The Assessment of Organic Matter Sources in Florida Bay: A biomarker and Compound Specific Carbon Isotope Ratio Approach

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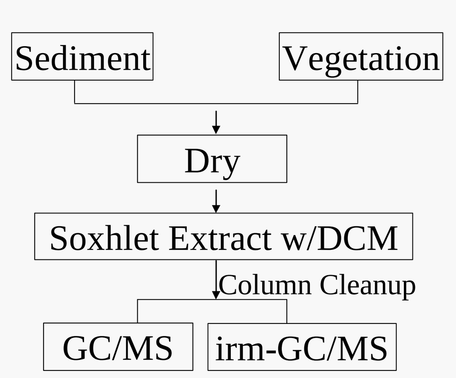
Abstract

Organic geochemical studies to determine the origin, transport, and ultimate fate of organic matter are the crucial to understanding the global carbon cycle. This study was undertaken using specific molecular markers, geochemical proxies and compound specific carbon isotope measurements to assess organic matter sources in sediments of Florida Bay from the dominant local biomass species, *Thalassia testudinum* and *Rhizophora mangle* . An n-alkane based proxy (Paq) and the n-alkan-2-one C_{25}/C_{27} ratio were successfully used to assess the relative contributions of mangrove derived organic matter on the composition of OM in seagrass beds throughout the bay. Mangroves were found to be particularly significant as an OM source in the northeastern and central section of Florida Bay**.** The decreasing trend in mangrove influence on sedimentary OM from the NE to the SW section of the Bay was further confirmed through the distribution of Taraxerol, a regional, mangrove specific biomarker, and the changes in the stable isotopic composition of n-alkanes as determined by GC-ir/MS. Throughout the bay, the influence of additional OM sources such as cyanobacterial mats and marine plankton (diatoms) on sedimentary OM was assessed through the relative abundance of the C_{20} and C_{25} highly branched isoprenoids (HBIs). These molecular characterizations are presently being applied to paleoenvironmental assessments with the aim of determining the historical variability of seagrass abundances in Florida Bay.

Methods

Sediments were collected using an Eckman dredge and the surface layer of sediment was used for analysis. All samples were placed into solvent rinsed, Teflon lined glass jars and frozen until analysis. Sediments were decalcified by using 10% HCl and allowed to stand until effervescence ceased before bulk sediment characteristics, such as ^{13}C measurement was determined. The bulk isotopic analysis was performed on a continuous flow EA-IRMS. Molecular marker analysis of the sediments was performed by solvent extraction of the sediment followed by column cleanup of the neutral fraction. All samples were analyzed on an HP 6890 GC with a 5973 MS. The compound specific ^{13}C stable isotope analysis was measured by Finnigan Delta Plus coupled to a HP 6890 gas chromatography. (Fig. 1)



➢Samples for CS-irm-GC/MS were treated with a molecular sieve when the *n*-alkanes were not clean well resolved.

➢Analytical precision for CS-irm-GC/MS analysis was typically better than ± 0.3 ‰ and samples were done in triplicate

Fig. 1 Flow chart of analytical method

Study Area

Fig. 2 shows the geographic locations of grab samples. Those eight sampling locations distribute from the northeast (NE) to southwest (SW) in Florida Bay.

Results

The molecular distributions of several biomarker compounds (such as n-alkanes, n-alkane-2-ones and taraxerol), ^{13}C stable isotope and compound specific stable isotopes were used to determine the origin and transport of organic matter in Florida Bay surface sediments.

1) Bulk Sediment Parameters

Table 1 Stable isotope ratio

	TC	DK	BK	RK
$\delta^{13}C$	-19.9	-16.0	-14.7	-12.9
	TSPH9	TSPH10	TSPH 11	Rabbit key
$\delta^{13}C$	-15.4	-11.5	-16.0	-12.6

Stable carbon isotopes are widely used to differentiate organic matter sources in estuarine sediments. Generally, the$d^{13}C$ values are c.a. - 10.0‰ and c.a. - 26.7‰ for seagrass and mangrove OM respectively. From table 1, the$d^{13}C$ values show an isotopic enrichment (heavier signal) from the northeast to the southwest portion of Florida Bay. This was likely caused by a gradual change in mixed input of organic matter from mangroves, which mainly occupy coastal fringe areas, and seagrasses, which are the dominant vegetation in Florida Bay.

