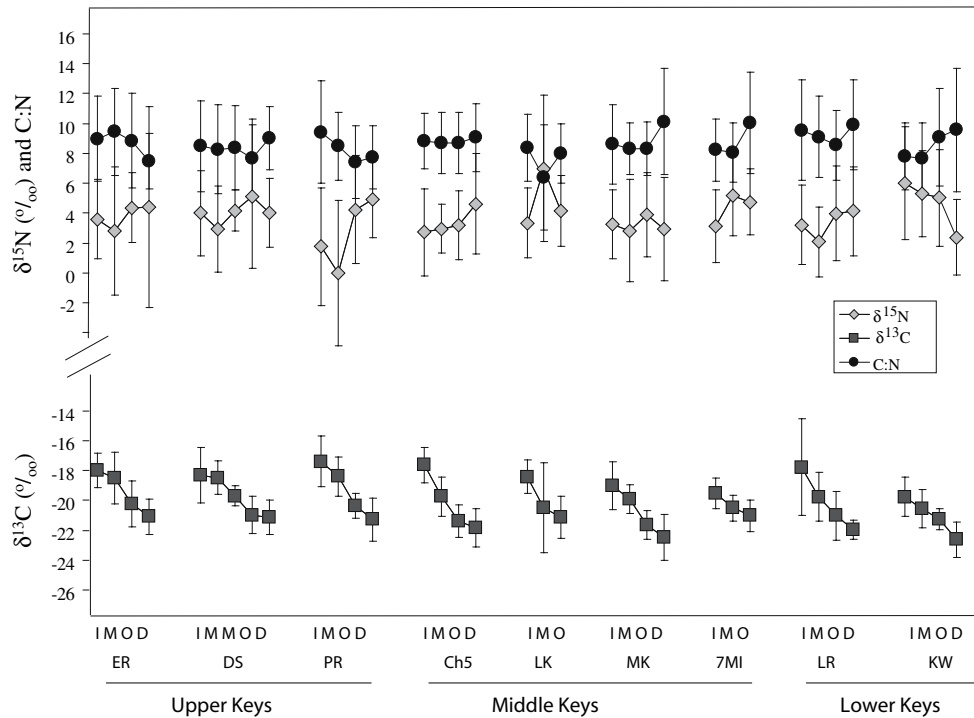
For the purposes of this study three transects were chosen, from the Upper Keys, Middle Keys and Lower Keys. Each transect consisted of three sites (Upper Keys 223–225, Middle Keys 238–240, and Lower Keys 271–273) and are in the general area of the POM samples taken in this investigation (Fig. 1). These data are shown in Fig. 5.

### Organic nitrogen

The concentrations of total organic nitrogen varied from 1.66 to 67.72  $\mu\text{M}$  (mean = 12.11  $\mu\text{M}$ ) and showed no consistent inshore to offshore trend (Fig. 5). There were also no statistically significant differences in concentration between the Upper, Middle and Lower Keys.

