12-hour cycle of matter transformation in the sea surface microlayer in the offshore waters of the Gdańsk Basin (Baltic Sea) during spring

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KEYWORDS
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Abstract

Short-term measurements of nutrient and DOC concentrations and suspended matter (particles, chlorophyll *a*, phaeophytin, algae and ATP concentrations) carried out in seawater layers of varying thickness (10, 90, 250 μm and the underwater layer – 15 cm depth) in spring form the basis for a discussion of the diurnal fluctuations of nutrient and suspended organic matter concentrations. Quantitative and qualitative differences in the composition of neuston species were recorded in selected sub-layers of the chemically stratified sea surface microlayer. The non-linear regression equation was applied in a mathematical model of the diurnal fluctuations of nutrients and organic matter. Two maxima and two minima were found in the diurnal cycle of nutrient concentrations and organic suspensions in sub-layers of different thickness selected from the sea surface. The first maximum, expressed by the proliferation of phytoneuston, lasted from the very early morning till mid-morning. The second maximum occurred in the afternoon. The chlorophyll *a* concentration, and ATP and neuston abundance declined markedly around noon, when the biologically-damaging radiation dose increased, compelling the downward migration of organisms. At the same time, the photo-oxidation of dissolved organic matter intensified and the concentrations of inorganic forms of nitrogen and phosphorus rose. A shift (up to 2 h) between the maximum and minimum neuston concentration in these sea surface layers was indicative of phototaxis occurring within the entire surface microlayer and in the underwater layer. After sunset the decline in phytoneuston abundance could be related to zooplankton grazing as well as to respiratory breakdown.

1. Introduction

The seawater surface is a common interface of profound importance to both the oceanic and atmospheric environments. This is where numerous spatially and/or temporally variable processes occur, which affect the accumulation and exchange of biologically active substances and components detrimental to the irradiation budget. These processes appear to play a key role in supporting life in the ocean and are decisive in the global radiation balance. Studies of the sea surface microlayer in the last 40 years have shown it to be a unique environment as regards its physical, biological and chemical properties (Liss & Duce 1997).

Organisms and their abiotic environment are interlinked and influence each other. Nitrogen and phosphorus compounds are important components of the protoplasm, circulating in the biosphere from the abiotic environment to organisms and back to that environment. Solar energy, converted into thermal and chemical energy (the latter being stored in the organic compounds), is the driving force of this circulation.

Besides stimulating life processes, solar energy plays an important role in photodegradation processes. Radiation, especially UV–B, is responsible for the inhibition of chemical processes, including photosynthesis, within the microlayer and subsurface water (Hardy & Gucinski 1989, Behrenfeld et al. 1993, Herndl et al. 1993).

Although the diurnal cycles of organic matter transformation in the euphotic layer of the sea have been discussed in numerous articles (Dietz et al. 1976, Mopper & Lindroth 1982, Johnson et al. 1983, Sieburth 1983, Falkowska 1998), and the daily rhythms of variations in the microlayer of lakes, ponds and marshes also described in detail (Hardy 1973, Freedman et al. 1982, Maki & Ramsen 1989, Maki & Herwig 1991), the part played by the microlayer of the sea-atmosphere interface requires further extensive study. Such investigations should focus on the variability in concentrations of substances closely related to photosynthesis and their effects in retarding CO_2 input from the atmosphere (the 'flux capping' hypothesis – GESAMP 1995). The main aim of the present article is to provide evidence that short-term fluctuations in the concentrations of chemical substances related to assimilation processes and the destruction of organic matter within the sea surface microlayer are not incidental but periodic in nature.

2. Material and methods

Seawater samples from the surface microlayer and underwater layer were collected in the offshore area of the Gdańsk Basin on 29 April–5 May 1994, 8–12 May 1995 and 19 June 1996 from an anchored vessel (Fig. 1). Three

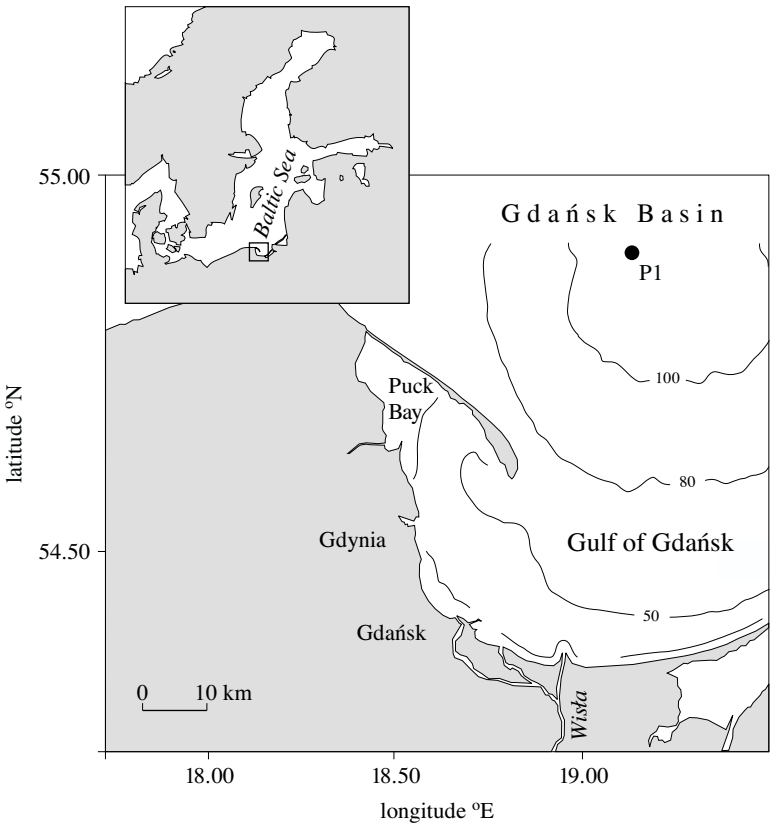

Fig. 1. Location of the sampling stations P1 – Gdańsk Deep

sampling techniques were applied: teflon plate, glass plate and Garrett (polyethylene) screen. Each technique yielded samples of a specific thickness: teflon plate 5–25 μm (TPM), glass plate 50–130 μm (GPM), polyethylene screen 180–340 μm (SM). Samples from the underwater layer at about 15 cm depth (UWL) were taken with a polyethylene sampler. Sampling by all techniques was repeated every 4 h in the first sampling period, and every 2 h and 1 h in the subsequent periods (Table 1). The sampling devices were lowered into the water from a special platform protruding from the bows of the ship. Once on deck, the samples were screened from direct sunlight. Sampling was done only when the sea state was 1–4°B. No slicks were observed.

Nutrients (nitrate, nitrite, ammonia, phosphate and total phosphorus) were determined according to Grasshoff et al. (1983) directly on board ship.

