Temporal and spatial changes in the bio-optical properties of seawater in the Nordic Seas – AREX'2003 and 2006

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Abstract

For many years the Nordic Seas have been the subject of research into ocean circulation carried out by the Institute of Oceanology PAS, especially the inflow of Atlantic water and the intensive turbulent mixing of these waters with Arctic and shelf waters. Ocean currents affect various biological processes, among them the supply of organic matter and oxygen, which constitute the foundation for the unique flora and fauna of the Svalbard islands.

Spectrophotometric examinations of surface waters using an M32 B spectrofluorophotometer (LDI Ltd.) were carried out repeatedly during Arctic cruises on board r/v 'Oceania'. The results presented in this paper come from the AREX campaigns of 2003 and 2006. Analysis of the chlorophyll *a* fluorescence excitation spectra recorded shows an increase in phytoplankton abundance and the changes in the spatial distribution of the phytoplankton species characteristic of Atlantic, Arctic and shelf waters. The spatial patterns of the phytoplankton pigments and their abundance were compared with the physical characteristics of water masses. The analysis confirmed that phytoplankton species move together with the Atlantic water as this flows into northern latitudes.

1. Introduction

The sea water in the coastal and open zones of the Nordic Seas (the Greenland, Iceland and Norwegian Seas) has a complex biophysical structure caused by the mixing of different water masses and a huge area with water fronts and glacial activity. The oceanic fronts are multiscale in both space and time and are associated with various phenomena and processes, such as high biological productivity and abundant fishing, abrupt changes of sea colour and powerful vertical movements. Large-scale fronts have important effects on both the weather and the climate (Kostianoy & Nihoul 2009). The main source of the currents circulating in the Nordic Sea is the warm, saline Atlantic Water (AW) that is carried northwards. The eastern branch flows around the Norwegian shelf, the Barents Sea slope and the west Spitsbergen shelf break, forming the eastern branch (the core) of the West Spitsbergen Current (WSC). The western branch of WSC, less saline and cooler than the core, is the continuation of the offshore westerly stream formed and guided by the topography (Piechura &Walczowski 1995, Walczowski & Piechura 2007). These water masses meet again west of Spitsbergen, converging as a result of the bottom topography at latitude 78°N and then diverging again in the Fram Strait. Moreover, the Svalbard Archipelago is surrounded by a cold (< 0°C) Arctic water mass penetrating from the Barents Sea shelf off the eastern coasts of the Svalbard Archipelago (Svendsen et al. 2002, Kostianoy & Nihoul 2009). The organic matter contained in the surface layer of the euphotic zone is a consequence of the history of the routes taken by the water masses, flowing both far from land and along the shelves and shorelines, as well as of the conditions in local biological systems (Drozdowska 2007). Finding such features of organic matter that are typical of the individual study areas, that is, typical of different water masses, is the purpose of this research.

Our in vivo spectrofluorometric investigation of seawater samples, taken from several depths in the Nordic Seas, was conducted together with measurements and analysis of the fluorescence excitation spectra of phytoplankton. Excitation spectra of living phytoplankton characterize the pigment composition of algal cells and energy transfer processes from accessory pigments to chlorophyll *a* (Chl *a*). Analyses of these spectra provide information about the spatial distribution of these pigments in different vertical and horizontal transects, and enable the phytoplankton community situation in coastal and open-sea waters to be established.

In order to study the trends of phytoplankton changes, quite a long time-series is needed. The spectrofluorometric studies are therefore being continued in order to determine the interannual variability and longer-term changes in the marine ecosystem of the archipelago (Cisek et al. 2010). The

Fluo-imager M32 B flow-through spectrofluorometer measures visible light excitation spectra and can be applied to the fluorescent constituents of phytoplankton pigments. The excitation wavelength from 400 to 600 nm is scanned by the monochromator; emission is at 680 nm. The aim was to reveal the fluorescence of Chl *a* induced by accessory pigments. The Chl *a* fluorescence emission at 680 nm, observed at several excitation wavelengths that are coincident with the accessory pigment absorption maximum, is treated as an indicator of the abundance of different phytoplankton pigments (Poryvkina et al. 2000).

The most important advantage of spectrofluorometric measurements is that the in vivo measurements of recent water samples on board ship and the data-processing are both carried out quite quickly.

The concentration of absorbing molecules can be calculated from the recorded excitation spectra of Chl *a* in seawater samples.