### Ammonia

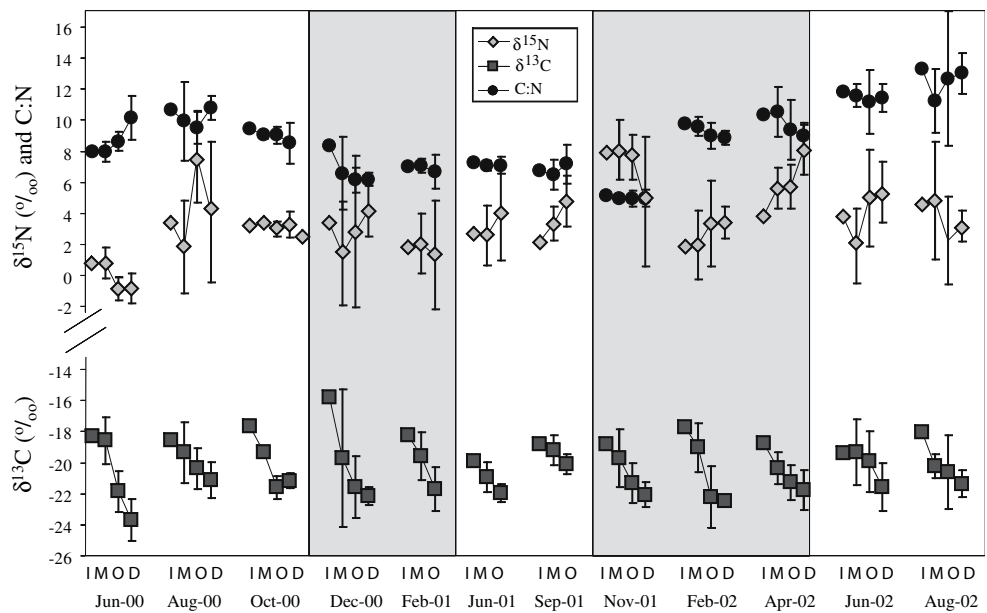
The concentrations of  $\text{NH}_4^+$  varied from undetectable amounts to 2.73  $\mu\text{M}$  and showed no statistically significant onshore to offshore trend (Fig. 5) or any statistically significant differences between the Upper, Middle and Lower Keys. In the Middle Keys transect there was a decrease in the concentration of ammonia from ~1999 through 2002, a trend mirrored in the data from the Lower Keys. In both the Lower Keys (Sites 223–225) and Upper Keys (Sites 271–273) there was a slight elevation in the concentration of  $\text{NH}_4^+$  prior to a larger increase in the concentration of  $\text{NO}_x$ . The inner shore site in the Middle Keys transect showed statistically significant elevated concentrations of  $\text{NH}_4^+$  with respect to the offshore sites and the other transects.



**Fig. 3** Mean  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and C/N ratios collected during 12 separate cruises between 2000 and 2002. *I* Inner, *M* middle, *O* outer and *D* deep. *ER* Elbow Reef, *DS* Dixie Shoals, *PR* Pickles Reef, *Ch5*

Channel 5, *LK* Long Key, *MK* Marathon, *7MI* 7 Mile Bridge, *LR* Looe Reef and *KW* Key West. *Error bars* represent SD

**Fig. 4** Mean values  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and C/N ratios from all sites categorized into *I* inner, *M* middle, *O* outer and *D* deep during 12 separate cruises between January 2000 and August 2002. The stations in each grouping are arranged inshore to offshore, left to right. The shaded area represents the dry season in South Florida. *Error bars* SD



*Nitrate and nitrite*

The concentrations of  $\text{NO}_x$  ( $\text{NO}_3^-$  and  $\text{NO}_2^-$ ) varied from undetectable amounts to  $1.87 \mu\text{M}$ . The concentrations showed no statistically significant onshore to offshore trend (Fig. 3) or any statistically significant differences

between the Upper, Middle and Lower Keys. The only exception to this is Site 238, the inshore site on the Middle Keys transect, which showed elevated concentrations. The  $\text{NO}_x$  shows a peak concentration in 2000 in both the Upper and Lower Keys transects decreasing to low levels by 2000.

**Table 3** Mean  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$ , and C:N values ( $\pm$ SD) for samples taken during a specific month