Dissolved organic carbon (DOC) was analysed on land with a Shimadzu TOC 5000 Analyser (Kyoto, Japan) accurate to 2%. The samples were

Table 1. Number of samples from the sea surface microlayer and the subsurface water layer collected for analysis in 1994–96

Layer	29 April – 5 May 1994	8–12 May 1995	19 June 1996
TPM		40	12
GPM	69	40	12
SM	86	41	12
UWL	110	41	12
Cycle	every 4 and 1 h	every 4 and 2 h	every 2 h
		Analytes	
	NO_3^-, PO_4^{3-}, NH_4^+ particles,	NO_3^-, NH_4^+, PO_4^{3-}, $P_{org.}$, DOC absorption spectra chl *a*, algae	ATP, chl *a*, phae *a*

prepared (filtering through roasted Whatman GF/F filters and conservation with $HgCl_2$) on board ship following the procedure described by Sugimura & Suzuki (1988) and by Benner & Strom (1993).

The samples for UV absorption spectra were immediately filtered on board through 0.22 μm pore size Millipore filters and their absorption measured in a 10 cm quartz cell in a double-beam Perkin Elmer Lambda 3UV/VIS spectrometer against deionised water from a Milli-Q column.

Chlorophyll *a* concentration was determined after extraction in acetone solution according to the procedure recommended by BMB (Edler 1979). The water volumes necessary for complete analysis were 0.5 or 1.0 dm^3 from the respective microlayers and 2 dm^3 from the subsurface layer. Phaeophytin was extracted from the same water samples with acetone and, after acidification of the acetone extract, measured spectrophotometrically (Parsons et al. 1985).

Samples for suspended particle size analysis were collected in late April and early May 1994 and stored deep-frozen for analysis on land. The measurements were done immediately after thawing in a Multisizer-II Coulter Counter. The methodology of this procedure was described in detail in Falkowska & Latała (1995).

Adenosine triphosphate (ATP) was measured by the luciferone-lucrose method as originally described by Holm-Hansen & Booth (1966). Water samples (50 cm^3) were filtered through 0.22 μm pore size Millipore filters. After ATP had been extracted in TRIS buffer, the samples were deep-frozen ($-20°C$) for further analysis on land. The procedures in the land laboratory included the use of a Beckman LS 6000TA scintillation counter.

Samples for the qualitative and quantitative determination of algae were preserved in Lugol solution containing acetic acid. Phytoplankton and phytoneuston species were analysed in the land laboratory with a reverse microscope.

The methodological details concerning sampling techniques and sample volumes, as well as the statistical evaluation of the chemical and biological parameters obtained from the teflon plate, glass plate and screen samplers are described in Falkowska (1999a, b).

The chlorophyll *a* and nutrient concentration changes, and the fluctuations of the number of particles in the respective size classes, were modelled mathematically with the aid of the Marquard algorithm:

$$A(\tau) = a_0 + a_1 \sin(\omega\tau + \varphi_1) + a_2 \sin(2\omega\tau + \varphi_2), \tag{1}$$

where

$A(\tau)$ – concentration of analytes at time τ,
a_0 – mean concentration of analytes,
a_1 – diurnal amplitude of analyte concentration,
a_2 – 12-hour amplitude of analyte concentration,
φ_1 – phase displacement of the diurnal component [rd],
φ_2 – phase displacement of the half-day component [rd],
ω – $2\pi\ \mathrm{T}^{-1}$; T – 24 hours.

3. Results

A series of data on temporal variations in the concentrations of nutrient and organic substances in sea surface layers of different thickness were obtained from measurements carried out in the offshore area of the Gdańsk Basin in spring. This data indicated that significant differences in the concentrations of the substances analysed existed between particular layers and also that these concentrations were diurnally variable (Fig. 2). The concentration amplitudes of the analytes were of considerable magnitude both within each layer as well as between the layers. The increased sampling frequency on the third day of the experiment in May 1994 yielded even greater fluctuations of the substances in question. Similar results were obtained the following year when samples were taken every 4 and 2 hours (Figs. 3, 4). Very high daily amplitudes were found in the case of organic phosphorus, ammonia, algae abundance and chlorophyll. The periodic nature of the variations in the concentrations of the analytes was tested using eq. (1). The results obtained from the regression analysis

