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Tracing water mass mixing in the Baltic–North Sea transition zone using the optical properties of coloured dissolved organic matter

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ABSTRACT

The distribution and characteristics of coloured dissolved organic matter (CDOM) in the Baltic – North Sea transition zone were studied. The aim was to assess the validity of predicting CDOM absorption in the region on the basis of water mass mixing alone and demonstrate the utility of CDOM as an indicator of water mass mixing in coastal seas. A three-end-member mixing model representing the three major allochthonous CDOM sources was sufficient to describe the patterns in CDOM absorption distribution observed. The three-end-member water masses were the: Baltic outflow, German Bight and the central North Sea. Previously, it was thought that water from the German Bight transported northwards in the Jutland coastal current only sporadically influenced mixing between the Baltic and North Sea. The results from this study show that water from the German Bight is detectable at salinities down to 12 in the Kattegat and Belt Sea. On average, 23% of the CDOM in bottom waters of the Kattegat, Great Belt, Belt Sea, Arkona Sea and the Sound originated from the German Bight. Using this conservative mixing model approach, local CDOM inputs were detectable but found to be limited, representing only 0.25% of CDOM in the surface waters of the Kattegat and Belt Sea. The conservative mixing of CDOM makes it possible to predict its distribution and characteristics and offers a powerful tool for tracing water mass mixing in the region. The results also emphasize the need to include the Jutland Coastal current in hydrodynamic models for the region.

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1. Introduction

Coloured dissolved organic matter (CDOM) is one of the major light-attenuating components of sea water. It is responsible for much of the ultraviolet light attenuation and, when present in high concentrations, also influences visible light attenuation. The CDOM UV–visible absorption spectrum (300–650 nm) can be modelled using an exponential relationship (Jerlov, 1968; Lundgren, 1976; Bricaud et al., 1981).

$$a_{(\lambda)} = a_{(\lambda_0)} e^{-S(\lambda_0 - \lambda)} \quad (1)$$

where λ_0 is a reference wavelength λ and S is the spectral slope coefficient, characterizing the exponential decline in absorption with increasing wavelength. The absorption at a specific wavelength (e.g. 300 nm (a_{300})) can be used as an estimate for CDOM concentration.

CDOM originates primarily from the degradation of terrestrial and aquatic plant matter. In regions influenced by freshwater run off, terrestrial CDOM often dominates and it is only when this source is considerably diluted that the presence of autochthonous marine CDOM can be detected (Blough et al., 1993; Stedmon et al., 2000; Stedmon and Markager, 2003). When allochthonous supply and mixing rates exceed autochthonous production and degradation rates, the concentration and characteristics of CDOM behave conservatively. There is a considerable allochthonous supply of CDOM in the coastal waters of the North Sea and Baltic Sea and this led early studies to conclude that CDOM represents purely terrestrial material (Højerslev, 1979). Measurements from oceanic regions far from the influence of rivers, however, have since revealed a lower intensity, pelagic, autochthonous CDOM source (Jerlov, 1976; Bricaud et al., 1981; Nelson et al., 1998).

In sub-surface open ocean waters, temperature and salinity are used to trace water mass mixing, since both parameters behave conservatively. In coastal or surface waters temperature is not a conservative parameter as it varies seasonally as a result of heat

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exchange with the atmosphere. So for these waters alternative parameters are required. In combination with salinity, CDOM absorption at specific wavelengths can be used instead of temperature to trace water mass mixing in coastal waters (Kalle, 1949; Højerslev, 1988; Karabashev et al., 1993). In the Skagerrak and Kattegat, the brackish Baltic Sea water with high CDOM absorption mixes with saline North Sea water with low CDOM absorption (Fig. 1). The Jutland coastal current, flowing north along the western coast of Jutland from the German Bight, also influences the Skagerrak and Kattegat (Højerslev et al., 1996; Warnock et al., 1999; Nielsen, 2000). The current carries water from the rivers flowing into the Southern North Sea, which contain high CDOM concentrations (Laane and Kramer, 1990; Højerslev et al., 1996; Warnock et al., 1999). However, the effect of the German Bight water in the Skagerrak and Kattegat is thought to be limited in comparison to the effect of the large volumes of water transported from the North Sea and Baltic Sea (Aarup et al., 1996; Nielsen, 2000). It has been shown that salinity–CDOM relationships can characterize and quantify the mixing of these three water masses (Malmberg, 1964; Aarup et al., 1996; Højerslev et al., 1996). Despite this seemingly conservative behaviour, Højerslev and Aas (2001) did not find systematic trends in *S*. Stedmon and Markager (2003) estimated the variability of *S* during conservative mixing of two end members, facilitating analysis of field data and the identification of non-conservative processes acting on CDOM, such as local autochthonous production (Kowalczuk et al., 2006; Guo et al., 2007). The aims