	$\delta^{15}\text{N}$ (‰)	<i>n</i>	$\delta^{13}\text{C}$ (‰)	<i>n</i>	C:N	<i>n</i>
<b>June 2000</b>						
Inshore	+0.82 ( $\pm$ 1.00)	6	-18.31 ( $\pm$ 1.53)	6	7.98 ( $\pm$ 0.50)	6
Midshore	+0.77 ( $\pm$ 0.74)	9	-18.58 ( $\pm$ 1.30)	9	7.97 ( $\pm$ 0.41)	9
Offshore	-0.87 ( $\pm$ 0.95)	5	-21.86 ( $\pm$ 1.34)	5	8.64 ( $\pm$ 0.55)	5
Deep	-0.82 ( $\pm$ 1.09)	5	-23.68 ( $\pm$ 1.26)	5	10.16 ( $\pm$ 0.55)	5
	<i>p</i> < 0.05		<i>p</i> < 0.05		<i>p</i> < 0.05	
<b>August 2000</b>						
Inshore	+3.40 ( $\pm$ 3.00)	5	-18.52 ( $\pm$ 0.68)	5	10.67 ( $\pm$ 2.52)	5
Midshore	+1.83 ( $\pm$ 2.94)	8	-19.35 ( $\pm$ 0.54)	8	9.94 ( $\pm$ 1.02)	8
Offshore	+7.66 ( $\pm$ 4.51)	6	-20.37 ( $\pm$ 0.62)	6	9.50 ( $\pm$ 0.79)	6
Deep	+4.10 ( $\pm$ 2.13)	4	-21.14 ( $\pm$ 0.76)	4	10.81 ( $\pm$ 2.27)	4
	<i>p</i> < 0.05		ns		ns	
<b>October 2000</b>						
Inshore	+3.22 ( $\pm$ 0.11)	3	-17.66 ( $\pm$ 0.24)	3	9.48 ( $\pm$ 0.24)	3
Midshore	+3.35 ( $\pm$ 0.49)	5	-19.31 ( $\pm$ 0.74)	5	9.04 ( $\pm$ 0.53)	5
Offshore	+3.01 ( $\pm$ 0.83)	3	-21.57 ( $\pm$ 0.49)	3	9.04 ( $\pm$ 1.35)	3
Deep	+3.27 ( $\pm$ 0.68)	3	-21.15 ( $\pm$ 1.04)	3	8.52 ( $\pm$ 0.05)	3
	ns		<i>p</i> < 0.05		ns	
<b>December 2000</b>						
Inshore	+3.37 ( $\pm$ 3.34)	5	-15.79 ( $\pm$ 4.45)	5	8.34 ( $\pm$ 2.35)	5
Midshore	+1.41 ( $\pm$ 4.89)	7	-19.70 ( $\pm$ 1.98)	7	6.58 ( $\pm$ 0.81)	7
Offshore	+3.17 ( $\pm$ 1.59)	5	-21.74 ( $\pm$ 0.40)	5	6.19 ( $\pm$ 0.46)	5
Deep	+4.16 ( $\pm$ 0.82)	2	-22.17 ( $\pm$ 0.35)	2	6.20 ( $\pm$ 0.29)	2
	ns		<i>p</i> < 0.05		ns	
<b>February 2001</b>						
Inshore	+1.81 ( $\pm$ 1.93)	7	-18.23 ( $\pm$ 1.55)	9	7.01 ( $\pm$ 0.45)	9
Midshore	+2.08 ( $\pm$ 3.49)	7	-19.58 ( $\pm$ 1.39)	12	7.07 ( $\pm$ 1.10)	12
Offshore	+1.32 ( $\pm$ 2.73)	4	-21.70 ( $\pm$ 0.96)	8	6.70 ( $\pm$ 0.44)	8
	ns		<i>p</i> < 0.05		ns	
<b>June 2001</b>						
Inshore	+2.69 ( $\pm$ 1.93)	7	-19.90 ( $\pm$ 0.95)	7	7.29 ( $\pm$ 0.31)	7
Midshore	+2.60 ( $\pm$ 3.11)	9	-20.92 ( $\pm$ 0.58)	9	7.06 ( $\pm$ 0.53)	9
Offshore	+4.06 ( $\pm$ 1.76)	7	-21.98 ( $\pm$ 0.64)	7	7.10 ( $\pm$ 0.63)	7
	ns		<i>p</i> < 0.05		ns	
<b>September 2001</b>						
Inshore	+2.17 ( $\pm$ 1.09)	6	-18.84 ( $\pm$ 0.96)	6	6.75 ( $\pm$ 0.96)	6
Midshore	+3.34 ( $\pm$ 1.61)	7	-19.21 ( $\pm$ 0.63)	7	6.50 ( $\pm$ 1.25)	7
Offshore	+4.79 ( $\pm$ 2.25)	5	-20.10 ( $\pm$ 1.27)	5	7.18 ( $\pm$ 0.62)	5
	ns		ns		ns	
<b>November 2001</b>						
Inshore	+7.92 ( $\pm$ 1.92)	8	-18.80 ( $\pm$ 1.85)	9	5.14 ( $\pm$ 0.24)	9
Midshore	+1.41 ( $\pm$ 4.89)	8	-19.70 ( $\pm$ 1.29)	11	4.98 ( $\pm$ 0.50)	11
Offshore	+8.10 ( $\pm$ 1.45)	9	-21.29 ( $\pm$ 0.83)	9	4.96 ( $\pm$ 0.54)	9
Deep	+4.75 ( $\pm$ 4.37)	3	-22.05 ( $\pm$ 0.33)	4	4.98 ( $\pm$ 0.47)	4
	ns		<i>p</i> < 0.05		ns	
<b>February 2002</b>						
Inshore	+1.84 ( $\pm$ 2.20)	8	-17.73 ( $\pm$ 1.58)	8	9.77 ( $\pm$ 0.62)	8
Midshore	+1.97 ( $\pm$ 2.77)	11	-19.03 ( $\pm$ 1.99)	11	9.59 ( $\pm$ 0.83)	11
Offshore	+3.36 ( $\pm$ 1.02)	8	-22.24 ( $\pm$ 0.22)	8	9.00 ( $\pm$ 0.43)	8

