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On the influence of dissolved organic matter on remote sensing of chlorophyll in the Straits of Skagerrak and Kattegat

Remote sensing Chlorophyll Light absorption Skagerrak Kattegat

Télédétection Chlorophylle Absorption de la lumière Skagerrak Kattegat

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ABSTRACT

An experimental techniques to estimate the influence of dissolved organic matter (DOM) on remote sensing of chlorophyll in water has been developed, based on the relationship between fluorescence and absorption of light by a substance. The profiles of fluorescence, chlorophyll content in sea water and estimates of light attenuation in water samples were used in the paper. These data have permitted to calculate the regressions linking fluorescence and light absorption at 450 nm by chlorophyll (ABC<sub>450</sub>) and by DOM (ABD<sub>450</sub>). The remote sensing needs no correction for DOM if  $M_{450} = 100*$  (ABC<sub>450</sub>/ABD<sub>450</sub>) >> 100. This technique has been applied to data collected during the international *Skagex* field experiment in the straits of Skagerrak and Kattegat in spring and autumn of 1990. It was found that  $M_{450} <= 100$  everywhere in the subsurface layer. Unfavorable conditions for remote sensing of chlorophyll prevailed in the straits because of the uptake of DOM-rich water from the continent and the accumulation of phytoplankton in deeper layers. These and another processes can increase relative content of colored DOM even in waters of open ocean.

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RÉSUMÉ

Effet de la matière organique dissoute sur la télédétection de la chlorophylle dans le Skagerrak et le Kattegat

Une méthode expérimentale est développée pour évaluer l'effet de la matière organique dissoute (DOM) sur la télédétection de la chlorophylle. Elle est fondée sur la dépendance entre la fluorescence et l'absorption de la lumière par une substance. Les données utilisées dans ce travail sont des profils de fluorescence, des concentrations de chlorophylle et les valeurs d'atténuation spectrale de la lumière. Ces résultats ont permis d'obtenir des régressions entre la fluorescence et l'absorption de la lumière à 450 nm par la chlorophylle (ABC<sub>450</sub>) et par la matière organique dissoute (ABD<sub>450</sub>). La télédétection peut être utilisée sans correction si la condition suivante est remplie :  $M_{450} = 100*$  (ABC<sub>450</sub>/ABD<sub>450</sub>) >> 100. Cette méthode a été appliquée aux résultats obtenus pendant la campagne internationale *Skagex* dans les détroits du Skagerrak et du Kattegat, au printemps et à l'automne de 1990. Dans la couche de subsurface, M est partout inférieur à 100. Cette situation peu favorable à la télédétection de la chlorophylle est due à l'afflux des eaux continentales riches en matière organique dissoute et à l'accumulation du phyto-

plancton dans les couches plus profondes. Ces processus sont, entre autres, capables d'augmenter la concentration relative de la matière organique, même dans les eaux du large.

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# INTRODUCTION

The remote sensing of chlorophyll in water is effective when phytoplankton and its byproducts determine water color and the stratification of the water body is simple (Sathyendranath and Morel, 1983; Sathyendranath and Platt, 1989; and others). These features are common in the open ocean. Additional sources of coloured substances acting in nearshore areas render the techniques and algorithms for successful remote sensing offshore inadequate. One of these substances is dissolved organic matter (DOM, or "Yellow substance"). Planktonic and allochtonous DOM are difficult to distinguish by their optical properties; both degrade much more slowly than particles suspended in sea water (Daumas, 1978) and absorb light within the same spectral range as chlorophyll. For these reasons the relationship between the absorption of light by chlorophyll and DOM at local scales must be studied to develop algorithms forthe remote determination of chlorophyll in coastal zones.

Direct estimates are impossible because there are no instruments for the separate measurement of light absorption by DOM or chlorophyll *in situ*. It is worthwhile developing indirect techniques using measurements of specific properties of DOM and chlorophyll that can be converted into estimates of light absorption coefficients. The purpose of the present work is to elaborate this technique and to reveal the role of DOM as background by remote sensing of chlorophyll in waters containing DOM of different origins (case-2 waters according to Sathyendranath and Morel, 1983).

### PRINCIPLES AND SITE OF OBSERVATIONS

The proposed technique is based on profiling of fluorescence of DOM and chlorophyll together with water sampling. The latter gives the quantities permitting the conversion of fluorescence intensity into light-absorption coefficients of a substance. These quantities are concentration C mg $*m^{-3}$  or coefficient of light absorption:

$$AB = SAB * C \tag{1}$$

where SAB m<sup>-1</sup> (mg\*m<sup>-3</sup>)<sup>-1</sup> is the specific coefficient of light absorption of a substance; The fluorescence intensity F in diluted solution of a substance excited with light of moderate intensity  $F_e$  is described with the expression:

$$\mathbf{F} = \mathbf{q} \, \mathbf{F}_{\mathbf{e}} \, \mathbf{SAB} \, \mathbf{C} \tag{2}$$

where q is a normalizing factor (Parker, 1968). From (1) and (2) it follows that coupled measurements of F and C or F and AB are needed to carry out above mentioned conversion.