The advantages and limitations of the application of fluorescence actively induced in living phytoplankton analysis are discussed. The focus is on making correct predictions of pigment concentrations from fluorescence data. The results of the high resolution mapping of chlorophylls and phycobilins in the Nordic Seas during the summers of 2003 and 2006 are presented. Dynamic spatial maps of phytoplankton pigments were registered with a Fluo-Imager flow-through spectrofluorometer. Characteristic patterns of the phytoplankton distribution in the study area and their evolution in time are discussed.

2. Material and methods

The schedule of the r/v 'Oceania' polar cruise included the Greenland and Iceland and Norwegian Seas, known as the Nordic Seas. Figure 1 shows a map of the stations where the optical and CTD measurements were carried out.

Water collection

Water samples were collected from the surface layer (from 0 to 0.5 m) using a special pail from on board ship. The samples were poured into the flow-through system of the Fluo-Imager that allows in vivo measurements of natural water, without prior sample preparation.

Instruments

Fluorescence excitation spectra of seawater samples were measured with a Fluo-Imager M32 B spectrofluorometer at one emission wavelength, 680 nm, at the halfwidth of the optical filter $\Delta\lambda = 5$ nm. The spectral range of the instrument (excitation 400 to 660 nm, emission 680 nm) was used

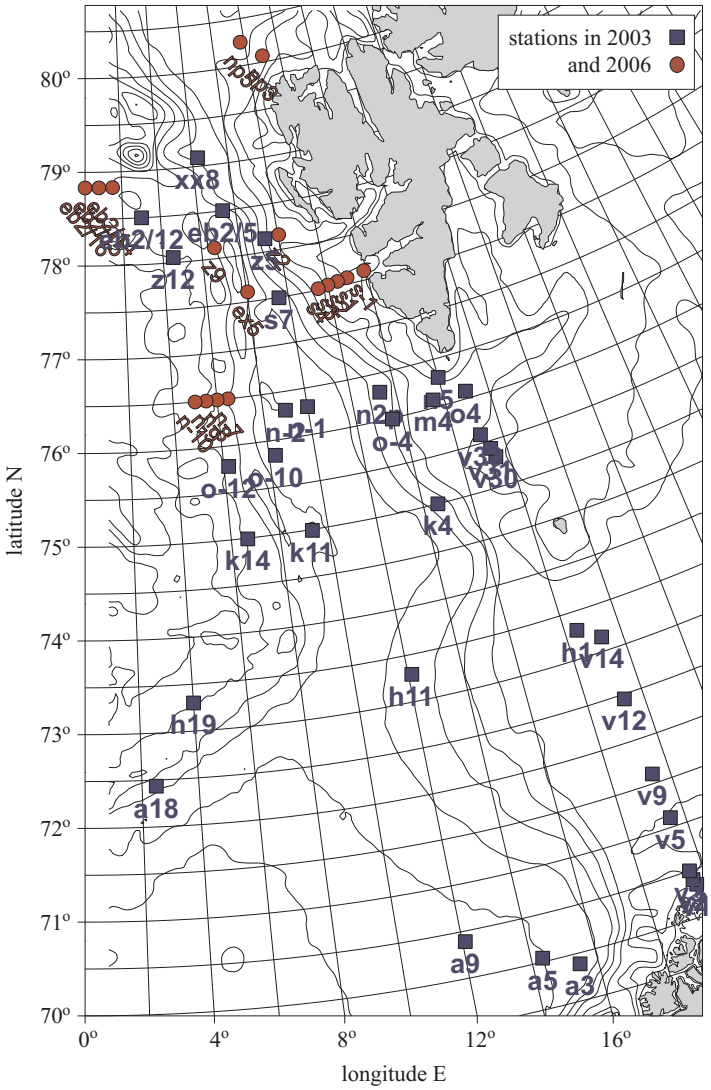

Figure 1. Map of the stations where optical measurements were made during AREX'2003 and 2006

to determine the fluorescence intensity of Chl *a* at 680 nm induced by accessory pigments. A xenon lamp (150 W) was used as the continuous light source. The fluorescence of the sample in the flow-through quartz cuvette is induced by the excitation monochromator and recorded by the optical filter with a photomultiplier tube (PMT) with further digital processing. Spectral data analysis and instrument control was ensured with specially designed software. The excitation spectra were not corrected for the spectral distribution of the lamp source.

