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# in the Gulf of Riga☆

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**Abstract**

The results of field studies of phytoplankton and dissolved organic matter (DOM) in the Gulf of Riga in August–September 1993, June 1994 and April 1995 are presented. Actively excited fluorescence in UV- and visible spectral regions was used to investigate spatial distributions of DOM, Chl *a*, carotenoids and phycoerythrin in surface water. The fluorescent data were collected by means of laser remote sensing spectrometer (LIDAR), spectrofluorometers in underway flow-through mode and in the measurements of the water samples. Pronounced variable spatial structures of phytoplankton were observed in spring 1995 and late summer 1993, while in early summer 1994 the pigment distribution was rather homogeneous. The spatial modulation of high-resolution profiles of phytoplankton with the period 3.5–5 km was detected across the gulf in all seasons probably caused by variability of hydrophysical conditions. A negative correlation of DOM concentration in surface waters and salinity was revealed in August–September 1993 and June 1994. 

*Keywords:* phytoplankton; in vivo fluorescence; accessory pigments; dissolved organic matter

## 1. Introduction

The long-term investigations in the Gulf of Riga from 1920 to 1990 showed the seasonal variability of chemical and biological variables as well as the spatial hydrological subdivision of the gulf waters (Andrushaitis et al., 1995; Jansone, 1995). The hydrological dynamics of the Gulf of Riga is determined mainly by exchange of water masses with Baltic Sea and river discharge. The Baltic waters intrude the gulf through the bottom layer of the Irbe sound and move along the western coast and to the northern deep-water zone. In spring and early summer the water from Gulf of Finland inflow the gulf along the Muhu sound. The eastern coastal area of the gulf is characterised by low saline waters originated by river discharge (Berzinsh, 1995). The quasi-permanent Irbe front and some distinct hydrographic structures in the northern gulf related to the water exchange were repeatedly observed in 1993–1994 (Lips et al., 1995).

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The dissolved organic matter (DOM) in coastal waters may be either of marine origin, derived primarily from in-situ activities of planktonic organisms, or it may be of terrestrial origin, transported via rivers (Moran et al., 1991). It has been shown that DOM has seasonal and spatial variability (Visser, 1984), especially in the areas of interaction of marine and freshwater masses (Poryvkina et al., 1992). The distribution and variability of DOM in the Gulf of Riga has been rather sporadically studied. Nevertheless the long-term data of annual dynamics of biological oxygen demand (BOD) showed that the influence of labile DOM transported by rivers to the amount of organic materials in the Gulf of Riga may be considerable. This statement is based on a high correlation of BOD load by river discharge and weighted mean BOD values in the Gulf of Riga (Andrushaitis et al., 1995).

Generally, the phytoplankton of the Gulf of Riga is similar to that in the Central and Northern Baltic but the features of brackish water complex (*Aphanizomenon flos-aquae, Anabaena baltica,* etc.) are more expressed (Nikolaev, 1953). The number of phytoplankton taxa is varied from 222 in central part (Jansone, 1995) to 442 in eastern coastal area of Gulf of Riga (Tenson, 1995). Phytoplankton pigments in the Gulf of Riga have not been studied up to 1972. The investigations carried out in the following years showed that during a year the Chl *a* concentration (average for 0–10 m layer) varied broadly: in spring (April–May) from 5 to 25 $mg/m^3$, in summer from 1 to 5 $mg/m^3$, in autumn (October–November) from 1 to 15 $mg/m^3$. The redistribution of the pigment concentration between the parts of the Gulf of Riga and long-term increase in Chl *a* dynamics observed in all studied seasons in the period 1978–1986 were most probably caused by an intensification of nutrient supply with freshwater inflow from the rivers (Tenson, 1995). The increase of Chl *a* concentrations started in the southern part of the gulf, while in the next years the increase of Chl *a* concentrations spread at the eastern coast and central gulf regions (Jansone, 1995).

The present work was aimed to study the spatial distribution and seasonal variability of phytoplankton pigments and DOM in the Gulf of Riga by continuous measurements. Such investigations were not done before in the region. The laser remote sensing and flow-through spectrofluorometry were applied to produce the profiles of phytoplankton pigments and DOM with spatial resolution of 100–150 m on board of steaming vessel. The characteristic spatial scales were determined by Fourier analysis of measured transects. Such techniques allow one to obtain the data continuously to record the small-scale spatial variability and general trends in distributions of phytoplankton and DOM. To analyse the composition of phytoplankton pigments and DOM in water samples the approach of Spectral Fluorescent Signatures (SFS) was used as a basic technique (Poryvkina et al., 1994). The SFS method comprise the measurement and analysis of spectral signatures of water sample as a two-dimensional matrix of fluorescence intensity in co-ordinates of excitation and emission wavelengths. Spectral signature includes the complete set of excitation and emission spectra of object and can be treated as a two-dimensional fluorescence spectrum. The topography of SFS (the number of fluorescent maxima, their co-ordinates ($\lambda_{ex}$, $\lambda_{em}$) on the plot of spectra, the shape of contour lines of equal intensity on the plot) allows one to identify organic compounds in a water and to estimate their concentration (Babichenko et al., 1996). Visible and UV spectral ranges are used to measure the fluorescence of phytoplankton pigments and DOM, respectively. DOM fluorescence signal with maximum at the excitation wavelength 350 nm and emission wavelength 450 nm is dominated by the fluorescence of fulvic acids. For longer excitation wavelengths the maximum of emission spectrum of DOM is red-shifted proportionally to the mean molecular weight of the fluorescing material (Belin et al., 1993).

The advantage of the technique in application to phytoplankton studies is the possibility to determine accessory pigments which have no own fluorescence in vivo. The SFS maxima with excitation/emission wavelengths 440/680, 460/680, 480/680 nm correspond to Chl *a*, Chl *c*, and Chl *b* or carotenoids, respectively (Yentsch and Yentsch, 1979; Anderson and Barrett, 1986; Hilton et al., 1989). The separate spectral structures with excitation/emission co-ordinates 560/580 and 620/640 nm are due to phycoerythrin and phycocyanin (Watras and Baker, 1988).

The method of selective excitation of fluorescence of phytoplankton pigments was applied in laser re-

mote sensing measurements (Babichenko et al., 1995).

## 2. Material and methods

The measurements were performed in the Gulf of Riga on 24 August–2 September 1993, 19–23 June 1994, and 20–26 April 1995 on board of RV *Marina*. Fig. 1 shows the cruise lines and location of sampling stations in the study area. The laser remote sensing was carried out in the cruises of 1993 and 1994. Fluorometric measurements by using water samples were performed in August–September 1993 and by flow-through mode in April 1995.

