Seasonal and spatial variability of surface seawater fluorescence properties in the Baltic and Nordic Seas: results of lidar experiments*

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Abstract

The paper analyses experimental measurements of laser-induced fluorescence (LIF) spectra in different seawaters. The fluorescence parameters, calculated from LIF spectra as the ratio of the integrals of fluorescence and Raman signal intensities, provide information about the relative changes in the concentrations of fluorescing molecules. Gathered during several cruises in 1994–2004 in the Baltic and Nordic Seas, all the data are presented as scatter plots of the fluorescence parameters of chlorophyll *a* (Chl *a*) and coloured dissolved organic matter (CDOM). Satisfactory correlations between these two parameters were found a) for open Nordic Seas waters, b) for the southern Baltic in blooming periods only, and c) for the Gulf of Gdańsk in non-blooming periods only.

1. Introduction

The structure of the water masses specific to the Baltic Sea is due to its resembling a quasi-enclosed estuary supplied with huge amounts of fresh water from river runoff and sporadic deep inflows of saline Atlantic

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water through the Danish Straits. It has therefore been deemed necessary to investigate and monitor the eutrophication of the Baltic (Darecki & Stramski 2004, Woźniak et al. 2000). Since 1993, lidar measurements of in situ seawater fluorescence spectra have been carried out on board r/v 'Oceania' during Baltic cruises as well as during two summer Arctic campaigns (AREX 2001 and 2002) in the Norwegian, Iceland and Greenland Seas. Baltic waters, seriously affected as they are by human activities, have been classified as Case 2 waters; the open waters of the Nordic Seas are Case 1 waters. The difference is due to the quantity and quality of organic matter contained in the upper seawater layer. The present paper analyses the results of the above-mentioned lidar investigations, which were obtained within the framework of a Ph. D. thesis (Drozdowska 2005, unpublished).

Our lidar investigations of seawater have made it possible to obtain continuous fluorescence spectra of seawater in the visible light region, in real-time and without disturbing the aquatic medium. The method can thus be applied to detect the main fluorescent constituents of seawater: phytoplankton pigments, humic-type dissolved organic matter, and oils (Piskozub et al. 1998, Drozdowska & Kowalczuk 1999, Drozdowska et al. 2002, 2004, Drozdowska & Darecki 2005, Drozdowska & Król 2005, 2006). These spectra provide information on the concentration of chlorophyll *a* (Chl *a*) and coloured dissolved organic matter (CDOM). The concentration of Chl *a*, for which the fluorescence parameter obtained from the lidar-induced fluorescence spectra is a proxy, is an indicator of phytoplankton abundance (Babichenko et al. 1993, Determann et al. 1994, Fadeev 1999, Barbini et al. 2001). The amount of CDOM is also determined from the CDOM fluorescence parameter calculated from the seawater fluorescence spectrum. The position of the CDOM fluorescence spectral band shifts towards the blue or red wavelengths, depending on the dominant fractions of humic substances (HS). High-molecular-weight HS molecules produce a red shift in the fluorescence and absorption spectra and typically, a lower quantum yield of fluorescence; low-molecular-weight HS molecules give rise to a blue shift in these same spectra and a high quantum yield of fluorescence (Babichenko 2001).

Analyses of seawater fluorescence spectra obtained by the lidar method yield the fluorescence parameters of Chl *a* and CDOM, which allow seawater masses to be distinguished according to their individual biophysical and fluorescence properties (Barbini et al. 1998). The classification of seawaters with the aid of lidar-induced fluorescence spectra parameters is based on the correlation coefficient (r^2) between the fluorescence parameters of Chl *a* and CDOM. For Case 1 waters these values are large (close to 1), for Case 2 waters, they are low (close to zero). Moreover, according to

Salyuk and his co-workers (Pavlov et al. 2000, Salyuk et al. 2003), the positive linear regression coefficients (when r^2 is close to 1), a and b, respectively supply information about the rate of CDOM formation from phytoplankton communities and the initial content of organic matter in the aquatic environment. Hence, if the correlations between the Chl a and CDOM fluorescence parameters obtained in a given waters are linear, this means that those waters have similar bio-optical properties.