3. Results

In vivo fluorescence excitation spectra of phytoplankton cultures in natural waters were measured at the emission wavelength 680 nm (Figures 2 and 3).

In all the water samples from the Nordic Seas were chlorophyll *c* – containing algae (Archibald & Keeling 2002, Howe et al. 2008, Liu et al. 2009). Different combinations of peaks fill the wide range of excitation

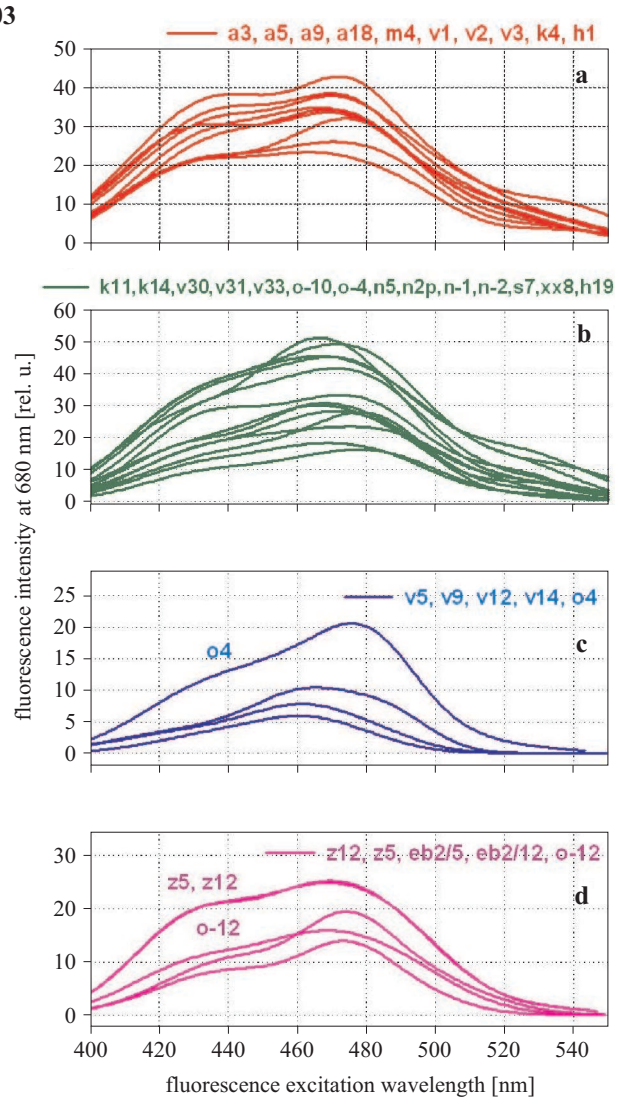

Figure 2. Fluorescence excitation spectra of phytoplankton cultures at 680 nm obtained in different transects – 2003

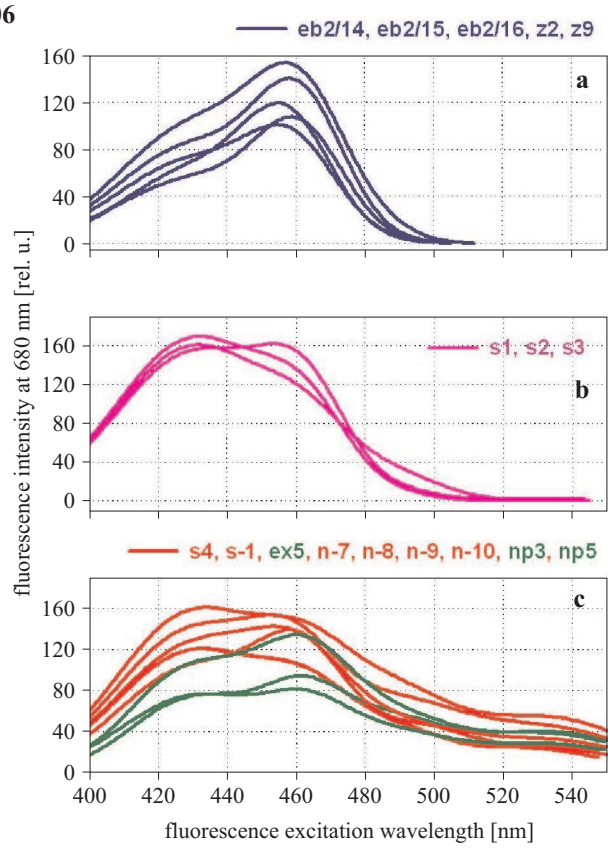

Figure 3. Fluorescence excitation spectra of phytoplankton cultures at 680 nm obtained in different transects – 2006

