Chemical Analysis of CDOM Sources in Danish Coastal Waters of the Baltic Sea-North Sea Mixing Zone

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LONG-TERM GOALS

The long term goal is to improve the Navy's prediction of the distribution of chromophoric dissolved organic matter (CDOM) in the littoral battlespace through measurement of its specific chemical properties. In the larger context of water mass mixing, the long term goal is to model the distribution of CDOM inputs from multiple sources. The study site is the Kattegat and Belt Sea at the entrance to Baltic Sea, however the approach was designed for implementation is other regions of Navy interest.

OBJECTIVES

The objective of this project is to provide the means to chemically validate the multiple sources of CDOM in a complex mixing environment through advanced chemical measurements of CDOM.

APPROACH

The field work of this project was carried out in the Baltic Sea-North Sea mixing zone at the entrance to the Baltic Sea. The Baltic Sea is a large fjord greatly influenced by freshwater inflow from its large drainage basin and having a limited exchange with the North Sea (Atlantic Ocean). As a result its waters have a high content of terrestrially derived organic material. Danish marine monitoring cruises with R/V *Gunnar Thorson* were used as a sampling platform for the project. The cruises covered 26 stations (Fig. 1). Samples were taken for optical and chemical measurements of CDOM. Data for other water constituents and properties were made available from the monitoring program (temperature, salinity, chlorophyll, nutrient concentrations). At ~90% of the monitoring stations, samples for dissolved organic carbon (DOC) concentration and stable isotope value (δ^{13}C-DOC) were taken.

In Figure 1, the red squares indicate stations where dissolved lignin was measured on select surface and bottom water samples at stations 444, 905, 925, and 1001, following solid phase extraction onto C_{18} resins (Louchouarn et al. 2001). The spatial distribution meant to capture the flow of terrestrial DOM out from the Baltic Sea through the Danish straits to the mixing zone. The measurement of lignin served as an additional check on the δ^{13}C-DOC values, in which phytoplankton signals may overlap with terrestrial signals.

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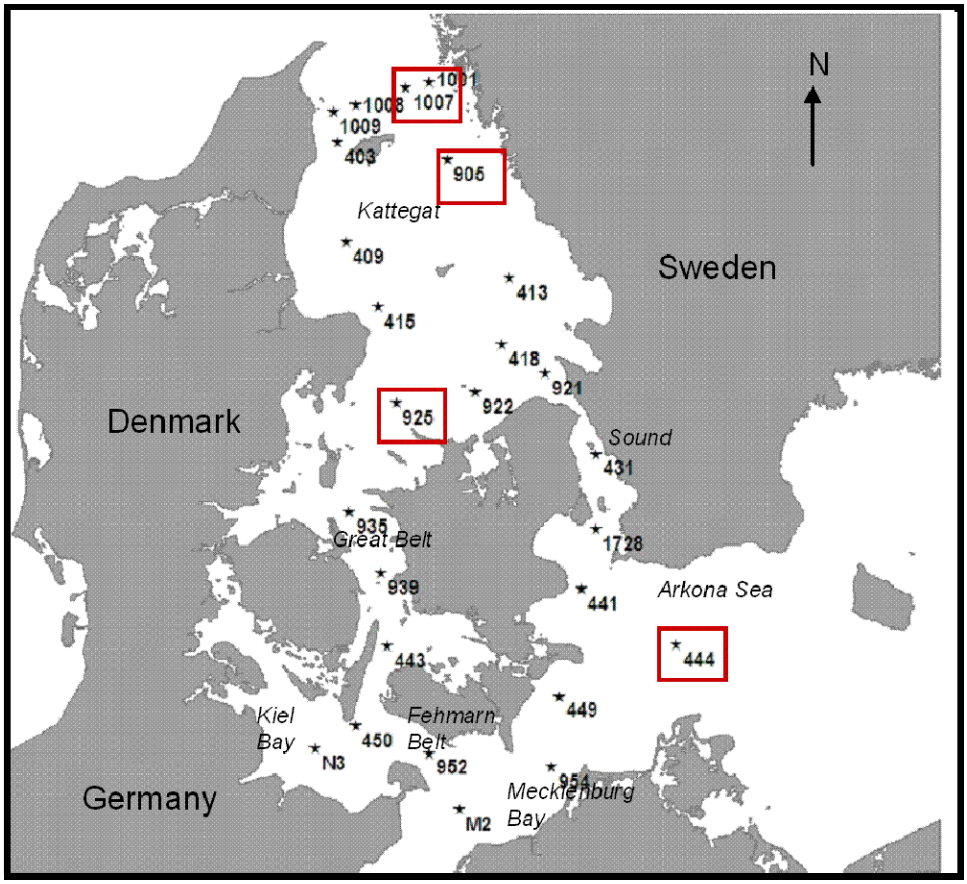

