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Estimating the seasonal impact of optically significant water constituents on surface heating rates in the western Baltic Sea

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In situ and remotely sensed data used for climatologies

In situ measurements and remotely sensed data from the MERIS ocean colour archive of CDOM absorption at 443 nm were used to develop a climatologies of CDOM absorption which support the evaluation of our modelled estimates of CDOM absorption. Below, the source and processing of the different data sets are briefly described.

In situ CDOM measurements and climatology

A time series (1994 - 2017) of in situ observations of CDOM absorption at 443 nm was reprocessed into seasonal means for our study area (Figure 2 in article). This data set was collected as a result of the implementation of numerous research projects and statutory research programs conducted by the Remote Sensing Laboratory at the Institute of Oceanology, Polish Academy of Sciences (IOPAN), Sopot Poland in the whole Baltic Sea. The main aim of the study on CDOM optical properties was the assessment of its temporal and spatial variability (Kowalczuk and Kaczmarek, 1996, Kowalczuk, 1999) and its relation to hydrodynamic conditions and Baltic Sea productivity (Kowalczuk et al., 2006). As the primary goal of this research was the development and validation of ocean colour remote sensing algorithms (Kowalczuk et al., 2005a), the vast majority of samples for determination of CDOM absorption spectrum were collected in the surface layer. However, since 2014, samples were also collected within the water column, depending on the thermohaline stratification of water masses and depth distribution of autotrophic protists, in order to better resolve the impact of non-linear processes (i.e. photo-degradation, autochthonous production by phytoplankton, diffusion from bottom sediments) influencing CDOM optical properties (Kowalczuk et al., 2015). The sampling program is conducted in the whole Baltic Sea and is designed to resolve the spatial variability of the CDOM absorption coefficient. We use a subset of this time series located in our study area. Most of the samples were taken in spring and autumn, with a smaller number of samples collected in winter and summer mostly due to adverse weather conditions or unavailability of research vessels in summer months. Water samples were collected by Niskin bottle and were filtered first through acid-washed Whatman glass fibre filters (GF/F, nominal pore size 0.7 mm). The water was then passed through acid washed membrane filters with 0.2 mm pore to remove fine-sized particles. From 2014 until the present, water for CDOM absorption spectra were gravity filtered directly from Niskin bottles through Millipore Opticap XL4 Durapore filter cartridge with nominal pore size 0.2 μm. Filtered water was kept in acid washed amber glass 200 ml sample bottles until spectrophotometric analysis, which was performed with use of various models of bench top research grade, double beam spectrophotometers both in land base laboratory (Kowalczuk and Kaczmarek, 1996; Kowalczuk, 1999) and on the ship (Kowalczuk et al., 2005a,b, 2006). The cuvette pathlength was 5 or 10 cm depending on the spectrophotometer model. MilliQ water was used as the reference for all measurements. The absorption coefficient aCDOM(λ) was calculated as follows:

$$a_{CDOM}\left(\lambda\right)=\frac{2.303A\left(\lambda\right)}{L} \tag{S1}$$

where L is the optical path length, A is the absorptance (the flux that has been absorbed) and the factor 2.303 is the natural logarithm of 10.

The whole CDOM absorption data base in the IOPAN repository, collected between 1994 and 2017, was reprocessed to calculate the spectrum slope coefficient, S. A nonlinear least squares fitting method using a Trust-Region algorithm implemented in Matlab was applied (Stedmon et al., 2000, Kowalczuk et al., 2006) in the spectral range 300-600 nm, as follows:

$$a_{CDOM}(\lambda) = a_{CDOM}(\lambda_0) e^{-S(\lambda_0 - \lambda)} + K \qquad \text{(S2)}$$

where λ_0 is 350 nm, and K is a background constant that allows for any baseline shift caused by residual scattering by fine size particle fractions, micro-air bubbles or colloidal material present in the sample, refractive index differences between sample and the reference, or attenuation not due to CDOM. The parameters aCDOM (350), S, and K were estimated simultaneously via non-linear regression using Eq. (S2).