### *2.1. Spectrofluorometric measurements*

In August–September 1993 the water samples were collected from the depth 2.5 m at the 27 stations throughout the Gulf of Riga. The two-dimensional fluorescence spectra of water samples were measured by spectrofluorometer RF-5000 (Shimadzu) not later than one hour after sampling. No pre-treatment of the samples was carried out. Each spectral signature was formed out of 25 emission spectra at different excitation. The start wavelength of emission scans at each excitation wavelength was off by 10–20 nm to eliminate excitation light passing through the registration monochromator. In the visible spectral range the excitation wavelength was changed in a range 400–640 nm with a step of 10 nm. The fluorescent spectra were recorded by consequential scanning of the fluorescent intensity in the spectral range of 300 nm with the spectral resolution of 5 nm. In the UV-region the excitation was changed from 240 to 360 nm with a step of 5 nm, and emission was measured in the spectral range of 200 nm. Fig. 2 presents the examples of two-dimensional fluorescence spectra for DOM (Fig. 2a) and phytoplankton in vivo (Fig. 2b) measured in the Gulf of Riga.

The flow-through spectrofluorometer FS M32B (LDI, Estonia) was used in continuous mode in April 1995 to measure the excitation spectra of living phytoplankton at the emission wavelength 680 nm. The water pumped from the depth of 1 m was

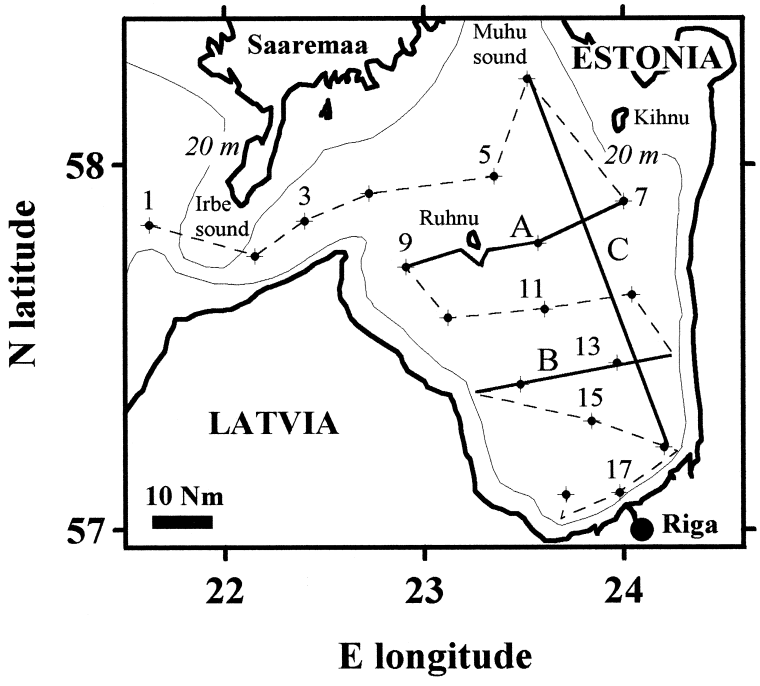


Fig. 1. Study area, sampling stations, cruise lines (dashed) and selected tracks: A, from Stn. 9 to Stn. 7; B, through Stn. 13 and Stn.14; C, from Stn. 16 to Stn. 6.

