Stratification of particulate organic carbon and nitrogen in the Gdańsk Deep (southern Baltic Sea)

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Abstract

Particulate organic carbon (POC) and nitrogen (PON) concentrations and fluxes were measured during an experiment in the Gdańsk Deep in late spring (30.05.–06.06.2001). The vertical POC and PON concentration profiles were characterised by the highest values in the euphotic layer, a gradual decrease with depth, and an increase below the halocline. The hydrophysical conditions had a decisive impact on POC and PON fluxes in the water column.

Preferential removal of nitrogen from suspended mater was observed in the entire water column (maximum – in the vicinity of thermocline). There were also differences in the diurnal effectiveness of nitrogen removal as compared to carbon removal. The removal rate was highest at night.

1. Introduction

Recent studies of the input and removal of organic matter in the marine environment have for the most part investigated aspects of the coastal zone, which is highly polluted and sensitive to eutrophication (Heiskanen et al. 1998, Emeis et al. 2000, Struck et al. 2004). The organic matter concentration in the water column and bottom sediments of coastal waters is usually high, owing to the direct input of organic matter from the land and an already high primary production further enhanced by nutrient discharges. Both processes affect organic matter degradation and the overall cycling of organic matter.

The relationship between the productivity of a water body and the net export of POC and PON can be roughly described by a exponential function (Wassmann 1991). According to Schneider et al. (2002), only about 15% of the entire organic matter pool produced in the euphotic layer in deep basins of the Baltic Sea actually reaches the sea bottom. Most of the organic matter undergoes mineralisation on its way to the bottom, but this process takes place sufficiently close to the surface to allow effective recycling of the metabolic products in the upper layer (Colombo et al. 1996). The vertical flux of organic matter links the pelagic and benthic trophic levels (Billet et al. 1983, Graf 1989), thereby determining the transport of nutrients and anthropogenic substances to the sea bottom (Honjo 1980, Fowler & Knauer 1986).

Conducted in Baltic waters, the present study aimed to determine the quantitative and qualitative seasonal changes in the vertical fluxes of organic matter. The highest POC and PON fluxes reaching the sea bottom were usually observed in spring. After the spring phytoplankton bloom, nitrogen removal was significantly more efficient than carbon removal (Heiskanen et al. 1998, Reigstad et al. 1999, Struck et al. 2004). The location of the sampling site was an additional factor influencing organic matter fluxes.

The hydrology of a water body is an important factor influencing vertical fluxes of organic matter (Reigstad et al. 1999). A stable density stratification and the reduction of turbulent diffusion can slow down suspended matter transport through a thermocline by as much as 20 times (Lande & Wood 1987). The aim of the present work was to determine short-term changes in suspended carbon and nitrogen, their downward fluxes reaching particular water layers, and the settling loss of major elements (C and N) in organic matter. The investigations were conducted during the low primary production period in the diurnal cycle. The results were considered with reference to changes in the thermohaline stratification and pigment concentrations (chl a, phae a) in the water column.

2. Material and methods

The measurements were carried out during the spring research cruise (30 May–6 June 2001) on board the Polish Navy vessel ORP 'Kopernik'. Water samples were collected in offshore waters at station P1 – Gdańsk Deep ($\phi = 55°1'$N, $\lambda = 19°10'$E, Fig. 1). Table 1 contains the list of parameters measured during the cruise.

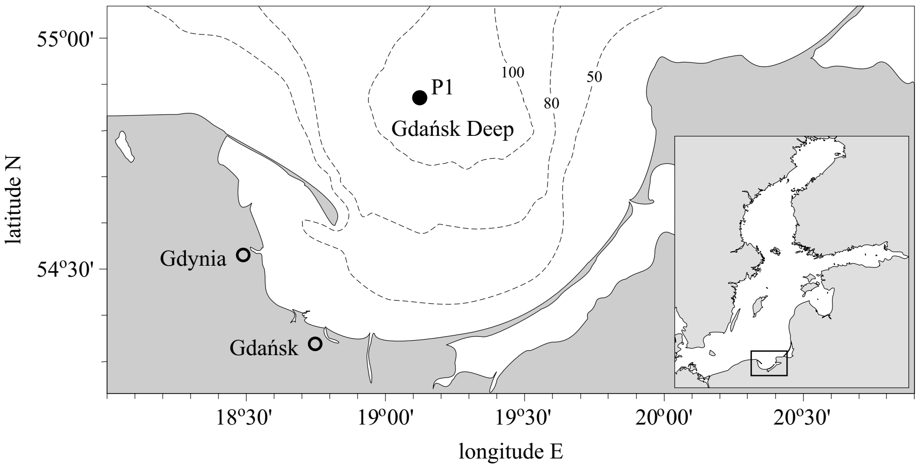

Fig. 1. Location of the sampling station: P1 – Gdańsk Deep

Table 1. List of parameters analysed during the field experiment (Gdańsk Deep 30.05.–06.06.2001)