Remotely sensed data

MERIS FRS L2 (full resolution level 2) product from 2003 to 2012 was used to create a monthly climatology of CDOM absorption for the Western Baltic Sea region. The MERIS FRS L2 product was processed with the C2RCC algorithm (Doerffer and Schiller, 2007) which has been trained with data-sets from European coastal waters. Full details of the post processing of the MERIS data into a climatology can be found in Röhrenbach (2019). A monthly climatology for the complete time frame of the MERIS archive was created and includes the mean value, standard deviation and number of observations for each point.

Figure S1 shows the difference between a snapshot of the MERIS data product (01.04.2004) and the corresponding April climatology. The snapshot has almost complete data coverage, which is quite rare compared to other time periods where only a small part of the region of interest is in the frame or free of cloud coverage. The climatology smooths the spatial variability, providing the average spatial distribution and gradients in CDOM absorption. High values of aCDOM(443) can be seen around the river mouths of the Vistula river (≈ 1.7 m^{-1}) and the Oder river (≈ 0.7 m^{-1}), whereas offshore areas show lower values (≈ 0.2 m^{-1}) and spatial variability. The snapshot image presents the typical situation at the beginning of the spring freshet. Both Vistula and Oder rivers have similar hydrographic properties with maximum flow observed in April and May and minimum flow in June and February. The land use in the catchment is also similar and consists of a mixture of agriculture, forestry and urbanised areas. The difference in aCDOM(443) values and the spatial extent of fresh water plumes seen as areas with elevated CDOM absorption results from the geomorphology of the outlets. The Vistula River has artificial outlets, built in 1895, and this channel carries up to 90 % of the flow with only a small fraction feeding old deltaic branches, cut off by locks and dikes. The Oder river outlet is less transformed by human activity, and the Oder River feeds the Szczecin Lagoon which is connected to the coastal Baltic Sea via three inlets: two located in Poland (Swina and Dziwna) and one in Germany (Peene). The shallow Szczecin Lagoon acts as a buffer and biogeochemical reactor, where photochemical, microbial and physical (flocculation) transformation of CDOM may occur leading to effective decreased absorption values recorded on the marine side of the estuary.

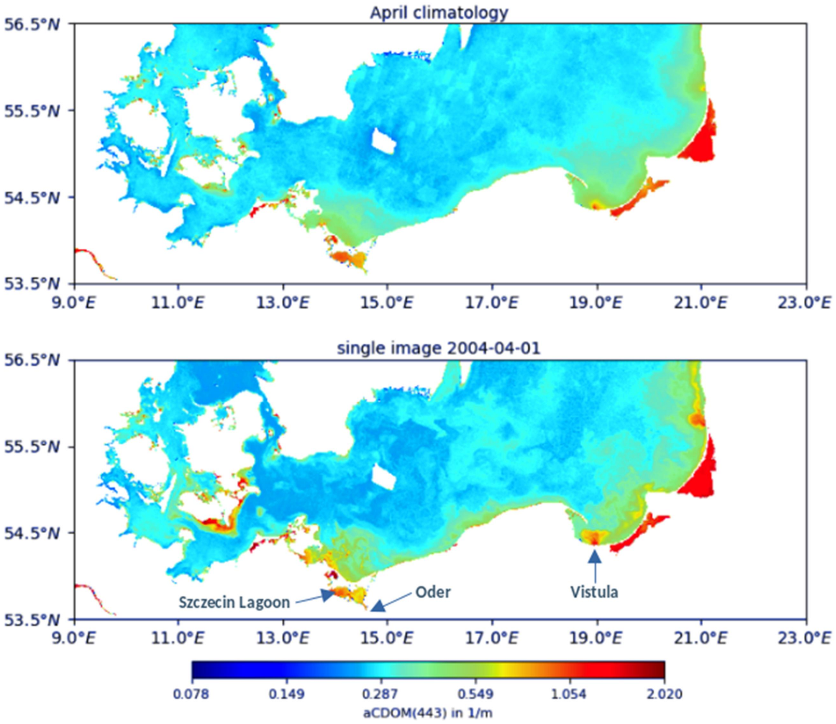

Figure S1: April climatology (top) and snapshot (01.04.2004) (bottom) of CDOM absorption at 443 nm (adapted from Röhrenbach, 2019).