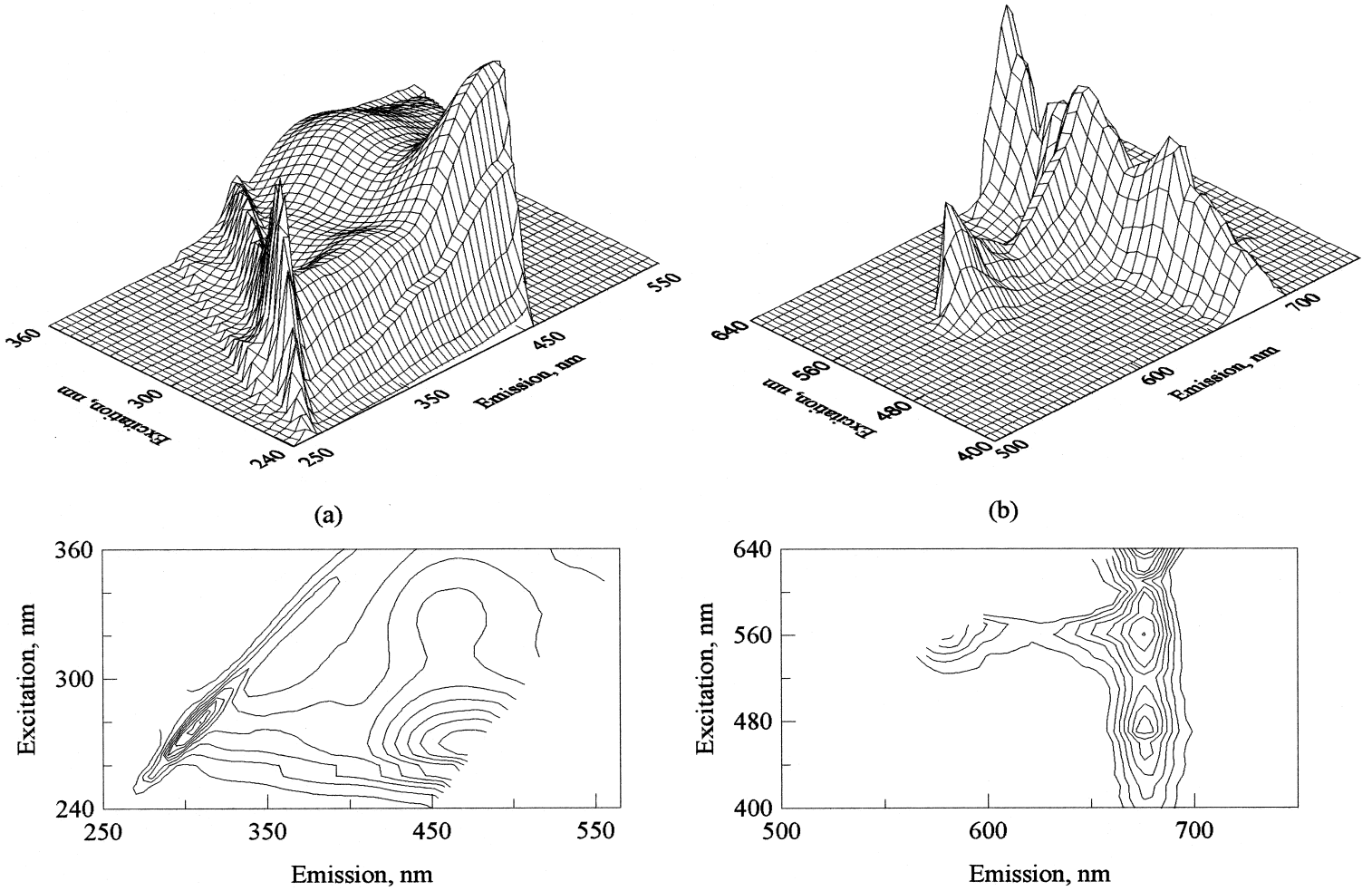


Fig. 2. Spectral fluorescent signatures of dissolved organic matter (a) and phytoplankton (b) in the Gulf of Riga (Stn. 16, 24 August 1993).

flowing through the quartz cuvette. After the cuvette filling the excitation spectra were measured in region 400–650 nm with a step of 5 nm (Fig. 3a). The measurement procedure was carried out with a time delay of 20 s after pumping to eliminate turbulent effects in the cuvette. The measuring procedure was repeated with a time interval of 40–120 s depending on the vessel speed to provide the spatial resolution of about 150 m. FS M32B was controlled by PC, measurements and analysis were performed in automatic mode.

### 2.2. Laser remote sensing

The laser remote sensing was carried out in August–September 1993 and June 1994 by LIDAR system FLS-S (LDI Ltd., Estonia). The LIDAR is based on two lasers: the XeCl excimer laser is used to pump the dye-laser. The dye-laser serves as a sensing source with variable monochromatic radiation. By changing the dyes and tuning radiation wavelength one can provide selective excitation of various pigments of phytoplankton and DOM. Linear

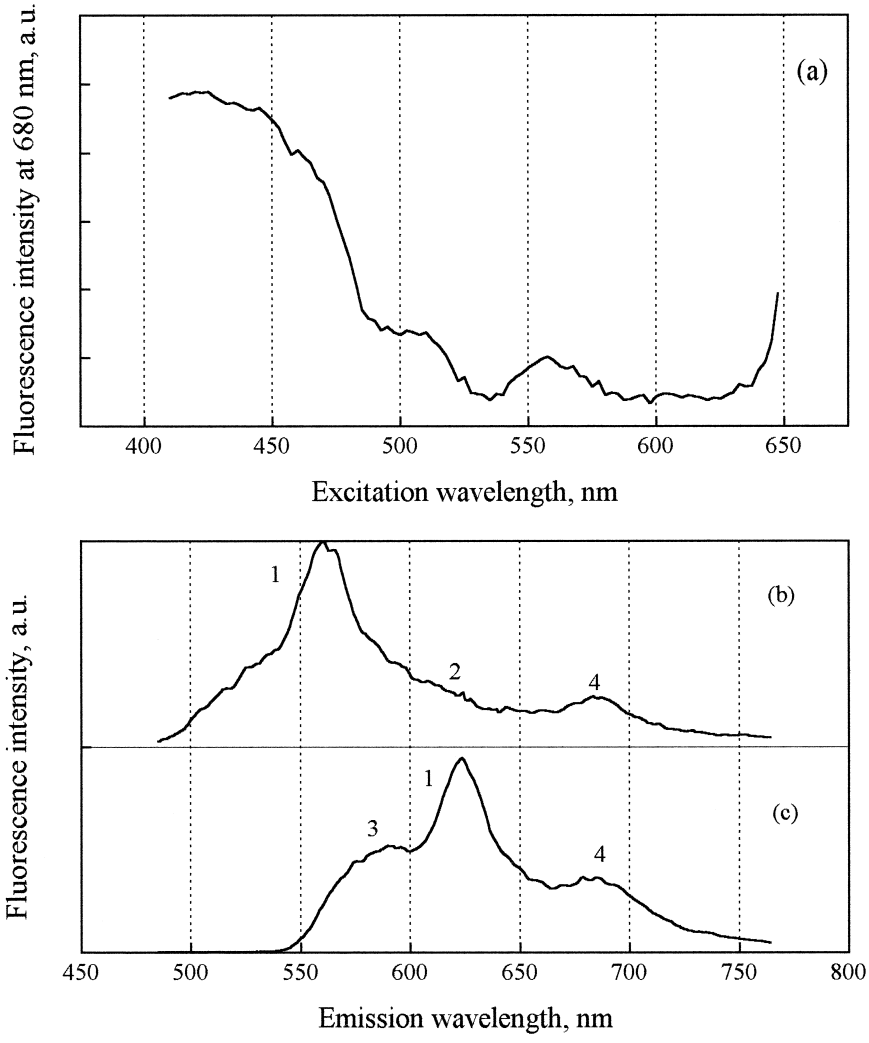


Fig. 3. (a) Example of excitation spectrum of phytoplankton in the Gulf of Riga; (b,c) Gulf water emission spectra at the laser excitation 480 nm (b) and 520 nm (c): 1, Raman scattering line, 2, DOM fluorescence, 3, Phycoerythrin fluorescence, 4, Chl *a* fluorescence.

multichannel detector (500 channels) with gated image intensifier coupled with modified Neuton telescope and compact polychromator, records fluorescence spectra of water at each laser pulse. Short gating time of detector (100 ns) eliminates the influence of sun light to the fluorescence spectra. The LIDAR was installed on the upper deck of the research vessel. The laser beam was passed into the water via a quartz mirror, the same mirror was used to pass the fluorescent signal from water to the telescope. The underway sensing was made along the tracks of 15–50 km with spatial resolution of about 100 m. The spectral signals were integrated over the depth from 0 to 15 m. Thus the registered spectra contained information about average abundance of phytoplankton in a water column. The schematics of LIDAR measurements and detail description of the device can be found in the paper (Babichenko et al., 1993).

The laser emission wavelengths 480 and 520 nm were used to sense the phytoplankton pigments. Fig. 3b and c show the typical emission spectra of gulf water recorded by LIDAR. At the excitation wavelength 480 nm the long-wavelength part of fluorescence spectra of DOM was registered (Fig. 3b). When using the excitation wavelength 520 nm, the fluorescence of phycoerythrin is revealed as well (Fig. 3c).