	Parameters analysed	Units	Time intervals [h]
Suspended particles	• concentration of suspended particulate matter (SPM)	mg dm^{-3}	2/4
	• concentration of suspended particulate carbon and nitrogen (POC, PON)		2/4
	• organic carbon and nitrogen content in SPM ($POC_{\%}$, $PON_{\%}$)	%	2/4
	• concentration of chlorophyll *a* and phaeophytin *a* (chl *a*, phae *a*)	μg dm^{-3}	2
Sediment traps	• fluxes of suspended particulate carbon and nitrogen (POC, PON)	mg m^{-2} h^{-1}	12
Physical parameters	• temperature	°C	2
	• salinity	PSU	2
	• wind speed	m s^{-1}	1

The water samples from the water column were taken with a rosette sampler (Ocean Test Equipment Inc.) and measurements of water temperature, conductivity and depth were done with a CTD profiler (Falmouth Scientific Inc.).

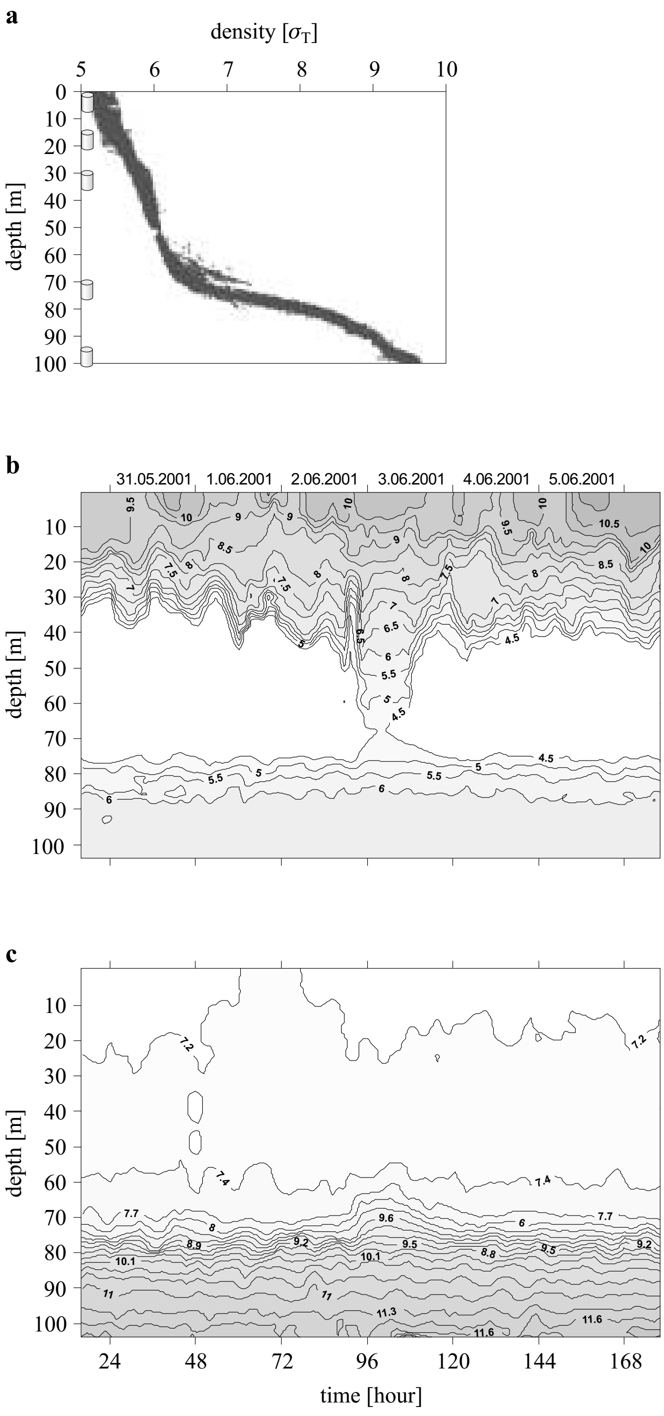

Fig. 2. Fluctuations of density [σ_T] (a) temperature [°C] (b) and salinity [PSU] (c) in the water column of the Gdańsk Deep (30.05.–6.06.2001)

The organic matter fluxes at each water level were measured with cylindrical sediment traps with a length-to-width ratio of 5.57 (length 585 mm and width 105 mm). Sediment traps were located at the following depths: 1.5, 15, 30, 70, 95 m, which reflected the density stratification of the water column during whole measurement period (day: 07:00–19:00 hrs night^{-1}: 19:00–07:00 hrs) (Fig. 2a). Before deployment, each of the cylinders was filled with water from the sampling depth (1.5, 15, 30, 70, 95 m). No preservatives were used inside the cylinders because of the short deployment time. Calculated flux values were corrected for the ambient concentration of suspended organic carbon and nitrogen.