2. Methodology

The most important advantages of applying the lidar in marine campaigns is that the results of lidar measurements are obtained in real time without any disturbance to the aquatic environment (Babichenko et al. 1993, Determann et al. 1994, Patsayeva 1995, Barbini et al. 2001). The lidar light penetrates the seawater, where part of it is absorbed, emitted as fluorescence quanta or transformed into some other kind of energy. The emitted light disperses equally in all directions, but only the fraction reaching the telescope's field of view is recorded by the lidar. So the important parameter of the geometry set-up is the ratio of the solid angle from which the light is collected by the telescope to the full solid angle (4π). It is the ratio of the telescope area to the surface area of the sphere into which the light is dispersed. The radius of this sphere **r** is equal to the distance between the target that emits the return signal and the telescope. The number of photons reaching the telescope decreases with the square of **r** and is proportional to the surface area of the telescope.

Intended to create a database of in situ fluorescence spectra of seawater, the lidar experiments were performed on board r/v 'Oceania' with the FLS-12 (LDI, Estonia) lidar system (Babichenko et al. 1989). This consists of an excimer laser (308 nm) used as the pumping source to a tuneable dye-laser, the lidar light source, and the receiving block, which includes the telescope, polychromator and electronic block. The tuneable range of emission is 320–670 nm. Time-gated fluorescence spectra of seawater are recorded in the 400–850 nm range.

The time-gated detection of the return signal permits control of both the optimal distance to the sensing layer (time-gate delay of the receiver) and the thickness of the sensing layer (time-gate duration of the receiver). The return signal is a continuous spectrum and can be divided into separate spectral bands due to Rayleigh scattering (elastic scattering of the laser emission at the water surface and in the water column), Raman scattering (inelastic scattering of the laser emission at water molecules, shifted 3420 cm^{-1} from the excitation wavelength) and CDOM and Chl a fluorescence (Fig. 2). The total intensity of the recorded fluorescence

