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On the variability of "yellow substance" in the Skagerrak and the Kattegat

"Yellow substance"
Fluorescence
Light attenuation
Skagerrak
Kattegat

«Substance jaune»
Fluorescence
Atténuation de la lumière
Skagerrak
Kattegat

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ABSTRACT

The variability of "yellow substance" in waters of the Skagerrak and the Kattegat was studied during the international *Skagex* programme in 1990 and 1991. Data on attenuation of light and fluorescence of dissolved organic matter (DOM) in sea water were collected with a spectral transmissiometer and a submersible fluorometer within a depth range of 0-250 m at several stations. More than fifty-fold variations of fluorescence intensity over space and time were due to the combined action of different sources of DOM in the straits. The surface maximum of fluorescing DOM, related to river outflow, was spreading from Oslo fjord to the central Skagerrak in late spring. This maximum may be ecologically important because it diminishes shortwave PAR. In the autumn the brightest DOM fluorescence was found in the Kattegat and along the Norwegian coast in accordance with earlier studies. The local minima of DOM fluorescence are associated with the Jutland current. Both the instability of the current and a ten-fold difference in DOM content between deep layers of the Skagerrak and Kattegat resulted in strong synoptic variability of fluorescence in the transitional area between the straits. Seasonal and synoptic variabilities of "yellow substance" were minimal in the southern Kattegat. The vertical gradients of DOM fluorescence were mostly negative at the depth of the thermocline of the open Skagerrak in spring, reaching values of 40-50 % m^{-1}. Fine structure and complex shape were inherent to fluorescence profiles from areas of intensive water mixing. DOM fluorescence closely covaried with attenuation of UV light: the correlation coefficient was + 0.9 for wavelength w <= 350 nm regardless of season. The inverse dependence between wavelength derivative and magnitude of UV attenuation in the straits did not change with season. DOM fluorescence and water salinity were negatively correlated at depths of 25-50 m but they varied independently in the upper 10 m. No significant correlation between fluorescence and nitrates has been found. Estimates of correlation with phosphates ranged from 0.7 to 0.8. In general, the changes of fluorescence were due to variations of DOM content in sea water but not to variability of DOM composition or state. The properties of DOM fluorescence in the Skagerrak-Kattegat area make it a useful natural tracer of water movements suitable for active remote sensing with airborne lidar.

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RÉSUMÉ

Variabilité de la «substance jaune» dans le Skagerrak et le Kattegat

La variabilité de la «substance jaune» dans les eaux du Skagerrak et du Kattegat a été étudiée dans le cadre du programme international *Skagex* en 1990 et 1991. L'atténuation de la lumière et la fluorescence de la matière organique dissoute (MOD) ont été mesurées à l'aide d'un transmissiomètre spectral et d'un fluorimètre submersible dans la couche 0-250 m. L'intensité de la fluorescence a varié d'un facteur cinquante dans l'espace et dans le temps sous l'effet combiné des différentes sources de MOD dans les détroits. A la fin du printemps, le maximum superficiel de MOD fluorescente, lié à l'apports des rivières dans le fjord d'Oslo, s'étend jusqu'au centre du Skagerrak; ce maximum pourrait avoir une importance écologique car il réduit la contribution des courtes longueurs d'ondes dans le rayonnement actif en photosynthèse. A l'automne la fluorescence de la MOD est la plus importante dans le Kattegat et le long de la côte norvégienne, en bon accord avec les travaux antérieurs. Les minima locaux sont associés au courant du Jutland; l'instabilité de ce courant et une différence d'un facteur dix dans la teneur en MOD entre les couches profondes du Skagerrak et celles du Kattegat sont à l'origine d'une grande variabilité synoptique de la fluorescence dans la zone de transition entre les détroits. Les variabilités saisonnière et synoptique de la «substance jaune» sont minimales dans le sud du Kattegat. Au printemps, les gradients verticaux de fluorescence de la MOD sont généralement négatifs à la profondeur de la thermocline à l'ouverture du Skagerrak, atteignant des valeurs de 40 à 50 % par mètre. La structure fine et la forme complexe inhérentes aux profils de fluorescence sont liées à l'atténuation de l'ultraviolet, avec un coefficient de corrélation de + 0,9 aux longueurs d'ondes inférieures à 350 nm en toutes saisons. La dépendance inverse entre la sélectivité spectrale et l'atténuation de l'ultraviolet dans les détroits ne varie pas avec la saison. La fluorescence de la MOD et la salinité sont corrélées négativement entre 25 et 50 m de profondeur, mais elles varient de manière indépendante dans les dix mètres superficiels. Aucune corrélation significative n'est trouvée entre la fluorescence et les nitrates; la corrélation avec les phosphates est de l'ordre de 0,7 à 0,8. En général, les variations de fluorescence sont dues aux variations de la teneur en MOD et non pas à la variabilité de la composition ou de l'état de la MOD. Les caractéristiques de la fluorescence de la MOD dans la région Skagerrak-Kattegat en font un traceur naturel des mouvements des eaux qui peut être observé par télédétection au moyen du lidar.

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INTRODUCTION

Coloured fluorescing dissolved organic matter DOM (or "yellow substance") is widespread in the ocean. It forms there from decomposing organisms or enters the marine environment from land by air or with river outflow (Kalle, 1963). The "lifetime" of molecules of DOM is 10^3 years (Romankevich, 1984) and hence "yellow substance" has been suggested as a tracer of water movements offshore and in coastal areas (Karabashev and Solov'ev, 1973; Zimmerman and Rommets, 1974, and others). DOM absorbs light and fluoresces, producing a natural background which can limit the ability of optical methods to detect other constituents of sea water. Hence there are three reasons to study the variability of optical properties of "yellow substances": 1) to increase knowledge of DOM; 2) to examine the advantages and limitations of using DOM as a natural tracer of water movements in the sea; 3) to provide algorithms for the background correction of optical determinations of chlorophyll, petroleum hydrocarbons or other ecologically important substances in water.

These topics are particularly urgent in areas where several sources of DOM are acting. The straits of Skagerrak and Kattegat represent such an area. Here the waters of the Atlantic Ocean and the Baltic Sea are mixing and rivers with large catchment zones bring DOM-rich waters into the sea (Fonselius, 1990). For these reasons, studies of the variability of "yellow substance" have been included in the programme of the international experiment *Skagex* aimed at complex investigations of the dynamics and biological processes in the straits. The experiment was conducted under the aegis of ICES. The measurements were carried out on board research ships from several countries in four cycles in 1990-1991, mainly at sections crossing the straits. In this paper the optics of "yellow substance" are studied from three cycles of *Skagex.*

The lack of a technique for direct *in situ* determination of the coefficient of light absorption by DOM represents one of the main obstacles in studies of this kind. The coefficient of attenuation of a collimated light beam, c(w), measurable with a transparency meter is:

$$c(w) = a(w) + b(w) \qquad (1)$$

where $a(w)$ and $b(w)$ are coefficients of light absorption and scattering at wavelength w. The $a(w)$ itself is a sum of absorption by "yellow substance" $a_y(w)$, photosynthetic pigments of plankton $a_P(w)$, "pure water" $a_w(w)$, salts $a_s(w)$, *etc*. The spectral window where $a_y(w)$ is likely to become comparable with $c(w)$ is in the wavelength range 300-400 nm (Jerlov, 1976; Kopelevich, 1983).