Modelled surface water constituent concentrations in 2018

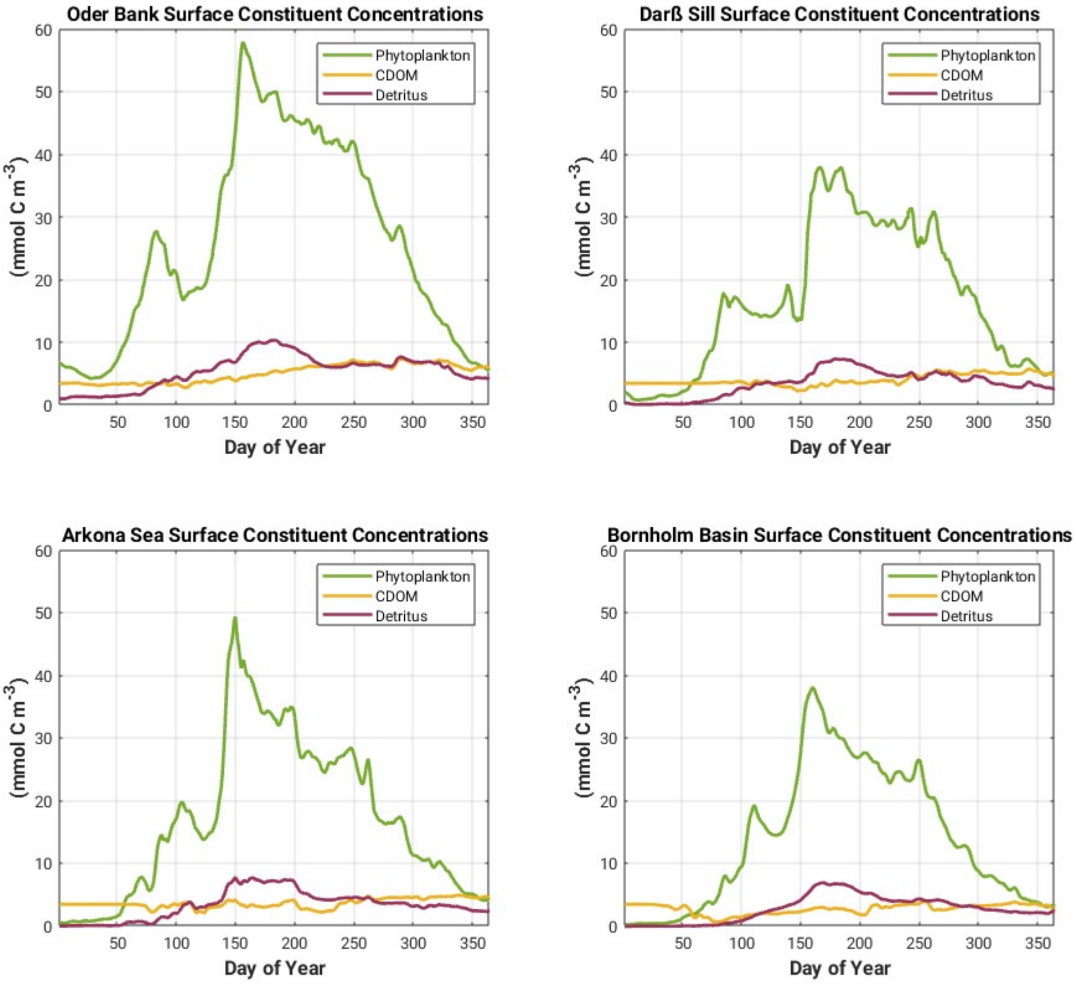

Figure S2: Modelled surface water constituent concentrations in 2018 at Oder Bank, Darß Sill, Arkona Sea and Bornholm Basin.

