

# Optical and Geochemical Tracers of Terrestrial DOM in the Coastal Ocean

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**ABSTRACT:** Terrestrial inputs of DOM to the coastal ocean are important features of the marine carbon cycle. The optical and chemical properties of terrestrial DOM are related, but bulk properties are difficult to resolve. However, molecular chemical information, such as the stable isotope values of DOM and the quantity of biomarkers such as dissolved lignin, are more specific to DOM sources and that information might better correspond to optical measurements such as ultraviolet-visible absorption and fluorescence. Recent advances in stable isotope analyses and statistical data processing offer the possibility for high-resolution studies that might better resolve these measurements. Here, results from the Gulf of Mexico and from the Baltic Sea show the relationships between DOM stable isotope values, dissolved lignin, and absorption and fluorescence. The goal is to develop models based on high resolution empirical observations to fine-tune optical measurements of terrestrial DOM in coastal waters.



FIGURE 1a: Location of the Baltic Sea-North Sea mixing zone. Red squares indicate the study site.

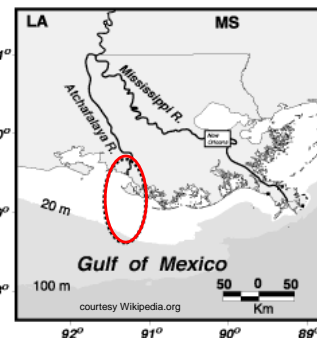


FIGURE 1b: Location of the study site for the Gulf of Mexico data. Red oval indicates the primary sampling site.

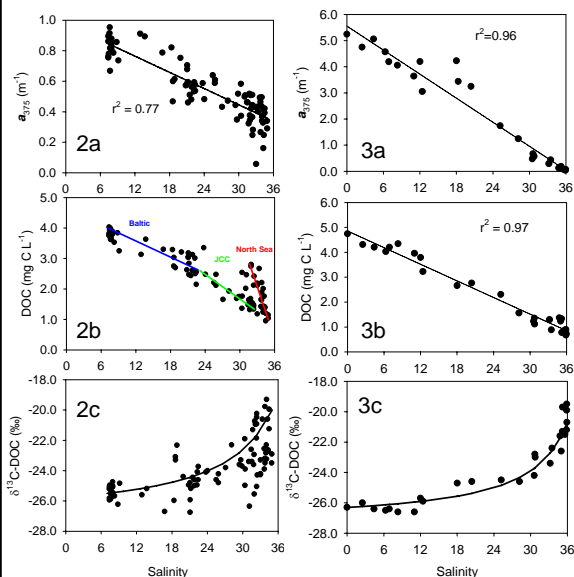
**STUDY SITE AND METHODS:** For the Gulf of Mexico, samples were collected aboard the R/V *Pelican*, near the Atchafalaya River, 07-10 May 2007. For the Baltic Sea, samples were collected aboard the R/V *Gunnar Thorsen* on three research cruises (GT237, GT238, and GT239) conducted from August to October 2006.

All samples were filtered directly from Niskin bottles through 0.7  $\mu\text{m}$  GF/F filters into cleaned glassware. DOC samples were immediately acidified to pH 2-3 with 85%  $\text{H}_3\text{PO}_4$ . CDOM samples were filtered into amber bottles and kept at 4  $^\circ\text{C}$  until absorption and fluorescence were measured on Varian Cary 300 and Eclipse instruments, respectively, using standard methods. For the Gulf of Mexico samples, Shimadzu UV-1601 and RF-5301 instruments were used. Dissolved organic carbon (DOC) concentration and carbon stable isotope ( $\delta^{13}\text{C}$ -DOC) values were measured according to Osburn and St-Jean (2007). Dissolved lignin was measured by microwave-assisted  $\text{CuO}$  oxidation of lignin into phenolic subunits (Montgomery and Goni, 2000) which were then quantified by GC-MS as trimethylsilyl (TMS) derivatives (Louchouart et al., 2000).