It is much easier to determine DOM by fluorescence methods with excitation by either UV or visible light. The spectral band of DOM fluorescence is shifted by 100-200 nm towards a longer wavelength relative to the excitation wavelength. The chlorophyll emits fluorescence in the far red. This makes it possible to separate measurements of DOM and chlorophyll fluorescence in natural sea water if the spectral windows for excitation and detection of fluorescence are properly chosen (Karabashev, 1987).

The quantum intensity of fluorescence for a diluted solution of a substance by wavelength w_f is:

$$F(w_f) = B\, q\, F(w_e)\, a(w_e)\, L \qquad (2)$$

where $F(w_e)$ and $a(w_e)$ are excitation intensity and absorption coefficient by wavelength w_e, L is thickness of the excited layer and q is quantum yield of fluorescence (Parker, 1968). The presence of $a(w)$ in (1) and (2) promises that combined measurements of $F(w)$ and $c(w)$ may be useful in studies of "yellow substance" in the case where the latter strongly influences the attenuation of light. This approach was used in the *Skagex* missions.

Kalle (1949) discovered an inverse dependence of light absorption and fluorescence of DOM on salinity in the surface layer of the Baltic Sea and interpreted this as due to the uptake of fresh, DOM-rich water from land and penetration of clear saline water from the straits. Measuring light attenuation at 380 and 665 nm with a submersible instrument, Malmberg (1964) estimated the absorption coefficient of "yellow substance" and its relation to the temperature, salinity and the dynamics of water in the Skagerrak. The variability of DOM fluorescence in the Skagerrak and the Kattegat had been described by Højerslev (1971). A rapid decrease of the fluorescence intensity of Elbe river water due to mixing with the North Sea water, has been demonstrated by Gienapp (1979). Investigations of this kind provided evidence that studies of DOM fluorescence and light attenuation may improve understanding of oceanographic processes in the Skagerrak and the Kattegat.

MATERIALS AND METHODS

A multichannel submersible fluorometer MZF was employed to give vertical profiles of DOM fluorescence (Karabashev and Khanaev, 1988). Two light beams from a strobe lamp excite fluorescence and scattering in sea water outside the watertight housing of the instrument. The first beam excites DOM fluorescence in the spectral window 350-390 nm. This fluorescence is detected with a photomultiplyer in spectral window 440-530 nm. The colour filters forming the windows protect the photomultiplier from scattered light including Raman scatter from water. The red component of the same beam scattered in sea water is detected with another photomultiplier at wavelengths $w \geq 680$ nm. The second beam excites chlorophyll fluorescence in window 420-550 nm and this fluorescence is detected with the third photomultiplier at $w \geq 680$ nm. The spectral and spatial separation of the beams prevents crosstalk between optical channels. These channels together with depth and water temperature were logged eight times per second by an onboard computer. The profiles were averaged over 0.5 m thick layers. The intensities of fluorescence and scattering values were expressed in arbitrary units of linear scale, temperature and depth in °C and m.

The reproducibility error, E, for the fluorometer measurements was estimated *in situ* as the lower limit of data scattering about the average value when repeated observations were made in steady homogeneous water layers of the straits. Temperature errors were $E_T = \pm 0.03$°C. The errors of fluorescence measurements were 4-6 %. These errors increased twice in deep waters poor in fluorescing DOM.

A shipboard spectral transmissiometer (Karabashev *et al.*, 1987) was used to measure spectral light attenuation $c(w)$ in water samples. They were collected with titanium water bottles. The sampled water fills short and long stainless steel tubes tightened with flat quartz glasses. The light from a halogen lamp is beamed through one of the tubes and a monochromator. A photomultiplier monitors the intensity of the light beam. After selecting a wavelength w_i with the monochromator, an operator places short tube in the light beam and measures intensity Fs_i. Then he replaces short tube with the long one and measures intensity Fl_i. The procedure is repeated at w_{i+1}. In this way the spectrum is scanned from 310 to 590 nm with steps of 10-20 nm. The second scanning begins just after refilling both tubes with the same water sample. The attenuation coefficient of the sample at w_i is calculated according to:

$$c_i = LN(Fl_i * Fs_i^{-1}) * x^{-1} \qquad (3)$$

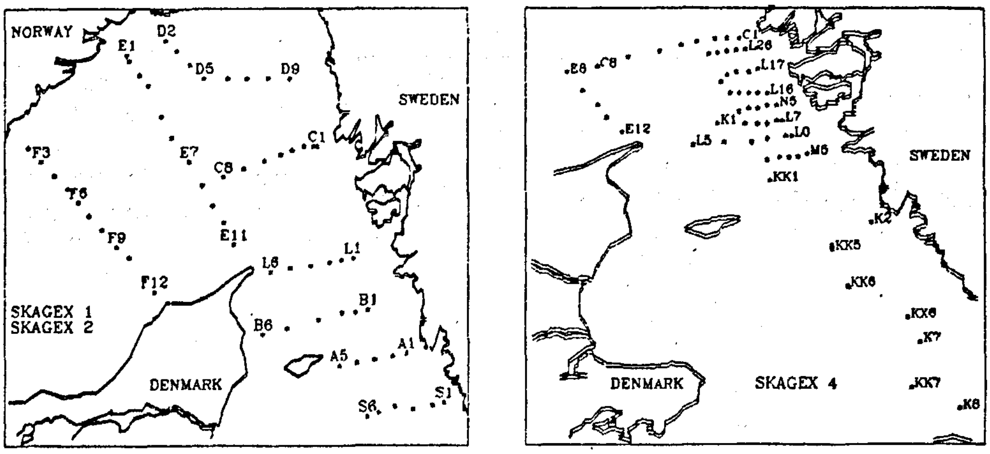
where x = 1 m is the path difference of the beam in the long and the short tubes. The data from two runs are used to compute the average attenuation spectrum $c_{av}(w_i)$ and reproducibility error E_0 of a sample. As a rule $0.01 < E_0 < 0.02\ m^{-1}$. Then a constant attenuation for "pure water" $c_{pw}(w_i)$ [Kopelevich, 1976] is subtracted from $c_{av}(w_i)$ and their difference $c(w_i)$ considered as the spectral signature of the sample.

