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Front.
Yellowisch river water with light reflection
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Summary

The Baltic Sea is optically a multi-componental water and has exceedingly high levels of colored dissolved organic matter (CDOM, also referred as yellow matter, gilvin or gelbstoff). CDOM is a complex mixture of chemical bonds originating from the decay of photosynthetically produced organic matter. It influences the aquatic light field substantially. A quantitative description of the dynamics and variability is often required to predict accurately light penetration and hereafter e.g. primary production.

The present study is a first attempt to include CDOM into a Baltic Sea model. The model integrations are based on a fixed concentration in the 30 major rivers. In the absence of comprehensive measurements, a river inflow proportional to total organic carbon is assumed. Since origin and fate are still a matter of discussion, we test various decay rates of CDOM and compare the results with satellite observations. Best results are obtained when assuming a light dependent decay, compared to a temperature or time dependent decay. Treating CDOM as a conservative tracer does not lead to satisfactory results.

Sammanfattning

Vattnet i Östersjön är optiskt sett uppdelat i många beståndsdelar och har ytterst höga halter av färgade lösta organiska ämnen (colored dissolved organic matter, CDOM), även kallade för gulämnen, gilvin eller gelbstoff. CDOM är en komplex blandning av kemiska bindningar skapade vid nedbrytningen av fotosyntetiskt producerat organiskt material och de tha r en avsevärd påverkan på ljusfältet i vattnet. En kvantitativ beskrivning av dynamiken och variabiliteten behövs ofta för att få en riktig beskrivning av ljusets nedträngning och där efter av t.ex. primärproduktionen.

Denna studie är ett första försök att inkludera CDOM i en modell för Östersjön. Modellförsöken baseras på en fix koncentration i de 30 största floderna. I brist på omfattande mätningar antas en flodtillförsel som är proportionell mot totalt organiskt kol. Eftersom ursprunget och ödet fortfarande är föremål för diskussioner testar vi olika hastigheter av CDOM sönderfall och jämför resultaten med satellitobservationer. Jämfört med temperatur eller tidsberoende sönderfall uppnåddes bäst resultat med ett ljusberoende sönderfall. Att behandla CDOM som ett konservativt spårämne leder inte till tillfredsställande resultat.

1 Introduction

The Baltic Sea is located in central Europe and about 85 million people are living in it's drainage basin (e.g. Leppäranta and Myrberg (2009)). This optically multi-componental water comprises extremely high levels of colored dissolved organic matter (CDOM, also referred as yellow matter, gilvin or gelbstoff), contained by the low exchange of Baltic waters with the North Sea (Jerlov (1968), Siegel et al. (2005), Kratzer and Tett (2009)). CDOM is, by definition, the part of dissolved organic matter which is capable to absorb light. It is a complex mixture of chemical bonds originating from the decay of photosynthetically produced organic matter and can play a substantial role in the biogeochemistry of natural waters merely through its influence on the aquatic light field (e.g. Bidigare and Ondrusek (1997), Blough et al. (1993), Blough (1996), Moran and Zepp (2004), Whithead et al. (1997)). Thus, a quantitative description of the dynamics and variability of CDOM is often required to predict accurately light penetration and hereafter e.g. primary production.
The origin and fate of CDOM is still a matter of discussion (del Vecchio and Blough (2006)). Siegel et al. (2002) analysed global satellite data of colored detrital and dissolved materials (CDM). Here, detrital particulated are assumed to make only a small contribution to CDM. The authors point out the different origin of coastal and open ocean dissolved organic matter. Near coastal CDOM, like in the Baltic Sea, is mainly regulated by land-ocean interactions and originates mainly from land drainage and river runoff. Entering the ocean, CDOM is mixed vertically, advected and decomposed (e.g. by photobleaching, flocculation), while new production is assumed to play a minor role. The importance of a CDOM sink compared to other effects (e.g. dilution) is still under discussion. In the absence of a sink of terrestrial CDOM, it would take about 35, 000 years for the ocean to reach average river CDOM absorption when assuming the present-day total annual river flow. The existing large gradient between fresh water and 'blue water' implies the presence of a loss mechanism acting on far shorter time scales (Blough and Del Vecchio (2002)). It has been shown by a large number of field studies that photochemistry alone can act as a substantial sink of terrestrial CDOM (Mopper and Kiebler (2002)) Also, laboratory experiments on (optically) thin natural waters have shown absorption losses