The intensity of fluorescence, when measuring in remote mode, is influenced by a number of external parameters, first of all by waving of water surface. To eliminate this influence the fluorescence intensity is normalised by the intensity of Raman scattering of laser emission on the water molecules. This ratio named Fluorescent Factor $\Phi\ (\lambda_{ex})$ serves as an indicator of phytoplankton abundance (Hoge and Swift, 1981).

### *2.3. Data calibration*

As the fluorescent measurements produce the data in relative units, the calibration of the fluorescence of phytoplankton pigments by concentration of pigments and calibration of fluorescence of DOM by quantity of dissolved organic carbon (DOC) is required. The relationship of the fluorescence intensities in spectral signatures and volume concentration of pigments were studied earlier in an experiment with natural phytoplankton community (Kaitala et al., 1994). The intensities of fluorescent peaks of SFS were compared with the data of pigment concentration obtained by HPLC. In this work it was shown that the fluorescence intensity depends on the pigment concentration as well as on the growth phase of the phytoplankton community. In a stationary phase the intensity of fluorescence had a linear dependency on the pigment concentration. In the exponential phase the correlation of fluorescence intensities and concentration of pigments decreased, and the accuracy of calibration was rather bad. At the same time the fluorescent ratio of accessory pigments to Chl *a* did not depend so much on the growth phase and corresponded to the taxonomic composition of phytoplankton (Kaitala et al., 1994). More detailed investigations revealed that the quantum yield of fluorescence of Chl *a* in vivo depends on the growth phase of the phytoplankton (Leeben, 1995). The laboratory experiments with pure cultures showed that the quantum yield of fluorescence is decreased sharply at the beginning of exponential phase and then slowly increased during this phase. Thus the coefficient of correlation between in vivo intensity of fluorescence and pigment concentration can vary depending on the growth phase of phytoplankton community.

The correlation of in vivo and in vitro data in August 1993 and June 1994 was quite high ($r^2_{n=26} = 0.75$ and $r^2_{n=23} = 0.71$, respectively), while on April 1995 it was lower than 0.5 ($n = 15$). The possible reason could be variable physiological conditions and taxonomic composition of phytoplankton during algae bloom detected in the gulf this time (Seppälä and Balode, 1999).

As the fluorescent data of phytoplankton pigments and DOM were collected by different devices, the intercalibration of LIDAR FLS-S and RF-5000 (Shimadzu) spectrofluorometer was performed in August–September 1993. The intensity of fluorescence of Chl *a* of living phytoplankton was calibrated by spectrophotometric method using the extracts of Chl *a* in acetone (Jeffrey and Humphrey, 1975). The Fluorescent Factors $\Phi\ (\lambda_{ex})$ at the excitation wavelength 350, 480 and 520 nm were calculated in LIDAR spectra at the sampling stations to compare them with the corresponding values in fluorometric measurements. The intercalibration allowed

to produce the compatible fluorescent ratios of accessory pigments to Chl *a* by LIDAR and fluorometer. The flow-through fluorescent data in April 1995 are given in relative units because of low correlation with in vitro Chl *a* data.

## 3. Results and discussion

### *3.1. Distribution of phytoplankton pigments*

The measured distributions of phytoplankton pigments over the Gulf of Riga are shown in Fig. 4 and Fig. 5. In August–September 1993, the contour maps were obtained by in vivo fluorescent analysis of water samples at 27 sampling stations throughout the Gulf of Riga. In June 1994 and April 1995 they were produced in remote and flow-through mode, respectively. Chl *a* fluorescence served as an indicator of abundance of phytoplankton. The ratios of fluorescent peaks of accessory pigments to Chl *a* were used to map the spatial distribution of pigments.

#### *3.1.1. August–September 1993*

The SFS of phytoplankton measured in late summer 1993 contained the spectral structures of Chl *a*, carotenoids, and phycoerythrin (Fig. 2b). As the data on phytoplankton biomass showed the high amount of cryptophytes at the sampling stations in this time (up to 60% of total biomass, Seppälä and Balode, 1999), the SFS maximum near the excitation 480 nm was probably due to carotenoids typical for cryptomonads.

Fig. 4a presents the distribution of Chl *a* in August–September 1993. The Chl *a* values were generally higher in the coastal area than in the central part of the gulf. The highest amount of Chl *a* (up to 5 mg/m$^3$) was observed in the northern part of the gulf near the Muhu sound. Chl *a* content decreased quite rapidly when moving from western coast to Ruhnu island with slow increase towards the eastern coast. The distribution of Chl *a* in the southern gulf was inhomogeneous (Fig. 4a).

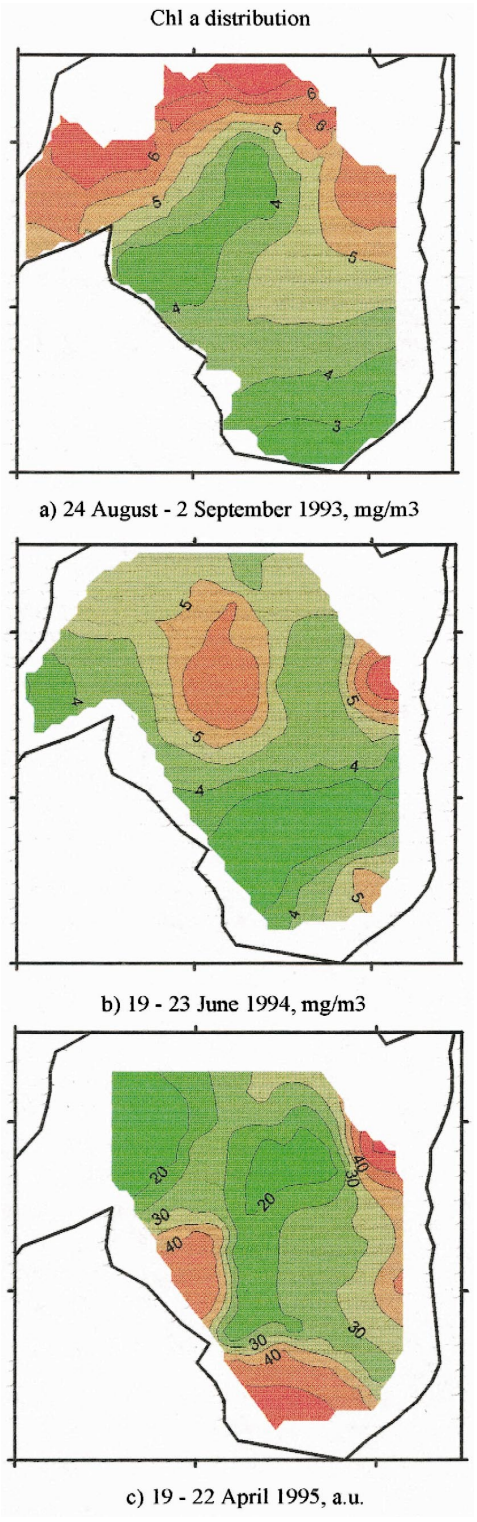


Fig. 4. Distribution of Chl *a* in the Gulf of Riga: (a) 24 August–2 September 1993, mg/m$^3$; (b) 19–23 June 1994, mg/m$^3$; (c) 20–24 April 1995, relative units.