spectra from 400 to 600 nm. The 420–440 nm spectral range is related mainly to Chl *a*, and the peaks in the 460–470 nm range are due to diverse combinations of chlorophylls *c1*, *c2* and *c3*. The carotenoid peaks lie between 480 and 580 nm. Fucoxanthin (530 nm) is the predominant carotenoid in *Bacillariophyceae*, *Chrysophyceae* and *Dinophyceae*. In general, the spectra recorded in 2003 and 2006 had different spectral features in the 460–480 nm range. The chlorophyll *c* peak in the excitation spectra was located at 480 nm in 2003 and at 460 nm in 2006.

All the Chl *a* fluorescence excitation spectra recorded were divided into four groups with certain dominant spectral characteristics; they are colour-coded (red, green, pink and blue) in Figures 2 and 3. The first type (red) has a wide excitation spectrum with two distinctive peaks at 440 nm and 480 nm (2003) (Figure 2a) and two distinctive peaks at 440 nm and 460 nm (2006) (Figure 3c). The overlapping of the Chl *a* fluorescence excitation spectral

bands from individual accessory pigments and the different intensities of these bands in the complex spectra cause a shift in the maximum positions of spectral bands in a complex spectrum.

The second type has a broad spectrum with one dominant peak at 480 nm (2003) and at 460 nm (2006), marked in green in Figures 2b and 3c. Both the red and green spectra exhibit a weak fucoxanthin shoulder at 530 nm. The first type of spectrum was recorded at stations in the Atlantic water (AW) domain, while the second type was recorded in the offshore area above the mixing zone of Atlantic and Arctic water masses. The third and fourth groups are typified by the absence of excitation bands in the 500–530 nm range, marked in pink and blue on Figures 2c, 2d and 3a, 3b respectively. The pink spectra have two distinctive bands, whereas the blue ones have a single dominant band.

The portions of fluorescence intensities at excitation wavelengths 440, 460, 490 and 530 nm were investigated in order to analyse how the excitation spectra structure varies with the algal pigment composition (see Figures 4 and 5).

The results in Figures 4 and 5 are divided as in Figures 2 and 3. One can see that the contribution of the main excitation spectra peaks is quite stable for a given area, despite the fact that the concentration can vary considerably. From this point of view the data in the figures represent the fluorescent fingerprint of the dominant species of phytoplankton. The

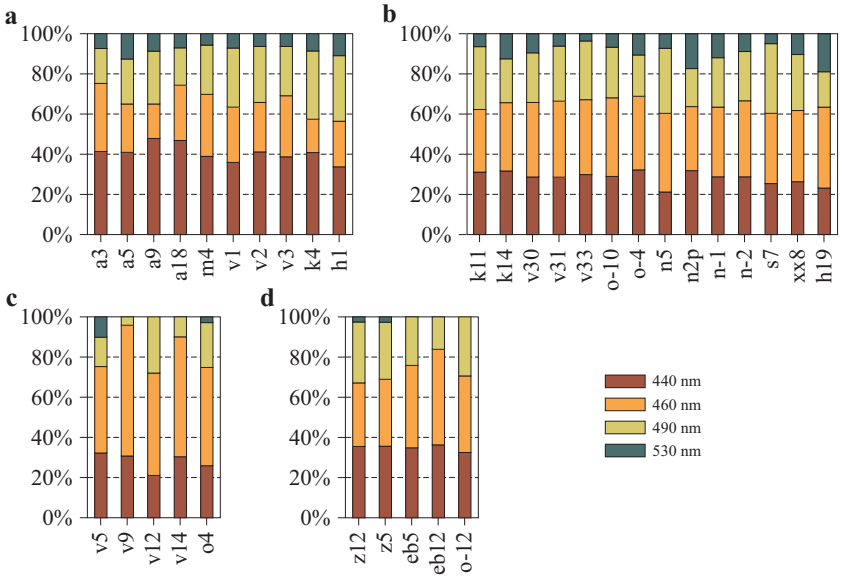

Figure 4. Composition of Chl *a* fluorescence at 680 nm induced at 440, 460, 490 and 530 nm – 2003