**Table 3** continued

	$\delta^{15}\text{N}$ (‰)	<i>n</i>	$\delta^{13}\text{C}$ (‰)	<i>n</i>	C:N	<i>n</i>
Deep	+3.41 ( $\pm$ 0.55)	3	-22.48 ( $\pm$ 0.21)	3	8.86 ( $\pm$ 0.42)	3
	ns		$p < 0.05$		ns	
April 2002						
Inshore	+3.36 ( $\pm$ 1.31)	8	-18.78 ( $\pm$ 1.02)	8	10.34 ( $\pm$ 1.62)	8
Midshore	+5.14 ( $\pm$ 1.40)	11	-20.34 ( $\pm$ 1.14)	11	10.54 ( $\pm$ 1.91)	11
Offshore	+5.23 ( $\pm$ 1.61)	8	-21.28 ( $\pm$ 1.30)	8	9.39 ( $\pm$ 0.87)	8
Deep	+7.60 ( $\pm$ 1.50)	3	-21.76 ( $\pm$ 0.94)	3	8.99 ( $\pm$ 2.62)	3
	$p < 0.05t$		$p < 0.05t$		ns	
June 2002						
Inshore	+3.71 ( $\pm$ 2.43)	4	-19.36 ( $\pm$ 2.10)	4	11.82 ( $\pm$ 0.74)	4
Midshore	+1.90 ( $\pm$ 3.11)	4	-19.32 ( $\pm$ 1.96)	5	11.60 ( $\pm$ 2.04)	5
Offshore	+4.99 ( $\pm$ 1.98)	6	-19.92 ( $\pm$ 1.56)	7	11.19 ( $\pm$ 0.88)	7
Deep	+5.36 ( $\pm$ 1.75)	5	-21.56 ( $\pm$ 0.82)	5	11.45 ( $\pm$ 2.25)	5
	nst		ns		ns	
August 2002						
Inshore	+4.58 ( $\pm$ 3.79)	7	-18.04 ( $\pm$ 0.77)	7	13.29 ( $\pm$ 2.04)	7
Midshore	+4.84 ( $\pm$ 2.80)	9	-20.24 ( $\pm$ 2.36)	9	11.26 ( $\pm$ 4.32)	9
Offshore	+2.26 ( $\pm$ 0.99)	6	-20.60 ( $\pm$ 2.36)	6	12.69 ( $\pm$ 1.32)	6
Deep	+3.19 ( $\pm$ 1.07)	4	-21.35 ( $\pm$ 0.90)	4	13.03 ( $\pm$ 1.59)	4
	nst		$p < 0.05t$		ns	

