



Estimating Organic Matter Source Contributions to the Lower Shark River , Everglades National Park

Ralph Mead and Rudolf Jaffe

Environmental Geochemistry Group and Department of Chemistry
Florida International University
Miami, Florida 33193

Introduction:

Everglades National Park (ENP) is about to undergo the world's largest wetland restoration. Historically, freshwater discharge was greater throughout ENP but with current management practices the volume of water is controlled thus less water travels throughout the park. The restoration of ENP will bring back pre-drainage hydrodynamic characteristics.

As a parcel of water flows from the freshwater marsh to the ocean, a certain proportion of different organic matter sources contribute to the organic carbon that is being carried by the water. The quality of the organic matter can be significantly different in the parcel and thus support different groups of organisms that live off of the organic matter. When historical freshwater flows are restored to ENP, a new proportion of organic matter will be present in the parcel of water. The question arises as to how this will change the organic matter dynamics of ENP.

To understand if the change in freshwater flow will have an effect on organic matter delivery and transport, a baseline study must be done to determine current conditions. The main objective of the work is to compare different methods of estimating organic matter sources based on molecular and isotopic data.

Methods:

Sediment samples were collected using an Eckman dredge and the surficial layer of sediment was used for analysis. All samples were put 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. 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.



Results:

Three approaches were used to estimate organic matter source contributions to the study sites. The first two approaches follow mixing of two separate endmembers, terrestrial and marine, using a combination of stable carbon isotopic ratios and molecular markers. The third approach follows up to the first two by including a third component that is represented by mangroves. The three components are freshwater marsh, mangrove and marine that are represented by a specific molecular marker.

Approach 1:

Bulk Isotope Measurements:

Stable carbon isotope ratios were used to estimate the terrestrial organic matter contributions to the SRS sediments following the method of Shult and Calder (1976). The equation:

$$\% \text{ Terrestrial} = \frac{\delta^{13}\text{C}_{\text{sample}} - \delta^{13}\text{C}_{\text{marine}}}{\delta^{13}\text{C}_{\text{terrestrial}} - \delta^{13}\text{C}_{\text{marine}}} \times 100$$

where $\delta^{13}\text{C}_{\text{sample}}$, $\delta^{13}\text{C}_{\text{marine}}$ and $\delta^{13}\text{C}_{\text{terrestrial}}$ are respectively the isotope ratio of sample, isotope ratio of marine endmember and isotope ratio of terrestrial, endmember. $\delta^{13}\text{C}_{\text{marine}}$ is taken to be MH 7 and $\delta^{13}\text{C}_{\text{terrestrial}}$ is SRS 2 was used for this purpose. Simply inserting into the equation the variables the % terrestrial contribution at each site can be calculated. Table 1 shows the terrestrial ratios along the transect steadily decrease from SRS 2 (100%) to MH 7 (0%). The trend seen is to be expected of dilution of two endmembers with each other.

Approach 2:

Molecular markers:

n-alkanes are ubiquitous compounds in epicuticular waxes of plants with higher plants biosynthesizing higher molecular weight *n*-alkanes with a typical C_{max} between C_{29} and C_{31} (Eglington et al. 1969). Using this knowledge and assuming terrestrial contributions of organic matter will decrease with distance offshore, a regression can be used to estimate the terrestrial contribution to each site. Following the method of Prahl et al. (1994), table 1 shows the sum of C_{25} - C_{31} *n*-alkanes for each site and the corresponding % OC content. Figure 2 shows the scatter plot of the data and the corresponding regression value of .6164 that is a fair correlation, however, the non-zero fit of the line shows non-ideal behavior of the compounds.

The slope of the line can be used to constrain the quantitative relationship between the molecular markers and terrestrial organic carbon content of sediments along Shark River Estuary. Since the organic carbon along the transect is a mixture of terrestrial and marine sources, the terrestrial percentage of material is calculated by taking:

$$\% \text{ Terrestrial} = \frac{\Sigma C_{25}-C_{31}}{\text{slope of the line}} * 100$$