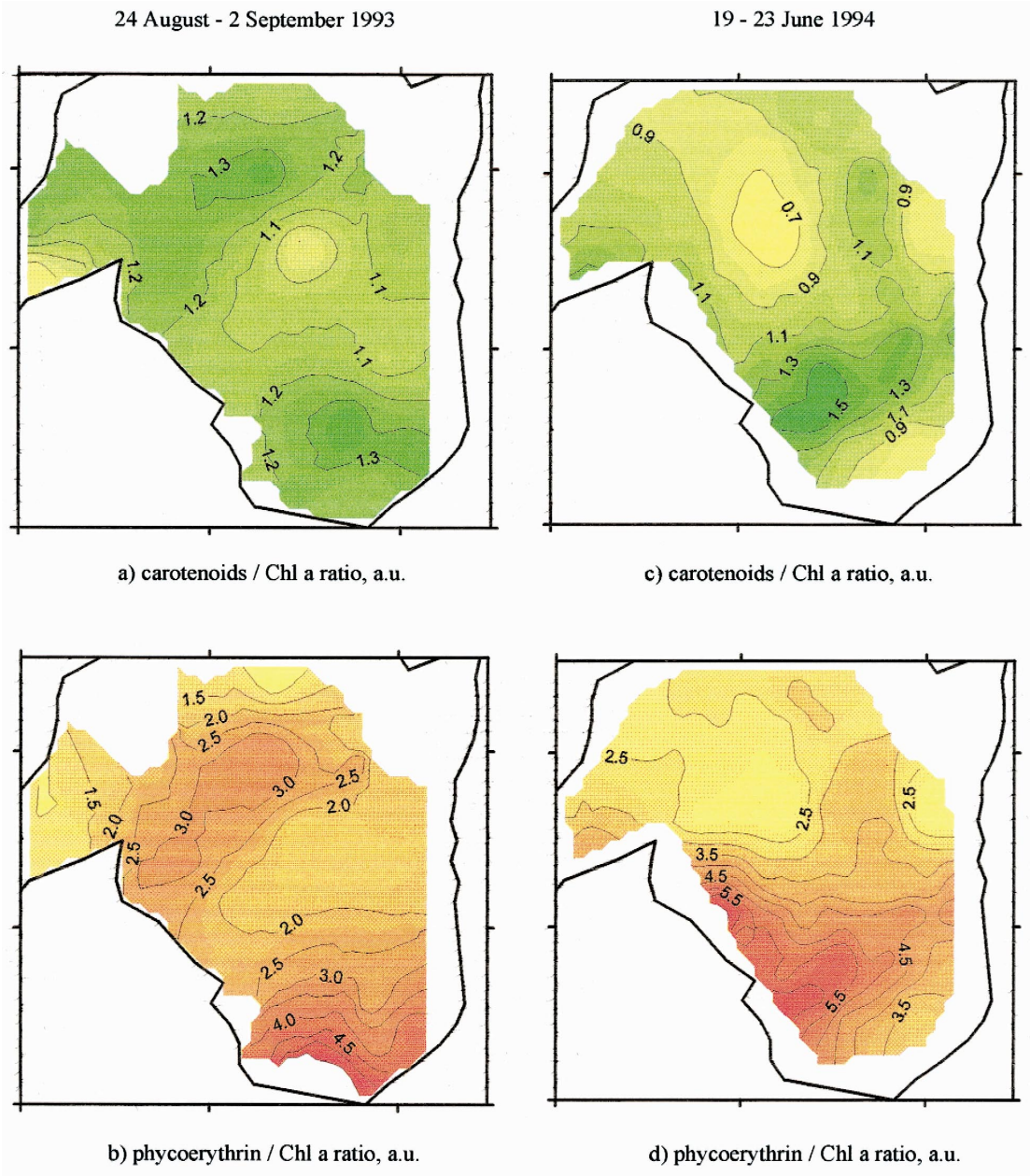


Fig. 5. Distribution of accessory pigments in the Gulf of Riga on 24 August–2 September 1993 (a,b) and 19–23 June 1994 (c,d): (a,c) ratio of carotenoids to Chl *a*; (b,d) ratio of phycoerythrin to Chl *a*.

The contour map of carotenoids distribution in this period is shown in Fig. 5a. The highest ratio of carotenoids to Chl *a* (1.3) was detected in the southern part of the gulf, while the lowest values of this ratio (to 0.9) were observed in the central gulf to the east of Ruhnu island. Pronounced spatial structures of carotenoids distribution were revealed in the Irbe sound and along the south coast of Saaremaa island.

The distribution of carotenoids derived by SFS method in August–September 1993 reflected mainly the distribution of dominant *Cryptophyceae* (compare with Seppälä and Balode, 1999).

When considering the phycoerythrin distribution, some specific patterns were observed (Fig. 5b). The content of phycoerythrin increased sharply when moving towards the mouth of river Daugava and Irbe sound. In the northern part the distribution was similar to Chl *a*. The *Cryptophyceae* biomass did not correspond to the variability of phycoerythrin fluorescence. Some correlation with *Cyanophyceae* biomass ($r^2_{n=26} = 0.62$) was obtained. Picocyanobacteria, probably rich in phycoerythrin, were not included in this correlation. Rather similar relationship between phycoerythrin fluorescence and cyanobacteria (not picosized) was observed during a cyanobacterial bloom in July 1994 in the Gulf of Riga (Seppälä and Balode, 1997).

