Characterization of particulate, dissolved, and black carbon exports from the Shark River Estuary

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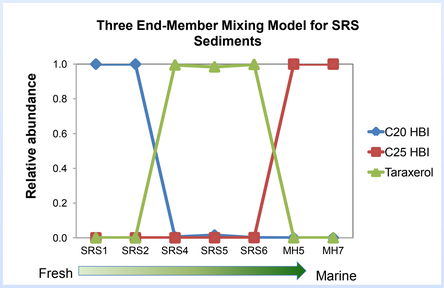
ABSTRACT:

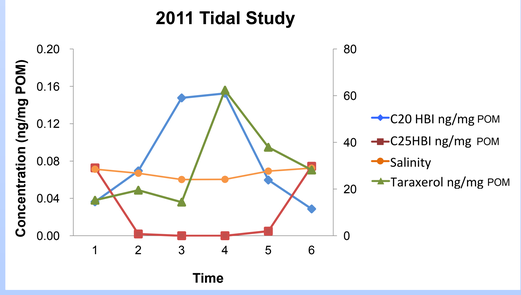
In order to evaluate carbon export from the Shark River Slough dissolved organic matter (DOM) concentration, $\delta^{13}C$ values, optical properties and black carbon concentrations were analyzed in conjunction with measurements of freshwater, estuarine, and marine biomarkers in particulate organic matter (POM) along a transect from the freshwater Tarpon Bay to the saline Gulf. The DOM concentration in the Shark River estuary shows net non-conservative behavior with additional inputs, possibly being mangrove-derived. Fluorescence data, however, showed that individual components of the DOM pool behave differently. Terrestrial humic-like components, similar to net DOC, showed non-conservative mixing due to mangrove inputs. An Everglades freshwater-derived component, C2, associated with soil inputs from the Northern Everglades behaved conservatively. In contrast, protein-like component, C7, behaved conservatively until reaching the mid-salinity range where its behavior changed to non-conservative due to degradation and loss. Dissolved black carbon, derived from wildfires in the freshwater Everglades exhibited conservative mixing behavior suggesting it is refractory. The $\delta^{13}C$ values of DIC and DOC show a non-conservative mixing pattern, confirming the mangrove DOC inputs in the estuary, and a significant degree of respired mangrove OM in the DIC pool. Source specific molecular markers, namely the C_{20} HBIs (highly branched isoprenoids), C_{25} HBIs and taraxerol, were used to trace the POM sources along Shark River transect from freshwater marsh (especially periphyton), coastal marine (mainly diatoms) and estuarine (mangroves dominated) environments, respectively. A novel three-end-member mixing model including the terrestrial end-member, the estuarine and the marine end-member contributions has been validated to assess the general organic matter dynamics and hydrologic processes that control the OM dynamics within this Shark River Estuary system. Interestingly, the incoming tide may be a major factor in the resuspension of mangrove-derived POM as well as a controlling factor for DOC mobilization. All in all, DOM, POM and black carbon studies combined to provide comprehensive information about organic matter sources as well as hydrologic transport dynamics of organic matter in the Shark River Estuary system, a typical subtropical estuary, and can be used in the creation of preliminary organic carbon budgets to assess changing organic matter dynamics with both natural and anthropogenic ecosystem change.

RESULTS AND DISCUSSION:

Particulate organic matter (Biomarkers approach)