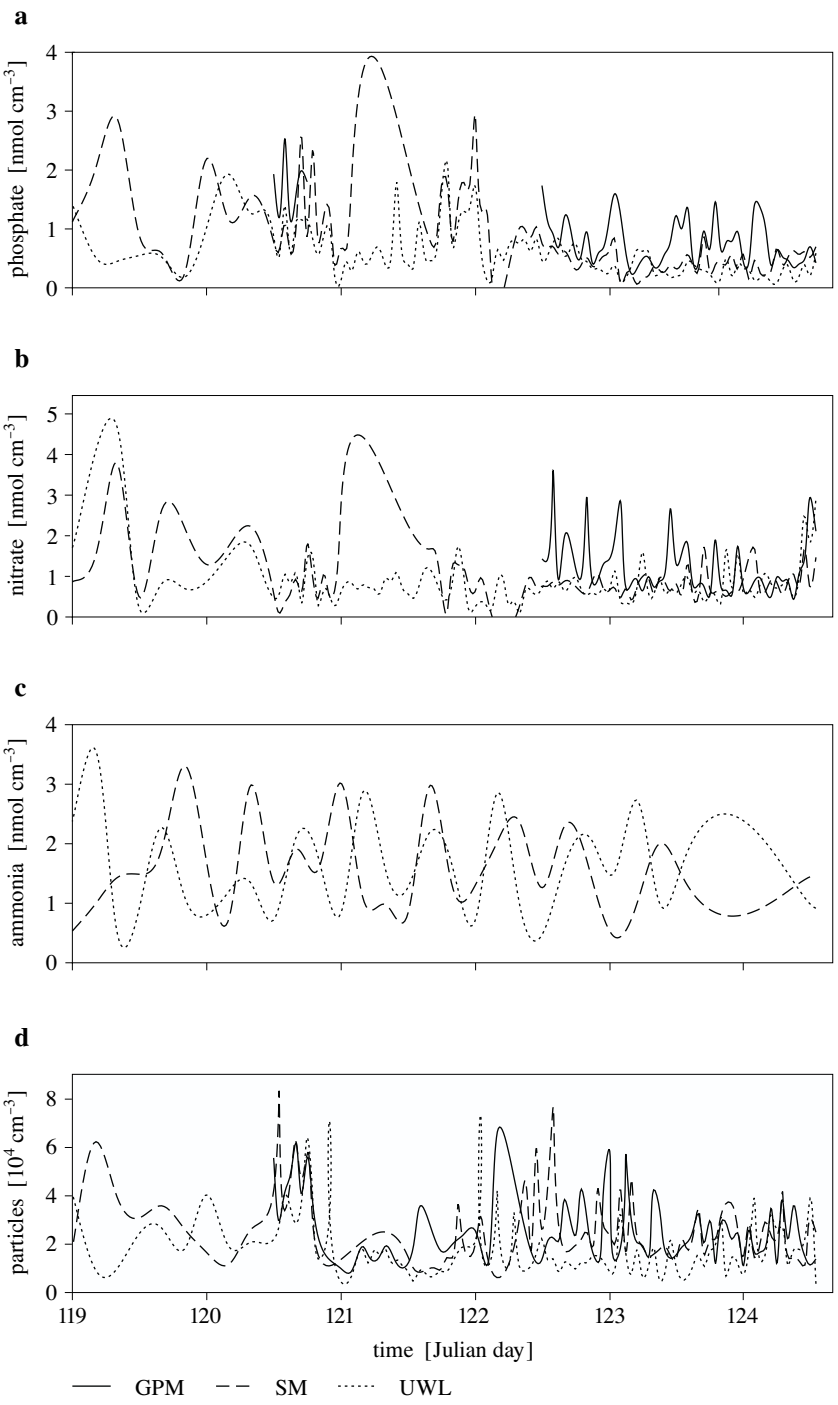

Fig. 2. Temporal changes in nutrient (a), (b), (c) and particle (d) concentrations in selected sea surface layers in the Gdańsk Basin (1994)

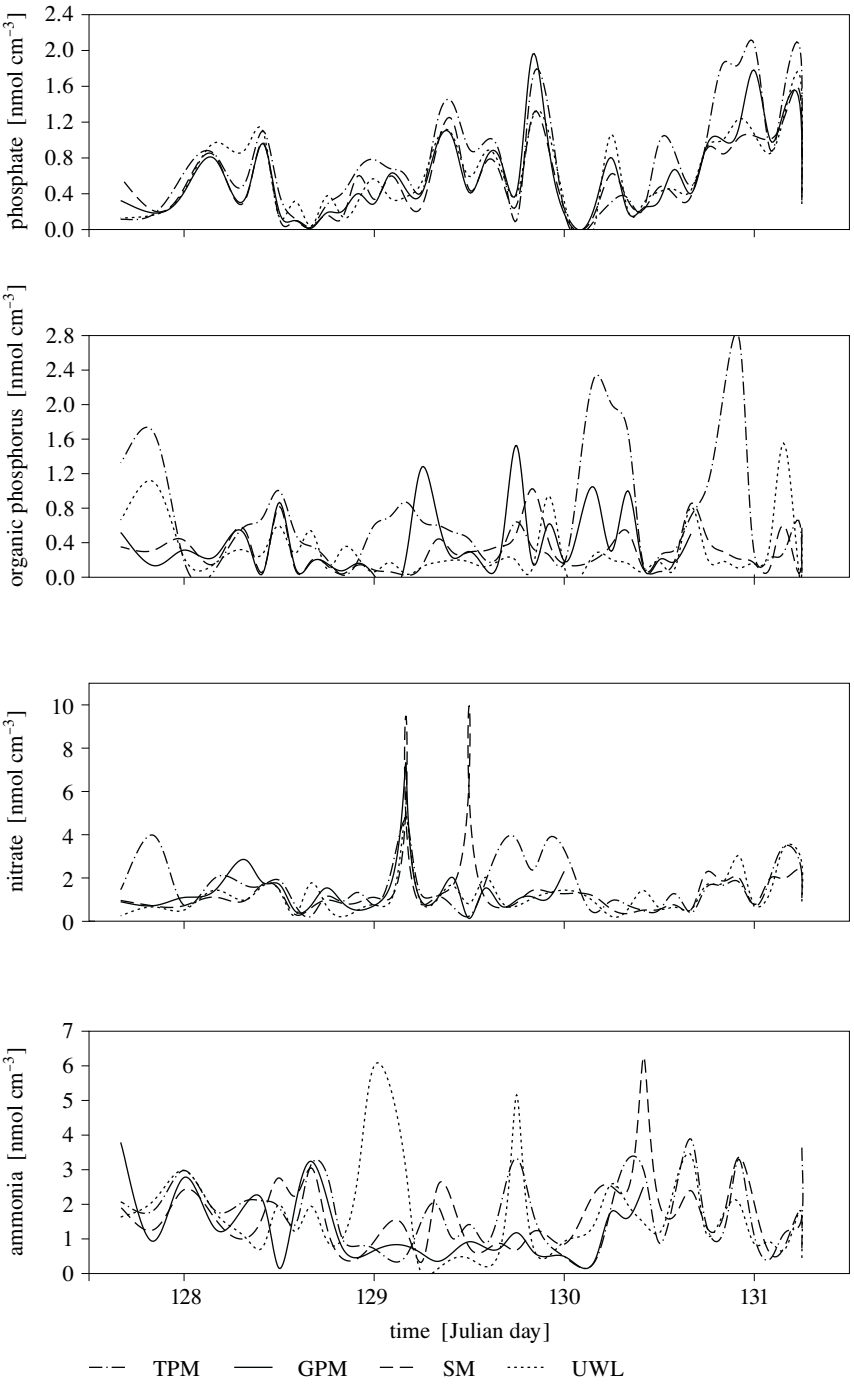

Fig. 3. Temporal changes in nutrient concentrations in selected sea surface microlayers in the Gdańsk Basin (1995)

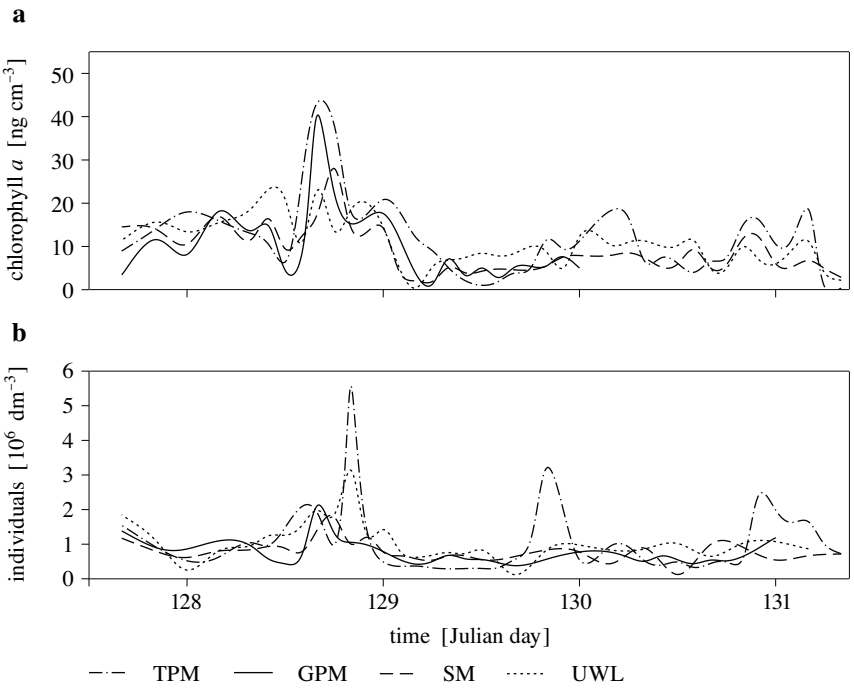

Fig. 4. Temporal changes in chlorophyll *a* concentrations (a), number of algae (b) in selected sea surface layers in the Gdańsk Basin (1995)

Table 2. Statistical evaluation parameters of the analytes and estimated from the model

Analytes from the relevant parts of the surface layer	R	p-level
GPM NO_3^-	0.77	0.002
SM NO_3^-	0.68	0.005
GPM PO_4^{3-}	0.63	0.008
UWL PO_4^{3-}	0.84	0.001
SM $NH4_4^+$	0.58	0.020
SM chl *a*	0.67	0.011
UWL chl *a*	0.58	0.030
GPM particles ≤ 2.11 μm	0.69	0.019
SM particles > 20.71 μm	0.62	0.009
SM particles	0.57	0.018

and the results of observations were tested by Spearman rank order correlation. In Table 2, the results are presented (10 items) from all the tests carried out for the particular data sets.