greater than 50% over irradiation periods of several hundred to thousand hours using sources approximating the surface solar spectrum. The time scale of these losses, on the order of weeks or month under natural irradiation conditions, is consistent with field studies by Vodacek et al. (1997) and Nelson et al. (1998) in the North Atlantic and the Saragossa Sea. On the other hand, in the presence of high CDOM-concentrations photobleaching is restricted to a very thin surface layer due to the high CDOM-absorption (Blough and Del Vecchio (2002)) and the net effect might be negligible. Some studies of the Baltic Sea - North Sea transition zone even treat CDOM as conservative tracer to identify the origin of water masses (Højerslev et al. (1996), Sedmon et al. (2010)). This assumption is based on the close relation between salinity and CDOM reported e.g. by Ferrari et al. (1998), Kowalczuk et al. (1998), Kowalczuk et al. (2006).

The present study is a first attempt to include CDOM in a Baltic Sea model. At this, we assume various decay rates of CDOM and compare the results with satellite observations. Also, we are testing the hypothesis that CDOM can be regarded as conservative tracer which is of great interest for mixing studies of water masses.

2 Methods and model

2.1 The ocean model

The oceanic component consists of the three-dimensional 'Rossby Centre Regional Ocean model' (RCO). The model setup is described in detail e.g. by Meier et al. (2003) and was successfully used in various climate related studies (Meier and Kauker (2003), Meier et al. (2004), Meier (2005)). RCO was originally a regionalized version of the OCCAM-model (Webb et al. (1997)). The model domain covers the Baltic Sea including Kattegat. The horizontal resolution used here is 2nm using 41 vertical layers. As surface boundary conditions air temperature, wind, cloud cover, sea level pressure, humidity and precipitation are required while surface restoring is not applied. Since as well common reanalysis data sets as well as global climate models have their limitations in regional detail, we use regional climate models with

a limited model domain and higher resolution to downscale coarser resolved data sets. Here, we use the Rossby Centre Regional Atmosphere model (RCA) at 25 km horizontal resolution (Jones et al. (2004), Samuelsson et al. (2011)). The boundary conditions for the atmospheric model are taken from ERA40 reanalysis data (Uppala et al. (2005)) .

2.2 Colored dissolved organic matter

CDOM is induced into the ocean model by assuming a certain concentration in the 30 major rivers. River runoff data are taken from Bergström and Carlsson (1994) and updated with results from a large-scale hydrological model (Graham (2004)). The crossover from observations to the hydrological model causes for some rivers a change in variability while the mean values remain basically unchanged. In the absence of comprehensive measurements of yellow substances (or dissolved organic carbon) we assume a river inflow proportional to total organic carbon (TOC). Measurements were provided by Humborg et al. (2008). For five of the rivers used by our model no measurements are provided and we assume basin mean concentrations. The position of the considered rivers is depicted in Fig. 1. The size of the dots is proportional to the inflow of yellow substances per river and results from the product of volume flow times concentration of TOC. The differences between the rivers are dominated by the volume of water inflow per river while, in general, the mean TOC concentration per river differs by less than a factor of two. Our modeling approach assumes, that new production of CDOM plays a minor role and that the North Sea has a negligible content of yellow substances. The latter assumption is in close agreement with the results presented by Højerslev et al. (1996). Under this assumptions we performed a set of experiments based on different decay rates of CDOM. All experiments are listed in Table 1.