OBSERVATIONS

The submersible fluorometer, MZF, was deployed at stations on several sections in the straits from the research ships "Shelf" (Russia) in *Skagex 1* and *2* and "Lev Titov" (Lithuania) in *Skagex 4*. Station positions are shown in Figure 1. Three surveys at sections L, B, A, S were completed on 27-29 May, 9-10 and 17-18 June 1990. Observations at section B were repeated as well on 2 June 1990. Measurements at sections E, D, F in *Skagex 1* were carried out on 31 May, 1 and 4 June 1990 respectively. In *Skagex 2*, fluorometer measurements were made at section

Figure 1

Location of the stations occupied by MZF fluorometer in the straits of Skagerrak at sections F, E, D, C and of Kattegat at sections L, B, A, S, K during field experiments Skagex 1, 2 *and* 4.



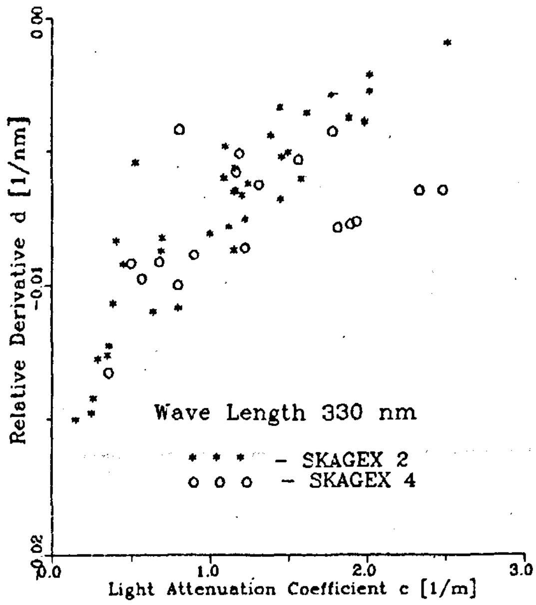


Figure 2

Dependence of relative derivative, d, on magnitude of coefficient of light attenuation, c, for 330 nm in Skagex 2 *and* 4.

E on 6 and 13 September 1990, at section C on 8 and 13 September 1990, at section D on 7 September 1990 and at sections A, B, S on 9 and 12 September 1990. Stations for sections C and E were occupied in *Skagex 4* on 13 and 17 May 1991. The survey at stations L, M, N in Figure 1 was completed between these data. Stations marked with K letters in Figure 1 were occupied when the ship sailed to and from *Skagex 4* area. The fluorometer was deployed 136, 61 and 72 times during *Skagex 1, 2* and *4*.

Transparency was measured in 44 water samples in *Skagex 2* and in 23 in *Skagex 4*. Depth of sampling took into account water column stratification according to the MZF fluorometer measurements.

RESULTS

As a rule c(w) spectra were structureless. Minimal values of c(w) were obtained at the red end of the spectrum and maximal at the UV boundary. The spectra of four samples from the surface layer at sections S and A were distinguished for maxima at 330-350 nm. They have been excluded from processing and analysis. Being similar in general the spectra essentially differed from each other by magnitude of attenuation and the rate of decrease with wavelength. The light attenuation was stronger in *Skagex 4* but more variable in *Skagex 2*. This difference was larger in the visible than in the UV spectral range. The smallest coefficients of light attenuation were found for samples taken from 100-250 m depth in the open Skagerrak. Here c(w) <= 0.05 m^{-1} at 450-500 nm. The maximal c(w) ≥ 1 m^{-1} in the surface layer of the straits at the same wavelengths. The ratio of maximal to minimal c(w) at 450-500 nm was 30-40 in *Skagex 2* and 10-12 in *Skagex 4*.

The wavelength derivative of c(w) has been computed as:

$$d(w_i) = [c(w_{i+1}) - c(w_{i-1})] * [2\, dw\, c(w_i)]^{-1} \qquad (4)$$

where dw = 20 nm is the scanning step. Expression (4) evaluates the spectral selectivity of light attenuation or steepness of $c(w_i)$ by w_i and provides a means of comparing shape of spectra regardless of their magnitude (Karabashev,

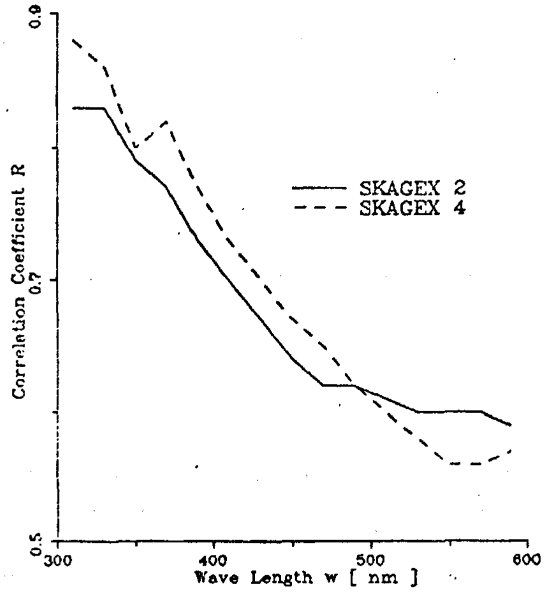


Figure 3

Correlation coefficient, R, of DOM fluorescence and light attenuation by wavelength, w, in Skagex 2 *and* 4.

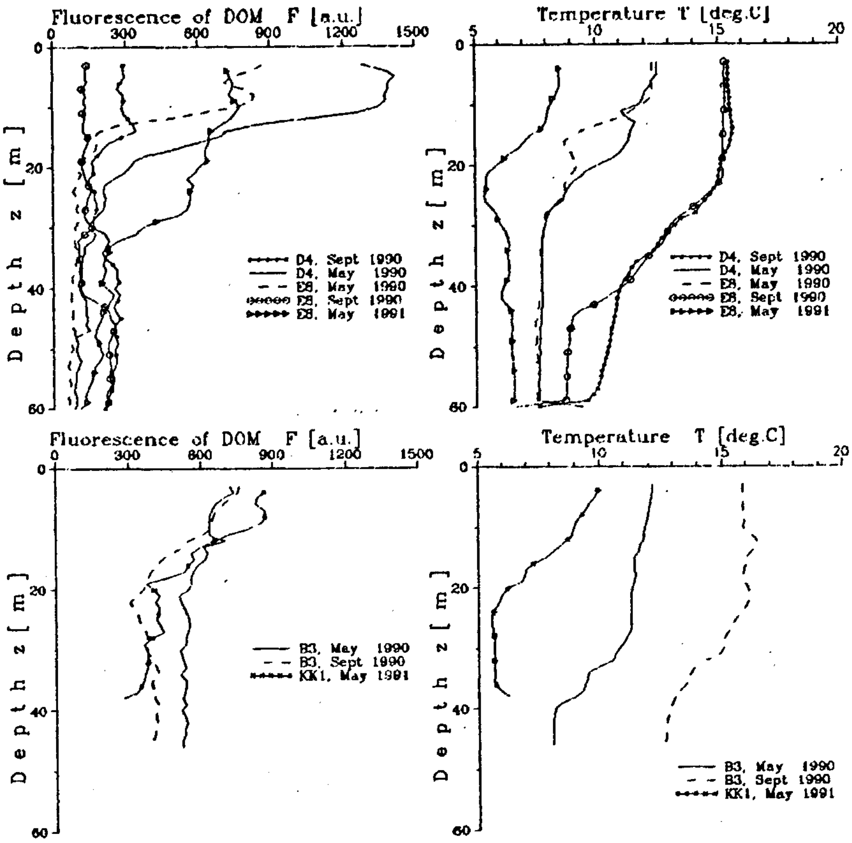


Figure 4

Seasonal variations of vertical profiles of DOM fluorescence F and water temperature T at stations for sections D, E, B and K in the Skagerrak and the Kattegat.

