Molecular Characterization of Dissolved Organic Matter(DOM) at Florida LTER Sites

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Abstract

Dissolved organic matter (DOM) is a large contributor to the pool of organic matter in coastal waters and thus plays an important role in the global carbon cycle. In order to better understand the global carbon cycle, significant research efforts have been placed to characterizing the sources and fate of DOM in the Florida Coastal Everglades. A variety of methods have been developed for this purpose. DOM bulk characterization can be performed by optical methods such as UV-vis and Fluorescence spectroscopy. More detailed structural information can be obtained using more labor-intensive methods, such as py-GC/MS, ^{13}C-NMR and FTIR. The former methods are faster, present less contamination problems and are more economical for long term water quality monitoring. The later are more helpful in obtaining molecular information about DOM, and to determine the origin and fate of organic matter. In this study, preliminary results of fluorescence analysis and examples of more detailed structural determinations of DOM are shown.

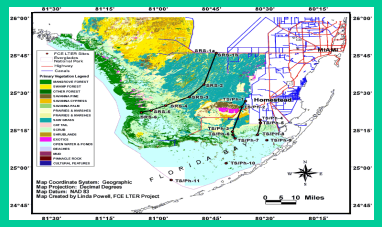


Fig. 1 LTER sampling sites SRS 1a - 6 and TS/PH 1 - 3, 6 - 7, 9 - 11

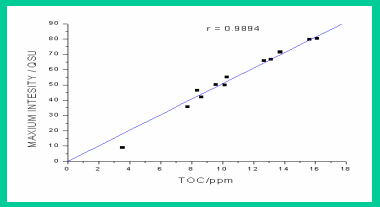


Fig. 2 Max intensity of fluorescence emission at Exitation 313 nm *vs* TOC. Max Intensity at Ex. 313 nm correlates very well with TOC at Shark Slough sites.

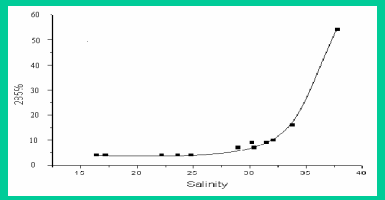


Fig. 3 Relative abundance of the synchronous fluorescence spectrum band at 285 nm *vs* Salinity.

Our data suggests that this peak corresponds to protein-like material, while those at 350nm, 385nm and 460nm correspond to humic substances . The 285%, or protein like material, increases with the salinity, suggesting a marine source of 'fresh' DOM and not simply a dilution of Everglades-derived DOM in coastal waters.

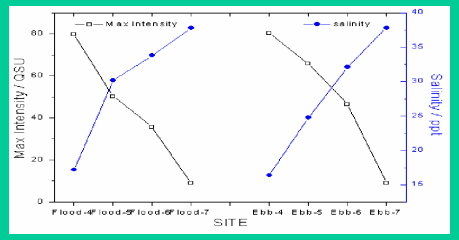


Fig 4. Max fluorescence intensity and salinity *vs* transect sampling sites in the Shark River (SRS4 to 6) tidal study. In flood and ebb tide, max intensity decreases with the salinity, suggesting that most DOM is derived . The max intensity changes due to dilution effect.

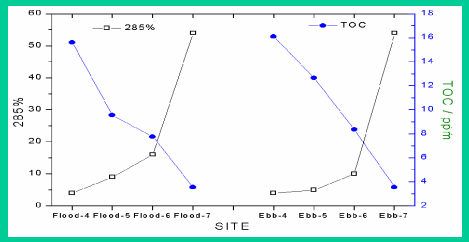
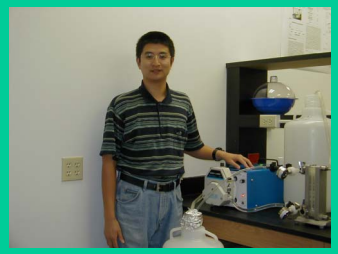


Fig. 5 285% and TOC *vs* transect sites

As though a large part of DOM is from terrestrial environment, protein-like material is mainly from marine. It suggest there is a obvious mixing effect on the composition of DOM in the Shark Slough, not merely due to dilution.



Isolation and Analysis of DOM

1. 25L of water were collected at 14 LTER sites, poisoned with NaN_3 and store on ice.
2. Samples were filter through GF/F, followed by ultrafiltration using two 1,000 Dalton membranes (see above) and concentrated to 100 mL.
3. The concentrate was desalinized with DD water if needed.
4. The concentrate was frozen, freeze dried, and then ready for analyses such as py-GC/MS, FT-IR, & ^{13}C-NMR.

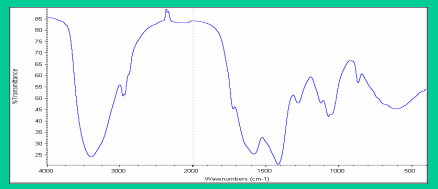


Fig. 6 FT-IR Spectrum of TS/PH 3

Peaks: 3440 cm^{-1} non- and bonded OH groups
2920 and 2800 cm^{-1} aliphatic groups
1630 cm^{-1} aromatic C=C and COO^- groups
1420 cm^{-1} COO^-, O-H and C-O groups

Acknowledgement

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References

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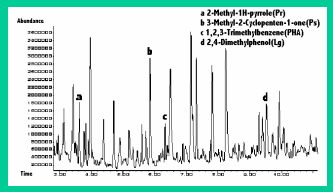

Fig. 8 Py-GC/MS chromatogram of TS/PH 3

Example of a pyrolysis-GC/MS run of a DOM sample. The freeze-dried DOM is pyrolyzed on-line for 20 seconds at 800 °C followed by GC/MS analysis. The pyrolysis products can be traced back to their origin such as Polysaccharides(Ps), Proteins(Pr), Lignins(Lg), and Polyhydroxy aromatics(PHA) from the original DOM. Some examples are indicated.

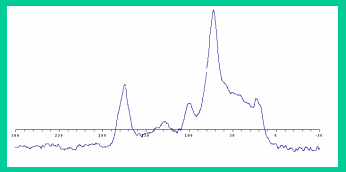

Fig.7 ^{13}C NMR Spectrum of TS/PH 3

For structural information, four broad-bands can be obtained. The integration of these will allow to obtain a relative abundance of functional groups from the DOM sample. These bands are:

0 - 45 ppm Alkyl Carbon
45 – 110 ppm O-alkyl Carbon
110 – 160 ppm Aromatic Carbon
160 – 200 ppm Carbonyl Carbon

Conclusion

1. The synchronous fluorescence method is very fast and sensitive. It can be widely applied for water quality monitoring.

2. Synchronous fluorescence data clearly indicates a mixing effect of Everglades-derived DOM with marine-derived DOM, and not merely dilution effect.

3. DOM isolated from water through ultrafiltration and freeze-drying can be analyzed by other techniques for more detailed research on the molecular composition and diangenesis of DOM .

4. All these analyses are being performed on DOM samples from the SRS and TSPH transects.