To determine concentrations of particulate organic carbon and nitrogen (POC, PON), 1–2 litres of seawater was passed through a heat-treated (450°C, 6 h) Whatman GF/F filter. The filtered samples were dried at 60°C in the laboratory on board ship. Afterwards, the samples were reacted with HCl vapour at room temperature for 12 h in glass desiccators to remove carbonate. The analyses were performed on a CHNS/O 2400 Perkin Elmer analyser according to acetanilide standards (Parsons et al. 1985, Kramer et al. 1994). The standard error of the mean was equal to $\pm 5\%$ for POC and $\pm 8\%$ for PON.

Chlorophyll *a* (chl *a*) and phaeopigment *a* (phae *a*) were determined with a spectrophotometer (Cadas 200) on acetone (90%) extracts (Edler 1979, Parsons et al. 1985). The standard error of the mean was $\pm 4\%$.

The standard meteorological observations were carried out during each measurement period.

3. Results

3.1. Hydrological conditions

Between May and June 2001, the water column of the Gdańsk Deep was stratified as a result of temperature and salinity gradients (Fig. 2). A deep isohaline upper layer with salinity 7.02–7.78 PSU at c. 65 m depth was separated from bottom waters of higher salinity (10.55–11.71 PSU) (Fig. 2c). The maximum width of the halocline was 20 metres, and the salinity gradient ranged between 0.12 and 0.19 PSU m^{-1}.

The original thermocline was observed at depths of 18 to 45 meters; only on the first and the last measurement day did it clearly separate warmer and mixed upper waters (9.60°C and 10.78°C) from colder isothermal middle waters (Fig. 2b). The maximum temperature gradient was noted on 31 May (0.36°C m^{-1}), the minimum temperature gradient on 3 June (0.08°C m^{-1}); the temperature decreased linearly down to a depth of 65 m. During the daytime, the temperature increase formed a second thermocline at 4 to 9 m.

However, the second thermocline was not stable and easily eroded by wind mixing. The maximum temperature gradient in the secondary thermocline ($0.28°C\ m^{-1}$) was noted on 2 June 2001.

The wind speed ranged from 0.3 to 9.4 $m\ s^{-1}$ during the measurement period. The strongest wind (5.0–9.4 $m\ s^{-1}$) was noted from 3 to 5 June 2001.

3.2. Suspended biomass

During the measurement time the suspended matter concentration varied from 1.34 to 12.96 $mg\ dm^{-3}$, achieving an average value of 4.24 $mg\ dm^{-3}$ (Table 2). The vertical profile of suspended particular matter (SPM) was characterised by a visible decrease from 0 to 20 m, constant values in the 30–50 m depth layer, and a gradual increase in concentration towards the sea (Table 2). Maximum variability ($RSD = (SD \times 100\%) \times \overline{X}^{-1}$) of SPM concentrations was noted in the surface layer from 0 to 5 m (RSD = 22%), the thermocline layer (RSD = 35%) and the halocline layer (RSD = 30%).

The changes in the proportions of carbon and nitrogen ($POC_{\%}$, $PON_{\%}$) in the suspended matter (Fig. 3) are indicative of qualitative differences