The summation of the diurnal and semi-diurnal components according to eq. (1) is presented as a diurnal cycle of the relevant chemical and biological parameters in the sea surface microlayer and in the underwater layer (Fig. 5). The results of non-linear regression analysis were normalised to fit the range 0–1 in relation to the maximum value because of the

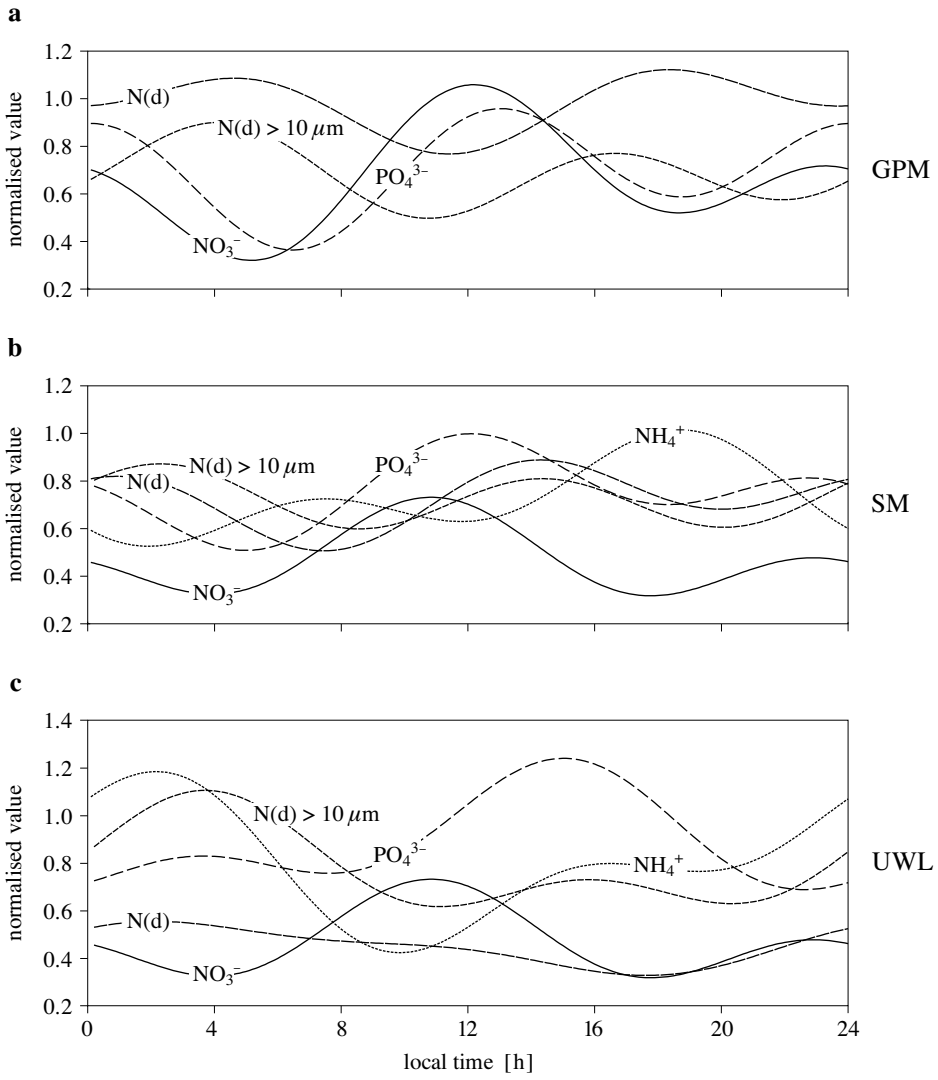

Fig. 5. Diurnal cycle of concentration variations of the analytes in selected sea surface layers in the Gdańsk Basin (May 1994); N(d) – total number of particles within the range 2–40 μm, N(d) > 10 μm – number of particles with diameter larger than 10 μm; GPM – thickness 50–130 μm (a), SM – thickness 180–340 μm (b), UWL – 15 cm depth (c)

considerable discrepancy between the abundance of particles and the great variability of nutrient concentrations.

The diurnal cycle of the analytes revealed 2 maxima and 2 minima in each sea surface layer and in the underwater layer. The number of planktonic organisms in the GPM layer (mean thickness 90 μm) increased both in the entire spectrum of size classes and in the size classes >10 μm, before sunrise (around 04:00 hrs) and in the afternoon. Around noon, the number of algae decreased significantly whereas the concentrations of inorganic nitrogen and phosphorus compounds increased, thereby showing that biological production was inhibited and that the processes destroying organic matter were intensifying.

In the SM microlayer (mean thickness 250 μm) assimilation and destruction displayed a similar pattern, although, as compared to the thinner GPM layer, the number of algae increased 2 hours earlier in both cases, before sunrise and in the afternoon. As a result, the increase in the number of algae was accompanied by a decrease in nitrate and phosphate concentrations.

The number of algae also rose in the underwater layer, especially in the cell size class >10 μm at sunrise. This strong maximum appeared prior to the highest daily concentration of ammonia, 2 hours before sunrise. In the SM layer, the ammonia concentration then fell to a minimum.

The particle concentrations in the various size classes (from 2.11 μm to 25.46 μm) from the 49-hour series (02–04.05.1994) were subjected to non-linear regression analysis, and the results averaged to 24 hours (Fig. 6).

The diurnal fluctuations of suspension concentrations revealed characteristic features clearly dependent on the particle size class:

- three groups of organisms were distinguishable in the GPM layer (Fig. 6a): with diameters I – <5.09 μm, II – from 5.10 to 16.25 μm and III – >17.00 μm;
- in the SM layer (Fig. 6b) similar diurnal changes in concentration were found in 5 groups of organic suspensions: I – <5.09 μm, II – from 5.10 to 14.02 μm, III – from 14.03 to 19.23 μm, IV – from 19.24 to 22.20 μm, V – from 22.21 to 25.18 μm;
- 8 groups were found in the underwater layer (Fig. 6c): I – <5.09 μm and within the 17.00–18.48 μm range, II – from 5.10 to 6.58 μm, III – from 6.59 to 14.02 μm, excluding particles of the 11.05–12.53 μm range, because these were grouped in class IV with particles of diameter 14.03–14.76 μm, V – from 15.51 to 16.25 μm and from 18.49 to 19.23 μm, VI – from 19.24 to 21.46 μm, VII – from 21.47 to 22.94 μm and VIII – from 22.95 to 25.18 μm.

