Available online at www.sciencedirect.com

SCIENCE DIRECT®

Marine Chemistry 101 (2006) 95 – 103

MARINE CHEMISTRY

www.elsevier.com/locate/marchem

# Fluorescence variability of marine and terrestrial colloids: Examining size fractions of chromophoric dissolved organic matter in the Damariscotta River estuary

Jennifer Boehme [a,*], Mark Wells [b]

[a] *University of Maine, Darling Marine Center, 193 Clarks Cove Road, Walpole, ME 0457, USA*
[b] *201 Libby Hall, University of Maine, Orono, ME 04469-5741, USA*

Received 24 August 2005; received in revised form 20 January 2006; accepted 1 February 2006
Available online 17 April 2006

---

## Abstract

Marine chromophoric dissolved organic matter (CDOM) imparts highly variable optical signatures in surface waters over short spatial and temporal scales, but the cause of that variability is poorly understood. A major fraction of dissolved organic matter in seawater is colloidal in size and can cycle quite rapidly, potentially contributing to the observed variability in CDOM. The relationship between marine colloids and CDOM optical variability was examined using flow field-flow fractionation (FlFFF) to partition the colloidal organic phase into a continuum of molecular sizes for optical characterization by excitation emission matrix spectroscopy (EEMS). Colloidal organic matter in surface seawater of the Damariscotta River estuary showed 2 major peaks in apparent abundance, spanning at ~1–5 kDa and ~15–150 kDa in size, respectively. The relative magnitude of these peaks changed systematically with the phase of phytoplankton blooms during 2003 and 2004, implying a relationship between colloid size distribution and bloom dynamics. Of the two colloidal sizes, the 1–5 kDa fraction was far more variable in apparent abundance than the larger colloidal matter. EEMS results reveal a compositional partitioning of protein-like and humic-like fluorescence between size fractions. Protein-like materials occurred primarily in the smallest colloid size fraction while humic-type materials resided mainly in the larger colloidal phase. These findings suggest that the fluorescence signature of bulk dissolved organic matter results from a collage of chromophores having optical characteristics that differ according to size of the molecular constituents. The colloidal-sized fluorescence characteristics of marine derived CDOM were contrasted with bulk CDOM to provide fundamental information on the distribution and forms of CDOM in Maine coastal waters. The findings here indicate that colloidal processes will have significant effects on the character and variability in the optical signature of surface seawaters.

*Keywords:* Chromophoric dissolved organic matter; Flourescence; Colloids; Flow field-flow fractionation; EEMs

---

## 1. Introduction

Chromophoric dissolved organic material (CDOM) represents a major fraction of dissolved organic matter (DOM) in seawater, and it can significantly hinder attempts to remotely sense chlorophyll in coastal waters. CDOM does not vary consistently with dissolved organic carbon (Nelson and Siegel, 2002), indicating that the chromophoric composition of DOM is not constant. The spatial and temporal variability in CDOM optical properties presumably reflects the balance between its production, transformation and removal

---

* Corresponding author.
*E-mail addresses:* jboehme@maine.edu (J. Boehme), mlwells@maine.edu (M. Wells).

0304-4203/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.marchem.2006.02.001

from surface waters. Production of new dissolved material and its subsequent modification likely involves both biological and physical processes, including production and transformations by bacteria and algae, degradation due to photobleaching, and changing composition due to physical mixing and aggregation. Changes in CDOM composition associated with these processes will be superimposed over regional variations in the chemical composition of CDOM, particularly in nearshore waters where inputs of terrestrial humic substances can be significant.