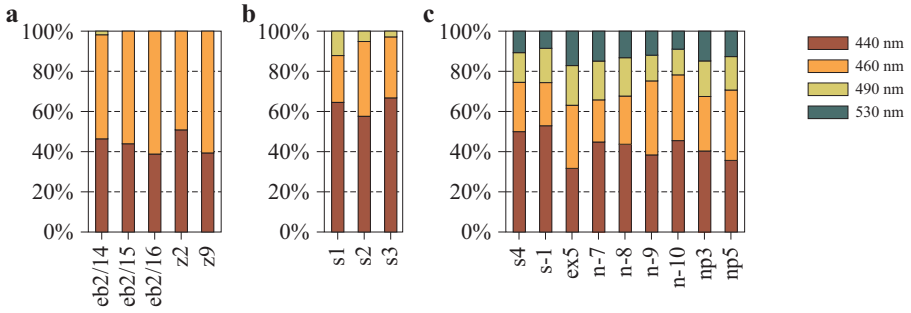

Figure 5. Composition of Chl *a* fluorescence at 680 nm induced at 440, 460, 490 and 530 nm – 2006

carotenoids that absorb light in the long-wavelength spectral range (490 nm and 530 nm) start to play a considerable role in light harvesting and energy transfer to Chl *a*. The fluorescence composition diagrams show that it is possible to distinguish chlorophyll *c* – containing algae by taking into account the differences in the carotenoid contribution to pigment composition.

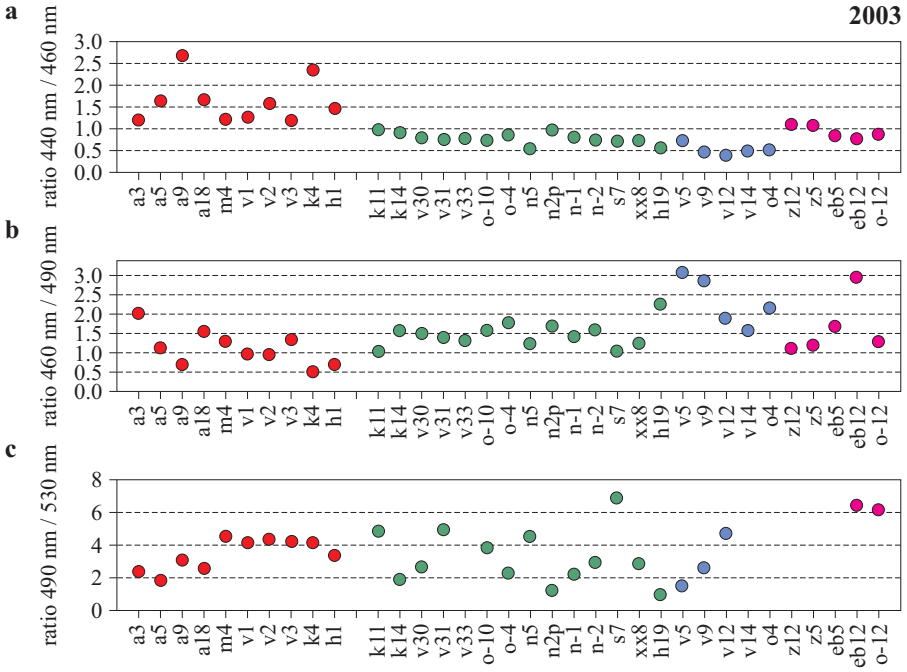

Figure 6. The fluorescence ratios at 680 nm induced at different wavelengths obtained in 2003; (a) $R_{440/460} = I_{440}/I_{460}$, (b) $R_{460/490} = I_{460}/I_{490}$, (c) $R_{490/530} = I_{490}/I_{530}$