Western Baltic Sea monthly mean surface irradiance

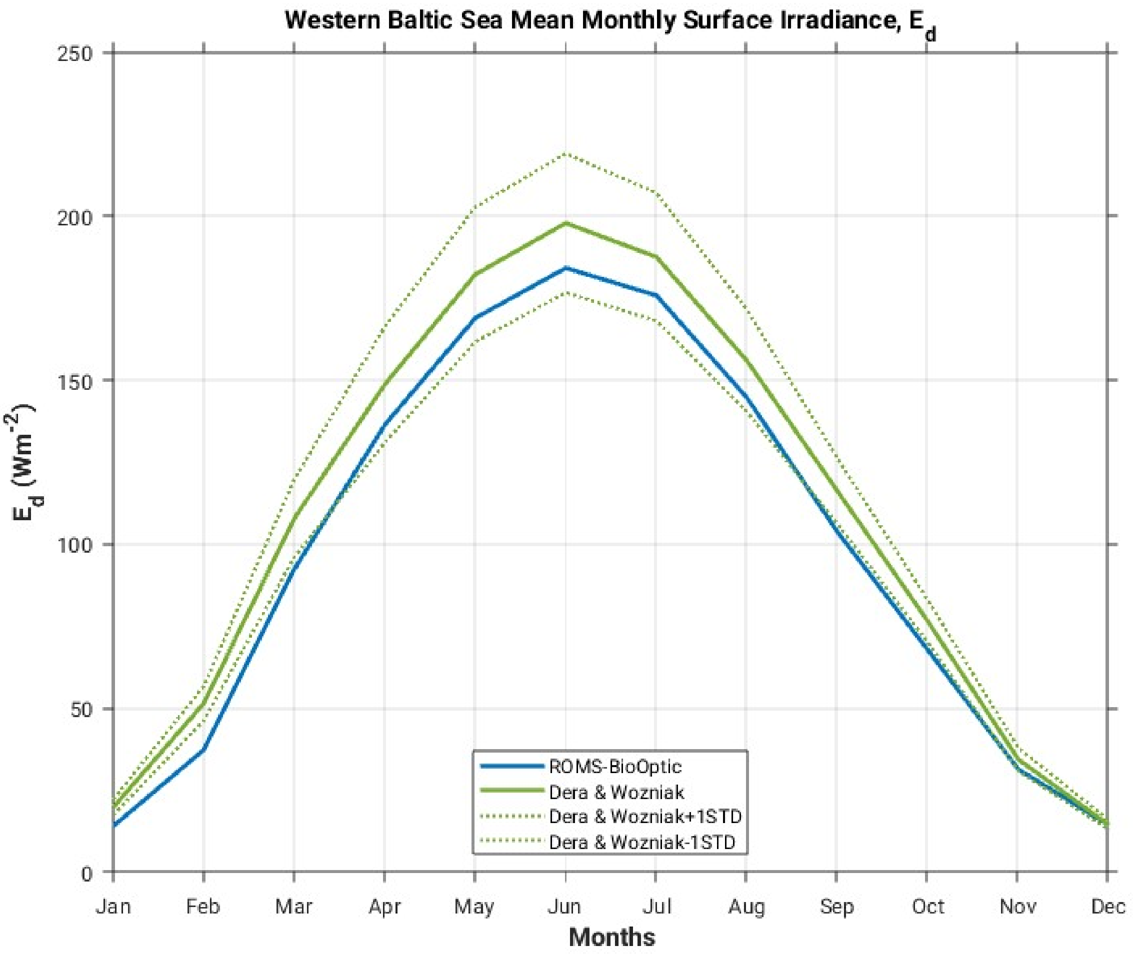

Figure S3: Modelled monthly mean surface irradiance in the Western Baltic Sea, ROMS-BioOptic versus Dera & Wozniak, 2010 (Dashed green lines represent Dera & Wozniak +/- one standard deviation).

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