1991). Selectivity of c(w) from *Skagex 2* had a greater variability than that from *Skagex 4* but the mean selectivity spectra were similar. The dependence of selectivity on the magnitude of UV attenuation was the same for *Skagex 2* and *4* at least in waters of low and moderate attenuation (Fig. 2). This dependence disappeared in the visible.

Covariability of the attenuation for different spectral bands was checked by computing the correlation coefficient R_Λ between c(310) and attenuation at wavelengths $w > 310$ nm. It was found that in *Skagex 2* the $R_\Lambda > 0.9$ for 310-590 nm and $R_\Lambda < 0.8$ for $w > 500$ nm in *Skagex 4*. To estimate the covariability of fluorescence and attenuation, the spectrum c(w) of a sample was matched for fluorescence intensity, F, measured at the corresponding depth and time of sampling. The pairs of c(w) and F were used to compute the correlation coefficient R for every w. It was established that $R >> 0$ at 95 % significance level for $w \le 400$ nm in *Skagex 2* and *4* (Fig. 3).

The intensity of DOM fluorescence varied in *Skagex 1, 2* and *4* in the ranges of 26-1420, 55-993, 80-1300 arbitrary units respectively. The brightest fluorescence was discovered at central sta-

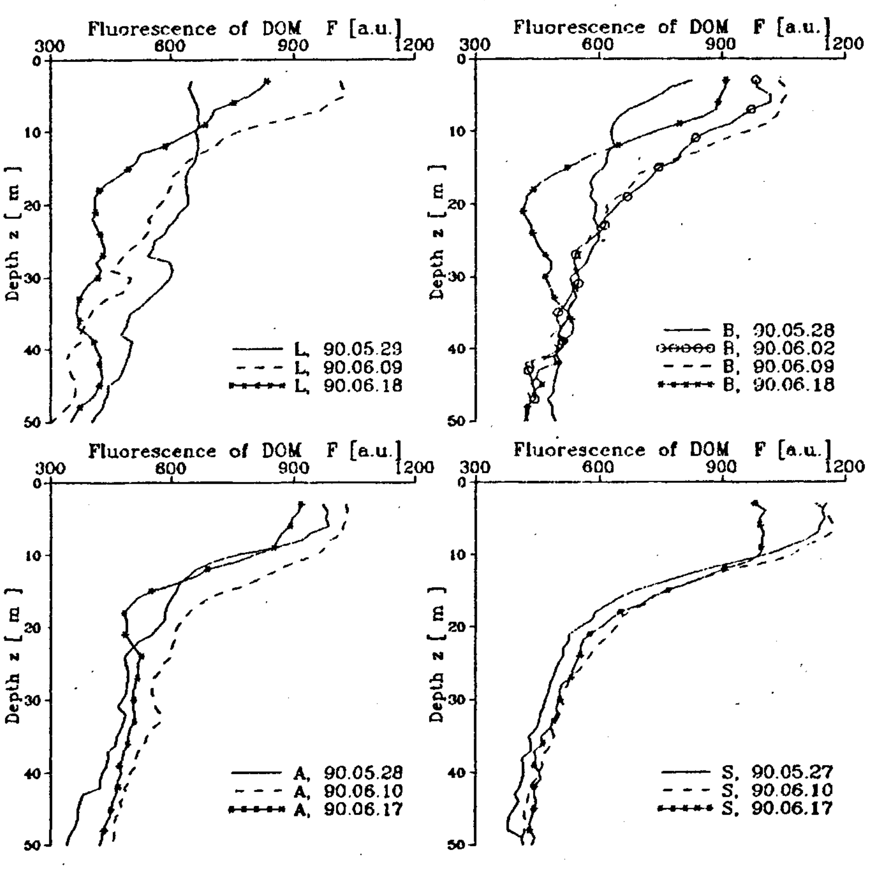


Figure 5

Average vertical profiles of DOM fluorescence F for sections L, B, A, S in surveys of Skagex 1.

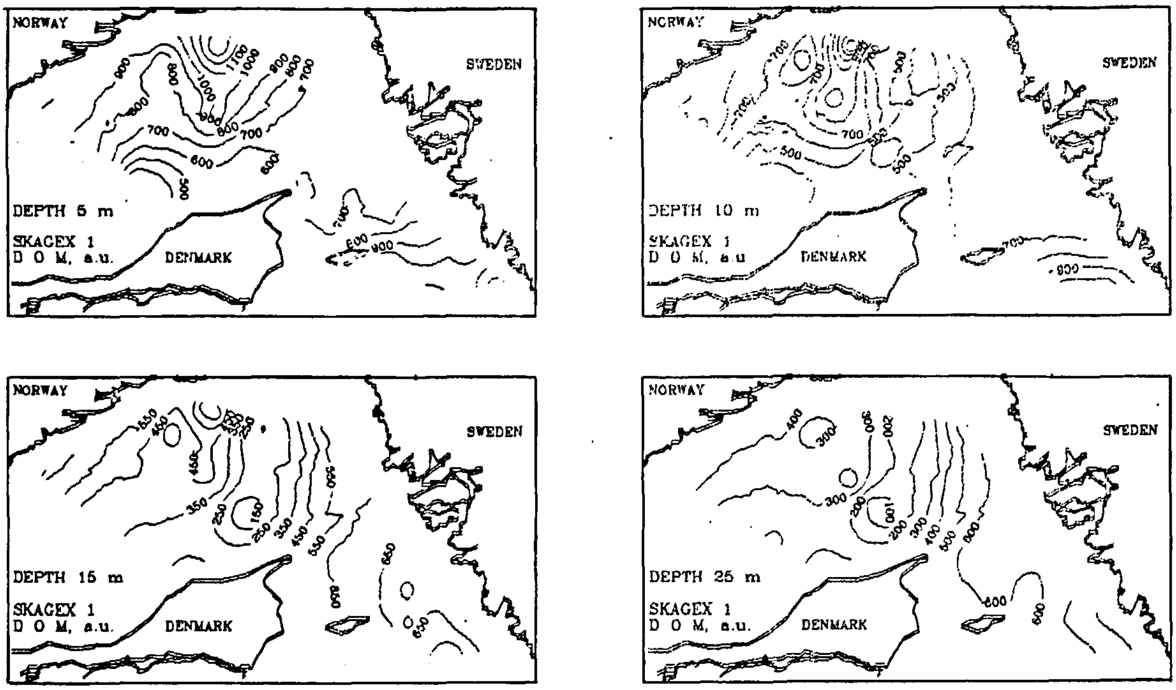


Figure 6

Distribution of DOM fluorescence in the Skagerrak-Kattegat area at depths of 5, 10, 15 and 25 m in Skagex 1. *The units are arbitrary.*