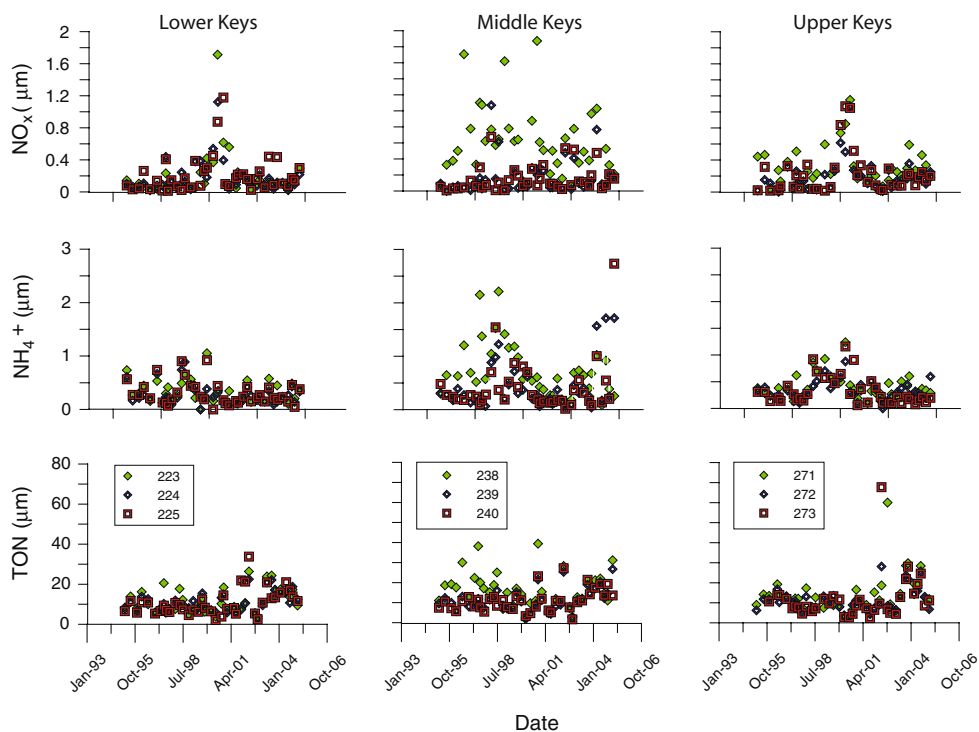
Samples are further subdivided based on station position along a transect. A *t*-test was performed between the inshore and the deep station and the statistical significance shown below each comparison

## Discussion

The  $\delta^{15}\text{N}$  of POM derived from sewage ranges from +2.3 to +7.9‰ (Sweeney et al. 1980; Heikoop et al. 2000a; Thornton and McManus 1994; Rogers 2003). This range is rather unexceptional and non-diagnostic as regards the

