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Modeling absorption by CDOM in the Baltic Sea from season, salinity and chlorophyll

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Abstract

In the Baltic Sea the underwater light regime is to a large extent governed by absorption by colored dissolved organic matter (CDOM), where the largest source is riverine input. We have applied a conservative mixing model of CDOMs optical properties to a dataset collected in the Baltic Sea during 11 years of continuous observations in 1993–2004. The majority of observations agreed well with the model indicating that conservative mixing is important in the area, as terrestrial organic matter is diluted with open sea water. Deviations from the conservative mixing pattern mainly occurred at salinities over 6.8, and chlorophyll a concentrations over 1.5 mg m^{-3}, and were located in open sea waters, coastal zone and Pomeranian Bay. The seasonal dependence between the light absorption coefficient by CDOM $a_{CDOM}(375)$ and salinity and chlorophyll a concentrations was explored. In March, April and November, months of intensive mixing and high riverine discharge, most of the variability in $a_{CDOM}(375)$ values could be explained by dilution of terrestrially derived CDOM alone. In February, May, and September, months of thermal stratification, reduced riverine discharge and enhanced biological activity, inclusion of chlorophyll a concentration resulted in significantly better models. Autochthonous production of CDOM was found to be a significant source of CDOM in the Southern Baltic Sea in these months. A series of algorithms for the prediction of CDOMs optical properties is presented.

Keywords: Colored dissolved organic matter; Optical properties; Baltic Sea

1. Introduction

Colored dissolved organic matter (CDOM) is a major determinant of the optical properties of natural waters and it directly affects both the availability and spectral quality of light in the water column (Jerlov, 1976; Del Vecchio and Blough, 2005; Hargreaves, 2003). Through its effects on underwater solar radiation CDOM may stimulate or hinder biological activity (e.g. Mopper and Kieber, 2002). In coastal water in particular, quantitative descriptions of the dynamics and variability of CDOMs optical properties are often required in order to accurately predict light penetration and hereafter for example, primary productivity. Another area where quantitative and qualitative assessment of CDOM optics is important is within remote sensing (Siegel et al., 2002; Blough and Del Vecchio, 2002). Algorithms for the estimation of chlorophyll concentrations often

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include corrections for CDOM effects (Garver and Siegel, 1997; Maritorena et al., 2002). Usually these algorithms use constant values for the spectral slope coefficient (S) because it is thought to vary unpredictably (Maritorena et al., 2002; Maritorena and Siegel, 2005). We hypothesize that these algorithms can be improved by applying empirical relationships for the variability of the optical properties of CDOM.

A number of physical, chemical and biological processes all influence the distribution and optical properties of CDOM (Whitehead et al., 2000; Siegel et al., 2002; Blough and Del Vecchio, 2002; Osburn and Morris, 2003; Zepp, 2003). Among the most important in open marine areas are dilution of terrestrially derived CDOM, photochemical bleaching, bacterial degradation and autochthonous production of CDOM by plankton. Modeling the behavior of the optical characteristics of CDOM during conservative mixing of two end member has shown that the relationship between light absorption at a given wavelength ($a_{\mathrm{CDOM}}(\lambda)$) and S is not linear but rather a hyperbolic curve (Stedmon and Markager, 2001, 2003). A quantitative understanding of underlying dilution effects that influence CDOM optical properties allows us to better identify occasions or locations where additional processes are important, for example where autochthonous production or removal of CDOM is occurring.

The objective for this study is to establish quantitative relationships between the optical properties a_{CDOM} (λ) and S of CDOM and their variability with respect to season, salinity and chlorophyll concentration. These relationships can be used to improve ecological models and algorithms for remote sensing. Moreover, they can help us to identify the occurrence of non-conservative processes in the dynamics of CDOM. The independent parameters in the models; season, salinity and chlorophyll a concentration, are parameters that are known, or to some extent can be estimated from hydrographic–ecological models or remote sensing. This allows the proposed algorithms to be incorporated into biogeochemical models or remote sensing algorithms. The proposed algorithms describe the conditions in the Baltic Sea, but we believe that the approach is relevant for estuaries and coastal waters in general.

2. Methods

2.1. Study area: the Baltic Sea

The study is conducted in the Southern Baltic Sea and based on 1610 measurements of absorption spectra of CDOM collected over a period of eleven years. The Baltic Sea has high concentrations of CDOM due to a high input of fresh water from a large drainage area and limited water exchange with the North Sea. Optical effects of CDOM are therefore particularly relevant in this area.

The Southern Baltic Sea is located in the temperate climatic zone. Maximum freshwater run off occurs in April/May and coincides with the phytoplankton spring bloom that is initiated by a stabilization of the water column and increased surface light. The freshwater carries with it both high concentrations of CDOM and a substantial load of inorganic nutrients. The nutrients enhance the spring bloom and combined with the CDOM cause an increase in light attenuation. In the summer, the local coastal upwelling caused by Ekman transport and periodic summer floods affect the optical properties in the coastal zone and bays. In the winter, wind driven mixing, vertical thermohaline circulation, decreased biological activity, and reduced riverine outflow all result in clearer surface waters (Sagan, 1991; Olszewski et al., 1992; Kowalczuk, 1999).

Field samples were collected between September 1993 and October 2004 as part of the Baltic Sea bio-optical observation program carried out by the Institute of Oceanology at the Polish Academy of Sciences. Water samples for CDOM absorption and chlorophyll a measurements were collected on 43 cruises in the southern Baltic Proper (Fig. 1) covering the months from February to May and September to November. The geographical coverage of the samples includes the Gulf of Gdansk, the Pomeranian Bay, Polish and German coastal waters and open sea (Baltic Proper). The coastal sites are under direct influence of two major river systems (Vistula and Odra) which drain the majority of Poland. Water samples were collected at fixed depths with Niskin bottles, with the majority of samples coming from the photic zone. Salinity data at each sampling station were taken from CTD casts. Chlorophyll a concentration was determined on a spectrophotometer according to HELCOM (1988).

2.2. CDOM optical properties

Water samples for CDOM underwent a two-step filtration process. The first filtration was through acid washed Whatmann glass fiber filters (GF/F, nominal pore size 0.7 μm). Water was then filtered through Sartorius 0.2 μm pore cellulose membrane filters to remove fine-sized particles. The first 500 ml was discarded and then 200 ml was collected and stored in darkness at ~4 °C in amber glass bottles. In the early cruises (1993–1997) 400 μL of 0.5 M $HgCl_2$ was added