The dependence between fluorescence and concentration in sea water or in living algal cells is likely to be not so simple as (2). Therefore it is desirable to use data varying within the widest range of their magnitudes. This requirement was satisfied by materials from the international multi-ship experiment Skagex, supported by ICES and intended as an interdisciplinary investigation of the Straits of Skagerrak and Kattegat. The experiment was carried out in May-June (Skagex 1) and in September (Skagex 2) of 1990. The waters of the Baltic Sea and the Atlantic Ocean mix in the straits, and the uptake of inland waters adds DOM to the marine environment (Fonselius, 1990). There is a grat deal of literature concerning the optical properties of waters in the straits (Joseph, 1950; Højerslev, 1971; Jerlov, 1976 and others), but published data are too incomplete to compare distributions of light absorption by DOM and chlorophyll under different environmental conditions.

#### INSTRUMENTATION AND COLLECTED DATA

Profiles of the intensity of fluorescence of DOM FD (z) and chlorophyll FC (z) were measured simultaneously on board R/V *Shelf* with a submersible MZF fluorometer (Karabashev and Khanaev, 1988) at stations of *Skagex* sections in the Skagerrak and Kattegat. Water sampling was added during *Skagex* 2. Samples were taken at depths  $z_i$  from 0 to 250 m. The spectra of light attenuation coeffi-



#### Figure 1

Positions of the Skagex sections B, D, E and F in the Straits of Skagerrak and Kattegat.

Positions des sections B, D, E et F de Skagex dans les détroits du Skagerrak et du Kattegat.

cient AT  $(z_i, w_j)$  were measured in water samples with a shipborne transmissiometer (Karabashev *et al.*, 1987) for wavelengths  $w_j$  ranging from 310 to 570 nm. Fluorescence of DOM was fixed at the moment of closing a water bottle mounted on the fluorometer. The first additional data set 1DS comprising 39 pairs of FD  $(z_i)$  and AT  $(z_i, w_j)$  was obtained in this way.

Since there was no possibility of determining chlorophyll on board *Shelf*, it was considered expedient to use data collected by other *Skagex* participants at the same stations as FC (z) with a time-gap not exceeding two days. The latter condition was satisfied by chlorophyll determinations carried out on board R/V *Arnold Weimer* (section F, 2 June) and R/V *A. Thiselius* (section B, 8 and 17 June, 12 September). Each chlorophyll concentration CC ( $z_k$ ) at depth  $z_k$  has been coupled with the corresponding FC ( $z_k$ ). Altogether 117 pairs of these quantities comprised the second, additional data set 2 DS.

The main data set included profiles FD (z) and FC (z) from sections E, D and B (Fig. 1) where observations have been carried out during both *Skagex 1* and 2.

## DATA ANALYSIS

The best ratio of signature of chlorophyll to that of DOM by passive remote sensing may be achieved within an absorption maximum of chlorophyll in the spectral window between 420 and 460 nm. The ratio of absorption of light by chlorophyll to DOM at 450 nm has been chosen to assess the role of the latter

$$M_{450}(z) \% = 100 * [ABC_{450}(z)/ABD_{450}(z)]$$
 (3)

The background from DOM may be regarded as negligible in the case of  $M_{450} >> 100$ . The final goal of data processing was to calculate ABC<sub>450</sub> and ABD<sub>450</sub> from measured data.

Attenuation of light by sea water in the UV spectral region is mainly due to colored DOM (Jerlov, 1976). There is close correlation between FD ( $z_i$ ) and AT ( $z_i$ ,  $w_j$ ) at  $w_j <$ 400 nm could exist. The data in 1DS have been used to calculate the spectrum of the corresponding correlation coefficient. Its estimates exceeds 0.8 at  $w_j <= 350$  nm.

Considering the scattering of light as main component of light attenuation in sea water at  $w_j \ge 530$  nm (Jerlov, 1976) and using expression linking light scattering coefficients at different wavelengths (Kopelevich, 1983), it is possible to calculate absorption of UV light by DOM.