Figure 1: Map of study region with red squares indicating focus of chemical characterization.

WORK COMPLETED

All DOC concentration and stable carbon isotope measurements have been completed. All measurements of dissolved lignin have been completed. Data synthesis and analysis is 80% completed. Due to the intensive nature of the lignin characterization this was only carried out on a sub set of samples. Preliminary results from the project were presented at the ASLO/AGU Ocean Sciences meeting in Orlando, 2008. Manuscript preparation is 25% completed.

RESULTS

The DOC concentration and δ^{13}C-DOC values were non-linear trends with salinity, whereas lignin concentration decreased linearly with salinity (Figs 2A-2C). When a three component model was used, DOC concentration was easily attributable to three sources, the relative proportion of each determined by mixing. For δ^{13}C-DOC values, clear deviations from a two end-member mixing model were apparent, yet δ^{13}C-DOC was well-correlated to lignin concentration. It thus appears that terrestrial DOC is a dominant feature of the North Sea-Baltic Sea mixing zone, but that multiple sources of DOC can confound otherwise straightforward properties.

Dissolved lignin properties show a distinct trend with dissolved lignin concentration (Figure 3). The S/V ratio is the relative proportion of syringyl to vanillyl phenols, where as the [ad/al]v ratio is the

relative proportion of acid moieties to aldehyde moieties in the vanillyl group. Both ratios decreased with increasing lignin concentration, likely reflecting the mixing of North Sea water with Baltic Sea water.