tions of section D at depths of 3 to 10 m. The surface waters in the Kattegat fluoresced less brightly. Minimal intensity was found below the thermocline of the Skagerrak at sections D, E, F. The waters below the thermocline of the Kattegat fluoresced five-ten times brighter than the deep waters of the Skagerrak.

The maximal intensity changed with season in the Skagerrak, being greatest in spring or early summer as shown in Figure 4. Seasonal variability of fluorescence has not been found in the Kattegat (Fig. 4, stations B and K). There was no direct correspondence between seasonal varaibility of vertical distributions of fluorescence and water temperature (Fig. 4). Three surveys in *Skagex 1* have revealed that fluorescence varied chaotically at each of the sections L, B, A, S over three weeks in May-June 1990. These variations decreased southward (Fig. 5).

The horizontal distributions of DOM fluorescence and temperature in the straits were mapped using the kriging interpolation of data collected in *Skagex 1* at sections S, A, B, L, D, E, F from 27 May to 4 June 1990 and in *Skagex 2*

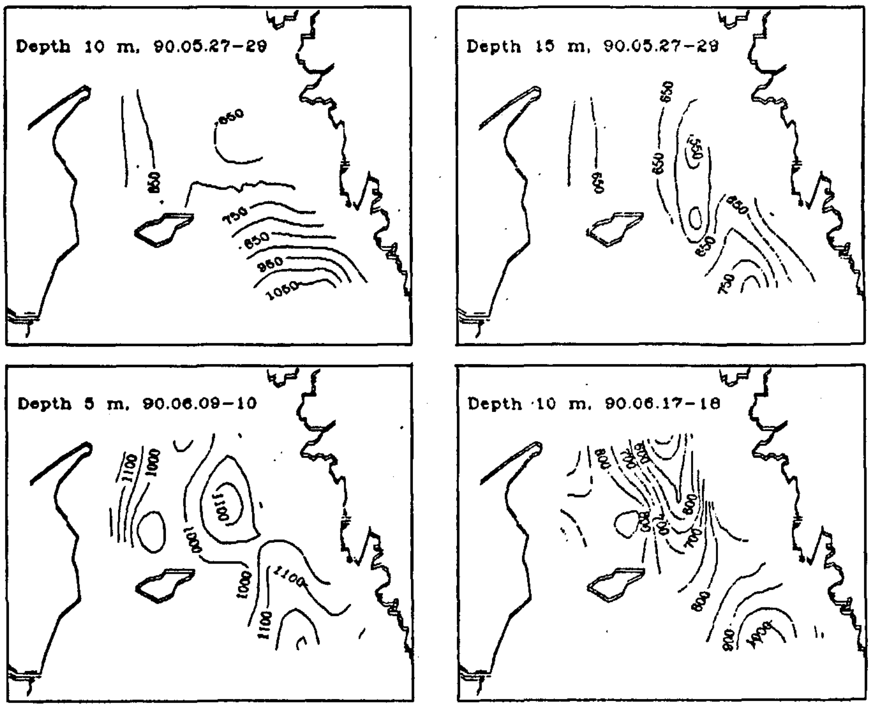


Figure 7

Distribution of DOM fluorescence in the Kattegat in Skagex 1. *The units are arbitrary.*

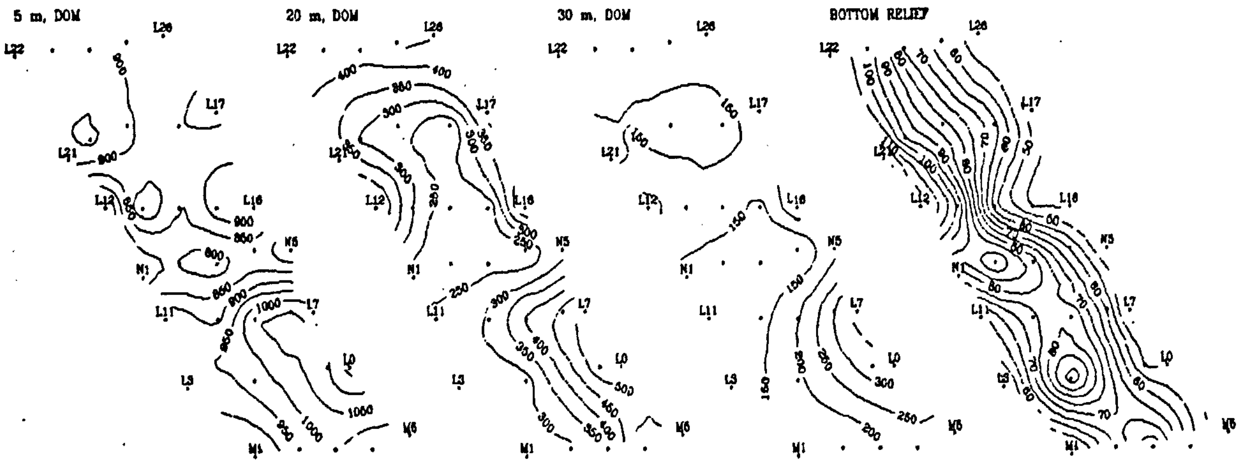
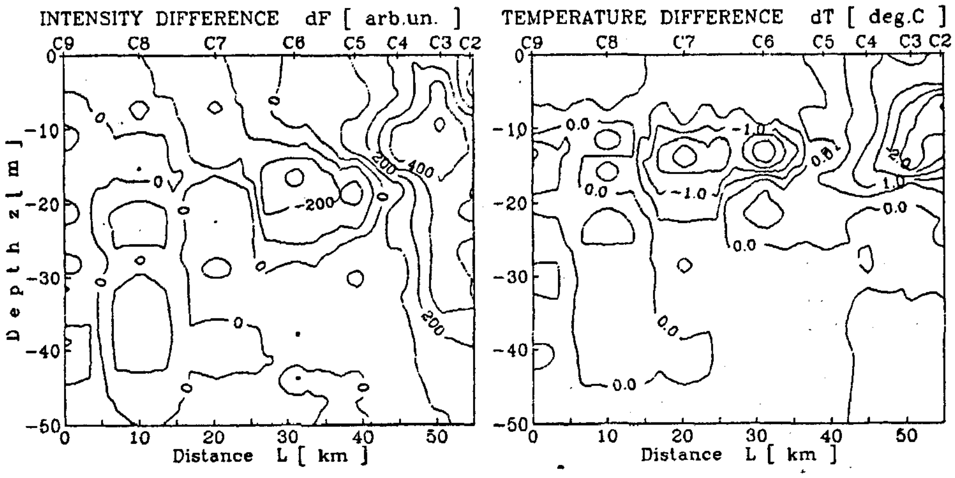


