

Response of a lidar-induced fluorescence signal to yellow substance absorption

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Abstract

The presence of yellow substances in seawaters was measured by the standard spectrophotometric (*in vitro*) and the lidar-induced fluorescence (*in vivo*) methods along a transect across the Pomeranian Bay towards the River Odra mouth, a local source of yellow substances. The experiment aimed to ascertain whether the fluorescent lidar method could be applied to yellow substance detection and whether there were any relationships and similarities in the absorption and fluorescence intensity values and their changes.

1. Introduction

The coloured dissolved organic matter CDOM (sometimes referred to as yellow substances or ‘Gelbstoff’) can contribute significantly to the total light absorption within the oceans. Like water, phytoplankton and crude oils and their products, yellow substances have a very high specific absorption coefficient in ocean water. On continental shelf margins the absorption of yellow substances can easily exceed the absorption of both phytoplankton and water in the blue region of the spectrum (Hoge *et al.* 1993b). The absorption spectra of CDOM and chlorophyll overlap, so the presence of the former can reduce photosynthetically active radiation and hence also the accuracy of satellite measurements of chlorophyll content. Direct measurement, the most commonly used spectrophotometric method

of estimating yellow substance absorption, is very sensitive to errors induced by sample filtration, storage and residual scattering within the sample. Despite these drawbacks, this method affords sufficient accuracy in coastal regions and marine basins affected by terrestrial runoff.

The remote lidar fluorescence method provides information on yellow substance fluorescence more rapidly and with good sensitivity. The theory of fluorescence spectroscopy links the fluorescent substance concentration with the intensity of fluorescence emission and absorption. Numerous authors have reported the correlation between fluorescence and absorption (Reuter *et al.* 1986b, Ferrari & Tassan 1991, Hoge *et al.* 1993b, Hoge *et al.* 1993a, Vodacek *et al.* 1995), but their experiments were carried out only in restricted geographical areas and over short periods of time. The relations they established cannot therefore be applied to the Baltic Sea.

The main aim of the present paper was to test the lidar response to terrestrial yellow substance content by comparing the results of lidar and absorption measurements. The experiment was carried out during two cruises on r/v 'Oceania' in the estuary of the River Odra (Oder) in the Pomeranian Bay in 1996 (Fig 1.).

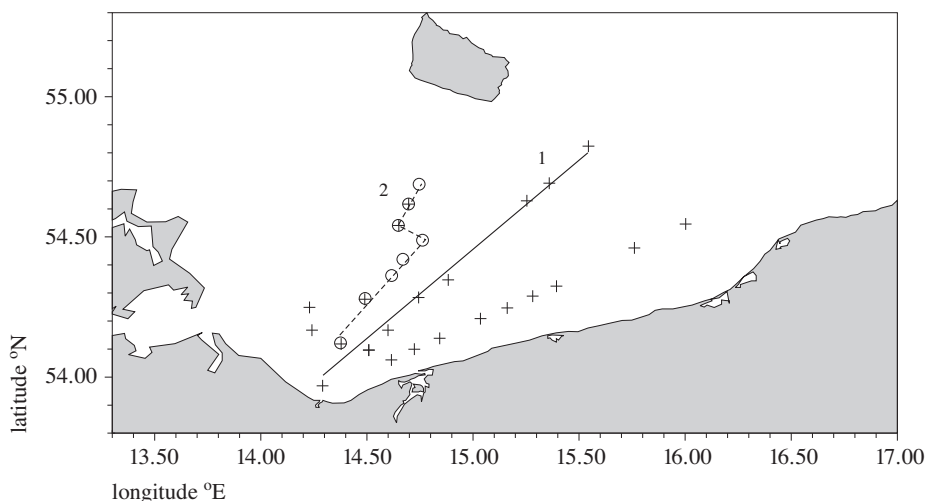


Fig. 1. Location of sampling stations. Stations visited during the March 1996 cruise (+); stations visited during the May 1996 cruise (o). 1 – March transect; 2 – May transect respectively (see text for explanation)

2. Methods

The FLS-12 lidar system used for the measurements is a tunable laser system designed for remotely sensing the aquatic environment in the visible

spectrum (Babichenko *et al.* 1995, Piskozub *et al.* 1996, Król *et al.* 1994). It consists of two lasers: a XeCl (308 nm) excimer laser, which is the UV pumping source, and the dye laser. The backscatter signal is collected by the telescope (receiver mirror diameter 280 mm) and recorded on CCD camera. The lidar-induced fluorescent maxima for the basic Baltic water components are as follows (Burlamacchi *et al.* 1983, Poryvkina *et al.* 1992, Babichenko *et al.* 1993): phycoerythrin – 575 nm, phycocyanin – 645 nm, chlorophyll *a* – 685 nm, and oils – 400–500 nm. If the maxima and half-widths of all the fluorescent bands are assumed known, the experimental curve can be approximated to the Gaussian function curve, and then reduced to component Gaussian function curves.