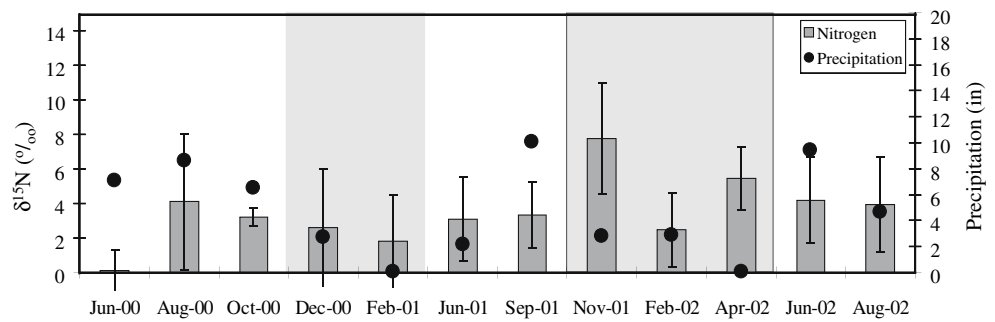
identification of sewage in the marine environment is concerned in that it is similar to values reported for marine derived POM. In contrast, the  $\delta^{13}\text{C}$  values of sewage derived POM have more isotopically negative values ( $\sim -22$  to  $-27$ ‰ vs.  $\sim -15$  to  $-22$ ‰) relative to marine samples. By using  $\delta^{13}\text{C}$  values, therefore, marine POM can

**Fig. 5** Inorganic  $\text{NH}_4^+$  and  $\text{NO}_x$  concentrations from three transects shown in Fig. 1. Data are from the Florida International University database (adapted from Boyer and Jones 2002). The *left three graphs* represent data collected from three stations in the Upper Keys. The site numbers are marked on Fig. 1. The *middle three graphs* show the data from the Middle Keys and the *right three graphs*, the data from the Lower Keys. TON total organic nitrogen





**Fig. 6** Mean  $\delta^{15}\text{N}$  of particulate organic material (POM) in comparison with mean precipitation in the Florida Keys during the study period, showing no clear relationship between rain events and nitrogen isotopic composition. The shaded area represents the dry season in South Florida. Error bars represent SD



be clearly separated from anthropogenically derived material. In this study the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  measurements on the POM, which averaged  $+3.6\text{‰}$  and  $-19.9\text{‰}$  respectively (Table 1), do not suggest a source of organic material which is mainly terrestrially derived. In fact the mean  $\delta^{13}\text{C}$  values more accurately depicts mixing between marine organic matter ( $\delta^{13}\text{C} = -22\text{‰}$ ) and marine benthic algae seagrasses ( $-10$  to  $-20\text{‰}$ ) (Burnett and Schaeffer 1980; Lathja and Michener 1994). The  $\delta^{13}\text{C}$  of the POM measured in this study showed a clear pattern ranging from more positive values ( $-16$  to  $-18\text{‰}$ ), close to the Florida Keys, to more negative compositions in deeper water further away from land ( $-21$  to  $-23\text{‰}$ ). The enrichment in the  $\delta^{13}\text{C}$  of the POM clearly implies that the origin of the POM at the stations closest to the Florida Keys was not principally derived from the Florida Keys mainland. The vegetation surrounding the Keys is composed primarily of isotopically more negative  $\text{C}_3$  plants, such as mangroves, or possibly organic material derived from human activities, both of which have relatively negative  $\delta^{13}\text{C}$  values, ranging from  $-20$  to  $-30\text{‰}$  (Burnett and Schaeffer 1980), respectively. Instead, materials which have relatively positive  $\delta^{13}\text{C}$  values such as seagrasses (Nichols et al. 1985; Anderson and Fourqurean 2003) and are extremely plentiful in the shallow waters close to the Florida Keys, are the dominant contributors to the POM in these areas. Recent work has shown that the algal-seagrass component has an average  $\delta^{13}\text{C}$  value of  $-9\text{‰}$  for the Florida Keys area (Fourqurean et al. 2005) and the data presented here suggests that approximately 52% of the nearshore POM  $\delta^{13}\text{C}$  component is derived from this source. The remaining possible sources for the POM (zooplankton, phytoplankton, terrestrial organic material and sewage), all of which possess  $\delta^{13}\text{C}$  values between  $-20$  and  $-30\text{‰}$ , contribute the residual amount.