Figure 8

Distribution of DOM fluorescence at depths of 5, 20 and 30 m and bottom relief in the area of stations L, M, N in Skagex 4. *The fluorescence is in arbitrary units and isobaths are in metres.*

Figure 9

Vertical distribution of differences of DOM fluorescence, dF, arb. un. and water temperature, dT, °C on 13 and 17 May 1991 at section C.



at sections S, A, B, D, E, C from 6 to 12 September 1990. The maps were plotted every 5 m in the depth range of 5-35 m. Some of the maps presented in Figure 6 show the distributions in the upper mixed layer (5 m), inside the seasonal thermocline (10 and 15 m) and below it (25 m). In *Skagex 1* there was large area of low fluorescence at 5 m, contouring the values of 700 arb.un. (Fig. 6). The area separated a strong maximum in the north of the Skagerrak from moderately fluorescing waters in the Kattegat. The maximum disappeared below the thermocline and a front-like structure emerged at 15-25 m in the transitional zone between the straits (Fig. 6). It coincided with the temperature front. Both fronts existed but the northern maximum of fluorescence disappeared in September. Minima in temperature and fluorescence gravitated towards the middle of section E in *Skagex 2*. In the Kattegat fluorescence increased southward (Fig. 6).

The maps plotted from data of three surveys in *Skagex 1* have shown that the southward growth of fluorescence in the Kattegat was not a permanent feature (Fig. 7). A "tongue" of low intensity fluorescence was discovered in the third survey at 10 m depth. The intensity increased southward inside the "tongue". Local fronts 20-30 miles long existed during the second and third surveys (Fig. 7).

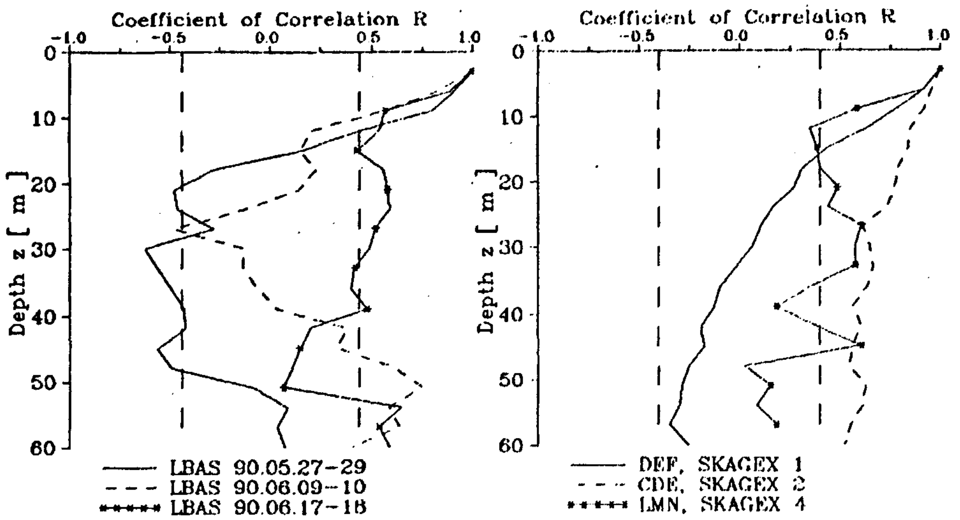
The frontal zone along the Swedish coast was studied in *Skagex 4* by seven close sections (stations L, M, N in Fig. 1). Observation of the boundary was expected between the Baltic waters along the coast and the waters of the straits. Front-like condensed isolines of fluorescence were located in the southern part of the zone but local decreases in intensity in its central part distorted the expected pattern (Fig. 8). The low fluorescence intruded into the northern part of the zone at depths of 14-22 m (Fig. 8, 20 m).

The changes of DOM fluorescence and water temperature occurring at section C from 13 to 17 May 1990 are presented in Figure 9. The DOM fluorescence diminished almost twofold in some layers at nearshore stations C2-C4 but became brighter by 15-25 % at central stations of C-section. The water had become more than 2°C cooler at C2-C4 and almost 1°C warmer at C5-C7. A long narrow strip of "boiling water" on the sea surface was crossed between stations C4 to C5 on 17 May 1991.

The vertical distributions of fluorescence with a maximum at the sea surface and negative gradients at depths of the thermocline were common in the Kattegat. The shape of DOM fluorescence profiles was more variable in the Skagerrak area. The profiles differed from each other by sign, magnitude and depth of maximal vertical gradients.

Figure 10

Correlation, R, between DOM fluorescence at depth 3 m and fluorescence at greater depths computed for different data samples.



The depth vertical gradient of fluorescence intensity given by:

$$g_i = 100\,\% * (F_{i+1} - F_{i-1}) * (z_{i+1} - z_{i-1})^{-1} * F_i^{-1} \qquad (5)$$

describes the variability of the shape of a fluorescence profile. The gradient shows what part of the fluorescence at depth z_i makes up its change between depths z_{i+1} and z_{i-1} per unit depth. The g_i is independent of units of fluorescence measurements and characterizes the steepness of profile F(z) at depth z_i.

The largest seasonal variations of g_i were observed at section E. Mean negative g_i in the layer of 8-12 m in May were 5-7 times larger than in September 1990. Positive g_i occurred much more often in September than in May in the upper 30 m, but below this layer there was no significant difference in the steepness of fluorescence profiles. The same tendency existed at section D in *Skagex 1* and *2* and at section C in *Skagex 2* and *4*.

The steepness of fluorescence profiles varied strongly within a section. The absolute steepness at stations E8-E10 culminated at 20-40 % m^{-1} in the layer from 8 to 18 m. It was about 20 % m^{-1} at 8-10 m at station E4 and dropped below 10 % m^{-1} at stations E1, E2. As a rule the depth of steepness maxima coincided with the depth of maximal temperature gradients. At some stations in the central Skagerrak, fluorescence changed proportionally to temperature at depths of the thermocline.