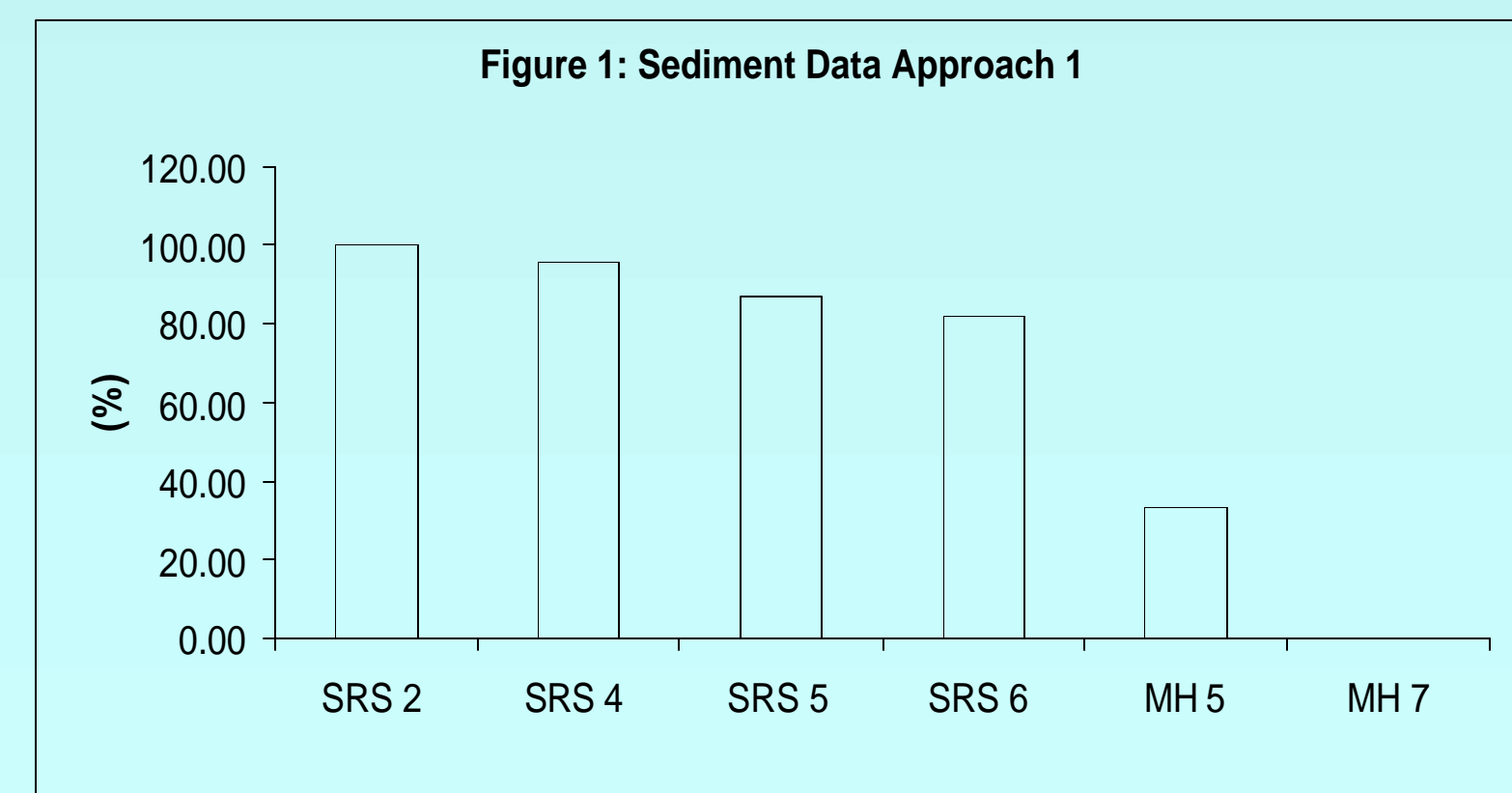
Table 1 shows the output of approach 2 and as can be seen, a steady decrease of terrestrial organic matter to the sediments moving seaward is seen.

Approach 3:

Specific Molecular Markers

Vegetation was analyzed from ENP to identify specific molecular markers for each. Molecular markers were identified for mangroves, periphyton and marine endmembers as can be seen in figure 4.

With this knowledge, a 3 way model was constructed based upon the concentrations of compounds found in sediments from SRS 2, 4-6 and offshore. As seen in Figure 3, SRS 2 had the highest concentration of freshwater marker, no marine markers and no mangrove markers. SRS 4 thru 6 showed a conservative mixing of freshwater marker and marine marker with the Freshwater marker decreasing moving offshore while the marine marker decreased moving inshore. There was a constant input of mangroves along SRS 4-6 with mangrove input absent at SRS 2 and the offshore sites.