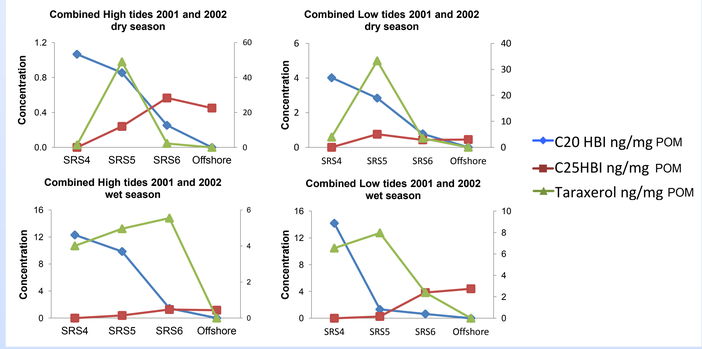


- Main source of C_{20} HBIs in the Everglades is freshwater periphyton.
- C_{25} HBIs are mainly produced by marine diatoms.
- Taraxerol, a type of triterpenoid, is a molecular marker for mangroves, representing estuarine organic matter inputs.
- Here, we show a three-end-member model established based on the concentration of each biomarker in sediments along the salinity transect, with freshwater (C_{20} HBI) OM high near SRS 1 and 2, estuarine OM (taraxerol) high in the mid-estuary, and marine OM (C_{25} HBI) dominating at high salinities.

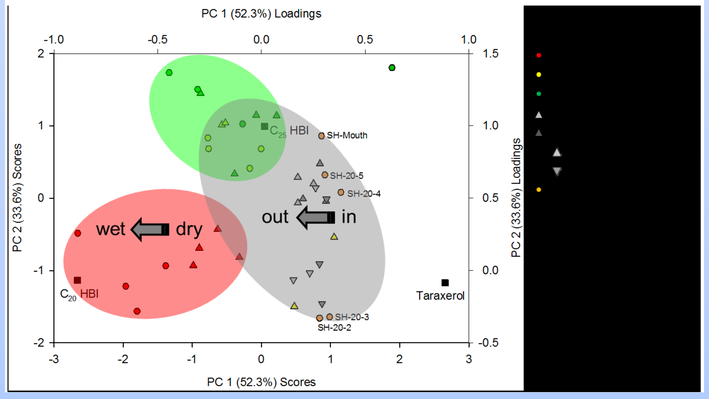


*Note: Salinity and taraxerol are plotted on the secondary axis of ordinates (right side); The units for taraxerol are ng/mg POM.

- For water column POM at SRS-5 during a tidal cycle, we see similar results to the 3-end member mixing model above.
- At the lowest salinities, C_{20} HBI concentrations peak, while C_{25} HBI concentrations are highest at the highest salinities (marine inputs).
- The taraxerol concentration was highest with the end of the outgoing tide and the start of the incoming tide, suggesting the incoming tide may be causing resuspension of organic matter.



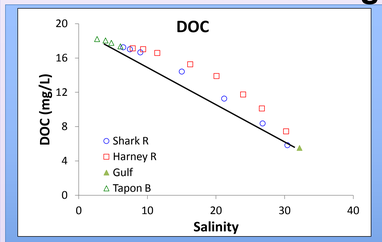
- Water column POM during wet and dry seasons also follows the proposed 3-end member mixing model, with highest concentrations of marine OM (C_{25} HBIs) at offshore sites, and highest concentrations of terrestrial OM (C_{20} HBIs) at lower salinities.
- Estuarine inputs, represented by the taraxerol concentration, typically peak at SRS-5, but may shift up or down estuary due to annual or seasonal variability.

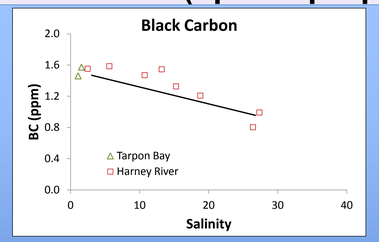


•Principal components analysis of log transformed concentrations of C_{20} HBI, taraxerol, and C_{25} HBI in POM from Shark River. Wet season samples represented by circles, dry season samples as triangles.

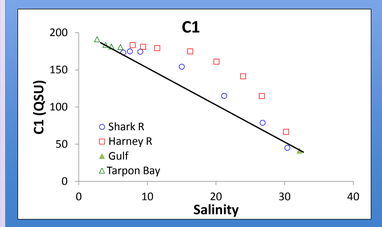
•The variability among the samples seems to be mainly controlled by OM sources, tide and season type. Samples from different locations (SRS4-SRS6) were clearly separated based on these three biomarkers. Incoming tide effect mimics the dry season.

