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Mixing anomaly in deoxygenated Baltic Sea deeps indicates benthic flux and microbial transformation of chromophoric and fluorescent dissolved organic matter

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ABSTRACT

Optical measurements have indicated an anomalous distribution of Colored Dissolved Organic Matter absorption coefficient – $a_{CDOM}(\lambda)$, and dissolved organic matter fluorescence – FDOM intensity, in the salinity gradient in deep Baltic Sea waters below the permanent pycnocline. The two steps mixing model of the $a_{CDOM}(\lambda)$ with salinity have been derived based on 3521 CDOM absorption observations done in Baltic Sea, from 1993 until April 2014 and 1011 CDOM absorption observation done in the Danish Straits from August 2006 until February 2008. Disproportionate decrease and even increase of CDOM absorption coefficient at 350 nm, $a_{CDOM}(350)$, with increased salinity was observed in deep waters. There was a significant increase of the $a_{CDOM}(350)$ mixing model residual values in deep water compared to overlaying waters. The $a_{CDOM}(350)$ mixing model residual values tended to increase significantly with increasing salinity in deep waters. The CDOM and FDOM composition has been assessed by spectral slope coefficient, $S_{300-600}$, the Humification Index (HIX), calculated from measured DOM fluorescence Excitation–Emission Matrix spectra and from ratio of the humic-like and protein-like DOM fluorescence measured in situ. The $S_{300-600}$ values decreased significantly in deep waters compared with overlaying waters. There was a strong ($R^2 = 0.705$) inverse linear relationship between $S_{300-600}$ and $a_{CDOM}(350)$ mixing model residuals. The HIX, and the values of the ratio of the humic-like to protein-like DOM fluorescence increased significantly in the deep waters, what indicated increase of humic-like and decrease of protein-like DOM fraction in the deep waters samples compared to control surface waters samples. An exponential relationship between the humic-like to protein-like FDOM intensity ratio and the apparent oxygen utilization – AOU was observed in the Gulf of Gdansk. Presented results suggested that possible DOM emission from sediments into the adjacent near bottom water in anoxic conditions, could explain the $a_{CDOM}(\lambda)$ mixing anomaly. Microbial DOM reprocessing in anoxic condition, documented by direct in situ measurements, significantly changed the CDOM and FDOM composition.

1. Introduction

CDOM has a significant influence on the spectral properties of the apparent optical properties of Baltic Sea waters. A high CDOM concentration strongly absorbs the solar radiation in the UV and blue and green spectral ranges and causes a shift in the maximum of its transmission towards longer wavelengths relative to clear oceanic water (Darecki et al., 2003; Kowalczuk et al., 2005a). The spatial and temporal variability CDOM in the surface waters and upper oligohaline layer of the Baltic Sea and Danish Straits has been studied over last 30 years (e.g. Højerslev, 1982, Aarup et al., 1996; Kowalczuk 1999; Kowalczuk et al., 1999; Stedmon et al., 2000; Kowalczuk et al., 2006, Stedmon et al., 2010). It has been shown that, rivers are predominant source of CDOM in the Baltic Sea, due to high input of fresh water from a large drainage area and limited water exchange with the North Sea and the mixing of fresh and saline waters can explain large proportion of CDOM variability. There was very significant negative trend between $a_{CDOM}(\lambda)$, DOM fluorescence and salinity in the Baltic Sea, (Kowalczuk, 1999; Kowalczuk et al., 2006; Kowalczuk et al., 2010). The mixing of CDOM in the Kattegat and Skagerrak is more complex. Baltic Sea waters outflow is regarded as one multiple end members in Danish Straits together with Jutland Current, that carries elevated CDOM

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concentrations from German Bight, and local fresh water inputs along the Danish, Swedish and Norwegian coasts. The northern part of the North Sea acts as the oceanic end member. Due to this complex hydrography in Danish Straits, there were observed multiple mixing lines between CDOM absorption and salinity in Kattegat and Skagerrak waters and multi end members mixing models were develop to estimate water masses composition in this region (Aarup et al., 1996; , Stedmon et al., 2010; Skoog et al., 2011; Kristiansen and Aas, 2015).

The transitional surface waters of Kattegat and Skagerrak that are transported over sills in the straits during the episodic inflows, are the source of the deep mesohaline waters of the Baltic Sea. Therefore in the absence of the autochthonous source, values of the optical characteristics of the DOM shall approximately follow the general decrease with salinity as observed on the published mixing diagrams. Recent observations of the vertical distribution of optical characteristics of the DOM revealed an anomalous distribution of the CDOM absorption or FDOM intensity in the function of salinity below permanent pycnocline in the Baltic Sea deeps (Kowalczuk et al., 2010; Skoog et al., 2011). This was the first documented indication of mixing anomaly of CDOM, However, neither quantification of this deviation nor assessment of its statistical significance were given.