The covariability of surface fluorescence at 3 m with the fluorescence at greater depths has been expressed by correlation coefficient R [F(3), F(z_j)] for six groups of fluorescence profiles measured at several sections. Correlations were computed within a group for the depth range of 3-60 m every 3 m. The covariability diminished with depth in the 3-18 m layer at sections L, B, A, S in all three surveys. R-profile for group of stations L, M, N in *Skagex 4* resembled that of the third survey at sections L, B, A, S in *Skagex 1*. The groups for sections D, E, F in *Skagex 1* and C, D, E in *Skagex 2* were geographically close but corresponded to different seasons. Their R-profiles show that surface fluorescence of DOM in Skagerrak covaried horizontally with fluorescence at greater depths in autumn but not in spring (Fig. 10).

The MZF fluorometer was deployed in *Skagex 4* just after water sampling performed by colleagues from the hydrochemistry team who kindly agreed to exchange data, thereby permitting a comparison of fluorescence, F, of "yellow substance" with salinity S, phosphate PO and nitrate NI in sea water. Three groups of data pairs F-S, F-PO, F-NI have been composed containing more than 125 pairs each. Salinity varied from 14 to 36 at sections C, E, K, L, M, N within depths of 0-50 m. The subgroup for S ≥ 32 yielded R (F, S) = - 0.90. This subgroup comprised data collected at different locations at depths z ≥ 25 m. The scatter plot and R (F, S) value for the subgroup indicated that a strong negative correlation between salinity and DOM fluorescence was inherent to any high salinity waters in *Skagex 4* area. The subgroup for S ≤ 32 containing 44 data pairs for the 5-10 m layer yielded R (F, S) not distinguishable from zero at 95 % significance level.

There was no significant correlation between fluorescence and nitrate content in water in any of the subgroups. The correlation of DOM fluorescence with phosphate content was computed for subgroup of stations C and E (45 data pairs), subgroup of stations L, M, N (75 pairs) and subgroup of K-marked stations (46 pairs). The estimates of R (F, PO) in the same order were - 0.81, - 0.79 and - 0.72 differing from zero at a 95 % significance level.

DISCUSSION

The lowest estimates of the spectral light attenuation in the visible were obtained in deep waters of the open ocean and make up 0.02 m^{-1} (Matlack, 1974). The attenuation of light in the deep of the Skagerrak measured in this study is rather close to these estimates. Most probably, this is due to the transparent waters from the Atlantic Ocean occupying the central Skagerrak (Danielssen *et al.*, 1991). The estimates of R [F, c(w)] exceeded + 0.8 for w ≤ 350 nm (Fig. 3). *Skagex 2* data sample included values of F and c(w) measured in extremely transparent deep waters from the open Skagerrak. In contrast, the data set for *Skagex 4* was sampled mainly in the transitional area between the straits at depths z ≤ 60 m. The spectra c(w) and R [F, c(w)] in Figure 3 agree well with the concept of an increase of the ratio $a_y(w)/b(w)$ in UV in comparison with the visible part of the spectrum (Jerlov, 1976). The coincidence of R [F, c(w)] for *Skagex 2* and *4* indicates that this ratio, conditioned by the relationship between "yellow substance" and suspended particles, did not change with season.

The values of R [F, c(w)] for w ≤ 350 nm are as high as estimates of correlation between DOM fluorescence and attenuation of UV light for the particle-free water sampled in the central Baltic (Karabashev and Zangalis, 1974) and in the Bothnian bay (Brown, 1974). This does not however mean that UV radiation in the straits was attenuated by "yellow substance" alone. It is possible to discriminate suspended matter using wavelength dependence of absorption of light by "yellow substance". This dependence is (Jerlov, 1976):

$$a_y(w_2) = a_y(w_1) \exp[- p (w_2 - w_1)] \qquad (6)$$

The estimates of p range from - 1.2 to - 1.7 % nm^{-1} (Karabashev and Zangalis, 1974; Lundgren, 1976; Morel and Prieur, 1976; Bricaud, 1979, *in* Prieur and Sathyendranath, 1981; Kopelevich, 1983, and others). The $p = - 1.5$ % nm^{-1} has been chosen in this work. Computing $a_y(310)$ and $a_y(350)$ relative to $a_y(330)$ with expression (6) and substituting $a_y(w)$ instead of c(w) in (4) yields $d_y(330) = - 1.5$ % nm^{-1}. This is very close to the minimal d(330) for the clearest waters of the Skagerrak (Fig. 2) and confirms the assumption that attenuation of UV light was controlled almost exclusively by "yellow substance" below the thermocline in the Skagerrak. In other cases the covariance of F and c(w) for w ≤ 350 nm could be due to correlation between "yellow substance" and suspended particles.

Close correlation between DOM fluorescence and light scattering by particles was observed in the Mediterranean (Ivanoff, 1962) and in the open ocean (Karabashev, 1987) in or above the seasonal thermocline. All water samples strongly attenuating light have been taken above the thermocline in *Skagex 2* and *4*. According to data collected at sections C, D and E in *Skagex 2*, light scattering and in particular fluorescence of chlorophyll covaried horizontally with DOM fluorescence in upper 10-15 m in Skagerrak but they were not related in deeper layers.

The scatter plots for *Skagex 2* and *4* in Figure 2 suggests that seasonal changes of DOM fluorescence and attenuation of light were mainly due to variations in the quantities of "yellow substance" and suspended particles and not caused by any variations in the state and composition of material. It is useful to discuss the changes of fluorescence in terms of "sources and sinks" of DOM in the straits if temperature, sunlight or other environmental factors do not affect the concentration dependence of DOM fluorescence.

The fluorescence intensity of a substance decreases with temperature (Parker, 1968). Almost nothing is known about this dependence for DOM fluorescence. Lyuzarev studied several samples of sea water and discovered that DOM fluorescence changes less than 10 % per 10°C (Lyuzarev, 1968, *in* Karabashev, 1987). There is no reproducible horizontal covariability of temperature and DOM fluorescence in the open ocean outside areas of upwellings (Karabashev, 1987). The same was true for *Skagex* observations. Degradation of fluorescing DOM by sunlight was reported by Kramer (1979) but later it was admitted that his findings could be artefacts (Laane and Kramer, 1990). There were no signs of photodegradation of DOM in the shape of fluorescence profiles even for tropical transparent waters (Karabashev, 1987). For these reasons we consider temperature dependence and photodegradation of DOM fluorescence to be insignificant for the purposes of the present study.

Kalle (1963) considered Baltic waters as a source of "yellow substance" in the straits. Højerslev (1971) has shown that river outflow specifically from Oslo fjord gives rise to maxima of DOM fluorescence along the coast of the Norway. An increase of fluorescence at these locations is seen in Figure 6 at 25 m and was established in the whole depth range of 5-35 m for *Skagex 2*; here fluorescence was not as bright as at the same depths in the Kattegat.