In the first five experiments, we assume different decay rates from no decay and light dependent decay with a maximum half live time 240, 480, 960 and 1920 hours. The decay rates are calculated for every grid box depending on the downward radiative flux in RCO which is parametrized by two exponential functions following Paulson and Simpson (1977). Maximal decay is reached in the surface grid box at an in-

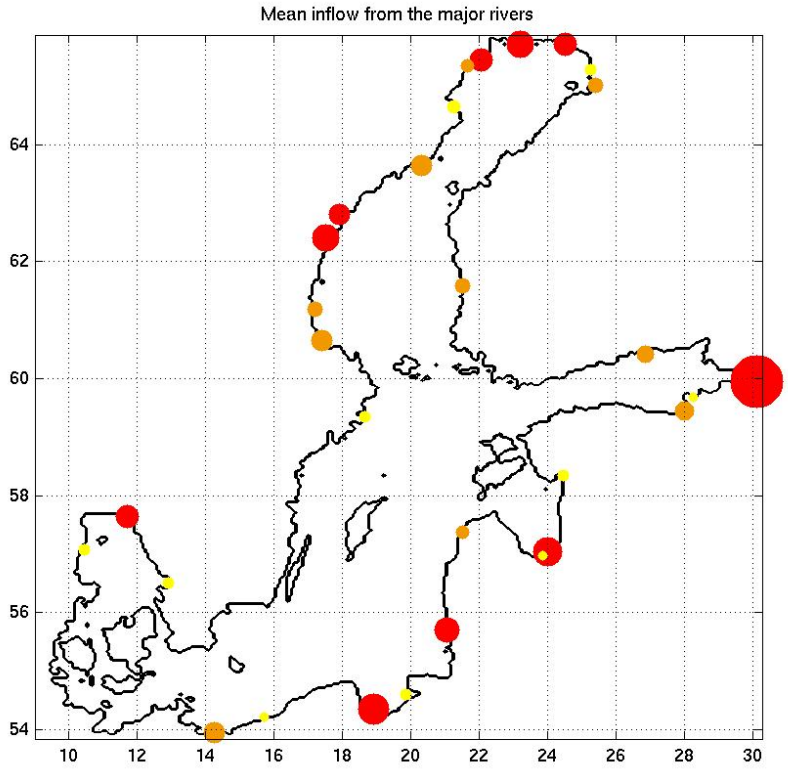

Figure 1: *Position of the rivers used in the model setup. The size of the dots is proportional to the amount of yellow substances discharged by the particular river. The amount of yellow substances results from water supply times concentration.*

Exp.	Description	Min. half life time
NODECAY	no decay of yellow substances	-
LIGHT240	light dependent decay	240 hours
LIGHT480	light dependent decay	480 hours
LIGHT960	light dependent decay	960 hours
LIGHT1920	light dependent decay	1920 hours
ZERF1920	constant decay	1920 hours
TEMP960	temperature dependent decay	1920 hours

Table 1: *Acronyms for model experiments discussed in the text (first column), a short description and the considered half life time.*

coming radiation of 900 W/m^2. Below this maximum this decay decreases linearly with the available light. The amplitude of the decay is given by the fraction of the effective mean radiation and the maximal mean radiation in the upper grid box. Two additional comparative experiments assume a constant and a temperature dependent decay of CDOM. The temperature dependent decay is designed such that the decay is maximal at 20°C and above. At lower temperatures (TEMP) the decay decreases by a factor of $TEMP/20$. A more systematic approach to test different decay rates is not possible due to the high complexity and long run-times of the ocean model. Following Meier (2005) we performed a 90 year spinup by repeating present day forcing (1962-2007) twice. Additionally, discharge experiments of the three major rivers were carried out.

2.3 Observational data

In the absence of comprehensive CDOM-measurements, we focus mainly on satellite data during the period 2003-2006 which were provided by the European Space Agency (http://www.esa.int/esaCP/index.html). Note, however, that satellite measurements in the Baltic Sea suffer from difficulties due to the atmospheric composition and the multi-componental water properties (Darecki (2003), Kratzer et al. (2003)).