2)Biomass-Specific Molecular Markers

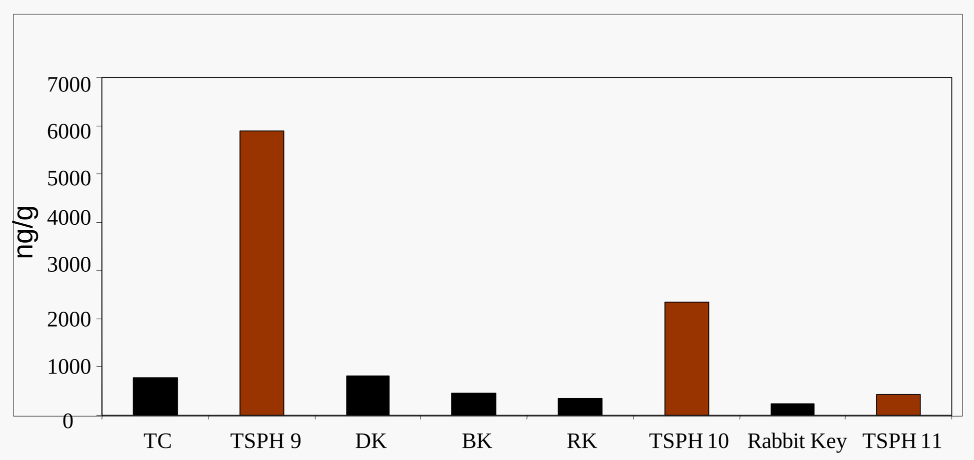


Fig. 3a Taraxerol in sedimentary samples from Florida Bay

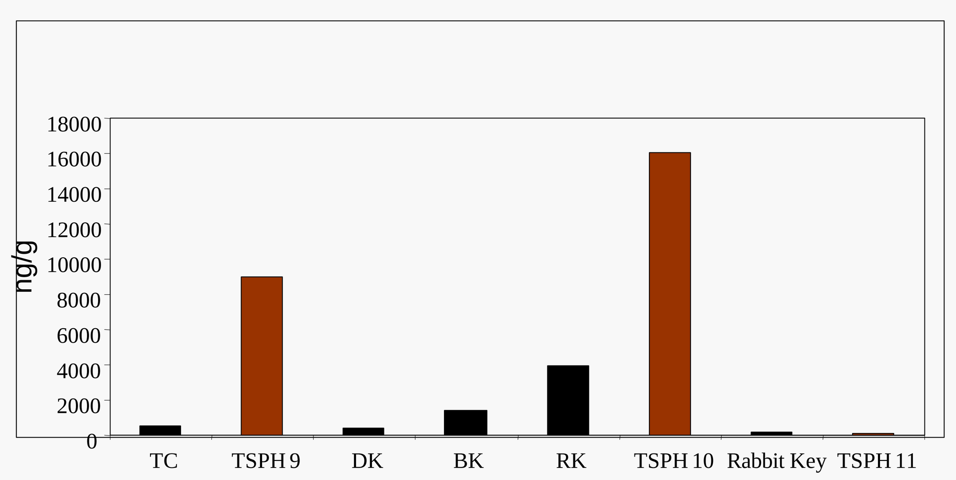


Fig. 3b C_{20} HBIs in sedimentary samples from Florida Bay

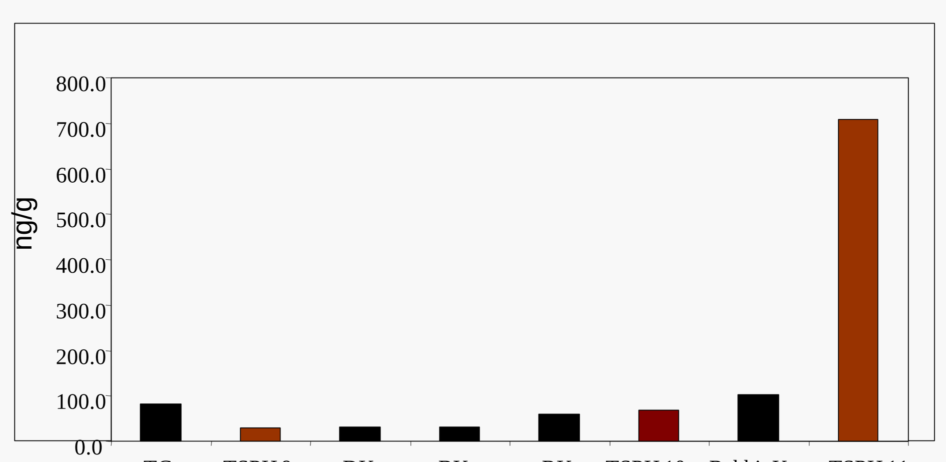
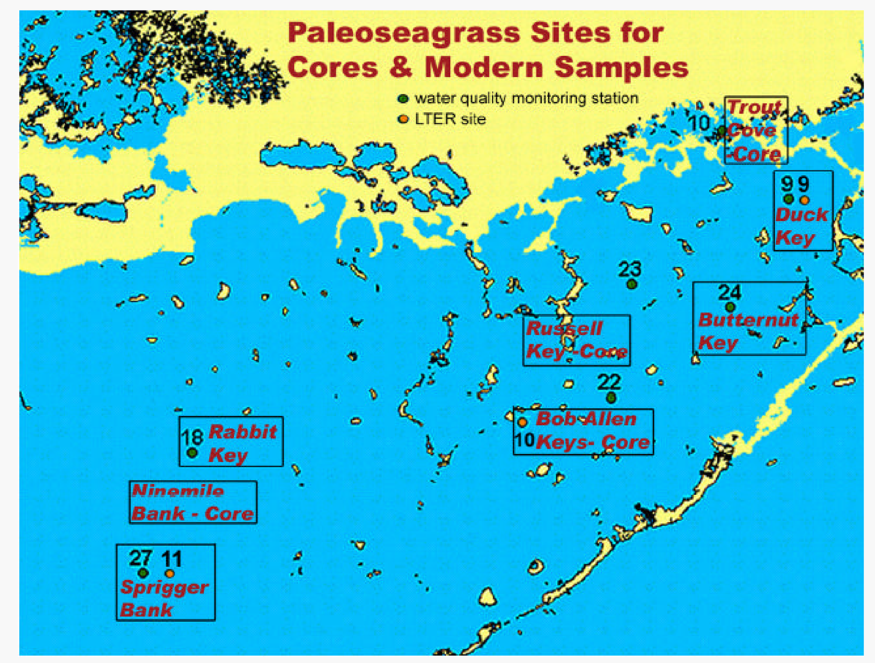


Fig. 3c C_{25} HBIs in sedimentary samples from Florida Bay

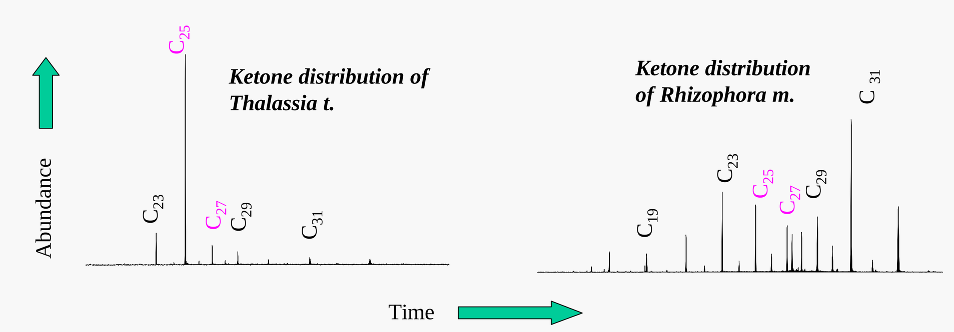


❖ TC= Trout Cove Core
DK= Duck Key
BK= Butternut Key
RK= Russell Key

Fig. 2 Location of the study area in Florida Bay

Taraxerol, C_{20} HBIs and C_{25} HBIs can be used as specific biomarker for mangrove, cynobacterial mat and diatom derived OM input in the FCE ecosystem, respectively. Taraxerol concentrations significantly decreased from the northeast to southwest portion of Florida Bay, suggesting that the proportion of mangrove derived organic matter decreases with the increasing distance from the coastal line, while the concentration of C_{20} HBIs is highest in the central section of the bay, reflecting the abundance of cynobacterial mats in this geographical area. The C_{25} HBI maximum in the SW portion of the bay provides a marine diatom OM source indicator.