ABD 
$$(z_i, 310) = AT (z_i, 310) - AT (z_i, 550) * (550/310)^s$$
 (4)

choosing s so that the correlation coefficient K1 between FD ( $z_i$ ) and ABD ( $z_i$ , 310) becomes maximal. It was found that K1<sub>max</sub> = 0.91 at s = 0.3. This value of s is inherent to light scattering by large particles in water (Kopelevich, 1983). Abundance of these particles in waters of the straits is quite probable. Using (4) at s = 0.3 gives a new set of pairs FD ( $z_i$ ) - ABD ( $z_i$ , 310). These were employed to determine the dependence of light absorption at 310 nm on fluorescence intensity of DOM

 $ABD_{310} = 3.19*10^{-9}*FD^3 - 5.30*10^{-6}*FD^2 + 3.65*10^{-3}*FD + 0.077$ 

This expression was used to convert profiles FD (z) to profiles  $ABD_{310}$  (z).

The absorption of light by DOM in sea water decreases exponentially with wavelength (Jerlov, 1976):

ABD 
$$(w_2) = ABD (w_1) * exp [p (w_2 - w_1)]$$
 (6)

The estimates of p obtained in different areas varies from - 0.012 to - 0.017 nm<sup>-1</sup> (Karabashev and Zangalis, 1974; Morel and Prieur, 1976; Bricaud, 1979, *in* Prieur and Sathyendranath, 1981; Kopelevich, 1983 and others). The value of  $p = -0.015 \text{ nm}^{-1}$  was accepted in this study as most probable and profiles ABD<sub>450</sub> (z) were calculated from ABD<sub>310</sub> (z) with the aid of (6).

The coefficient of correlation K2 [FC  $(z_k)$ , CC  $(z_k)$ ] for 2DS has turned out to be less than 0.5. >The scatter plot for 2DS has revealed three kinds of data pairs. The most numerous produced points gravitating towards a line with positive slope. The pairs of second kind were formed by high CC  $(z_k)$  and moderate FC  $(Z_k)$  was peculiar to pairs of the third kind. It was supposed that data pairs of the second and third kinds were due to the time-gap between profiling of FC and water sampling. Observations at sea and oceans have shown greater variability of chlorophyll near its maxima (Karabashev, 1987). Plenty of maxima existed in the Skagex area. Because of the time-gap there was a greater probability of obtaining corrupt data in layers with maxima of chlorophyll than above or below them. So the pairs of the second and third kinds have been excluded and the new set 3DS has emerged containing 92 data pairs of the first kind. For this set K2 [FC  $(z_k)$ , CC  $(z_k)$ ] = 0.78. This makes it possible to find a regression of chlorophyll on fluorescence

$$CC = 1.85 * 10^{-3} * FC + 0.19$$
<sup>(7)</sup>

It was used to calculate CC (z) from FC (z). Accepting coefficient of specific absorption of light by chlorophyll at 450 nm in living algae SABC<sub>450</sub> = 0.09 mg m<sup>2</sup> (Yentsch, 1960) and substituting it for (1) permits the transition from CC (z) to ABC<sub>450</sub> (z) and estimation of  $M_{450}$  (z).

### **RESULTS AND DISCUSSION**

The estimates of  $M_{450}$  at depths 5-7 m for sections E and D and at 3-5 m for section B are presented in the Table and Figure 2. These depths belong to a layer where optical

Table

Statistical characteristics of distribution of M-criterion at sections E, D and B during Skagex 1 and 2.

Caractéristiques statistiques de la répartition du critère-M aux sections E, D et B pendant Skagex 1 et 2.

	Skagex 1			SKAGEX 2		
	Е	D	· <b>B</b>	E	D	В
Mean	56.5	71.4	68.7	86.1	128.3	69.3
Std.dev.	15.4	12.1	13.5	18.4	44.6	12.4
Max.	84	88	91	125	210	91
Min.	33	58	55	58	65	55
Sample vol.	11	7	6	12	8	7

(5)





Profiles of light absorption at 450 nm by DOM and chlorophyll at stations E1 and E7 in Skagerrak.

Profils d'absorption de la lumière à la longueur d'onde 450 nm par la matière organique dissoute (DOM) et par la chlorophylle aux stations E1 et E7 dans le Skagerrak.

contrasts detectable from space are formed. It is here that the main features of  $M_{450}$  distribution in the straits are to be found: 1) It varied within wide range of magnitude but was never high enough to discount the influence of DOM on remote sensing of chlorophyll; 2) This influence was the strongest in central Skagerrak where the smallest  $M_{450} =$ 33 has been observed at station E7; 3) The DOM background was somewhat higher in early summer than in the autumn in Skagerrak but there were no significant interseasonal changes of  $M_{450}$  in the Kattegat.