*3.1.2. June 19–23, 1994*

The distribution of Chl *a* was more homogeneous with weak spatial structures than in August–September 1993, especially in the central gulf (Fig. 4b). The spatial structures were evinced weakly. Increased values of Chl *a* were observed in the south-eastern part of the gulf, near the Pärnu bay and to the north of Ruhnu island. The Chl *a* concentration decreased toward the Irbe and Muhu sounds. At the same time, the corresponding map of carotenoids had pronounced features (see Fig. 5c). The ratio carotenoids/Chl *a* varied from 0.7 in the northern part of gulf to 1.5 at the western coast. In the southern part of the gulf this ratio decreased in West–East direction, while Chl *a* values keep the mean level. The spatial distribution of phycoerythrin had rather similar features (Fig. 5c). Increased values of phycoerythrin/Chl *a* ratio were detected at the western coast. The data of phytoplankton counting showed, that quantity of *Cyanophyceae* was up to 40% of biomass in that area (Seppälä and Balode, 1999). Relatively high spatial variability of ratio of accessory pigments to Chl *a* at the rather smooth distribution of Chl *a* may be caused by changes in taxonomic composition of phytoplankton.

*3.1.3. 19-22 April 1995*

Only the Chl *a* distribution has been measured in this period. As the data of in vivo fluorescence had not high correlation with absolute amount of Chl *a*, the contour map was produced in arbitrary unit of fluorescence intensities (Fig. 4c). The spring bloom of phytoplankton dominated by diatoms has been detected this time. The spatial distribution of Chl *a* based on in-vivo fluorescence was characterised by pronounced structures in the coastal zones and high fluorescence in the southern part of the gulf. The fluorescence of Chl *a* increased sharply toward the mouth of Daugava river. Increased fluorescence values were detected also at the south of Kihnu island. The map was produced by using high-resolution underway fluorometric measurements. The smoothness of the isolines was influenced by small-scale spatial variability of phytoplankton distribution.

*3.2. Small-scale spatial variability of phytoplankton*

The horizontal profiles of phytoplankton distribution with 100–150 m spatial resolution were measured to investigate the small-scale variability of phytoplankton distribution. The underway measurements were performed by LIDAR (August–September 1993, June 1994) and by means of flow-through spectrofluorometer (April 1995). The profiles of Chl *a* and phycoerythrin measured by LIDAR are presented in Fig. 6a–d.

The Chl *a* profile recorded on 30 August 1993 across the gulf demonstrated sharp increasing of phytoplankton (up to three times) at the southern coast of Ruhnu island (Fig. 6a, see track A location in Fig. 1). As the front was located between the stations, it was not detected by analysis of water samples. The fluorescent ratio of phycoerythrin to Chl *a* was higher at the coastal areas than in central gulf. The horizontal profiles of phytoplankton across the gulf were modulated with the spatial scale about 4–5 km. The profiles registered in South–North direction were more smooth (Fig. 6b, see track C location in Fig. 1). The Chl *a* values increased towards the northern part of the gulf, while maximal values of fluorescent ratio of phycoerythrin to Chl *a* were registered in the southern part of the gulf. In spite of LIDAR data integration over the water column, the distribution of pigments corresponded well to the fluorescent data in upper water layer described in Section 1.

Fig. 6c and d presents the corresponding Chl *a* and phycoerythrin profiles along the tracks A and C

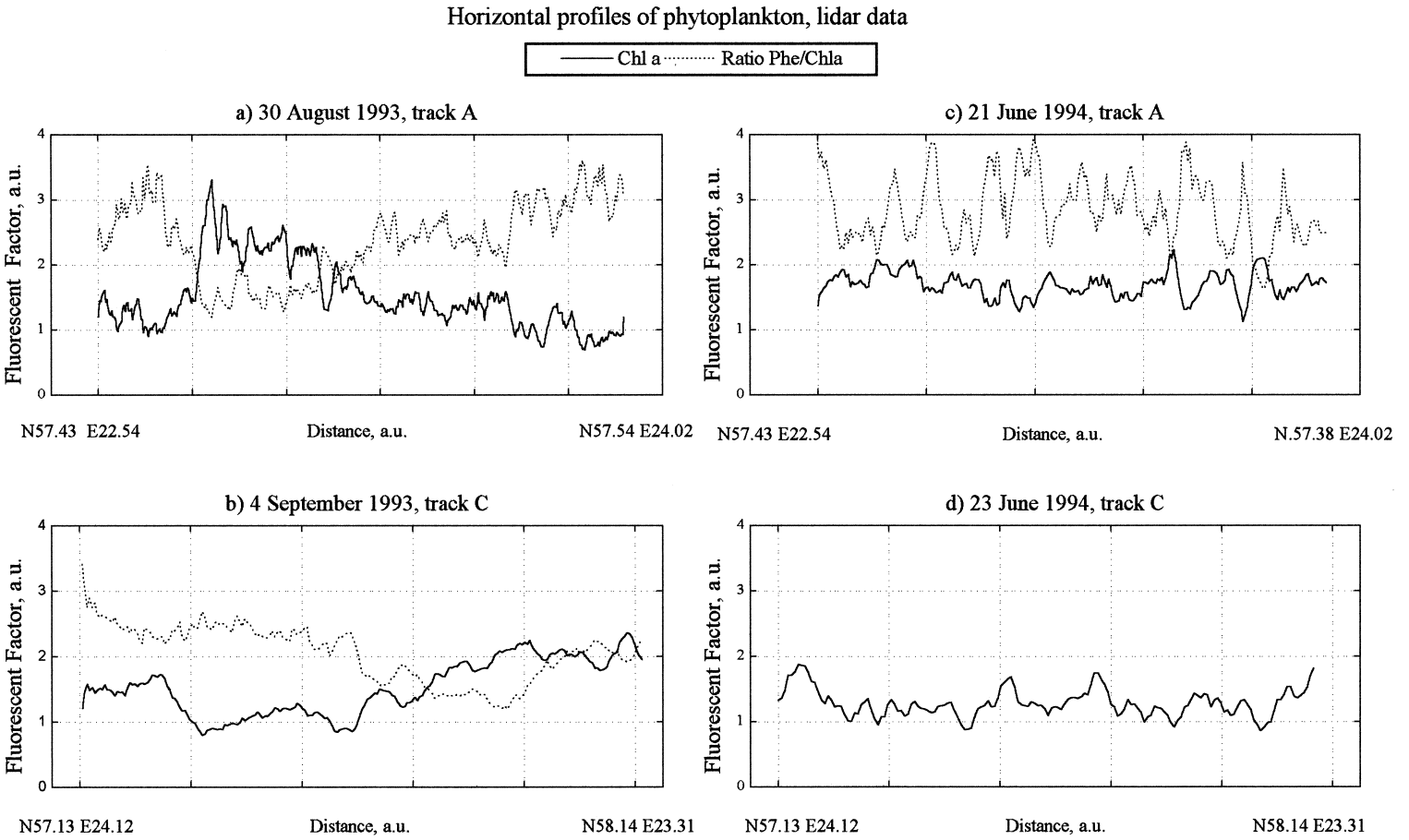


Fig. 6. Horizontal profiles of Chl *a* and phycoerythrin measured by LIDAR along the tracks A and C (see Fig. 1): (a,b) August–September 1993, (c,d) June 1994, relative units.

in June 1994. The underway measurements were performed in windy weather. Registered horizontal profiles had spatial modulation but did not reveal clear structures of phytoplankton distribution, except increase of Chl *a* values in the southern part of the gulf (Fig. 6d).