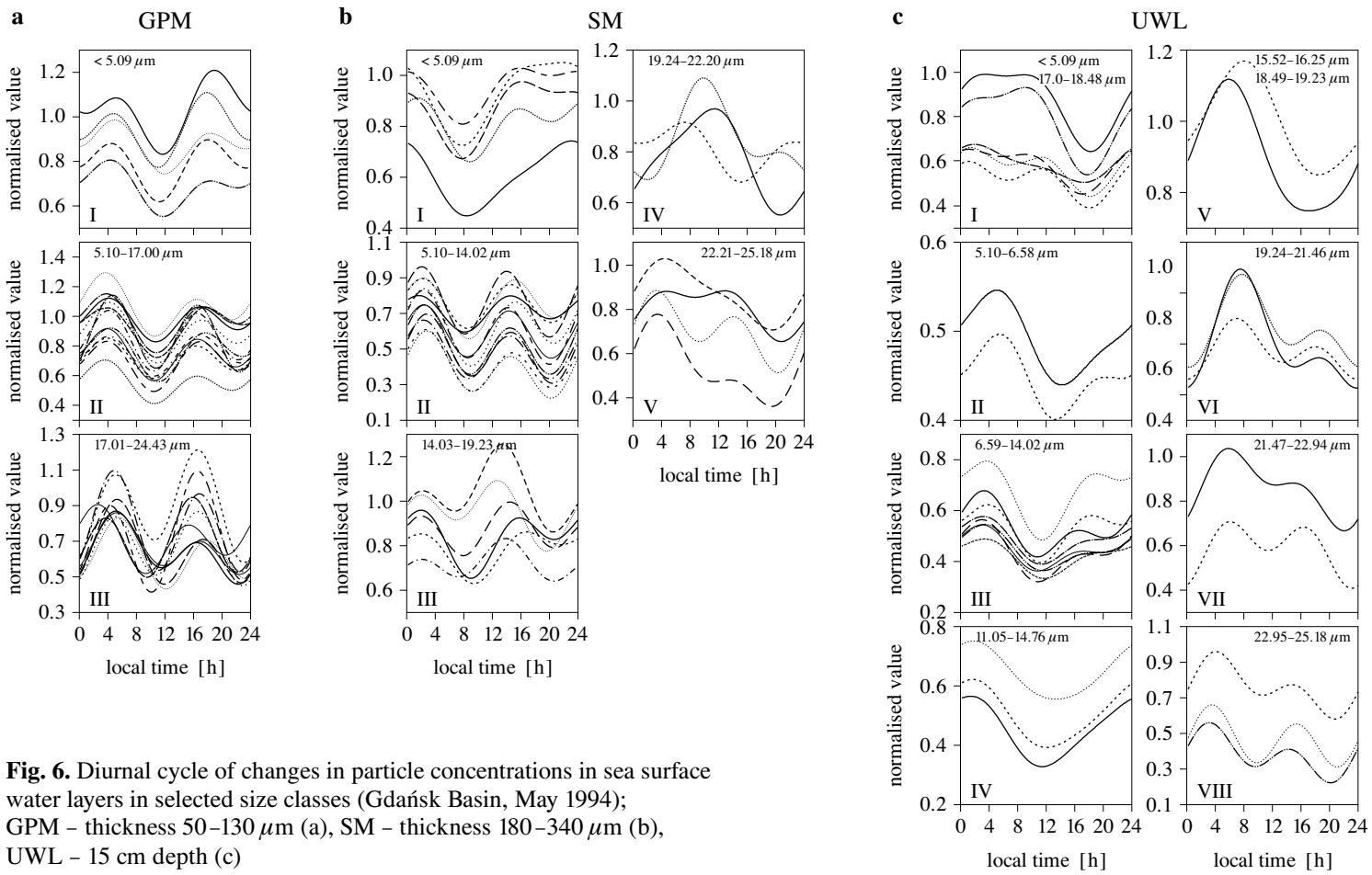

Fig. 6. Diurnal cycle of changes in particle concentrations in sea surface water layers in selected size classes (Gdańsk Basin, May 1994); GPM – thickness 50–130 μm (a), SM – thickness 180–340 μm (b), UWL – 15 cm depth (c)