Bristow *et al.* (1981) gives the theory of fluorescent substance concentration measurements by the lidar method. The fluorescence return signal is directly proportional to the concentration of fluorescing molecules. However, the spectrum of the fluorescence band contains errors due to light attenuation, to changes in the density of various substances dispersed in the seawater and to the instrument set-up. The solution to these problems is the concurrent laser-induced Raman emission of liquid water, which is used to indicate changes in the optical attenuation (Hoge & Swift 1980, 1983, Exton *et al.* 1983). In other words, since water has a constant density, it can be used as an internal standard. The ratio of the integral radiation intensity in the band characteristic of the fluorescent substance to the backscattered water Raman emission is a much more useful quantity, since it minimises the penetration effects and is independent of laser power and the altitude of the fluorosensor.

The relative concentration of components having their own fluorescence can be expressed by the fluorescence factor (Bristow *et al.* 1981)

$$\phi_0 = \frac{P_F}{P_R}, \quad (1)$$

where

P_F – peak detected fluorescence emission power at fluorescence wavelength,
 P_R – peak detected water Raman emission power at water Raman wavelength.

This expression depends mainly on the concentration of the fluorescent substance and is independent of a number of parameters that are the same for both bands. By always using the same wavelength to excite the seawater, one obtains the spectrum of the fluorescence factor ϕ_0 , which varies in a similar way to the changes in concentration of the fluorescent components.

Yellow substance absorption was measured as the UV–VIS transparency of the sample filtered *in vitro*. In accordance with the procedure recommended by Reuter *et al.* (1986a), samples were collected in Nansen bottles

and then filtered on board through Sartorius 0.2 mm cellulose membrane filters. The filtered water was stored in the dark at *ca* 4°C in 200 ml brown-glass bottles, to which 400 μ l 0.5 M HgCl₂ was added to prevent bacterial growth and decomposition of CDOM. Sample transparency was measured with Perkin-Elmer Lambda 4 and Specord double-beam spectrophotometers in a 10-cm quartz cell in the 300–700 nm spectral range. A similar 10-cm quartz cell filled with doubly distilled water was used as reference. The transparency (in units of absorbance $A_{10}(\lambda)$) was converted by means of the following relation into the absorption coefficient obeying the Lambert-Beer law:

$$a_{ys}(\lambda) = 23.03A_{10} \quad [\text{m}^{-1}]. \quad (2)$$

The accuracy of the measurements was found from the reproducibility of a blank sample, where both optical cells were filled with doubly distilled water. Differences in the spectra obtained were detected below an absorbance of 0.001, which corresponds to an absorption coefficient of 0.023 m^{-1} for 10-cm cells.

3. Results and discussion

The research cruises were planned in such a way that samples could be collected in different water masses – in the Pomeranian Bay and in the open southern Baltic. One transect for each cruise has been chosen, marked on Fig. 1 as 1 and 2, to show changes in yellow substance absorption and fluorescence along the transects from the Odra estuary towards the open sea. Sampling and simultaneous lidar measurements were done on a regular basis. The total yellow substance absorption coefficient ranged from 0.45 to 1.0 m^{-1} at $\lambda = 400$ nm. The highest values were recorded in the Pomeranian Bay (0.60 – 1.0 m^{-1} at $\lambda = 400$ nm); in open-sea waters they were lower (0.45 to 0.8 m^{-1} at $\lambda = 400$ nm). The total magnitude of the fluorescence factor variability ranged from 5 to 40 relative units. Figs. 2a–b illustrate the absorption and fluorescence changes plotted as a function of the distance from the mouth of the Odra (calculated from the river mouth towards the open sea). The curves rise and fall simultaneously, so the shapes of the absorption and fluorescence spectra *vs* distance are very similar. In both cruises the highest values of both a_{ys} and ϕ_0 were recorded near the mouth of the Odra. In stations farther away from the mouth and the coasts, the values decrease.