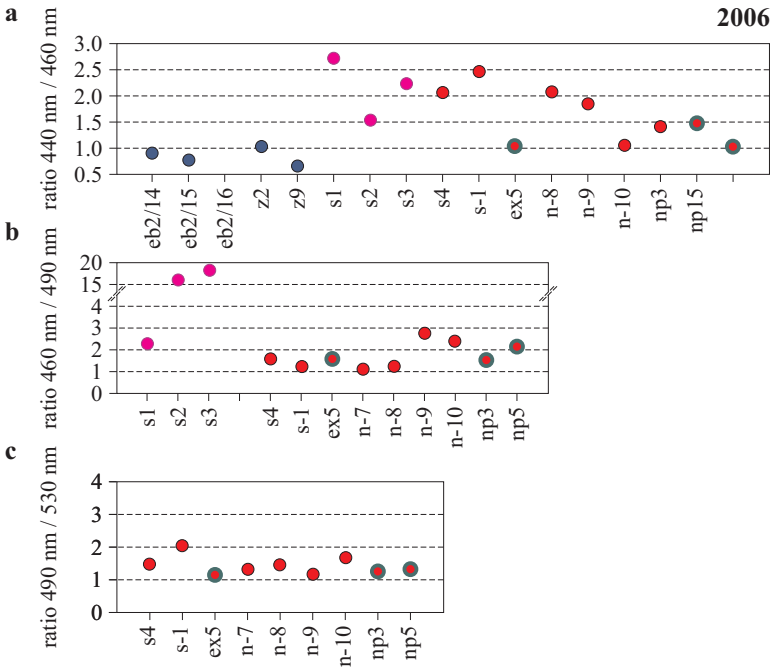

Figure 7. The fluorescence ratios at 680 nm induced at different wavelengths obtained during AREX'2006; (a) $R_{440/460} = I_{440}/I_{460}$, (b) $R_{460/490} = I_{460}/I_{490}$, (c) $R_{490/530} = I_{490}/I_{530}$

The Chl *a* fluorescence excitation spectra obtained in 2003 at the stations presented in Figures 4a and 4b exhibit all four pigments. The dominant pigment in plot 'a' has an excitation spectral band with a maximum at 440 nm, whereas that in plot 'b' has a maximum at 460 nm. The same properties describe the stations presented in Figure 5c (data from 2006). However, the areas presented in Figures 4c, 4d and Figures 5a, 5b are described by absorption spectral bands above 480 nm that are weak or lacking altogether; this indicates a shortage of carotenoids.

The ratio of the main intensity peaks for chlorophyll *c* – containing groups of algae were estimated and compared on the basis of the diagrams in Figures 4 and 5. The colours in Figures 6 and 7 signify the stations defined by the fluorescence excitation spectra presented in Figures 2 and 3.

In 2003, the stations marked in red had a high 440/460 ratio – >1; at the other stations the ratio was <1 (Figure 6a). In 2006 the 440/460 ratio reached values >1 at the stations marked in red, green and pink; the other stations (dark blue) had values <1 (Figure 7a). In 2003, the 460/490 ratio varied from 0.5 to 2 at the stations marked in red, and from 1 to 2.5 at the green stations; at the other stations the values varied from 1 to 3

(Figure 6b). In 2006, the 460/490 ratios calculated for the stations marked in red and green ranged from 1 to 3, whereas for the stations marked in pink they were spread over a much larger range of values (Figure 7b).

The 490/530 ratio is an indication of the carotenoid content. The ratio calculated for the 2003 results varied from 1 to 7, but from only 2 to 4 at the red stations. The 2006 ratio varied from only 1 to 2 at the red and green stations (Figures 6c and 7c).

The above results enable the chlorophyll pigment composition of surface water phytoplankton species to be determined precisely. The distribution of phytoplankton species classified on the basis of pigment fluorescence analysis is shown in Figures 8a and 8b. The coloured dots relate to the same stations as in Figures 2 and 3.

The phytoplankton species marked in red correspond to the warm AW penetration in the direction of Spitsbergen; those in green are characteristic of the masses of mixed warm Atlantic waters and cooler Arctic waters; those in pink are typical of these latter waters. That was the situation in 2003.