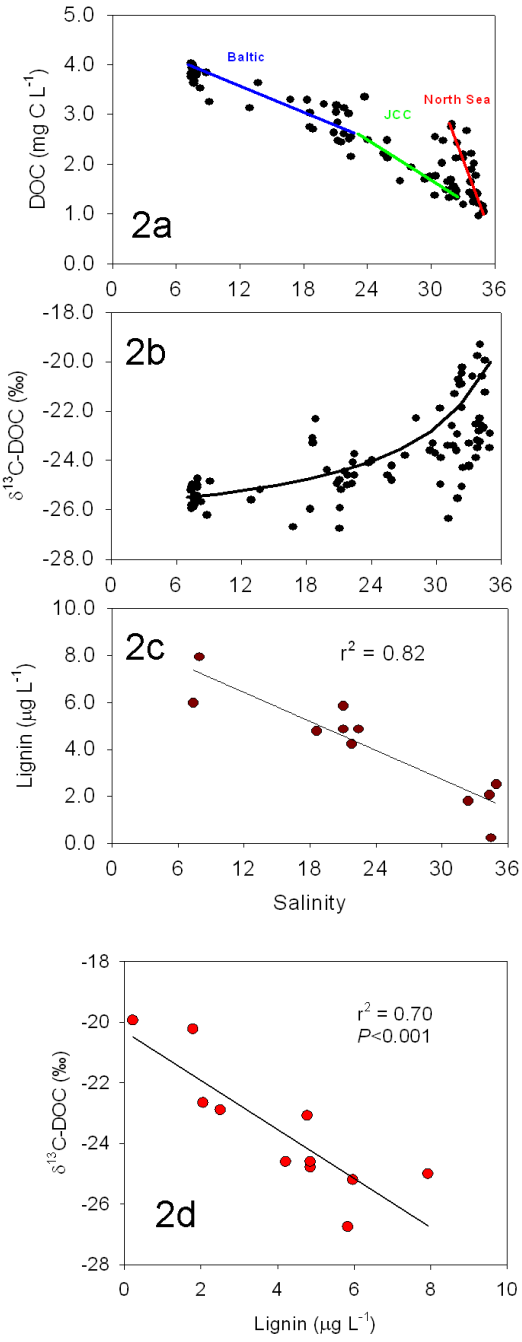

Figure 2: Change in CDOM chemical properties for the North Sea-Baltic Sea mixing zone of Danish coastal waters. DOC concentration was conservative with salinity when a 3-source mixing zone was employed (A). The stable isotope values for DOC (δ^{13}C-DOC) showed deviations from a mixing model based solely on terrestrial (-26‰) and marine (-20‰) sources (B). Lignin, however, decreased linearly (C) and was strongly related to δ^{13}C-DOC values (D).

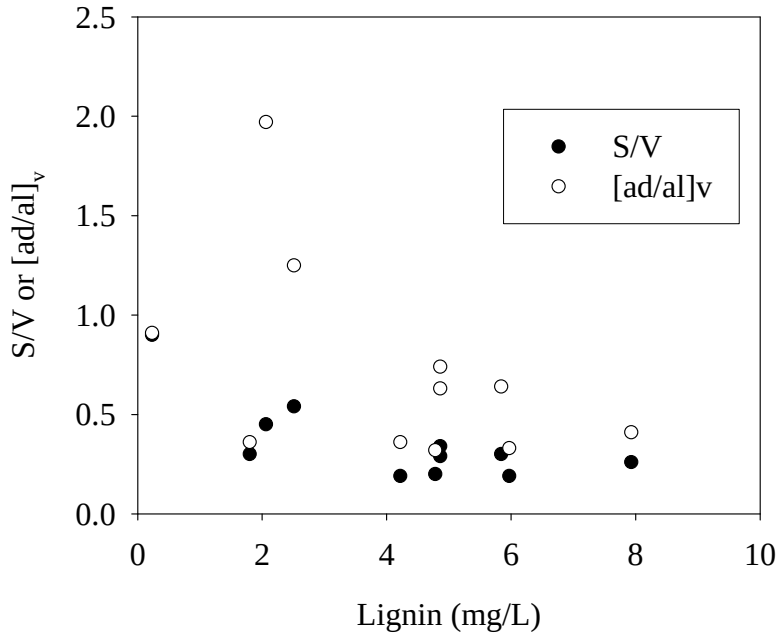

Figure 3: Change in lignin properties as a function of lignin concentration.

IMPACT/APPLICATIONS

With a more clear understanding of how the chemistry of CDOM behaves with salinity, and the realization of multiple CDOM inputs, estimates of CDOM optical properties can be used to understand water mass mixing. The distribution of CDOM in this region is complicated by a possible autochthonous input that is likely due to microbial generation of DOM from phytoplankton biomass. Hence, traditional optical algorithms derived for river-dominated margins will not likely operate in complex coastal environments such as those found in Danish coastal waters. Further algorithm development should isolate spectral changes occurring in CDOM due to changes in CDOM source, only validated through simultaneous description of CDOM chemistry using the techniques we have used here.

RELATED PROJECTS

"Quantitative and Qualitative Prediction of Light Absorption by Colored Dissolved Organic Matter in the Coastal Zone," PI Dr. Colin Stedmon, ONR Award N000140610357

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Osburn, C. L. and G. St-Jean (2007). The use of wet chemical oxidation with high-amplification isotope ratio mass spectrometry (WCO-IRMS) to measure stable isotope values of dissolved organic carbon in seawater. Limnology & Oceanography: Methods 5:296-308

PUBLICATIONS

Osburn, C. L.; Stedmon, C. A.: Resolving optical and chemical measurements of terrestrial DOM flux in the North Sea-Baltic Sea mixing zone. ASLO/AGU Ocean Sciences Meeting 2008, Orlando, Florida, USA. (Poster presentation).

Osburn, C. L.: Spectral light absorption by CDOM in the North Sea-Baltic Sea mixing zone: Modeling seasonality and dependency on water mass mixing. OCB Scoping Workshop on Carbon Cycling in the Gulf of Mexico, May 2008, St. Petersburg, Florida, USA. (Oral presentation)