3) Molecular Marker-based Proxies



Vegetation		Paq
Mangrove	*Rhizophora m.*	0.24
	Avicennia g.	0.15
Seagrass	*Halodule w.*	0.99
	Thalassia t.	0.93
	Syringodium f.	1.00
	Halophila d.	0.90

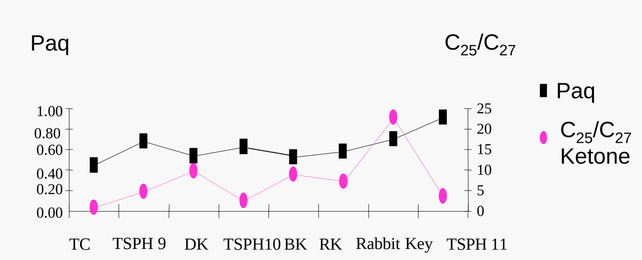


Fig. 4 Biomarker of Florida Bay samples

The n-alkane proxy, Paq, which is expressed as the ratio of the sum of C_{23}, C_{25} to C_{23}, C_{25} C_{29},C_{31} n- alkanes, can assess the relative proportion of the seagrass input to mangrove input. N-alkane distributions in seagrass and mangrove exhibit significant differences, resulting in Paq for seagrass of 0.90~1.00, while Paq for mangrove is only ~0.20. The overall Paq value increased from NE to SW Florida Bay. The ratio of C_{25}/C_{27} n-alkan-2-ones also a seagrass/mangrove proxy (see Chromatograms above) behaved similarly. Paq and C_{25}/C_{27} ketone ratio show a gradually increasing trend from northeast to southwest in Florida Bay, which reflects the increasing proportion of seagrass derived organic matter.

References:
[1] Jaffé, R., et al, Organic Geochemistry, 32 (2001), 507-526
[2] Hernandez, M.E., et al, Organic Geochemistry, 32 (2001), 21-32
[3] Ficken, K.J., et al, Organic Geochemistry, 31(2000), 745-749
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4) Compound specific carbon isotope ratios

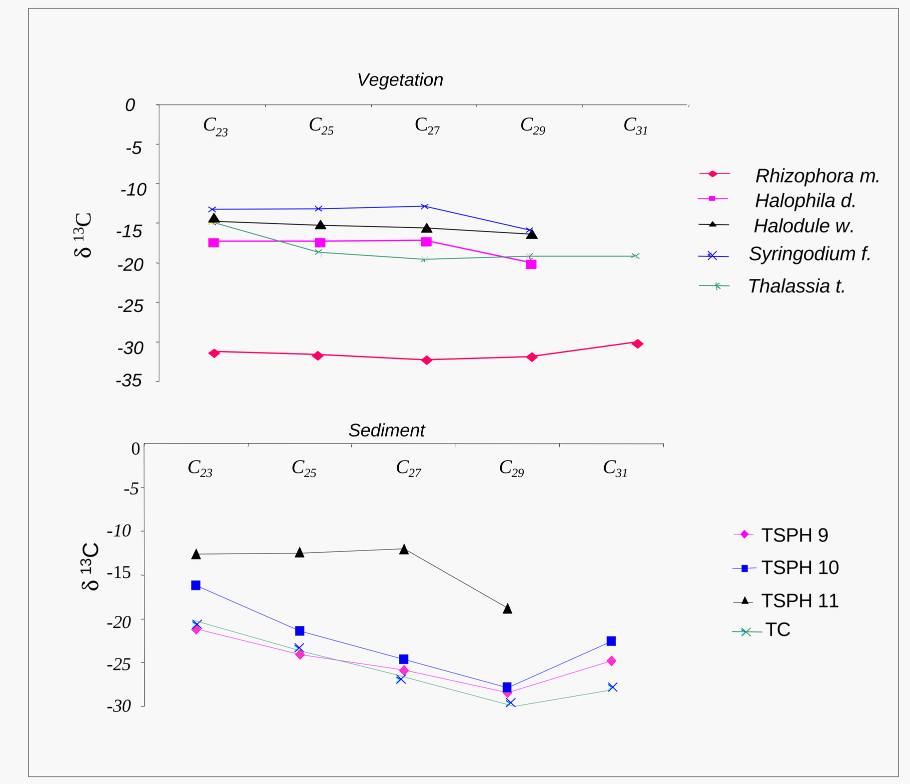
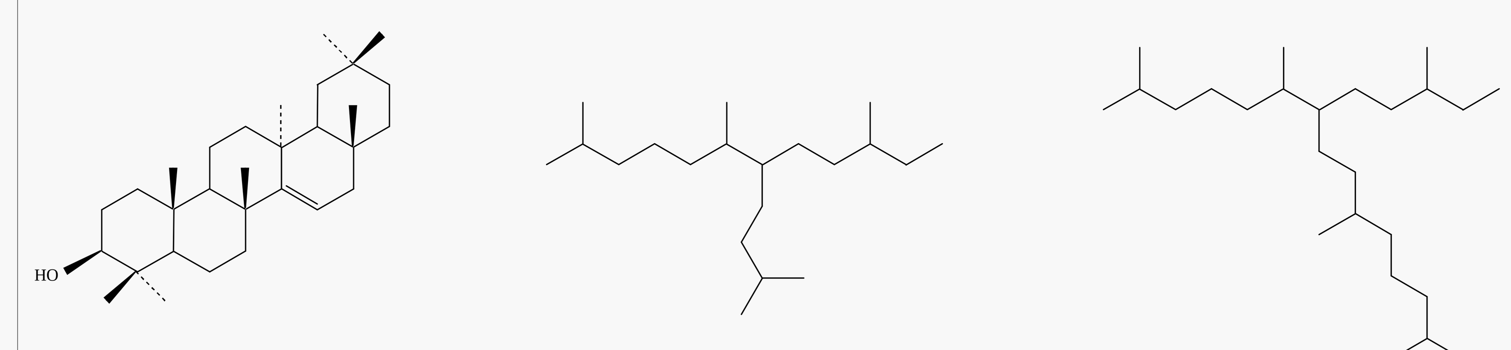