Spatial variability of  $M_{450}$  in a layer accessible for remote sensing may not be regarded as evidence of spatial variability of chlorophyll in the water column, even in the absence of significant changes of DOM. Profiles ABC<sub>450</sub> (z) and ABD<sub>450</sub> (z) from stations E1 and E7 with  $M_{450} = 84$  and  $M_{450} = 33$ , correspondingly, are compared in Figure 2. It is obvious that the lesser  $M_{450}$  at E7 is due to stratification of chlorophyll but not to a decrease of its content in water body relative to station E1.

The profiles  $ABD_{450}$  (z) have been calculated using data not submitted to any selection. On the contrary, the data processing for  $ABC_{450}$  (z) involved selection without strictly defined criteria. The validity of this procedure was checked employing data collected at section F where the time-gap between fluorescence measurements and water sampling amounted to two days. The values of  $ABC_{450}$  (5) have been computed by substituting estimates of chlorophyll content at 5 m depth from eleven stations and SAB<sub>450</sub> = 0.09 mg m<sup>2</sup> to expression (1). The values FD (5) from the same stations of section F have been used to calculate  $ABD_{450}$  (5) with expressions (5) and (6). The average of eleven estimates of M-criterion for section F made up 84 % with standard deviation 34 %. These estimates agree well with  $M_{450}$  in the Table, confirming their independence of properties of 2DS or 3DS.

Specific absorption of chlorophyll 0.09 mg m<sup>2</sup> (Yentsch, 1960) used in this study is among the greatest known estimates (Prieur and Sathyendranath, 1981). Such values of SABC are most common in oligotrophic waters but in eutrophic areas like Skagerrak and Kattegat the SABC<sub>450</sub> hardly exceeds 0.05 mg m<sup>2</sup> (Wozniak and Ostrowska, 1990). For this reason real  $M_{450}$  in the straits may be 1.5-2 times smaller than in the Table, signifying that the absorption of light by DOM but not by chlorophyll played a key role in the formation of optical contrasts within the upper layer of the straits accessible to remote sensing during *Skagex* field activities.

The growth of  $M_{450}$  in Skagerrak from early June to September was accompanied by an increase of salinity and a decrease of DOM fluorescence in the subsurface layer. Both events were due to seasonal variations in the uptake of continental waters to the strait [and, in the first place, from Glomma river in the North (Fonselius, 1990)]. In this connection it is worth noting that DOM of continental origin is able to change the optical properties of sea water at much greater distances from its source than in the Skagerrak. A patch of low salinity water with bright fluorescence of DOM had been observed offshore in the surface layer of the Bay of bengal. It was displaced 250 miles from mouth of river Ganga in direction of water circulation in the bay (Karabashev, 1987). The excess attenuation of UV light counter correlated with salinity of sea water has been measured in surface layer of tropical Atlantic more than 1,000 km north of Amazon river mouth (Karabashev and Kuleshov, 1985). Large patch of low salinity water strongly attenuating light has been observed by author to the east of Lesser Antilles in open Atlantic Ocean in 1984. The patch was believed to originate from Orinoco river. Large scale circulation bringing DOM rich waters from eutrophic to oligotrophic areas is likely to be another cause of excess colored DOM in surface layer of open ocean. The example of this kind of event in Indian Ocean is mentioned by Karabashev (1987).

### CONCLUSIONS

1) A new approach to the influence of DOM on remote sensing of chlorophyll in sea water has been realized, comprising *in situ* measurements of fluorescence of these substances and determination of chlorophyll and light attenuation in water samples. The data are used to compute the profiles of absorption coefficients by chlorophyll and DOM. Their ratio serves as a measure of estimated influence.

2) This ratio has been calculated for data collected in the Skagerrak and Kattegat in May-June and September of 1990. Absorption of light by DOM was comparable to or greater than absorption by chlorophyll in the subsurface layer of the straits, due to the uptake of inland waters rich with DOM as well as the accumulation of chlorophyll below waters accessible to remote sensing.

3) Observations evidence that these processes may act in open ocean because of long range influence of great rivers and radical differences of vertical distributions of chlorophyll and DOM in many areas of the ocean.

The influence of DOM on remote sensing of chlorophyll may be reduced by high resolution spectrophotometry of water surface considering that their absorption spectra are not the same. Another way is to employ discrimination of Fraunhofer lines (Stoertz *et al.*, 1969) for remote sensing of DOM together with sea surface radiance measurements in absorption band of chlorophyll. Subtracting processed DOM signal from radiance may yield "pure" chlorophyll signature. Remote sensing of DOM is meaningful itself for tracing water movements or revealing upwellings.

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