Abstract

Organic matter plays a key role in estuarine dynamics and understanding the sources and mixing of this organic matter is key to the local and ultimately global carbon cycle. Many researchers have used bulk isotopes and molecular markers in simply two way mixing models to estimate organic matter sources. This is not always the case in environments as diverse as estuaries where more than two major organic matter sources exist.

In this work 3 approaches using bulk stable isotopes and molecular markers are compared to estimate organic matter sources to Shark River Slough, Everglades National Park. The first two approaches use simply two models to estimate terrestrial and marine organic matter while the third approach uses specific molecular markers for freshwater, mangrove and marine endmembers.

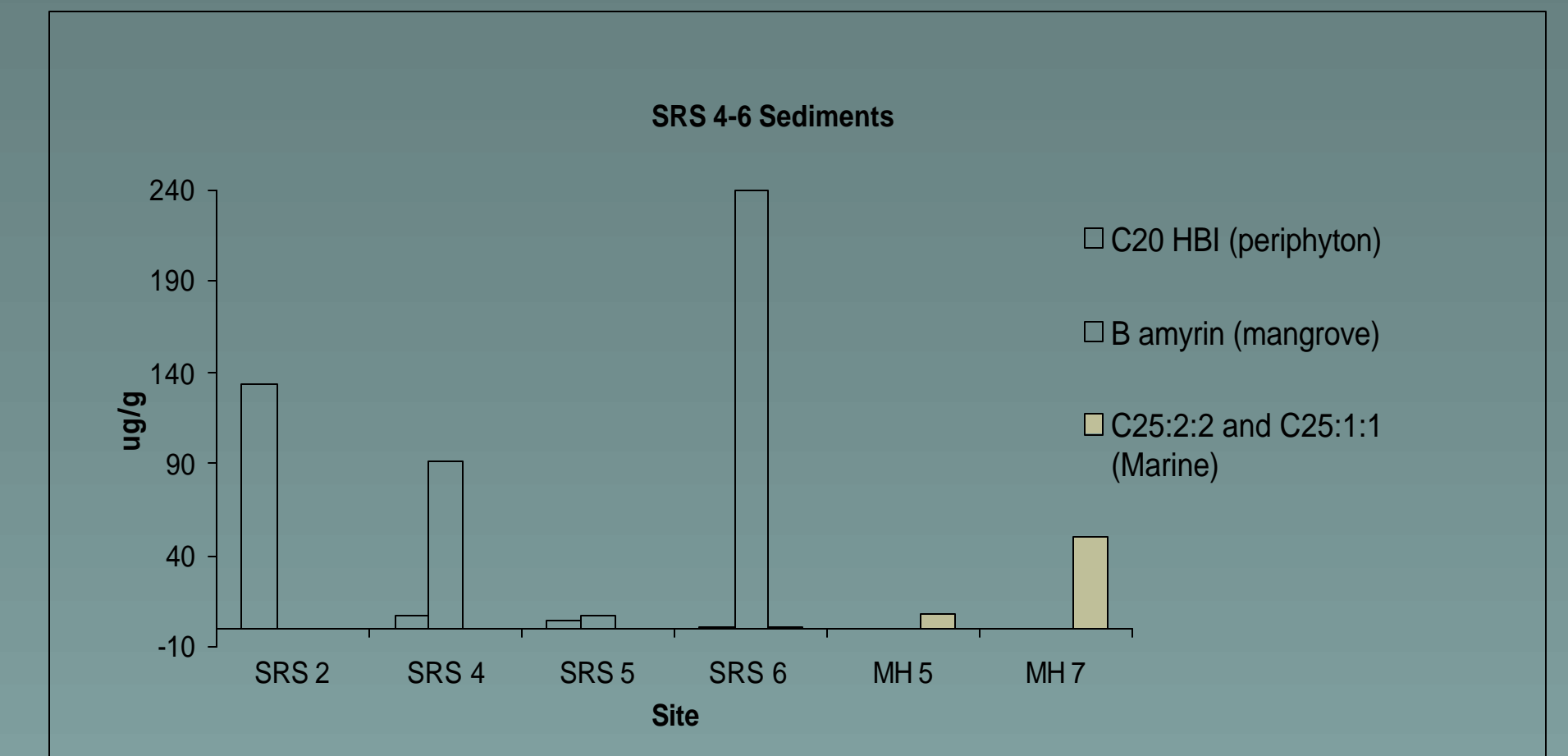
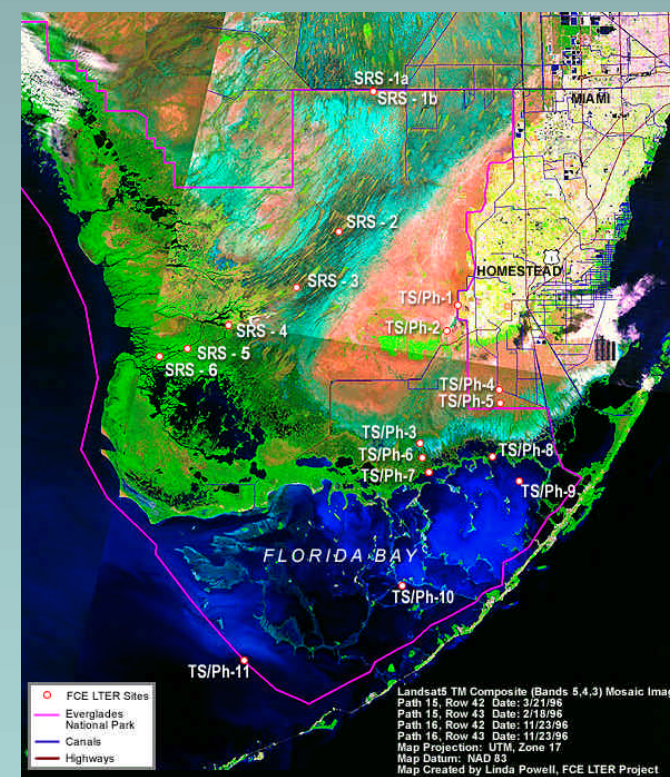
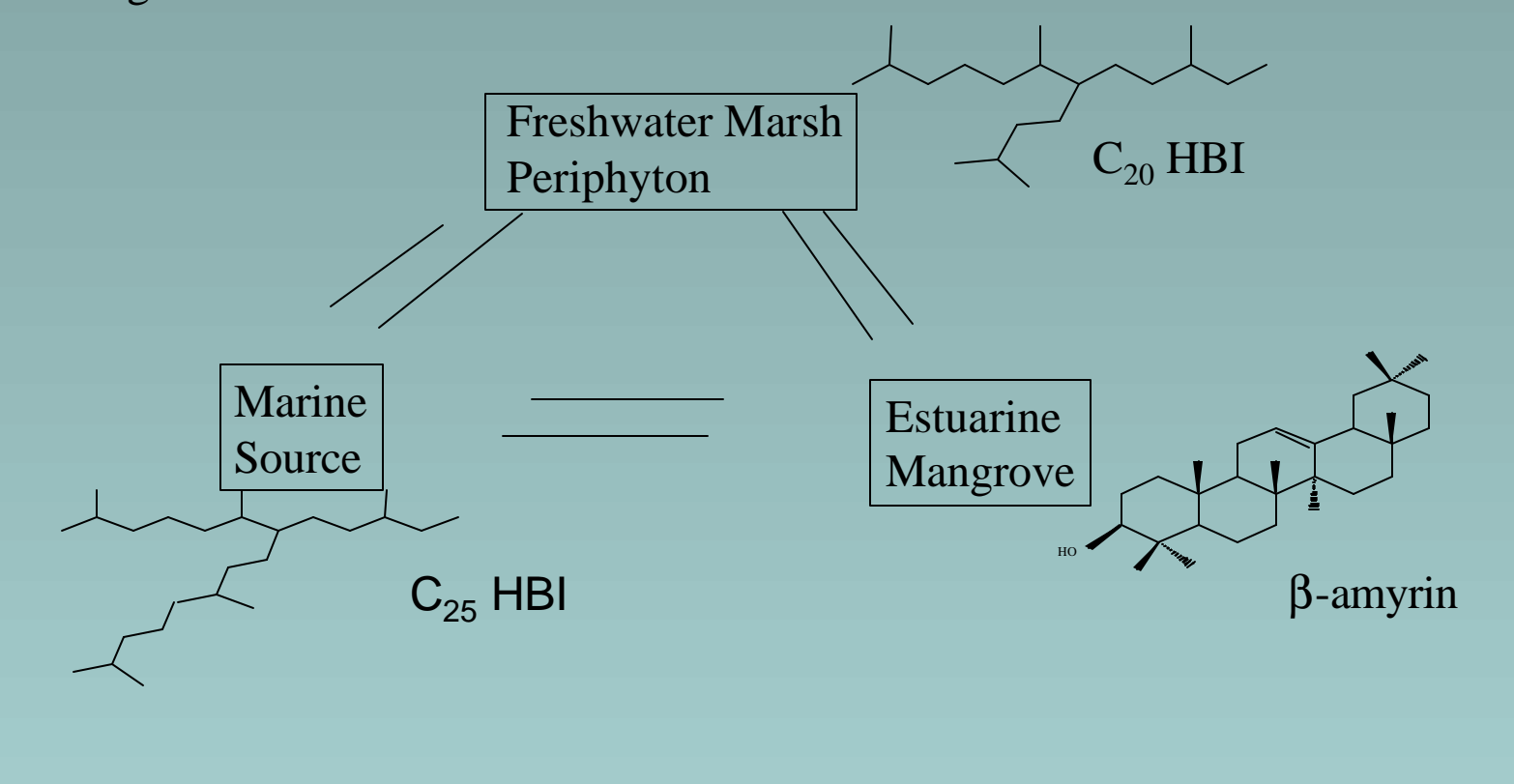