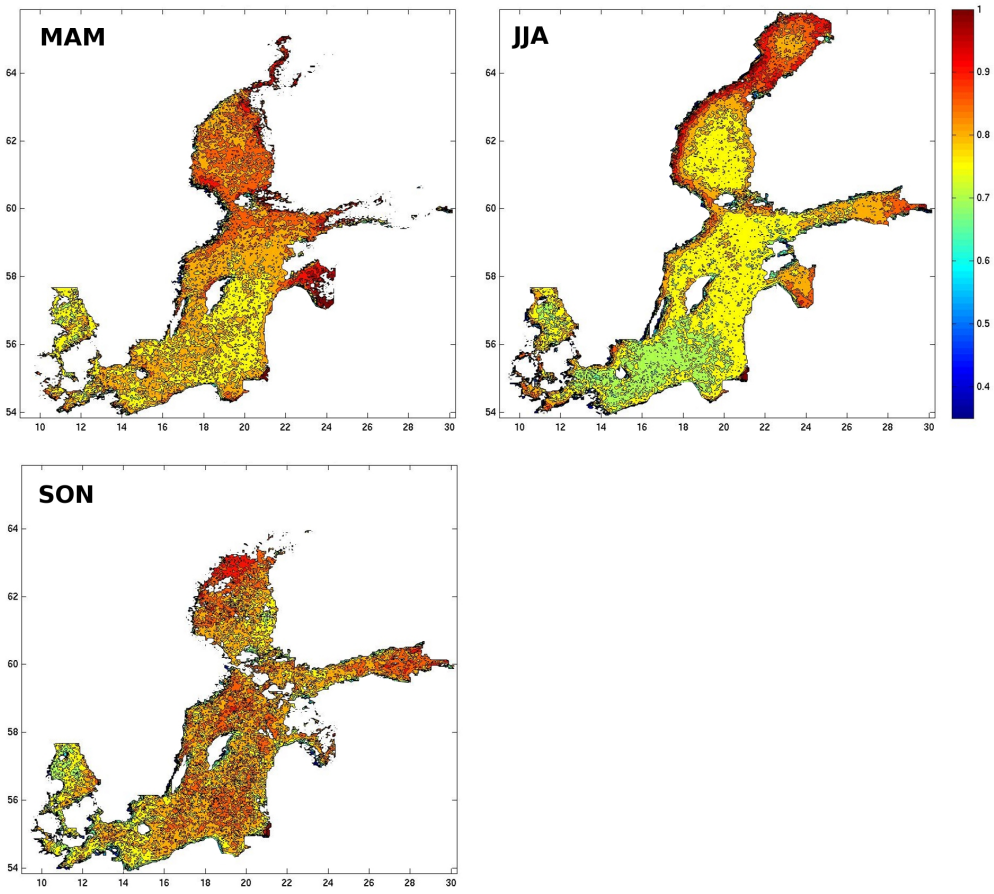

Figure 2: *Normalized seasonal mean concentration of yellow substances as observed by satellite (MERIS).*

According to Kratzer and Tett (2009) the MERIS standard processor underestimates

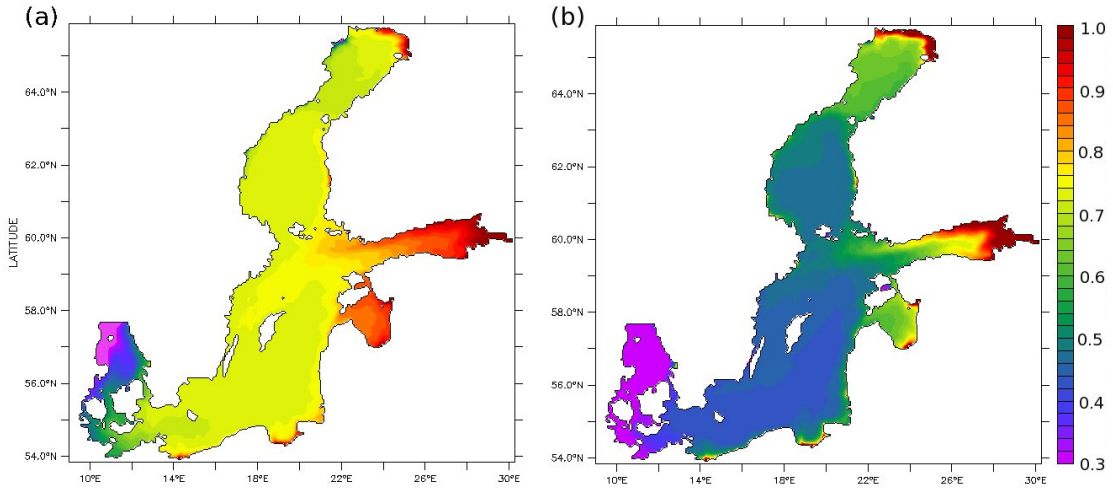

Figure 3: *Normalized seasonal mean concentration of yellow substances as modeled in summer in (a) experiment NODECAY and (b) in experiment LIGHT480.*