Fig. 5 GC-IRMS Data for n-alkanes

Compound specific ^{13}C isotope ratios of the individual n-alkanes can be useful to identify the origin of organic matter in sediments. From Fig. 5, the compound specific isotope ratios are significantly different between sea-grass & mangroves. The $d^{13}C$ for mangroves (~ - 30.0‰) are much more depleted than the values of seagrass (~ - 10‰ to - 17‰). Compound specific ^{13}C isotope ratios of four sediment samples (TSPH 9, 10,11 and TC) are shown to gradually decrease from short carbon chain n-alkanes (C_{23} , C_{25}) to long carbon chain n-alkanes (C_{29} , C_{31}). These results indicate different organic matter sources for short and long carbon n-alkanes; While the C_{23} and C_{25} may be mainly derived from seagrass, the mangroves are a major source of C_{29} and C_{31}. In addition, a clear NE to SW change in OM sources from mangrove-dominated to seagrass dominated OM was observed.

Discussion

Several geochemical proxies were applied to identify the sources of organic matter in Florida Bay. The bulk$d^{13}C$ data showed a mixed source of terrestrial (mangrove) and marine (seagrass) derived organic matter input for Florida Bay. A gradually increasing seagrass influence over that of mangroves, based on biomass-specific molecular markers (Paq, C_{25}/C_{27} ketone ratio and taraxerol abundance) in a general northeast to southwest transect was observed throughout the Bay. The compound specific ^{13}C isotopic composition can provide very useful and confirmatory information in this respect. The distributions of C_{20} and C_{25} HBIs in Florida Bay clearly reflect the geographical presence of cynobacterial mats and the abundant diatom inputs in the Phosphorus rich SW Florida Bay.



Taraxerol　　C_{20} HBIs　　C_{25} HBIs (exact structures are not determined)

Conclusions

➢Preliminary results indicate a significant influence of mangrove derived organic matter on the composition of organic matter in seagrass beds.

➢The molecular and isotopic data shows a significant decrease in the mangrove derived organic matter inputs from the northeastern to southwestern part of Florida Bay.

➢Biomass-specific biomarkers and geochemical proxies are useful in the assessment of organic matter sources in surface sediments of Florida Bay, and could be applied to paleo-environmental studies in the Bay.

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