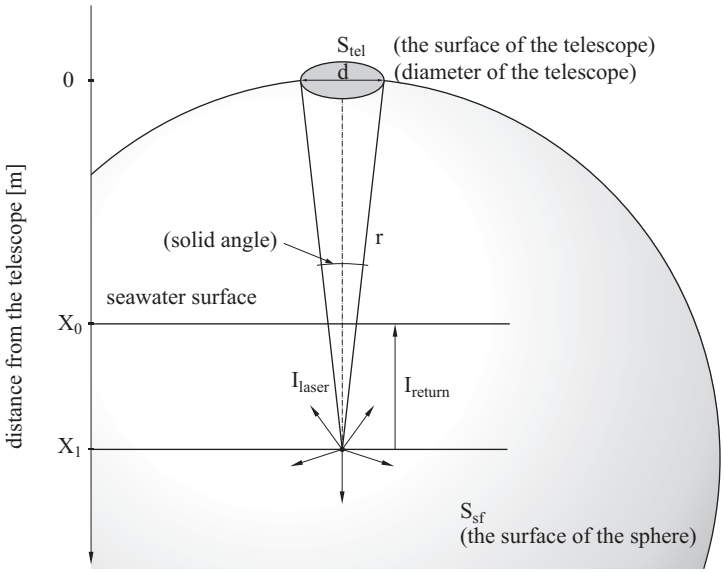

Fig. 1. Lidar set-up

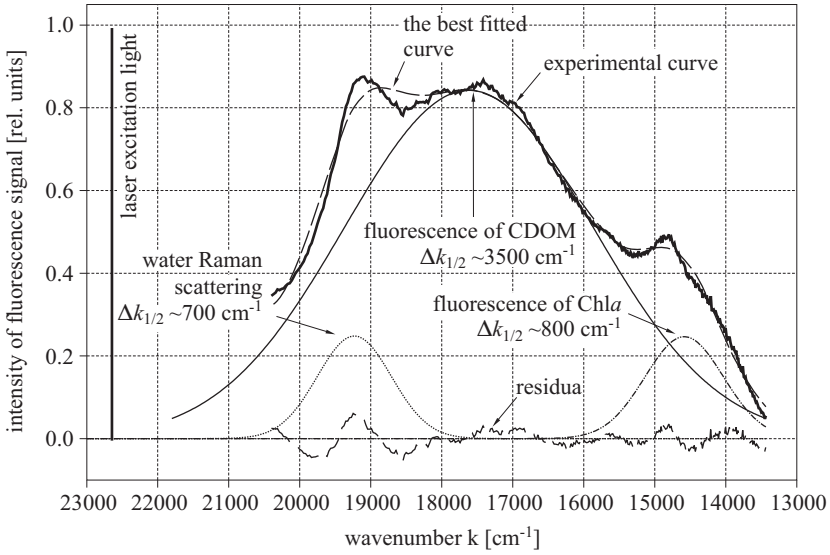

Fig. 2. Typical lidar-induced seawater fluorescence signal

signal comes from the upper layer. The Raman scattering signal is used to normalise the fluorescence signal in order to obtain the fluorescence parameter describing the relative concentration of the fluorescing molecules (Klyszko & Fadeev 1978, Babichenko 2001, Drozdowska et al. 2002).

3. Results and discussion

Extensive data were gathered on the occurrence and spatial distribution of natural organic matter – phytoplankton and humic substances – in the upper seawater layer.

In the Baltic Sea, the spatial distributions of Chl *a* during blooms are quite characteristic, which makes it necessary to use different axis scales during blooming as opposed to non-blooming periods (Fig. 3). During blooming periods, Chl *a* spatial distribution maps resemble complex, patchy, mosaic-like patterns of small areas with different fluorescence properties. In the other periods, Baltic waters are well mixed and characterised by huge areas with similar, homogeneous fluorescence properties.

Similar spatial distribution patterns of the Chl *a* and CDOM fluorescent parameters were observed in the Nordic (Norwegian, Iceland and Greenland)

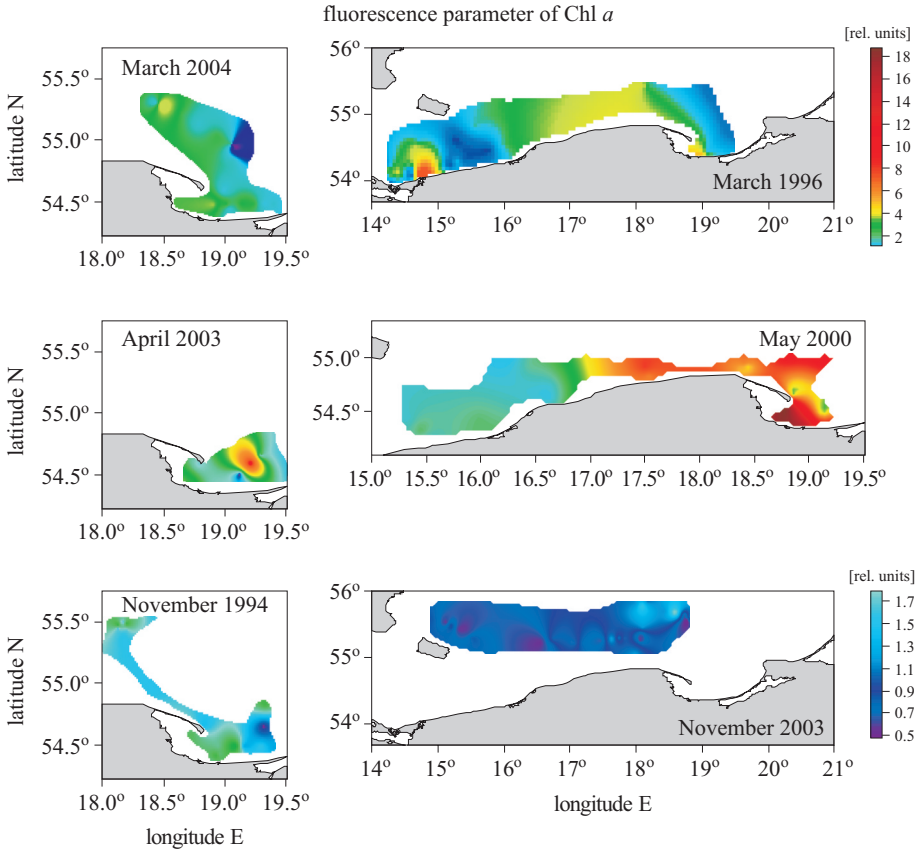

Fig. 3. Spatial distribution of the Chl *a* fluorescence parameter measured during several Baltic cruises during blooming and non-blooming periods