#### Wet and dry season

South Florida has distinct wet (May to November) and dry (December to April) seasons. It has been suggested that during the wet season greater amounts of

anthropogenic derived nutrients are washed into coral reefs, leading to more positive  $\delta^{15}\text{N}$  values during this time period (Lapointe et al. 2004). However, the results in the present study do not support this idea and in fact showed elevated  $\delta^{15}\text{N}$  values during the dry season (Table 1 and Fig. 6). Furthermore, if the C:N ratio is to be taken as an indicator of nutrient limitation as proposed by some authors (Fourqurean et al. 2005), the slightly higher values during the wet season indicate lower nitrogen availability and not higher nutrients as proposed by Lapointe et al. (2004).

#### Distribution of nutrients

The concentration of nutrients measured prior, during and after the study period showed values similar to those previously determined (Szmant and Forrester 1996) for the Florida Keys. With the exception of the Middle Keys transect (Fig. 5), there were no statistically significant differences in the concentration of any of the nitrogen species between the inshore and offshore sites. At the Middle Keys transect, high  $\text{NO}_x$  and  $\text{NH}_4^+$  values were measured at the inshore site close to Channel 5 (Site 238) (Figs. 1, 5). This area is probably high since it receives water from the Gulf of Mexico which has been influenced by Florida Bay and the Everglades. The elevated N at this site did not correspond to any differences in the  $\delta^{15}\text{N}$  of the POM.

Occasionally there were time periods during which concentrations of  $\text{NO}_x$  and  $\text{NH}_4^+$  were elevated. For example, between 1998 and 2000 concentrations of  $\text{NH}_4^+$  reached  $1 \mu\text{m}$  in both the Lower and Upper Keys and up to  $2 \mu\text{m}$  in the Middle Keys (Fig. 5). Following this period of elevated  $\text{NH}_4^+$ , the concentrations returned to levels of  $<0.5 \mu\text{m}$ , while the concentrations of  $\text{NO}_x$  at the Lower and Upper Keys increased to between 1 and  $2 \mu\text{m}$ . By 2001 however these values also had decreased to levels  $<0.4 \mu\text{m}$ . The explanation for these periods of elevated values, which lasted over 12 months, is not known, but they did not appear to correlate with any changes in the  $\delta^{15}\text{N}$  of the POM.

### Conceptual model to account for observed values

Based on the  $\delta^{13}\text{C}$  as well as visual observation, the POM that was measured in this study was determined as consisting primarily of a mixture of plankton and suspended detritus, derived from seagrasses and macroalgae, with very little contribution from land based material. It should be noted that nominal contributions from land based sources, including terrestrial vegetation and anthropogenic wastes, are possible to the nearshore environments. However, the spatial patterns of the  $\delta^{13}\text{C}$  of the POM, consistent with carbon derived from seagrass and the low reported  $\text{NO}_3^-$ ,  $\text{NO}_2$  and  $\text{NH}_4^+$  concentrations, all indicate that the Florida Keys reef tract has negligible exposure to intense and prolonged anthropogenic wastes.