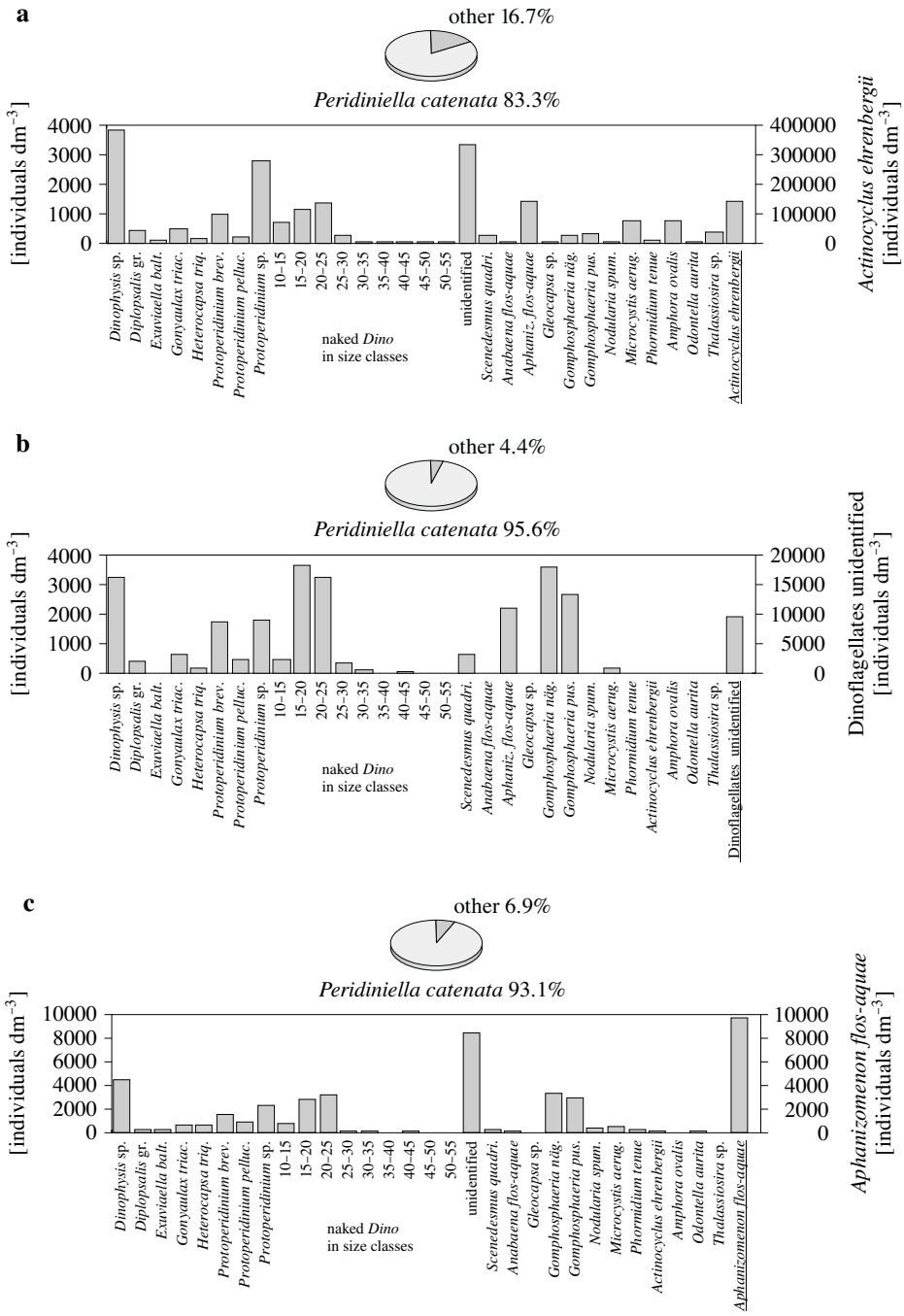

Fig. 7. Mean abundance of phytoplankton species collected from selected sea surface layers in the Gdańsk Basin (May 1995); the contribution of the dominant *Peridiniella catenata* is shown in the histograms: TPM (a), GPM (b), SM (c), UWL (d)

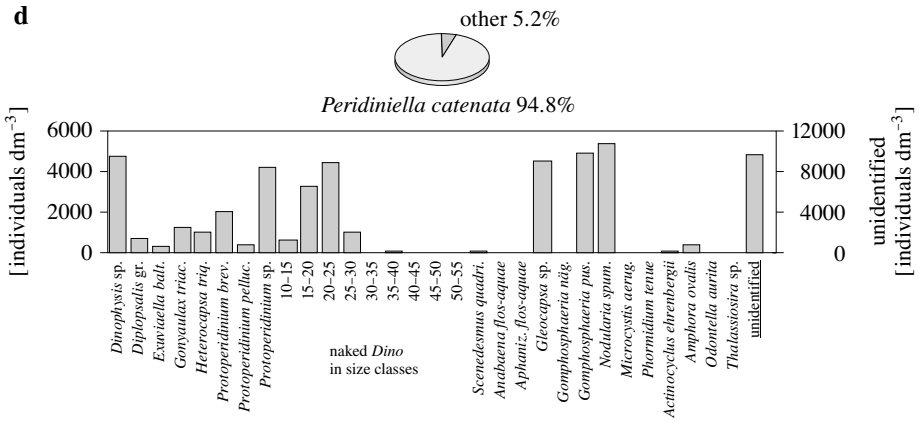

Fig. 7. (continued)

In the GPM layer, photosynthesis peaked twice: around sunrise and in the afternoon, though the process was much more intense among small planktonic organisms (pico- and nanoneuston) at sunset, and a higher number of larger algae was noted more often at sunrise (Figs. 5a, 6a).

In the SM layer, photosynthesis was similarly intense in three groups of organisms from 2.11 to 19.23 μm (Fig. 6b); however, the first intensity peak appeared about 2 hours earlier than in the GPM layer.

The underwater layer turned out to be where organisms congregated in large numbers once or twice a day (Fig. 6c). The maximum increase was found in the plankton size groups II, III, V, VI, VII and VIII between 04:00 and 08:00 hrs, when the abundance of algae in the GPM and SM layers had already begun to diminish. The highest number of algae was found in groups I and IV before sunrise.

The morphological criterion noticed in May 1994, which seems to suggest an increase in species diversity with increasing depth, was not confirmed by the investigation into species composition carried out in May 1995 (Fig. 7). *Peridiniella catenata* was the dominant organism in all the water layers examined. The maximum number of algae, including the dominant species, was noted in the thinnest TPM layer (Fig. 7a). Moreover, the species differentiation was greatest in this layer. Both diatoms (*Actinocyclus ehrenbergii*, *Amphora ovalis*, *Odontella aurita* and *Thallasiosira* sp.) and dinoflagellates displayed a preference for this layer.

The second-highest number of plankton was present in the underwater layer. Dinoflagellates were still the dominant species there, but blue-green algae *Nodularia spumigena* and *Geoclapsa* sp. (Fig. 7d) achieved peak numbers. The mean number of algae in the GPM layer was lower than in

the underwater layer (Fig. 7b), though the cyanobacteria *Gomphosphaeria nägeliana* were more abundant there than in the other water layers. The smallest number of algae was found in the SM layer (Fig. 7c), with *P. catenata* dominant and *Aphanizomenon flos-aquae* the second most abundant species. The green algae *Scenedesmus quadricauda* were present only in the TPM and GPM layers and were not detected at noon.

The non-linear regression analysis of the data obtained in May 1995 (Fig. 8) generally substantiates the daily cycle of carbon assimilation and dissimilation recorded during the experiment in May 1994 (Fig. 5). Significant differences were found with respect to concentration amplitudes.

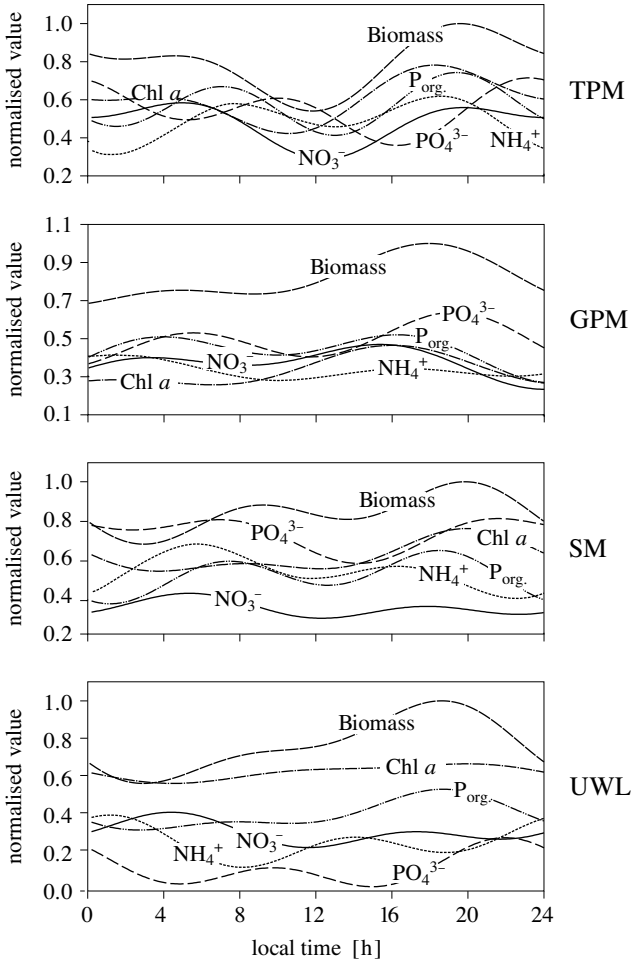

Fig. 8. Diurnal cycle of concentration variations of analytes in selected sea surface layers in the Gdańsk Basin (May 1995)