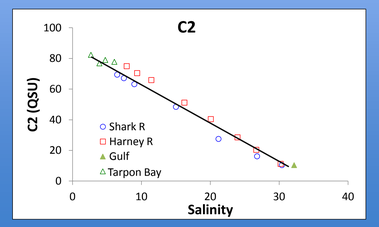
Dissolved organic matter (optical properties & stable isotopes)

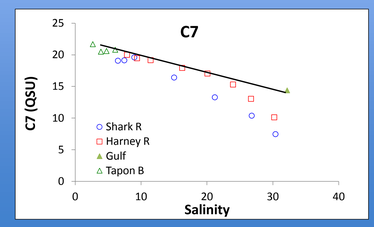




- Dissolved organic carbon (DOC) concentration is not conservative, with a DOC source, potentially mangroves (see isotope data below).
- Black carbon, derived from biomass burning in the freshwater FCE, shows conservative mixing behavior, suggesting its potential application as a freshwater Everglades conservative tracer.
- PARAFAC component C1, an indicator of humic DOM, shows non-conservative behavior similar to DOC => mangrove source!.
- PARAFAC component C2, which is EAA soil derived, is conservatively transported in the rivers from an upstream source.
- PARAFAC component C7, which is protein-like, shows non-conservative behavior and is reactive in the rivers at salinities where higher TP levels are expected.

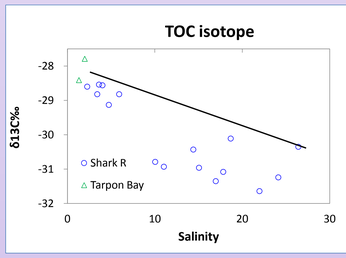


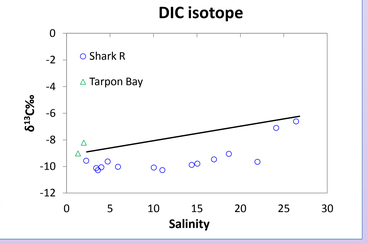




CONCLUSIONS:

- The three-end-member mixing model was constructed and confirmed for POM studies along SRS. The model reflects seasonal and tidal effects on POM dynamics. The incoming tide may be the major force of mangrove POM release.
- The DOC profiles and δ13C values for DOC and DIC show that there are net inputs to the DOM pool (from mangroves) in SRS that are exported to the Gulf as DOC and/or lost from the system through CO2 evasion.
- Optical properties show that different DOM components behave differently based on source and reactivity, with some being generated in the estuary (C1), conservatively transported throughout the estuary (black carbon and EAA soil derived organic matter), or being partially removed (protein-like organic matter) prior to discharge into the Gulf.
- Calibrations for these OM dynamics models will be used to assess C-losses in the system.





- The $\delta^{13}C$ values for DIC and DOC show non-conservative mixing patterns along a Shark River transect
- The $\delta^{13}C$ of DOC shows the most depleted values in the mid-salinity zone confirming OM inputs from adjacent mangroves, (C3 plants) which are expected to be more depleted compared to freshwater and marine OM sources .
- The $\delta^{13}C$ values for DIC confirm an important degree of respiration of mangrove-derived OM in the system.
- The dynamics and transportation of DOM showing by isotope well agree with the optical measurement.

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REFERENCES:

Jaffé, R., R. Mead, M. E. Hernandez, M. C. Peralba,O. A. DiGuida, 2001. Origin and transport of sedimentary organic matter in two subtropical estuaries: a comparative, biomarker-based study, Organic Geochemistry, Volume 32, pp. 507-526.

Mead, R., Xu, Y., Chong, J., Jaffé, R., 2005. Sediment and soil organic matter source assessment as revealed by the molecular distribution and carbon isotopic composition of n-alkanes. Organic Geochemistry 36, 363-370.

Xu Y. Mead R.N. and Jaffé R. (2006). A molecular marker-based assessment of sedimentary organic matter sources and distributions in Florida Bay. Hydrobiologia. 569: 179-192.

Xu Y., Wachnicka A., Gaiser E.E. and Jaffé R. (2006). Occurrence of C25 highly branched isoprenoids in Florida Bay: Paleoenvironmental indicators of diatomderived organic matter inputs. Organic Geochemistry 37:847-859.