The spatial modulation may be caused by the variability of hydrophysical and meteorological conditions and can be analysed by comparison of continuous fluorescent and CTD data (Babichenko et al., 1990). Such measurements were performed in April 1995 in flow-through mode. Fig. 7 presents high-resolution horizontal profiles of temperature, salinity and Chl *a* fluorescence, measured in the upper water layer along the track B (see Fig. 1 for track location). The Fourier analysis of the profiles was performed to determine the typical spatial frequencies. After filtration of near-zero frequencies, corresponding to the linear trends in spatial distributions, more higher harmonics were revealed. The typical spatial frequencies were quite similar in the profiles of temperature, salinity and fluorescence. They corresponded to spatial modulation with the scale 3.8–4.3 km. The similarity of spatial frequencies confirmed the correlation of hydrophysical variables and phytoplankton distribution.

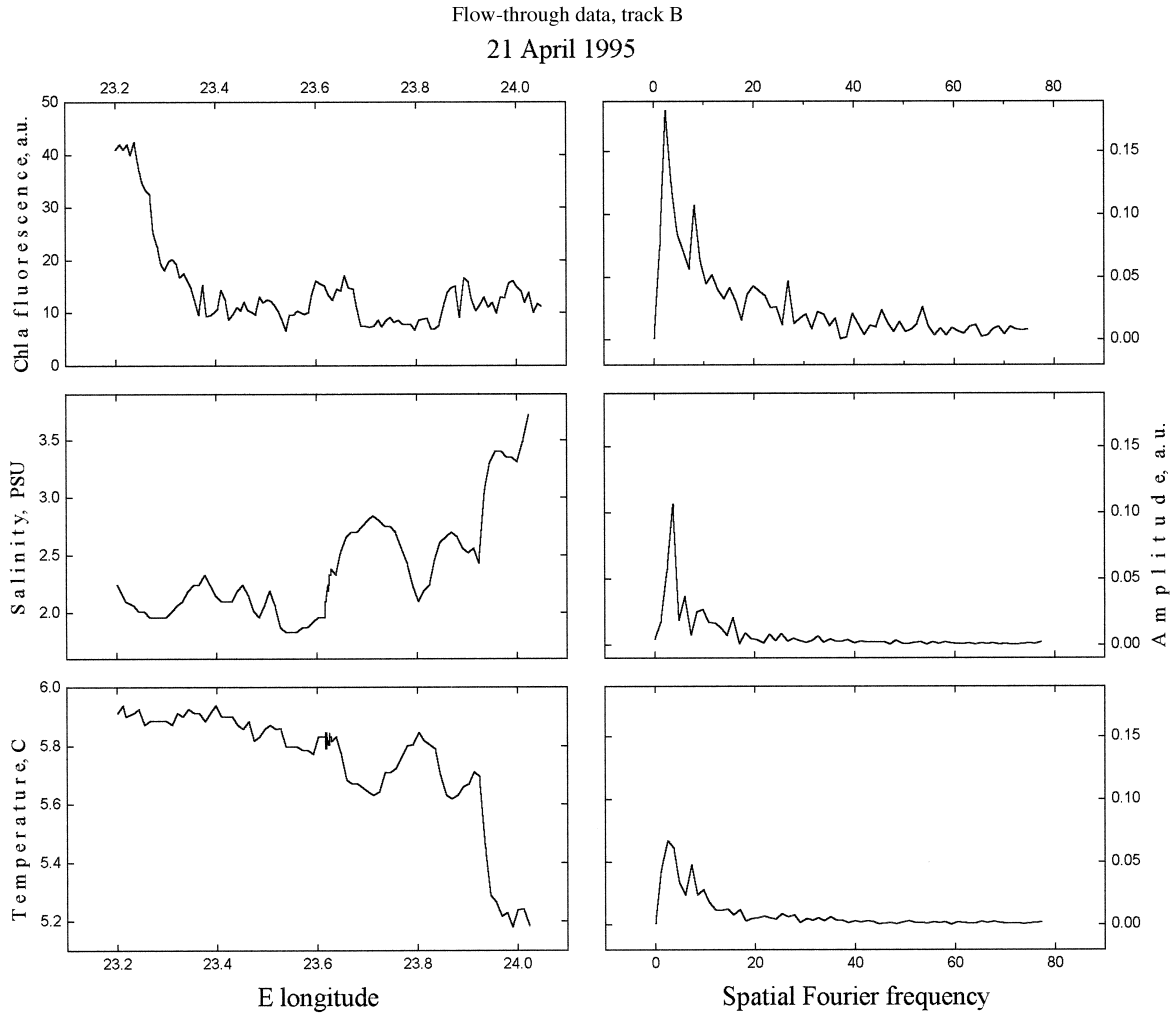


Fig. 7. Horizontal profiles of Chl *a*, temperature and salinity along the track B (see Fig. 1) and their Fourier spectra in April 1995.