yellow substances in the open Baltic by about 81%. This error is basically related to an off-set which implies that we have to focus on the pattern and the mean seasonal cycle rather than on absolute values. Before normalisation by dividing through the maximum value we added the offset (= 80% of the mean summer concentration of yellow substances at Gotland Deep) to obtain reasonable gradients in space and time. Note, that this is a rather rough approach which is due to the lack or more reliable data. In Fig. 2 the normalized pattern are depicted.

2.4 Model results

Comparing the spatial pattern of the modeled CDOM concentrations with satellite observations, reveals that the pattern roughly agree when considering experiment NODECAY (Fig. 3a). However, one apparent discrepancy is a somewhat too high concentration in the Gulf of Finland, too high concentrations close to the river mouth

and, apart from the regions very close to the coast, too weak spatial gradients. A light dependent decay basically enhances the spatial gradient while the overall pattern remains in principle unchanged (e.g. LIGHT480 in Fig. 3b).

Considering the large scale time behaviour shows as well an underestimation of the variability when no decay of yellow substances is assumed. Fig 4a depicts the mean seasonal cycle of CDOM in the centre of the Baltic proper (14°-19°E, 54°-58°N) in the experiment NODECAY in comparsion to observations. In contrast to the observations, which show a pronounced minimum during the summer month, CDOM is accumulating throughout the year until mixed layer depth increases during winter and run-off is reduced at the same time (Fig. 4). The observed seasonal cycle can not be reproduced by either a constant (ZERF1920) or temperature related decay (TEMP960). While a constant decay does not change the shape of the seasonal cycle at all, but increases the amplitude, a temperature dependent decay leads to a decrease of CDOM in late summer/autumn (Fig. 4a) when water temperatures are highest. As shown in Fig. 5, similar results are obtained in the northern Baltic Sea (16°-24°E, 60°-70°N). The assumption of a light dependent decay gives most satisfactory results (Fig. 4b and Fig. 5b) while the results concerning the strength are somewhat contradictory. In experiment LIGHT240 the amplitude of the seasonal cycle compares best to observations (though the seasonal cycle is still somewhat too weak and the increase in the yellow substance content is a bit too slow in autumn), but the spatial gradient is too strong and a weaker light dependent decay seems likely.

3 Conclusions

In the present study, CDOM was included into a Baltic Sea model assuming a river supply proportional to TOC. At first order, we assume that new production is of minor importance and that the North Sea has a negligible content of yellow substances. Given this assumptions, we obtain a reasonable agreement with observed pattern, while some large differences occur in detail. Our attempt to model yellow substances in the Baltic Sea was most successful when assuming a linear light dependent decay

of yellow substances with a half life time of 240-480 hours under maximum light exposure. Thus, according to our finding yellow substances can not be regarded as a conservative tracer. This result is inline to the results of Opsahl and Brenner (1998) who report a loss of 75% of total dissolved ligning during 28d of light exposure at the Missisippi river plume.