The natural fluorescence properties of CDOM have been used to distinguish water masses in the marine environment (Baker and Spencer, 2004; Cabaniss and Schuman, 1987; Chen and Bada, 1992; Coble, 1996; Zika et al., 1993) and characterize CDOM in both the water column and sediment porewaters (Benamou et al., 1994; Burdige et al., 2004; Chen and Bada, 1994; Coble, 1996; Coble et al., 1998; De Souza Sierra et al., 1994). Excitation emission matrix spectroscopy (EEMS) is particularly well suited to analyze a mixture of fluorophores such as CDOM in seawater, utilizing multiple excitation and emission wavelengths to examine the luminescence of CDOM as a three-dimensional representation. Previous studies using three dimensional fluorescence techniques have distinguished several CDOM components with distinct optical properties in a variety of environments (Coble et al., 1990, 1998; Coble, 1996; De Souza Sierra et al., 1994; Mopper and Schultz, 1993; Parlanti et al., 2000).

Recent information on the fate and cycling of marine colloids has added an interesting dimension to the study of DOM optical variability. The definition of “dissolved” organic matter is operational, based on filter pore size cutoffs generally accepted by the bio-optical community (0.2 to 0.7 μm). Given that colloids are defined traditionally as particles 1–1000 nm in size, “dissolved” samples would include a subset of the colloidal fraction and indeed colloids comprise a significant fraction (e.g., 10–40%) of the marine DOM pool (Benner et al., 1992; Buesseler et al., 1996; Wells, 2002). The persistence of marine colloids in surface waters is largely dependent on the rates of microbial degradation (Benner et al., 1992) and co-aggregation to form sinking particles (Baskaran et al., 1992; Chin and Gschwend, 1992; Kepkay, 1994; Moran and Buessler, 1992). In addition, recent work indicates that colloidal and dissolved fractions provide precursors for aquatic gel formation (Chin et al., 1998). The aquatic gel model implies not only that colloidal aggregation and degradation processes may be linked but also that microbial degradation of particulate gels may well induce the continued removal of their colloidal precursors (Wells, 1998). Marine colloidal processes are believed to be rapid, so small shifts in colloid production and removal dynamics might significantly impact the abundance of dissolved chromophores and fluorophores in seawater.

Isolation of colloidal organic matter has been undertaken using a variety of methods. One of the more popular methods is cross-flow filtration (e.g., Wells, 2002), however this approach provides only a single size cut-off, and membrane performance and fouling can be problematic (Buesseler et al., 1996). Flow field flow fractionation (FlFFF) represents a more recent advance in size separation that uses an open channel to partition constituents of the colloidal phase into a continuum of macromolecular size. FlFFF has been applied to analysis of terrestrial humic and fulvic acids (Beckett et al., 1987) and more recently to marine samples (Vaillancourt and Balch, 2000; Wells, 2004; Zanardi-Lamardo et al., 2002).

We examined the size distribution of marine CDOM and its optical variability as a function of phytoplankton bloom dynamics in the Damariscotta River Estuary. By employing FlFFF with absorbance detection, a range of different size fractions of colloidal CDOM ($\mathrm{CDOM_c}$) were collected for fluorescence analyses using EEMS. The optical variability and changes in apparent composition of $\mathrm{CDOM_c}$ were measured to determine whether the fluorescence signal of marine colloids varies with size and over time, and to provisionally assess the chemical variability of this under-explored pool of organic carbon. Evidence from fluorescence characteristics indicates that the chemical constituency of colloidal matter differs among colloidal size fractions. This study is part of a larger project studying the changes in colloid abundance and absorption coefficients as a function of colloid size and season (Floge et al., in preparation).

## 2. Materials and methods

Water samples were collected from the dock at the Darling Marine Center (Walpole, Maine) between January 2003 and June 2004. Using plastic gloves, glass bottles were opened and filled under the water surface to avoid contamination from the surface microlayer. Samples were immediately filtered in the adjacent lab using pre-cleaned plastic syringes and 0.22 μm syringe filters (Millex GV, Fisher Scientific). Salinities were measured with a refractometer (Fisher Scientific).

The theory of flow field flow fractionation has been described in detail elsewhere (Giddings, 1993). Briefly, a flow field is applied at right angles to the channel flow