The second, i.e. afternoon, maximum of the function describing diurnal changes in the plankton biomass and chlorophyll *a* was much higher in all the water layers, though a tendency towards attenuation was noticeable with increasing depth. This difference is explained by the different irradiation conditions in the two experiments. In May 1994, the measurements were carried out under a cloudless sky, whereas cloudy weather prevailed in May 1995, the weather being overcast nearly 50% of the time. Although both experiments were conducted under very similar conditions, considerable differences in the species composition and in the number of neuston organisms cannot be excluded.

4. Discussion

The following discussion is based on the hypothesis that the data from selected sea surface water layers of differing thickness supply evidence for the stratification of chemical substances as a result of life processes occurring at various levels in the microlayer (Hardy et al. 1997, Falkowska 1999b). Therefore, each of layer is dealt with separately.

Detailed analysis of the chemical and biological parameters measured allows one to model the diurnal organic matter transformations induced by solar activity in spring. The diurnal pattern characterises the greatest probability of maximum neuston concentration in the early morning and late afternoon. The maximum concentrations of nutrients can be expected at noon and midnight. This model of the diurnal cycle of organic matter transformations corroborates other observations of inhibitory effects due to solar radiation (Behrenfeld et al. 1993, Herndl et al. 1993, Hardy et al. 1997, Neale et al. 1998). These observations have indicated that biological damage increases exponentially with decreasing wavelengths within the UV radiation. Field studies suggest that cell size could be a key factor determining the ultraviolet fraction of solar irradiance with the greatest impact on the microlayer (Fig. 6). The observed stratification of phytoplankton species within the microlayer and underwater layer supports the earlier findings of Manzi et al. (1977) and Wandschneider (1979). Both these authors suggested that the different paths of migration resulted in the observed differences in the composition and number of phytoplankton species. During the most intensive solar radiation, some organisms sank, congregating in the underwater layer at a depth of about 2–5 m owing to negative phototaxis, while other organisms rose from the underwater layer to the microlayer.

The sea surface microlayer absorbs a significant portion of the solar energy. The commonly observed accumulation of DOM and the presence of many neustonic species in the sea surface microlayer are the main effects of light absorption. They are responsible for fundamental changes in

the MO cycle as expressed by the inclusion of DOC, the change in the light attenuation coefficient, and the depth distribution of planktonic organisms. DOC is an important source of carbon for bacterioplankton and is the major force driving energy through the ecosystem. The DOC concentrations and absorption spectra correspond well with the hypothesis discussed above (Fig. 9). At noon, the high level of solar radiation leads to photolysis of dissolved organic matter and the consequent formation of carbon dioxide (Zafiriou et al. 1984, Zepp et al. 1998). Photodegradation of DOM has also been shown to increase the biological availability of phosphorus and inorganic nitrogen (Francko 1990). For this reason low DOC and photodegradation were probably responsible for the decrease in the absorption potential of the microlayer in comparison to the underwater layer (Fig. 9a, d), this being the main cause of the photoinhibition of or photodamage to neustonic organisms. Weak solar radiation before noon and in the afternoon caused the DOC concentration to rise; the afternoon radiation was closely linked with the growth of bacterial population and reduced the penetration depth of UVR (Fig. 9b, c). The suggested scheme is supported by the results of experiments carried out by Herndl et al. (1993) and Kaiser & Herndl (1997). These authors mention the periodic nature of bacterial activity, the severe inhibition of their metabolic activity during periods of UVR stress and the utilisation of labile photoproducts formed during periods of low UVR.

At night, the biodegradation of dissolved organic matter (Fig. 9a) was probably much stronger in the microlayer than in the underwater layer, yielding negative differences between absorption coefficients (Fig. 9e). The decrease in chlorphyll *a* concentration and in the abundance of algae observed at night (Fig. 4) could have been the result of zooplankton grazing. This observation is confirmed by the increasing concentration of larger-sized particles (Figs. 5, 6). Zooplankton can migrate to the upper water layers at different times of the day, the extent of migration depending on the species, sex, and age (Bovbjerd et al. 1976, Zaitsev 1997). However, at this time of year the number of zooplankton specimens increased after sunset and remained stable until early morning (Ciszewski et al. 1983). The rapid rate of ammonification of zooplankton excreta was reflected in a steep increase in ammonia concentration. These concentrations reached a maximum in subsurface water from midnight to sunrise (Fig. 2c). Because this observation was specific to the underwater layer, no ammonia being detected in the SM layer, it is presumed that zooplankton congregate preferably in the underwater layer, where they encounter variable and copious food resources. Hence, the greatest abundance of zooplankton can be found in the milli- or centilayer.