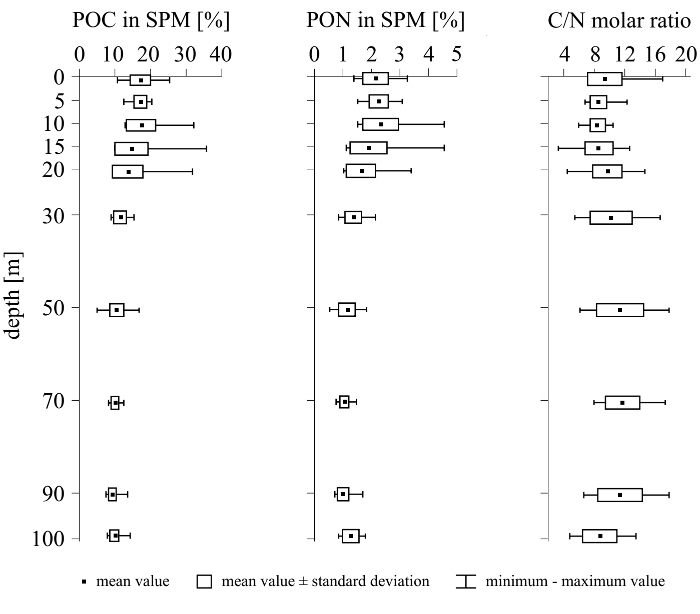

Fig. 3. Percentage content of particulate organic carbon and particulate organic nitrogen in suspended particular matter (SPM) ($POC_{\%}$, $PON_{\%}$) and the C/N molar ratio in the water column of the Gdańsk Deep (30.05.–06.06.2001)

Table 2. Statistical characteristics of suspended particulate matter (SPM), particulate organic carbon (POC) and nitrogen (PON) concentrations [mg dm^{-3}] in the water column of the Gdańsk Deep (30.05.–06.06.2001)

Depth	SPM			POC			PON	
[m]	n	$\overline{\mathrm{X}} \pm \mathrm{SD}$	Min–Max	n	$\overline{\mathrm{X}} \pm \mathrm{SD}$	Min–Max	$\overline{\mathrm{X}} \pm \mathrm{SD}$	Min–Max
0	40	**4.61** ± 0.83	3.40–8.11	27	**0.67** ± 0.21	0.29–1.43	**0.09** ± 0.03	0.04–0.18
5	42	**4.34** ± 1.08	2.97–10.26	31	**0.61** ± 0.11	0.34–0.80	**0.08** ± 0.02	0.05–0.13
10	40	**4.05** ± 0.57	2.10–5.25	32	**0.58** ± 0.17	0.36–1.23	**0.08** ± 0.03	0.04–0.18
15	42	**3.89** ± 0.38	2.90–4.62	31	**0.46** ± 0.22	0.23–1.44	**0.06** ± 0.02	0.03–0.08
20	41	**3.63** ± 0.84	1.34–6.71	33	**0.35** ± 0.11	0.22–0.80	**0.04** ± 0.02	0.02–0.09
30	29	**3.41** ± 0.33	2.45–4.31	29	**0.27** ± 0.06	0.17–0.42	**0.03** ± 0.01	0.01–0.06
50	42	**3.49** ± 0.60	2.29–5.47	31	**0.23** ± 0.07	0.02–0.46	**0.03** ± 0.01	0.00–0.06
70	40	**4.42** ± 1.35	2.82–9.55	34	**0.28** ± 0.10	0.15–0.64	**0.03** ± 0.01	0.01–0.08
90	40	**4.77** ± 0.60	3.34–6.92	32	**0.26** ± 0.07	0.18–0.48	**0.03** ± 0.01	0.01–0.06
104	40	**5.74** ± 1.57	3.70–12.96	30	**0.33** ± 0.07	0.20–0.52	**0.05** ± 0.02	0.02–0.09

n – number of data, $\overline{\mathrm{X}}$ – mean value, SD – standard deviation, Min – minimum, Max – maximum value.

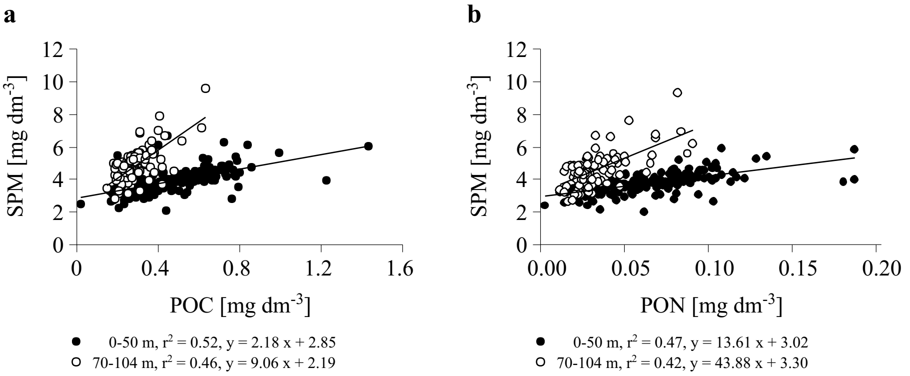

Fig. 4. Correlations between suspended particular matter (SPM) concentrations and concentrations of particulate organic carbon (POC) (a) and particulate organic nitrogen (PON) (b) (confidence coefficient 95%) in the Gdańsk Deep (30.05. –6.06.2001)