## RESULTS AND DISCUSSION

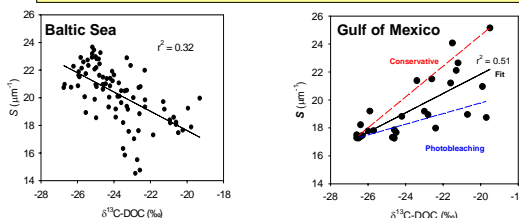
How conservative are DOM properties in coastal waters?

- Baltic Sea:** CDOM roughly conservative; DOC mixing with salinity could be represented with three sources: Baltic outflow, Jutland Coastal Current [JCC], and North Sea (Figs. 2a-2c)
- Gulf of Mexico:** CDOM conservative (Figs. 3a-3c)

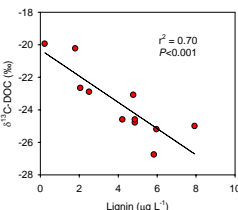


How well do optics and chemistry match up?

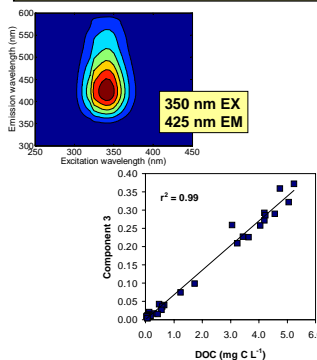
Spectral slope (S) was not well correlated to  $\delta^{13}\text{C}$ -DOC in the Baltic Sea, yet better correlated in the Gulf of Mexico. Possible addition of non-terrestrial CDOM or in-situ alteration (photobleaching)



Strong relationship between lignin and  $\delta^{13}\text{C}$ -DOC in Baltic Sea indicative of terrestrial input

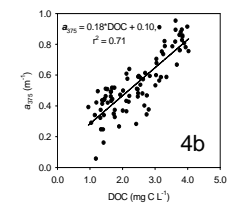
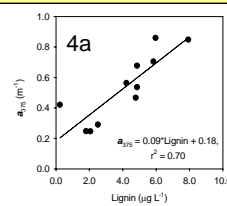


Component 3 of 5 from a PARAFAC model of EEM fluorescence in the Gulf of Mexico correlated well with DOC

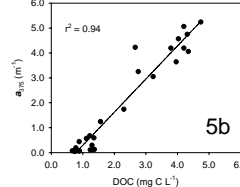
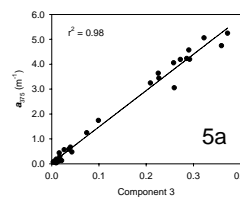


How good are the models?

**Baltic Sea:** CDOM at 375 nm had a higher correlation to lignin (Fig. 4a) than to DOC concentration (Fig. 4b)



**Gulf of Mexico:** CDOM at 375 nm was strongly correlated to Component 3 (5a) and to DOC (5b)



## SUMMARY AND FINDINGS

- Deviations from linear mixing of DOC properties with salinity likely resolved by three-component mixing models or allowances for production/degradation (e.g. photobleaching)
- Addition of DOC and CDOM obscure qualitative relationships between S and DOC stable isotope composition, requiring multi-component mixing.
- CDOM optics relate well to DOC chemistry and may be scaled to remote sensing wavebands, but regional models/algorithms are probably required due to nonconservative processes.

## References

- Louchouart, P., S. Opsahl, and R. Benner (2000). Isolation and Quantification of Dissolved Lignin from Natural Waters Using Solid-Phase Extraction and GC/MS. *Analytical Chemistry*, 72: 2780-2787.
- Goni, M.A. and S. Montgomery (2000). Alkaline  $\text{CuO}$  Oxidation with a Microwave Digestion System: Lignin Analyses of Geochemical Samples. *Analytical Chemistry*, 72: 3116-3121.
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