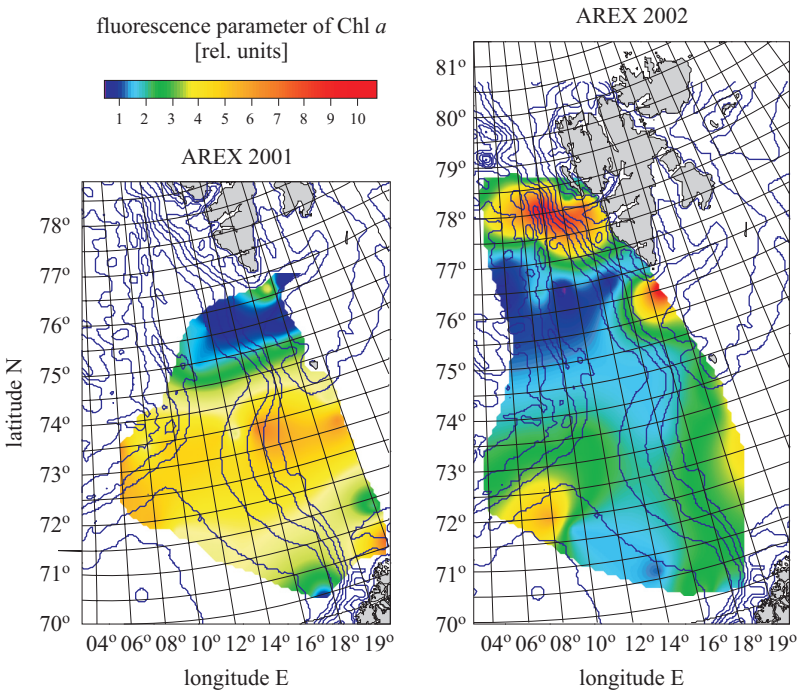

Fig. 4. Spatial distribution of the Chl *a* fluorescence parameter measured during AREX 2001 and 2002

Seas in 2001 and 2002 (Fig. 4). The largest amount of fluorescent organic matter was observed along the shelf of Spitsbergen and along the Scandinavian coast. Additionally, quite significant amounts of fluorescent organics were recorded in central parts of the seas, except for the area around Bear Island, where the fluorescence parameters were low.

Fig. 5 illustrates the relationships between the fluorescence parameters of Chl *a* and CDOM obtained during marine experiments carried out in different regions of the Baltic Sea at different seasons. To ensure clarity of the plots, the names of the stations have been removed from the figures. The values presented in Fig. 5a (each point is the average of > 50 measurements) were obtained during cruises during blooming (spring) and non-blooming (the other seasons) periods; the stations are marked as circles or triangles, respectively. In general, during algal blooms the fluorescence parameters of Chl *a* and CDOM obtained in the southern Baltic are subject to considerable variation and represent spatially diverse values. During the non-blooming periods, their values are smaller, and the changes in CDOM fluorescence parameters are much less than those affecting the corresponding parameters of Chl *a*. Therefore, in the blooming periods a positive correlation ($r^2 = 0.6$) for the Chl *a* and CDOM fluorescence parameters was obtained for all