Observed anomaly suggested that there could be a local production of the DOM from the hydrolysis of particulate organic matter – POM, in the oxygen deficit of the deep water, or the diffusion of DOM from bottom and enrichment of DOM in the stagnant waters below the pycnocline. The microbial mineralization of the POM and DOM in deep water decreases the dissolved oxygen – DO, concentrations, leading during the decade long stagnation periods in the Baltic Sea deeps to hypoxia and anoxia and increase of hydrogen sulfide concentrations causing the formation of the bottom dead zones (Meier et al., 2006). The extent of the bacterial respiration can be assessed by apparent oxygen utilization – AOU. Linkages between microbial respiration, and dissolved organic matter has been established in the mesopelagic and bathypealgic oceanic waters through regression between humic-like organic matter fluorescence and AOU (Jørgensen et al., 2011; Nelson and Siegel, 2013; Álvarez-Salgado et al., 2013: De La Fuente et al., 2014). Such relationships were poorly documented in the Baltic Sea. There was achieved a significant progress in the carbon cycle in the Baltic Sea in recent years (Kuliński and Pempkowiak, 2008, 2011). and budget for different carbon fractions has been estimated, yet the cycling of this element in the deeps and possible emission from bottom sediments was poorly understand and quantified (Hoikkala et al., 2015).

Inherent optical properties, that are easy to measure in situ with high spatial and temporal resolution, may act as useful proxies of many biogeochemical parameters: e.g. chlorophyll *a* concentration, DOC, POC (e.g. Woźniak and Dera, 2007; Kirk, 2011; Woźniak et al., 2014) and may directly contribute to carbon cycle studies. The CDOM absorption and FDOM in the Baltic Sea could be used as a convenient proxy for DOC concentration (Ferrari et al., 1996; Kowalczuk et al., 2010). CDOM and FDOM spectral indices may be used as the indicators of the qualitative transformation of dissolved organic matter in natural waters. The absorption spectrum spectral slope coefficient is often regarded as a proxy for the CDOM composition; typically a higher *S* indicates low molecular weight material or lower aromaticity and a lower *S* indicates DOM with a higher aromatic content and higher molecular weight (Blough and Del Vecchio, 2002; Helms et al., 2008; Guéguen and Cuss, 2011). Transformation of dissolved organic matter in natural waters during humification process can be quantified by Humification Index – HIX, calculated as a ratio of a long-wave emission band to a short-wave emission band excited in UV (Zsolnay, 1999; Kalbitz et al., 1999). Humification causes the fluorescing molecules become more condensed, and increases number of aromatic (phenolic) groups (Milori et al., 2002), which effect emission spectra to shift toward longer wavelength (Lakowicz, 2006).

The aims of this paper are: i) to compare observed values of DOM optical properties below the pycnocline in Baltic Sea deeps with those predicted from the conservative mixing model, that assumed negligible contribution of autochthonous CDOM production and decomposition processes ii) to assess relationship between derived mixing model residuals and CDOM spectral indices in mesohaline waters below pycnocline, iii) to assess the compositional transformation of CDOM and FDOM based on the distribution of spectral indices in distinct water masses, iv) to verify the linkages between the oxygen conditions and CDOM and FDOM spectral indices.

2. Material and methods

2.1. The study area

The vertical distribution and seasonal cycle of inherent optical properties are determined by thermo-haline structure of the Baltic Sea waters. Both the absorption coefficient and the beam attenuation coefficient are highest in the upper oligohaline layer, that is under influence of the fresh water inflow from the watershed. The seasonal cycle of warming and biological activity are the main sources of variability of inherent and apparent optical properties in the upper layer. Maximum freshwater runoff occurs in April/May and coincides with the spring phytoplankton bloom, initiated by the stabilization of the water column due to heating and increased surface light. The fresh water carries both high concentrations of CDOM and substantial loads of inorganic nutrients what enhances the spring bloom, and in combination with the CDOM, cause an increase in light attenuation. The accumulation of phytoplankton biomass over the time decreases water transparency in the mixed layers. This is mainly due to particle scattering, and – less importantly – to light absorption by phytoplankton pigments and detrital particles. Local coastal upwelling events caused by Ekman transport, as well as periodic summer floods, affect the optical properties in the coastal zone and bays. In spring and the summer, stratification of the water column forms a density boundary at the thermocline which, prevents mixing of the upper and lower water layers and distribution of less transparent waters to deeper layers. In the winter, from October to March, wind-driven mixing, the vertical thermohaline circulation, reduced biological activity and reduced riverine outflow all result in clearer surface waters (Sagan, 1991; Olszewski et al., 1992; Kowalczuk, 1999; Sagan, 2008). In the absence of thermal stratification, the convective vertical mixing distributes clearer waters into deep and forms almost homogenous vertical distribution of absorption and attenuation coefficients down to about 70–80 m of depth and forms optically clearest and homogenous water body of “Baltic Sea winter waters” (Leppäranta and Myrberg, 2009).

The permanent halocline, that is located at the depth range 60–80 m, forms strong physical boundary. Particulate material, formed in the euphotic zone during phytoplankton blooms and descending after its collapse, tends to accumulate at the halocline contributing to formation of the beam attenuation and scattering maximum. Below the permanent halocline, scattering remains much higher than in the upper 70 m due to the resuspension of sediment particles from the seafloor by currents. Absorption is only slightly raised at this depth in the spectral region between 412 nm and 555 nm. Below the permanent halocline, the absorption in these blue to green spectral bands increases slowly down to the sea floor (Sagan, 2008).