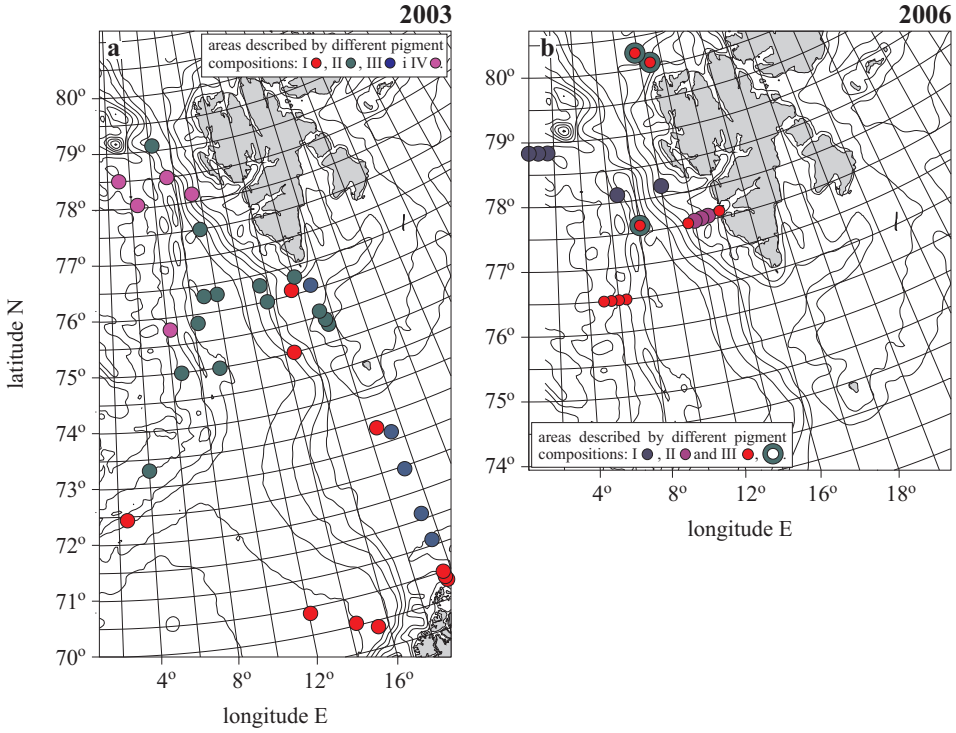

Figure 8. Distribution of different phytoplankton species recorded during the AREX campaigns in 2003 (a) and 2006 (b)

In 2006 the warm water spread closer to the island, and the red dots reflect these changes.

4. Discussion

The thermodynamic properties of the water masses, recorded during the same campaigns, are described in detail by Piechura & Walczowski (2009). The analyses of the CTD results obtained during the 2003 and 2006 campaigns, presented in that paper, show the shift of Atlantic Water into the region where the WSC had normally circulated (Figures 9a and 9b). Additionally, the luminescent properties of water samples taken from several different depths of the same seas combined with the thermodynamic properties of the water masses are given by Cisek et al. (2010).

Comparison of the results of our analysis and calculations with the CTD maps in Piechura & Walczowski (2009) obtained during the same campaigns shows good similarity between temperature and phytoplankton types. One may infer that the observed changes in the abundance and spatial

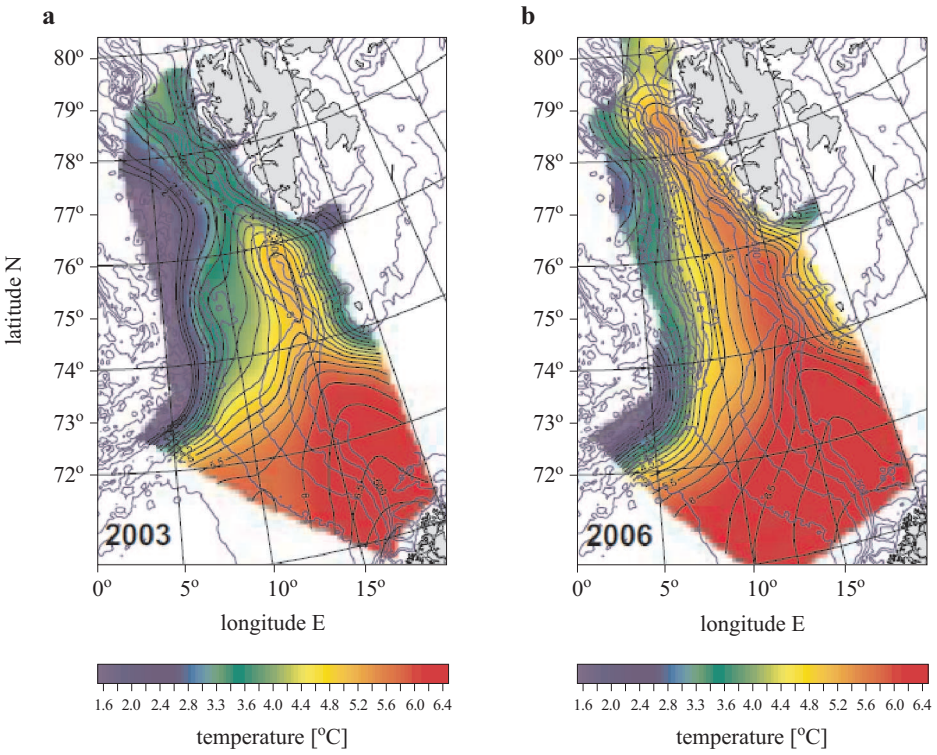

Figure 9. Temperatures in summer 2003 (a) and 2006 (b). Based on data from Piechura & Walczowski (2009)

distribution of phytoplankton species are controlled by the hydrophysical properties of the water masses in a given year, that is by the inflow of Atlantic waters into the Svalbard Archipelago.