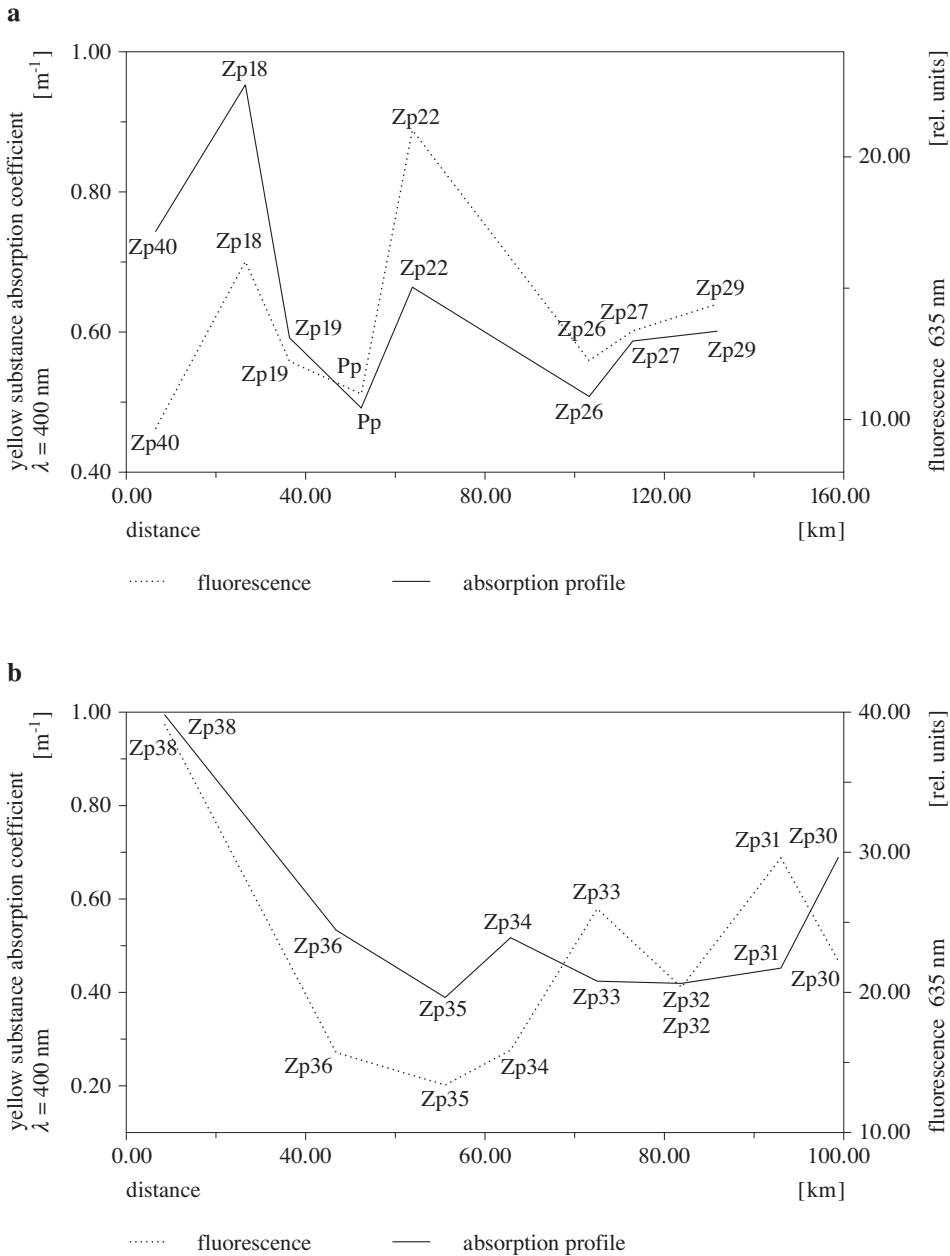


Fig. 2. Distance plots of yellow substance absorption coefficient and fluorescence 635 nm on transects during cruises in March (a) and May 1996 (b)

The available data set is too small for a meaningful quantitative statistical correlation analysis. Furthermore, the fluorescence data have not been normalised to the external standard, as was done, for example,

by Hoge *et al.* (1993). Therefore, converting induced fluorescence into equivalent absorption may be a source of serious errors, because the fluorescent properties of yellow substances vary significantly as a result of composition changes that depend on their origin. Variations in salinity and pH also bring about changes in fluorescent efficiency.

Closer to the river mouth the water contains a lot of products moved by the river from the land. The measurements carried out near the mouth of the river and shipping routes therefore exhibit higher values of yellow substance absorption and fluorescence than do stations more distant from the worst polluted areas of the sea. In the open sea, yellow substance absorption is usually much lower than in bay areas (Kowalczyk & Kaczmarek 1996), but a random oil slick or elevated chlorophyll concentration can affect the lidar signal (Otremba *et al.* 1993, Piskozub *et al.* 1996, Piskozub *et al.* 1998). The different measurement stations in the two cruises may have had some influence on the results, but as the measurement areas overlap, this effect is not thought to be serious.

4. Conclusions

Fluorescence and absorption were recorded during two cruises along transects extending from the mouth of the Odra north-eastwards across the Pomeranian Bay and the southern Baltic. The results demonstrate a correspondence between the changes in the rising and falling trends of the values of a_{ay} and ϕ_0 . The experiment demonstrates that the fluorescent lidar method is a good way of detecting yellow substances in the sea.

However, a much larger database is needed to establish a satisfactory empirical relationship between yellow substance absorption and lidar-induced fluorescence. Measurements of this kind are planned in the future. What is more, the results would be more accurate if the exact composition of the seawater were known. If water samples were chemically analysed, the lidar-induced return signal could be decomposed to Gaussian function curves according to the chemical composition of seawater and the luminescent properties of these components. In the future the application of chemical methods is planned.

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