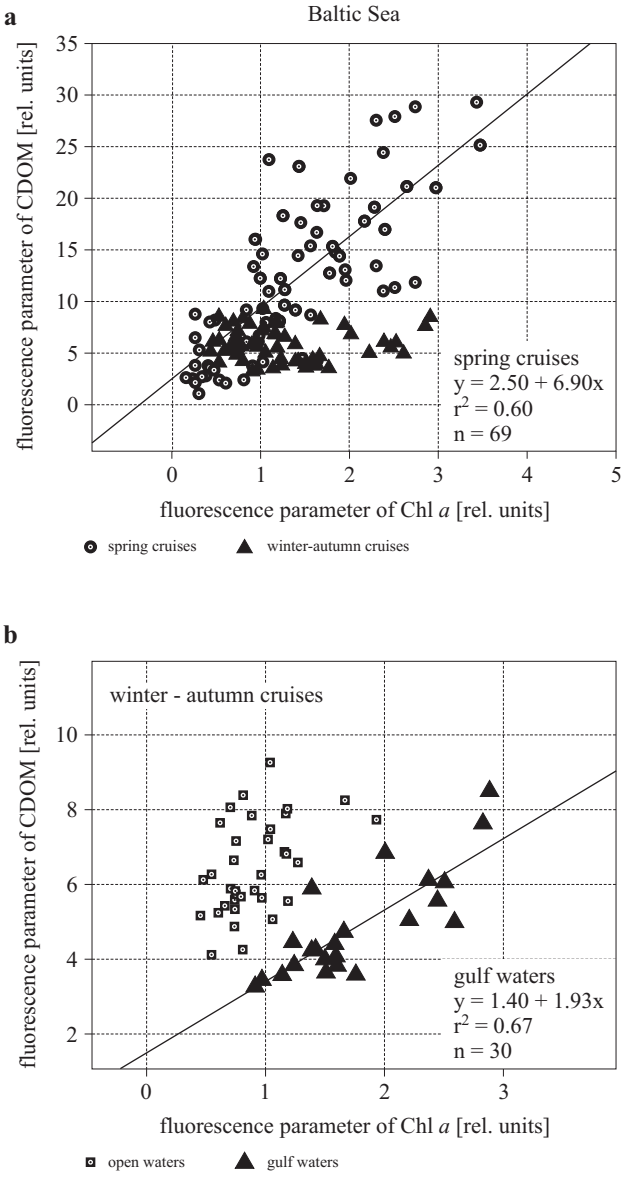

Fig. 5. Correlation coefficient between fluorescence parameters of Chl *a* and CDOM for the Baltic Sea obtained during (a) spring (blooming periods) and (b) autumn and winter (non-blooming periods)

the stations (number of samples: n = 69), regardless of which part of the Baltic was investigated (coastal or open waters). However, in non-blooming periods, the waters of the Gulf of Gdańsk and the Pomeranian Bay differed from the rest of the southern Baltic, the correlation being positive ($r^2 = 67$)

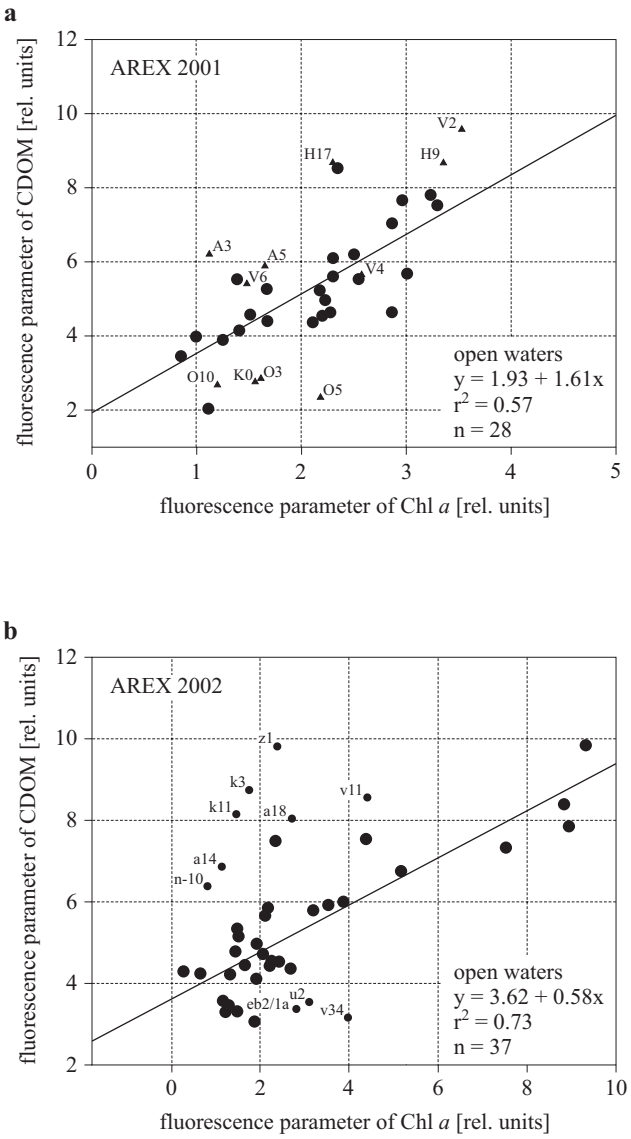

Fig. 6. Correlation coefficient between fluorescence parameters of Chl *a* and CDOM for the Nordic Seas obtained during AREX 2001 and 2002