Fluorescence of DOM in *Skagex 1* at station D4 was brighter than at any other place including southernmost section S. This means that the fluorescence maximum contoured by values of 900 arbitrary units in Figure 6 at 5 m cannot be caused by Baltic water and hence its source must be local. According to data collected on 5-6 June 1990 on research ship "T. Braarud", the salinity of water at section D at 5 m was less than 30 and the salinity minimum was located at stations D4, D5. These facts infer that DOM-rich waters from rivers entering Oslo fjord spread southward in the upper 10-15 m and reached the open Skagerrak at the central part of section E. On the basis of turbidity observations Malmberg (1964) supposed the arrival of Oslo fjord waters in the surface layer of the northern Skagerrak, but he could not discriminate effect of the Baltic waters.

There are two possible types of river outflow influence on "yellow substance" distribution in the Skagerrak. The first may be called "background". This results in steady maxima of DOM fluorescence along the Norwegian coast where brightly fluorescing water penetrates deeper than elsewhere in the Skagerrak because of mixing in the Norwegian current. The second influence is a "spring" one; most probably it is related to spring floods and depends on wind direction. The "spring" maximum waters fluoresce more brightly than the Kattegat waters but do not penetrate as deeply as waters of "background" maximum.

The formation of the "spring" maximum causes a local increase of light absorption three- to five-fold relative to the "background" pattern. This happens in the upper few metres above the layers where phytoplankton accumulates and therefore may considerably reduce the shortwave radiation available for photosynthesis. The data are too limited to quantify these effects.

The area of low fluorescence along the Danish coast coincided with colder water at places where the Jutland current appears (Fig. 6, depth 5 m). DOM fluorescence increased from sections F to E just as salinity increases downstream of the Jutland current because of entrainment of North Sea waters (Pedersen *et al.*, 1988). The current is unstable and does not always reach the Skagen peninsula. It may be supposed that this situation was encountered in *Skagex 2*, since no signs of the Jutland current have been found in the distributions of fluorescence and temperature.

Sometimes the same current hits the Swedish coast or intrudes into the Kattegat (Fonselius, 1990). We assume that the first of these events was observed in *Skagex 4* when waters of minimal DOM fluorescence entered the frontal zone occupied by stations L, M, N and turned north along the Swedish coast. Comparing the fluorescence isolines with the isobaths in Figure 8 leads to the conclusion that fluorescence distribution in the middle of the zone was shaped by the interaction of Jutland current with the bottom relief.

The turning of the current northward is consistent with the decrease of temperature and fluorescence during four days at nearshore stations of section C (Fig. 9). Taking into account the time and space scales of the event, the current speed may be approximately estimated as 0.5 knots. The phenomenon of "boiling water" observed between stations C4 and C5 traces on the sea surface a boundary between strong countercurrents (Fedorov and Ginsburg, 1992). This suggests that our observations were conducted at the beginning of interaction of the Jutland current with the underwater slope.

Intrusion of Jutland current in the Kattegat occurred during the third survey at sections L, B, A, S on 17-18 June 1990 (Fig. 7). The intruding waters tagged by low fluorescence were only a few metres thick. The tagging was due to differences in fluorescence stratification of intruding and intruded water bodies. The real thickness of the intrusion could be larger in the velocity field than was indicated by measured fluorescence or temperature.

The fluorescence profiles with surface minimum occurred in *Skagex 2* at stations C8 and E8 (Fig. 4) and could be connected with the presence of the Atlantic waters in the central Skagerrak (Danielssen *et al.*, 1991). Profiles of this kind are common for the oligotrophic waters of the open ocean (Karabashev and Solov'ev, 1977). The profiles with strong surface maximum emerged at places where river outflow overlay the waters from the Atlantic Ocean (Fig. 4, D4 in May). The DOM fluorescence profiles from the eutrophic areas of the open ocean also have surface maxima (Karabashev and Solov'ev, 1977) but the difference between surface and deep water fluorescence is smaller in the case of the eutrophic ocean. Mutual penetration of water bodies differing in fluorescence stratification resulted in fine structure and surprising diversity of DOM fluorescence profiles in *Skagex* area.

An inverse linear relationship between fluorescence, F, and salinity, S, observed in a 25-50 m layer during *Skagex 4* agrees well with earlier reported data on the F-S correlation for the North Sea-Baltic zone (Kalle, 1949; 1963; Gienapp, 1979; Laane and Kramer, 1990, and others). The lack of a similar relationship for the layer of 5-10 m seems strange because this relationship is common for the areas of river and sea water mixing.

Laane and Kramer (1990) discovered that in the Ems, Elbe, Weser, Rhine and Scheldt estuaries the DOM fluorescence diminished with salinity to one and the same limit but at quite different rates. This is possible if the concentration of fluorescing material is different in each of the rivers. In all estuaries mixing begins from one and the same zero salinity but from different concentrations of fluorescing material. Therefore a value of salinity may be associated with different values of fluorescence (and *vice versa*) in a sea water mixing area shared by the neighbouring estuaries. This effect decreases the F-S correlation for the area and is inherent to the sea surface layer. The similar effect seems to be relevant for the *Skagex 4* area because there is an inflow of brackish waters from different rivers, brooks and fjords. The addition of "yellow substance" in sea water from decomposing marine phytoplankton may also reduce F-S covariance.

CONCLUSIONS

The amount of DOM fluorescence changes more than fifty-fold in the relatively small area of the Skagerrak and is thus comparable with worldwide data (Kalle, 1963; Karabashev, 1987). This makes the Skagerrak a unique natural environment where all known sources of "yellow substance" are acting and where mixing waters are most dissimilar by origin and content of DOM. It is difficult to reach any "final conclusions" about the causes and mechanism of variability of "yellow substance" in such a complex medium with a limited data set.

But at least one conclusion can be drawn: namely, that the optical characteristics of "yellow substance" may be used as natural tracers of waters in the Skagerrak-Kattegat area. This is supported by two considerations: 1) the displacements of water masses in the area result in changes of DOM content by tens and hundreds of per cent; 2) unlike salinity, oxygen, nutrients or other natural tracers of currents, DOM fluorescence may be measurable remotely from aircraft or space.

Passive remote sensing of DOM fluorescence excited by sunlight may be achieved by the Fraunhofer lines method (Stoertz *et al.*, 1969). Active remote sensing of DOM fluorescence is attainable by airborne fluorosensors able to measure Raman scattering of water as a reference signal (O'Neil *et al.*, 1980, and others). Instruments of this kind provide amplitude resolution comparable to that of submersible fluorometers and allow oceanological observations to be made in "instantaneous" surveys of a study area regardless of weather or time of day.

Remote sensing instrumentation may be used to monitor the location of the Jutland current, to determine the spreading of waters from fjords to the open Skagerrak, to reveal local upwellings and to trace Baltic waters entering the straits. At the same time, strong attenuation of light in sea water and varying correlations between surface and deep water fluorescence restrict the employment of "yellow substance" remote sensing to the upper 5-10 m. The same advantages and limitations are to be expected for DOM remote sensing of water movements in other coastal or shelf areas. We hope that our findings will encourage new studies of "yellow substance" variability.

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