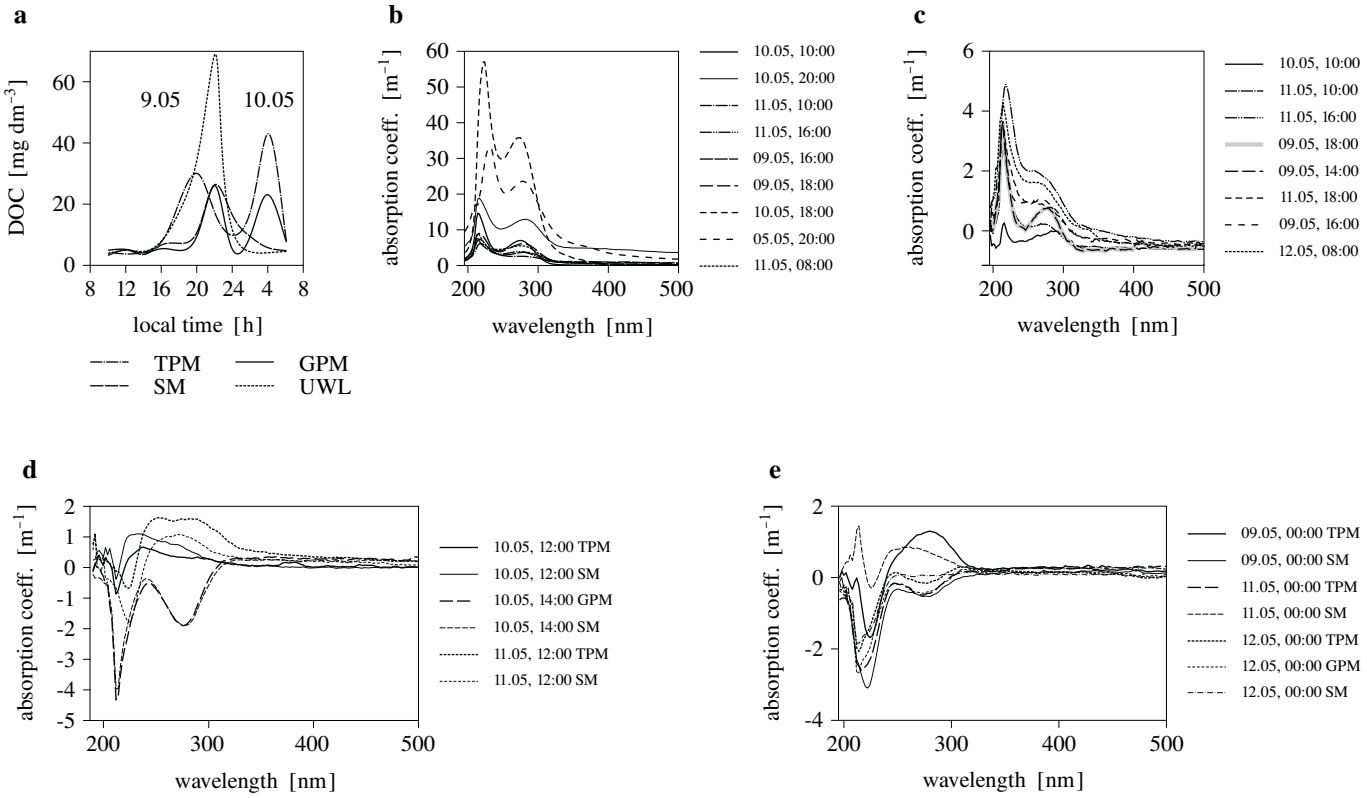

Fig. 9. Diurnal changes in DOC concentration (a) and differences in absorption coefficient between TPM sea surface microlayer and UWL subsurface water (b), between SM sea surface microlayer and UWL underwater layer (c), between selected sea surface microlayers and subsurface water at noon (d), and at midnight (e)

The conceptual model was validated by additional measurements of diurnal variations in ATP concentrations of chlorophyll *a* and phaeophytin in the sea surface microlayer with simultaneous measurements of solar radiation. This experiment was carried out in June 1996 (Fig. 10). These measurements indicated that under strong radiation, negative phototaxis in planktonic organisms was likely and any rise in chlorophyll *a*

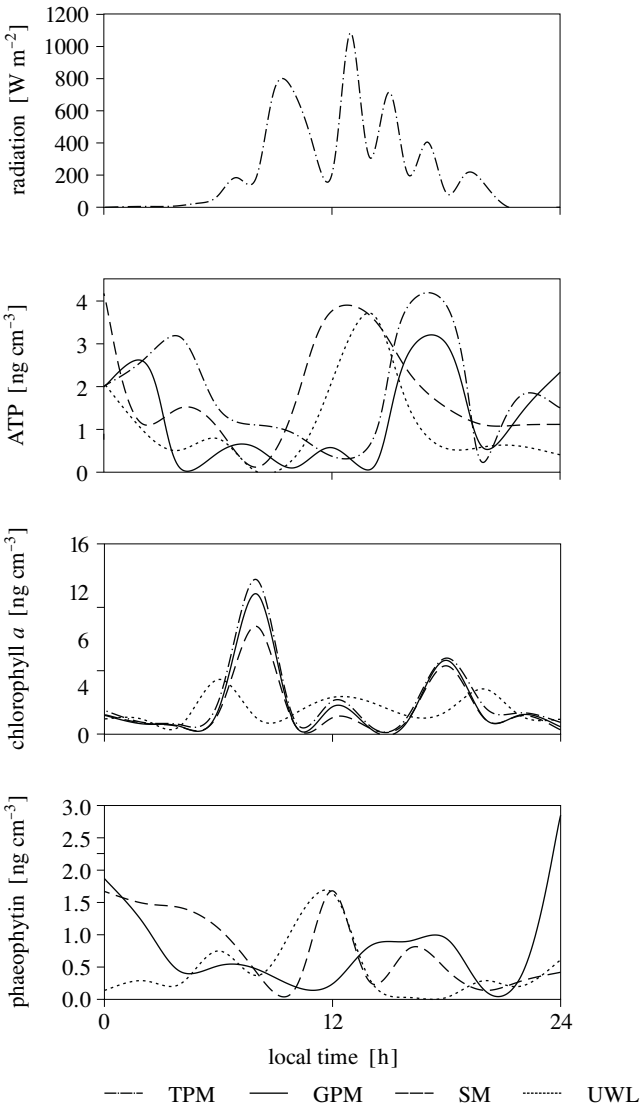

Fig. 10. Temporal changes in concentrations of suspended substances in selected sea surface microlayers during the diel cycle of radiation (300–1000 nm) in the Gdańsk Basin (19 June 1996)

concentration strongly inhibited. These effects were accompanied by intense direct photodegradation of organic matter, a process detected through the increasing concentration of phaeophytins. The proposed model of diurnal transformations of organic matter requires further study in other marine basins and at other seasons. Recently, in a polar aquatic ecosystem, a reduction in short-term growth rates and the primary production of a number of organisms was recorded; this had resulted from elevated UV–B radiation (Holm-Hansen et al. 1993, Prézelin et al. 1994, Neale et al. 1998). As suggested by several authors (Hardy & Gucinski 1989, Behrenfeld et al. 1993, Hardy et al. 1997, Zepp et al. 1998), the consequences of elevated UV-radiation, manifested by changes in the species composition of the phytoplankton and in the food web, could significantly alter the balance of several processes in the ecosystem (biogeochemical cycle, the microbiological contribution to food webs, zooplankton fecundity, etc.). These consequences could spread from polar to temperate regions, especially in spring. Future studies should focus on the vitality and activity of other components of microbial communities including viruses, bacterioneuston, protozoans and microzooneuston, as well as the kinetics of organic matter transformations brought about by solar radiation.

5. Conclusions

The normal, 24-hour rhythm of organic matter transformation in the surface microlayer was observed to undergo a distinct change in spring: a 12-hour component appeared as an effect of intense solar radiation.

Consequently, the processes of dissolved and suspended organic matter photoinhibition and photodegradation intensified at noon. This was evidenced by:

- an increase in inorganic nitrogen and phosphorus concentrations,
- a simultaneous decrease in the number of neuston,
- the appearance of negative differences between UV absorption coefficients in water samples collected from sea surface layers and the underwater layer.

The elevated solar radiation levels recorded at noon in spring probably led to respiratory breakdown and phototaxis within the entire sea surface microlayer and in the underwater layers as well. In consequence, this could upset the balance of several ecosystem processes, especially photosynthesis and sea-atmosphere gas exchange (O_2, CO_2), either within a single region of the temperate climatic zone or globally.

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