### 3.3. Distribution of dissolved organic matter

The fluorescence of DOM was measured by RF-5000 (Shimadzu) spectrofluorometer in water samples and by LIDAR in August–September 1993. In June 1994 only LIDAR was used for the measurements. Basing on the 1993 data, the intercalibration of LIDAR and spectrofluorometer were performed. The correlation of DOM Fluorescent Factors $\Phi(480)$ registered by LIDAR and corresponding values $\Phi(350)$ obtained by spectrofluorometer at 14 stations was quite well ($r^2_{n=14} = 0.91$). Fig. 8a and c show the contour maps of DOM distribution in two seasons. The maximal values of DOM content were detected in the central part of the gulf as well as in the mouths of the river Daugava and Pärnu Bay. The DOM concentration decreased toward the Irbe and Muhu sounds in both seasons. In June 1994 some spatial structure with increased DOM values was observed to the northwest of Ruhnu island. Generally the distributions were in accordance with hydrophysical regime of the Gulf of Riga (Berzinsh, 1995). The analysis of fluorescent data and salinity at the sampling stations in late summer of 1993 revealed

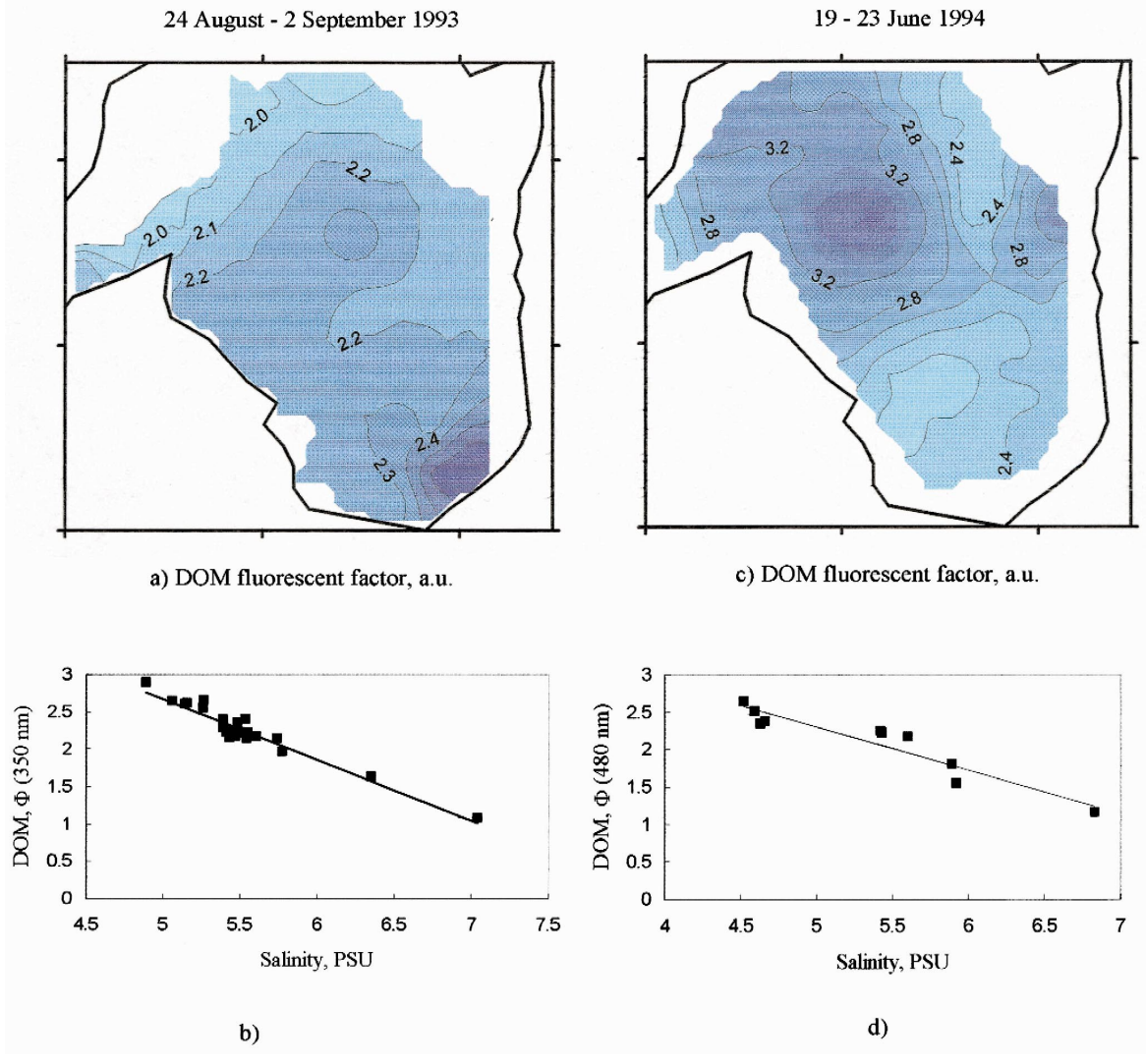


Fig. 8. Spatial distribution of DOM in August–September 1993 (a) and June 1994 (c) and corresponding correlation with salinity (b,d).

strong negative correlation between DOM content and salinity (Fig. 8b). In June 1994, the LIDAR and CTD measurements were carried out in different legs with the time shift of two weeks. Nevertheless, the negative correlation of DOM and salinity was repeatedly observed (Fig. 8d). It showed that the DOM content and its distribution over the gulf was strongly influenced by water impact from Daugava and Pärnu rivers and conservative mixing of marine and freshwater masses.

## 4. Conclusions

The investigations of phytoplankton pigments and DOM in the Gulf of Riga in 1993–1995 revealed their spatial and seasonal variability. In late summer 1993 the abundance of Chl *a* was higher in the coastal areas than in central gulf. The highest amount of Chl *a* (up to 5 $mg/m^3$) was observed in the northern part of the gulf near the Muhu sound, while the highest ratio of carotenoids to Chl *a* was revealed in the southern part of the gulf. Ratios of phycoerythrin and carotenoids to Chl *a* increased towards the mouth of river Daugava and Irbe sound. The features of carotenoids distribution corresponded to dominant *Cryptophyceae*. In early summer 1994 the distribution of Chl *a* was more homogeneous, but the ratio carotenoids/Chl *a* varied from 0.7 in the northern part of gulf to 1.5 at the western coast. Increased values of phycoerythrin/Chl *a* ratio were detected in the central gulf. Relatively high spatial variability of ratio of accessory pigments to Chl *a* was caused probably by changes in taxonomic composition of phytoplankton. The spatial distribution of Chl *a* during the spring bloom in April 1995 was characterised by pronounced structures in the coastal zones and high fluorescence in the southern part of the gulf. The horizontal profiles of phytoplankton abundance across the gulf showed spatial modulation with the scale 3.5–5 km caused probably by variability of hydrophysical conditions. Such a modulation has to be taken into account to produce representative data when sampling and analysis are carried out.

The negative correlation between DOM and salinity was detected in summer seasons 1993 and 1994. This fact shows that the impact of fresh water provided by the Daugava and Pärnu rivers influences strongly to DOM content in the Gulf of Riga, and mixing of marine and fresh waters is rather conservative. The spatial distribution in both seasons had common features: the maximal DOM content was detected in the central gulf decreasing toward Irbe and Muhu sounds. At the same time its concentration and spatial structures varied seasonally.

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