Particulate organic matter is often regarded as a food source for filter feeders, such as sponges, in marine environments. However, POM can also be mineralized to ammonium ( $\text{NH}_4^+$ ), which in turn undergoes nitrification to form nitrite ( $\text{NO}_2^-$ ) and nitrate ( $\text{NO}_3^-$ ). This DIN contribution, in addition to inorganic nitrogen sourced from upwelling (Leichter et al. 1996, 2007; Szmant and Forrester 1996), atmospheric deposition (Savoie 1987), groundwater (Reich et al. 2002), and anthropogenic wastes, is available in the water column to be utilized by benthic organisms, such as macroalgae. As organisms incorporate nitrogen, it has been shown that the  $\delta^{15}\text{N}$  of their tissue will reflect the  $\delta^{15}\text{N}$  of the nutrient source, after a fractionation factor is taken into account (DeNiro and Epstein 1981). Thus, many investigators have utilized the  $\delta^{15}\text{N}$  of various organisms as a proxy to characterize the primary source of N to ecosystems; studies that report enriched  $\delta^{15}\text{N}$  signatures in tissues often directly attribute those compositions to exposure to anthropogenic wastes. While this may be the case in some instances, there may be occasions where tissues, enriched in  $\delta^{15}\text{N}$  were never exposed to sewage, but instead are enriched as a result of various transformation processes of DIN pools, such as denitrification, nitrification and assimilation. Although the fractionation factors involved in these transformations of DIN vary between ecosystems and specific organisms, most of these processes result in the preferential use of the lighter isotope ( $^{14}\text{N}$ ), leaving the residual DIN pool enriched in the heavier isotope ( $^{15}\text{N}$ ). These normal ecosystem transformations of N can, at times, result in  $\delta^{15}\text{N}$  values that can be misinterpreted as evidence of anthropogenic influence. For example, the  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  would have the same initial value as the  $\delta^{15}\text{N}$  of POM, since there is very little fractionation in the mineralization of OM to  $\text{NH}_4^+$  [ $\alpha = \sim 1.000$ ; Kendall 1998]. However, subsequent nitrification can enrich the residual  $\text{NH}_4^+$  pool as the conversion of  $\text{NH}_4^+ \rightarrow \text{NO}_3^-$  has a large fractionation factor ( $\alpha = 1.020$ ; Miyake and Wada 1971). This fractionation can result in the depletion in the  $\delta^{15}\text{N}$  of the  $\text{NO}_3^-$  product

and a consequent enrichment in the  $\delta^{15}\text{N}$  of the residual  $\text{NH}_4^+$ . Since algae preferentially utilize ammonium rather than nitrate (Cifuentes et al. 1989), algae can have tissues that are relatively enriched in  $\delta^{15}\text{N}$  without ever being exposed to anthropogenic wastes.

It is evident that variations in the inorganic nitrogen in the Florida Keys and similar environments involves the input of DIN from many sources and this scenario provides an example of how variations and transformations of DIN sources might control the eventual isotopic composition of benthic organisms. Based on the  $\delta^{15}\text{N}$  of the POM presented in this study as well as the  $\delta^{15}\text{N}$  of the nitrate ( $\delta^{15}\text{N} = +5.5\text{‰}$ ) reported from upwelling (Leichter et al. 2007), the reported  $\delta^{15}\text{N}$  values for algae and benthic organisms in other studies from within the Florida Keys (Lapointe et al. 2004; Swart et al. 2005; Ward-Paige et al. 2005a, b) can be easily explained through natural variations in the DIN species as well as variations in mineralization, nitrification and assimilation histories without having to invoke anthropogenic sources. Changes in the  $\delta^{15}\text{N}$  of the POM over periods of years, such as observed in this study, or in the  $\delta^{15}\text{N}$  of organic material from gorgonians (Ward-Paige et al. 2005a) and corals (Swart et al. 2005), may be related to a combination of variations in the source of the POM, combined with fractionation during the nitrification and assimilation of DIN. Such considerations in combination with data presented in this paper imply that using a particular  $\delta^{15}\text{N}$  value as a threshold for determining pollution from anthropogenic sources is problematic. Instead, the complex issue of nutrient provenance must be considered within the context of such conditions as ambient ecosystem nutrient-state, subsequent nutrient transformations and fractionations, as well as species-dependant metabolism.

The main conclusion that can be drawn from this study is that the relatively positive values of the  $\delta^{13}\text{C}$  of the POM indicates that the principal source of organic material contributing to the POM in the nearshore was organic detritus derived from seagrasses and not from land based sources. As this material also provided the largest reservoir of nitrogen, input of anthropogenic derived nitrogen cannot be a major source into the Florida Keys. Instead it is proposed that variations in mineralization of organic material and nitrification, as well as changes in the input of DIN species derived from upwelling, runoff, diffusion from sediments, and atmospheric input can account for variations in the  $\delta^{15}\text{N}$  of all major benthic components on the reef tract, without having to invoke the input of major amounts of nitrogen from anthropogenic sources.

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