Figure 4:



Discussion:

All three approaches have tried to quantify mixing of 2 or 3 endmembers and have used a combination of isotopic, molecular marker and TOC values. Approach 1 and 2 are based upon a simple mixing of two endmembers, terrestrial and marine, while approach 3 uses absolute concentrations of specific molecular markers of vegetation from three endmembers, marine, mangrove and freshwater marsh.

Referring to table 1, the % terrestrial material calculated by methods 1 and 2 has a considerable different amount that could possibly be explained several ways. Approach 2 uses the assumption that higher molecular weight *n*-alkanes have only one endmember, however this is not the case. Vegetation analysis reveals mangroves have an *n*-alkane C_{max} 29 while sawgrass and spikerush have the same C_{max} . Therefore approach one calculations are possibly inflated due to shared sources. Approach 1 calculations rely heavily upon the values of each endmember plugged into the equation. Detailed endmember temporal and spatial variations must be understood to assign a meaningful value. In this study, and in others, no work was done to validate assigning an endmember with these considerations. Another problem with approach 1 has to do with mangrove leaves having a similar bulk $\delta^{13}\text{C}$ value (-27 to -32) compared with the freshwater marsh value of $\delta^{13}\text{C}$ -28.7. As with approach 2, mangrove contribution could have the potential to artificially inflate the % terrestrial calculation. A third potential problem with bulk isotopes is how microbial activity effects the isotope values as the material is transported through the estuary. Approach 3 is different from the 2 previous approaches due to the fact it takes into account mangrove input and a specific molecule represents each endmember. Approach 3 however, relies upon similar degradation rates of each compound and true specificity of each molecule.

Conclusion:

1) The percentage of terrestrial organic matter using approaches 1 and 2 were very different but a general trend of dilution was seen.

2) A simple two endmember approach of tracing terrestrial organic matter in mangrove estuaries is not enough due to mangrove organic matter input that can artificially increase the apparent terrestrial organic matter contributions.

3) A third endmember was recognized, mangrove, which had to be accounted for by using specific molecular markers for mangrove, periphyton and marine sources. The three compounds were used to plot absolute concentrations of each along the transect.

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Site	% OC	$\delta^{13}\text{C}$	$\Sigma C_{25}-C_{31}$ (ug/g)	β -Amyryn (ug/g)	C_{20} HBI (ug/g)	$\Sigma C_{25:2:2}$ and $C_{25:1:1}$ HBI (ug/g)	Approach 1 %Terrestrial Material	Approach 2 %Terrestrial Material
SRS 2	31.09	-28.7	16.49	0	133.68	0	56.11	100.00
SRS 4	27.78	-28.3	9.08	91.17	7.46	0.17717	30.89	95.70
SRS 5	15.72	-27.5	3.17	6.72	4.39	0.11575	10.80	87.10
SRS 6	8.15	-27	1.42	239.96	0.94	1.24	4.83	81.72
MH 5	1.01	-22.5	1.00	0.00	0.00	8.00	3.74	33.33
MH 7	0.99	-19.4	0.0943	0.00	0.00	50.25	0.32	0.00