The results of this field study of phytoplankton pigment distribution using fluorescence excitation spectra demonstrate that it is possible to specify the algae type and to monitor changes in the phytoplankton community. This application can be extended to the development of a method for the in vivo quantification of phytoplankton pigments. To achieve this, however, parallel measurements of extracted samples have to be made and the appropriate calibrations applied, depending on the composition of the phytoplankton community.

Field studies have confirmed that on-line spectrofluorometric methods can be effectively used to identify phytoplankton pigments. They were used to detect phytoplankton blooms, to investigate changes in phytoplankton composition, and to create spatial maps of photosynthetic pigments. With regard to the monitoring of large water areas or of temporary processes in a small area, the most productive way is a balanced combination of continuous on-line fluorescence measurements and sampling procedures, which allows to decrease the time-consuming manual analysis of water samples in the laboratory.

References

Archibald J. M., Keeling P. J., 2002, *Recycled plastids: a 'green movement' in eukaryotic evolution*, Trends Genet., 18 (11), 577–583, doi:10.1016/S0168-9525(02)02777-4.

Cisek M., Colao F., Demetrio E., Di Cicco A., Drozdowska V., Fiorani L., Goszczko I., Lazic V., Okladnikov I. G., Palucci A., Piechura J., Poggi C., Sighicelli M., Walczowski W., Wieczorek P., 2010, *Remote and local monitoring of dissolved and suspended fluorescent organic matter off Svalbard*, J. Optoelectron. Adv. M., 12 (7), 1604–1618.

Drozdowska V., 2007, *Seasonal and spatial variability of surface seawater fluorescence properties in the Baltic and Nordic Seas: results of lidar experiments*, Oceanologia, 49 (1), 59–69.

Howe C. J., Barbrook A. C., Nisbet R. E. R., Lockhart P. J., Larkum A. W. D., 2008, *The origin of plastids*, Philos. Trans. R. Soc. B, 363 (1504), 2675–2685, doi:10.1098/rstb.2008.0050.

Kostianoy A. G., Nihoul J. C. J., 2009, *Frontal zones in the Norwegian, Greenland, Barents and Bering Seas*, [in:] *Influence of climate change on the changing Arctic and sub-Arctic conditions*, J. C. J. Nihoul & A. G. Kostianoy (eds.), Springer, Dordrecht, 171–189.

Liu H., Probert I., Uitz J., Claustre H., Aris-Brosou S., Frada M., Not F., de Vargas C., 2009, *Extreme diversity in noncalcifying haptophytes explains*

a major pigment paradox in open oceans, PNAS, 106 (31), 12803–12808, doi:10.1073/pnas.0905841106.

Piechura J., Walczowski W., 1995, *The Arctic Front: structure and dynamics*, Oceanologia, 37 (1), 47–73.

Piechura J., Walczowski W., 2009, *Warming of the West Spitsbergen Current and sea ice north of Svalbard*, Oceanologia, 51 (2), 147–164.

Poryvkina L., Babichenko S., Leeben A., 2000, *Analysis of phytoplankton pigments by excitation spectra of fluorescence*, Proc. EARSeL-SIG-Worksh. 16–17 June 2000, Dresden/FRG, 9 pp.

Svendsen H., Beszczynska-Møller A., Hagen J. O., Lefauconnier B., Tverberg V., Gerland S., Ørbøk J. B., Bischof K., Papucci C., Zajączkowski M., Azzolini R., Bruland O., Wiencke C., Winther J.-G., Dallmann W., 2002, *The physical environment of Kongsfiorden-Krossfjorden: an Arctic fjord system in Svalbard*, Polar Res., doi:10.1111/j.1751-8369.2002.tb00072.x.

Walczowski W., Piechura J., 2007, *Pathways of the Greenland Sea warming*, Geophys. Res. Lett., 34, L10608, doi:10.1029/2007GL029974.