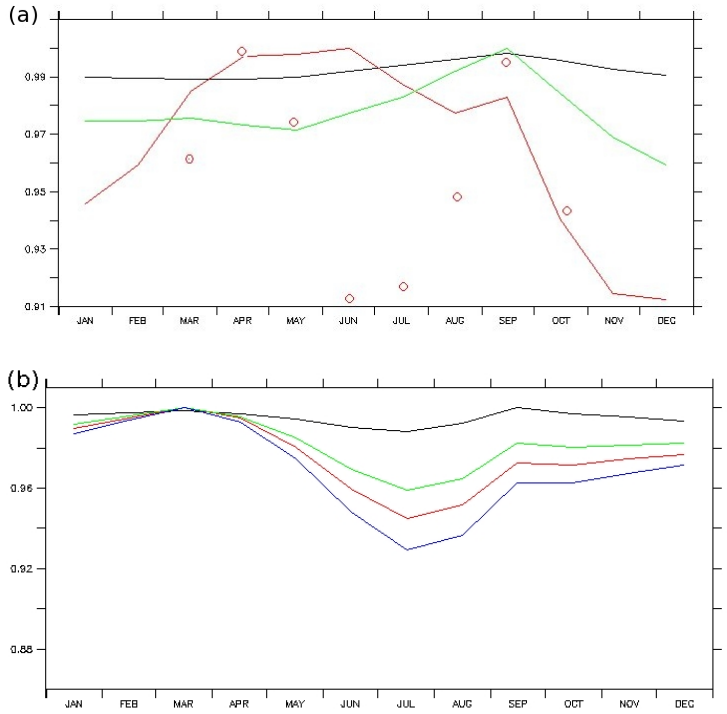

Figure 4: *Seasonal cycle of yellow substances (normalized by division through the maximum value) in the Baltic Proper as modeled. (a) NODECAY (black line), ZERF1920 (green line) and TEMP960 (red line). The observed, normalized values in the same region as observed by satellite (MERIS) are depicted as red dots. (b) LIGHT240 (blue line), LIGHT480 (red line), LIGHT960 (green line) and LIGHT1920 (black line).*

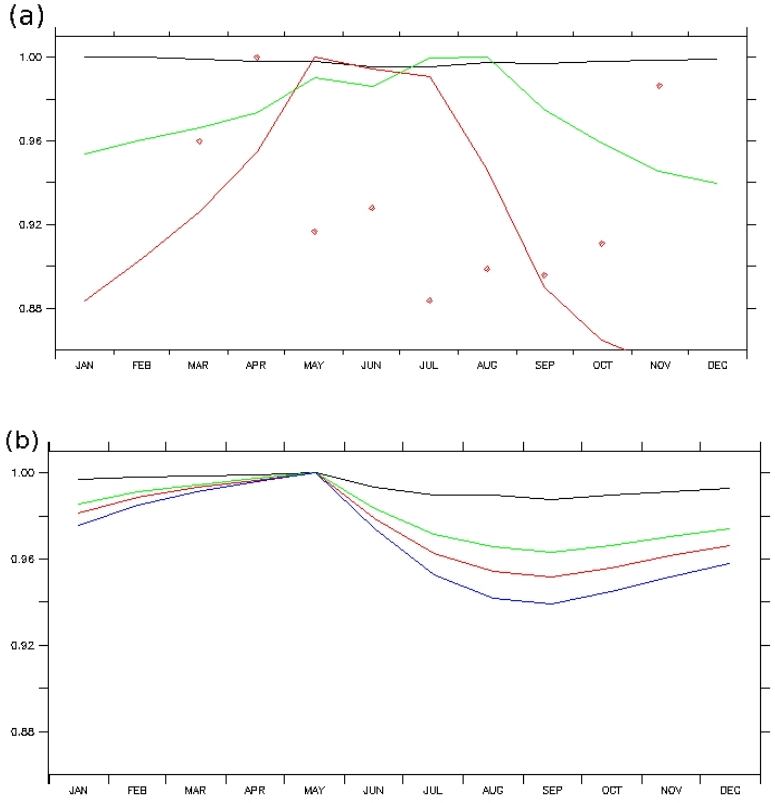

Figure 5: *Seasonal cycle of yellow substances (normalized by division through the maximum value) in the Bothnian Sea (16°-24°E, 60°-70°N) as modeled. (a) NODECAY (black line), ZERF1920 (green line) and TEMP960 (red line). The observed, normalized values in the same region as observed by satellite (MERIS) are depicted as red dots. (b) LIGHT240 (blue line), LIGHT480 (red line), LIGHT960 (green line) and LIGHT1920 (black line).*

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