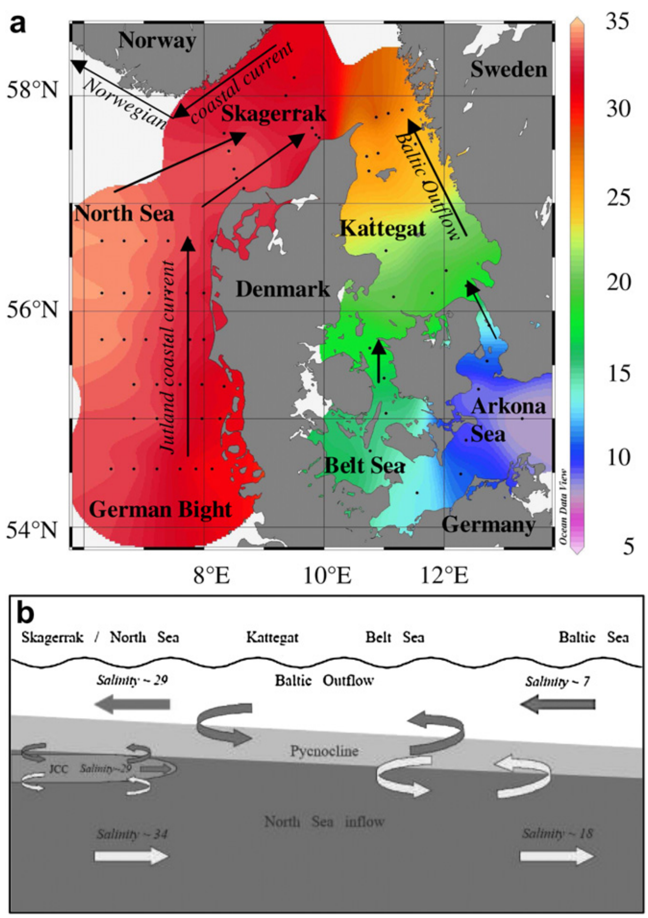

Fig. 1. (a) Map of study site indicating the different surface currents and regional seas. Also shown are the station locations and the coloured contours represent the average salinity at 5 m. (b) A diagram of generalized characteristics of the water column structure in the region. For a map of the bathymetry in the region, see Fig. 1 in Højerslev et al. (1996).

of this work are two fold. Firstly we aim to predict CDOM absorption of water masses in the region based on water mass mixing alone. We assume that mixing is the dominant process controlling both the distribution and character (*S*) of CDOM. If this is true, a three-end-member mixing model representing the three major allochthonous CDOM sources should be sufficient to describe CDOM absorption. If this assumption is invalid and autochthonous production and removal processes control the distribution and characteristics of CDOM, the model results will indicate the magnitude of these processes. Secondly, we aim to demonstrate the utility of CDOM as an indicator of water mass mixing in coastal seas. By applying simple mixing models water at different depths and locations can be fractionated into the relative proportion of the three dominant end member water masses.

2. Methods

2.1. Sampling and measurement

Water samples were collected using the national water quality monitoring cruises on the R/V Gunnar Thorson. Samples were obtained from ten cruises (Table 1) in the transition zone between the North Sea and the Baltic Sea (Fig. 1). Data from February 1999 originates from Stedmon et al. (2000) and is included to expand the data analysis. At each station, samples were collected at 1 m and 5 m intervals from 5 to 30 m. For stations deeper than 30 m, samples were taken at 10 m intervals below 30 m and at 1 m over the sediment. A rosette with a Seabird CTD and 12 5 L Niskin water samplers was used and calibrated according to accredited procedures required by the national monitoring program.

CDOM samples were gently filtered through pre-combusted GF/F filters (approximate pore size 0.7 µm) using a syringe, into acid-washed 100 mL brown glass bottles and stored refrigerated in the dark. Storage time varied from one to two weeks, since the cruise lasted 5 days and all the optical characteristics of the samples were determined during the week directly following each cruise. Stedmon et al. (2000) investigated the effects of storage on CDOM absorption for sample from these waters and found little change for periods up to 27 days. CDOM absorbance was measured on a Shimadzu UV-2401PC spectrophotometer using MilliQ water as a reference, according to Stedmon et al. (2000). A 10 cm quartz cuvette was used for all samples and the absorption coefficient was calculated from absorbance (*A*) according to Equation (2).

$$a_{(\lambda)} = 2.303A_{(\lambda)}/L \quad (2)$$

where *L* is the pathlength in meters (0.1 m).

The spectral slope, *S*, of the absorption curve from 300 to 650 nm was obtained by fitting Equation (1) to the data using the

Table 1
Cruise name, sampling time, number of stations and samples, and location of cruise track. Inner Danish waters include Arkona Sea, Belt Sea, Sound and Kattegat (Fig. 1).

Cruise	period	#Stations	#Samples	Description
GT189	Feb.1999	74	324	Inner Danish waters, Skagerrak and North Sea
GT191	Aug. 1999	72	136	Inner Danish waters, Skagerrak and North Sea
GT198	Sept. 2000	24	131	Inner Danish waters
GT237	Aug. 2006	24	182	Inner Danish waters
GT238	Sept. 2006	24	135	Inner Danish waters
GT239	Oct. 2006	24	138	Inner Danish waters
GT240	Feb. 2007	22	164	Inner Danish waters
GT242	Aug 2007	17	131	Inner Danish waters
GT243	Sept 2007	17	134	Inner Danish waters
GT244	Feb 2008	17	132	Inner Danish waters

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