only for the results (n = 30) obtained at stations located in these two water bodies (Fig. 5b). From this it follows that in algal blooming periods, the activity and concentration of phytoplankton in the southern Baltic are high – hence the homogeneity of the bio-optical and fluorescence properties of the surface waters. On the other hand, the fluorescence properties of southern Baltic waters in autumn and winter are governed mostly by the mixing of

the water masses and, with the exception of the Gulf of Gdańsk and the Pomeranian Bay, constitute quite a complex region. Very probably, the homogeneity of these latter waters as regards fluorescence properties is due to river runoffs, which are predominant in these areas and at these times.

Similar investigations were carried out in the Nordic Seas; the results are presented in Fig. 6. Each point represents the average of about 20–30 measurements. The unmarked points in Fig. 6 relate to open waters, whereas the points marked by letters refer to stations located in shelf waters and the western part of the Nordic Seas area under scrutiny. In 2001, the lidar investigations covered the central part of the Nordic Seas; during the 2002 campaign they extended as far north as latitude 81°N. Since maximum values were recorded along the western shore of Spitsbergen in 2002, the Chl *a* fluorescence factors obtained during these two campaigns differ significantly: 0–4 relative units in 2001 but 0–10 relative units in 2002. The plots (a) and (b) show that the correlations between the Chl *a* and CDOM fluorescence factors for the open waters were positive ($r^2 = 0.57$ for $n = 28$ and $r^2 = 0.73$ for $n = 37$, respectively). The open Nordic Seas waters are thus described by the same fluorescence properties. Where phytoplankton is the only source of CDOM formation, the relationship between the CDOM fluorescence parameters and the Chl *a* concentration is linear (Barbini et al. 1998); the open Nordic Sea waters are therefore Case 1 waters. Such a relationship was not, however, observed in the shelf waters off western Spitsbergen and on the border between the Barents and Norwegian Seas owing to the occurrence of additional advected organic matter.

4. Conclusions

The fluorescence parameters of Chl *a* and CDOM, which provide information about the relative concentrations of the main seawater constituents, could be calculated following analysis of laser-induced fluorescence (LIF) spectra of different seawater masses. The content of these constituents affects the radiative energy flux exchange between sea and atmosphere, which, in turn, governs numerous, environmentally significant biophysical processes and determines the biophysical status of waters. The analytical results highlighted changes in the fluorescence properties of the seawater constituents, enabling maps of their spatial distribution in different areas of Baltic and Nordic Seas to be constructed.

Spatial distribution patterns not only of Chl *a*, but also of CDOM can be discerned. Rivers constitute the principal source of CDOM in the sea, but another relevant source is partly decomposed phytoplankton, which exists mainly in areas where intensive blooms of phytoplankton have taken place. The relationships between the contents of CDOM and Chl *a* (their

fluorescence parameters) enabled waters with different bio-optical properties to be distinguished and a link between fluorescence parameters and CDOM sources in the seawaters to be established.

The specific bio-optical status of seawaters can be determined from the correlation of the linear relationships between the fluorescence parameters of Chl *a* and CDOM. A positive correlation for a given body of water indicates the presence of the same sources of CDOM runoff.

The results obtained in the Baltic Sea allow certain inferences to be drawn from the positive correlations obtained between the fluorescence factors of Chl *a* and CDOM: they exist only for local waters and are variable in time. During the spring algal blooms, the bio-optical properties of the entire southern Baltic are similar. In the other seasons, however, the dominant influence of the Vistula river runoff and mixing processes combine to produce the homogeneous fluorescence properties of Gulf of Gdańsk waters.

Similar measurements were carried out in Nordic Seas, where a positive correlation was found for the open waters; these can be classified as Case 1 waters.

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