between the isohaline surface water layer and the heterohaline deep waters. The correlations between the SPM and POC concentrations in these layers were different (Fig. 4): POC concentrations were responsible for c. 50% of the changes in SPM concentration in the 0–50 m layer, but for only 12% in the 70–104 m layer. The highest $POC_{\%}$ and $PON_{\%}$ values (35.1% and 4.5% respectively) were recorded in the euphotic layer (0–15 m). The carbon and nitrogen contents in the suspended matter in this layer (means: 14.6% and 1.9%) were twice as high as in the intermediate layer (20–50 m) and about 2.5 times as high as in the deep water layer (70–104 m). The highest POC and PON concentrations (mean values: 0.58 mg POC dm^{-3} and 0.08 mg PON dm^{-3}) a low C/N molar ratio were noted (mean values: 8.8) in the euphotic layer (Table 2, Fig. 3). The lowest POC and PON concentrations with a maximum C/N molar ratio in suspended matter (mean value: 11.6) were recorded in the 50–70 m layer, and a minimum C/N molar ratio in suspended matter (4.4–5.5) in the thermocline (15 –30 m) and at the sea bottom (104 m). The standard deviation of the C/N ratio at the different depths varied between c. 12% and 27% of the mean. The lowest variability of the C/N value was observed in the 5 to 10 m layer.

Chlorophyll *a* and phaeophytin *a* were used as factors to characterise the phytoplankton biomass and its physiological state. Pigment concentrations in the water column decreased with depth and were almost constant for chl *a* from 70 m to the sea floor and for phae *a* from 30 m down to the bottom (Fig. 5). The mean concentration of chl *a* in the euphotic layer amounted to 1.32 μg dm^{-3}; the extremes were from 0.16 to 4.23 μg dm^{-3}. Phae *a* concentrations ranged from 0.02 to 2.24 μg dm^{-3} and were, on

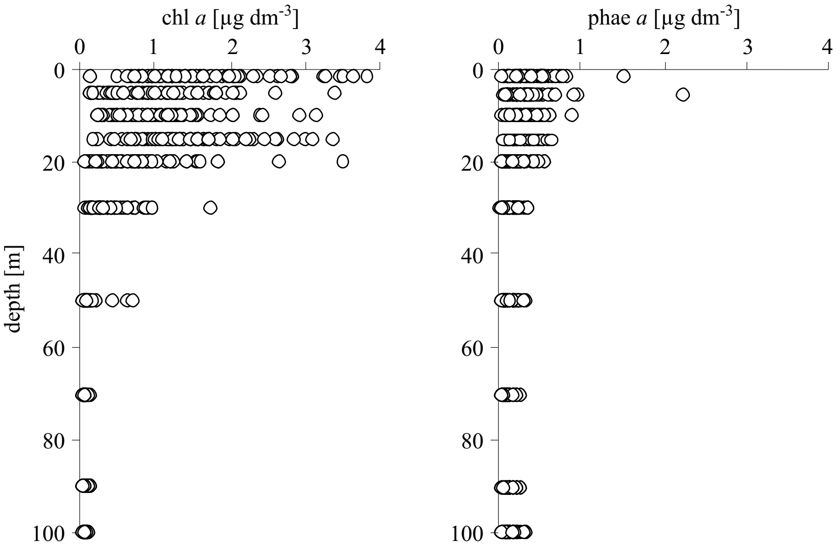

Fig. 5. Vertical profile of chlorophyll *a* (chl *a*) and phaeophytin *a* (phae *a*) [μg dm^{-3}] (number of samples = 70–80 for each level) in the waters of the Gdańsk Deep (30.05.–06.06.2001)

average, about 4 times lower than chl *a* concentrations. The importance of phae *a* increased with depth and its concentration below the halocline (0.13 μg dm^{-3}) was, on average, twice as high as that of chl *a*.

3.3. Sinking biomass

POC and PON flux values ranged widely, from 4.0 to 82.4 mg POC m^{-2} h^{-1} and from 0.2 to 16.0 mg PON mg m^{-2} h^{-1} (Figs 6a and 6b). The highest values of organic matter fluxes were usually observed in the surface layer (1.5 m) and beneath the halocline (95 m).

In 65% of samples $C/N_{settled} > C/N_{suspended}$, in the other 35% $C/N_{settled} \le C/N_{suspended}$. (Fig. 6c).

4. Discussion

Since the Gdańsk Deep waters are located at some distance from land-based sources, the main factors determining concentration, composition and vertical fluxes of suspended matter are changes in primary production and hydrodynamic conditions. Between May and June, primary production is controlled by a stable seasonal thermocline that prevents mixing and affects the mineralisation of organic matter and nutrient recycling in the surface layer both qualitatively and quantitatively (Falkowska et al. 1998).

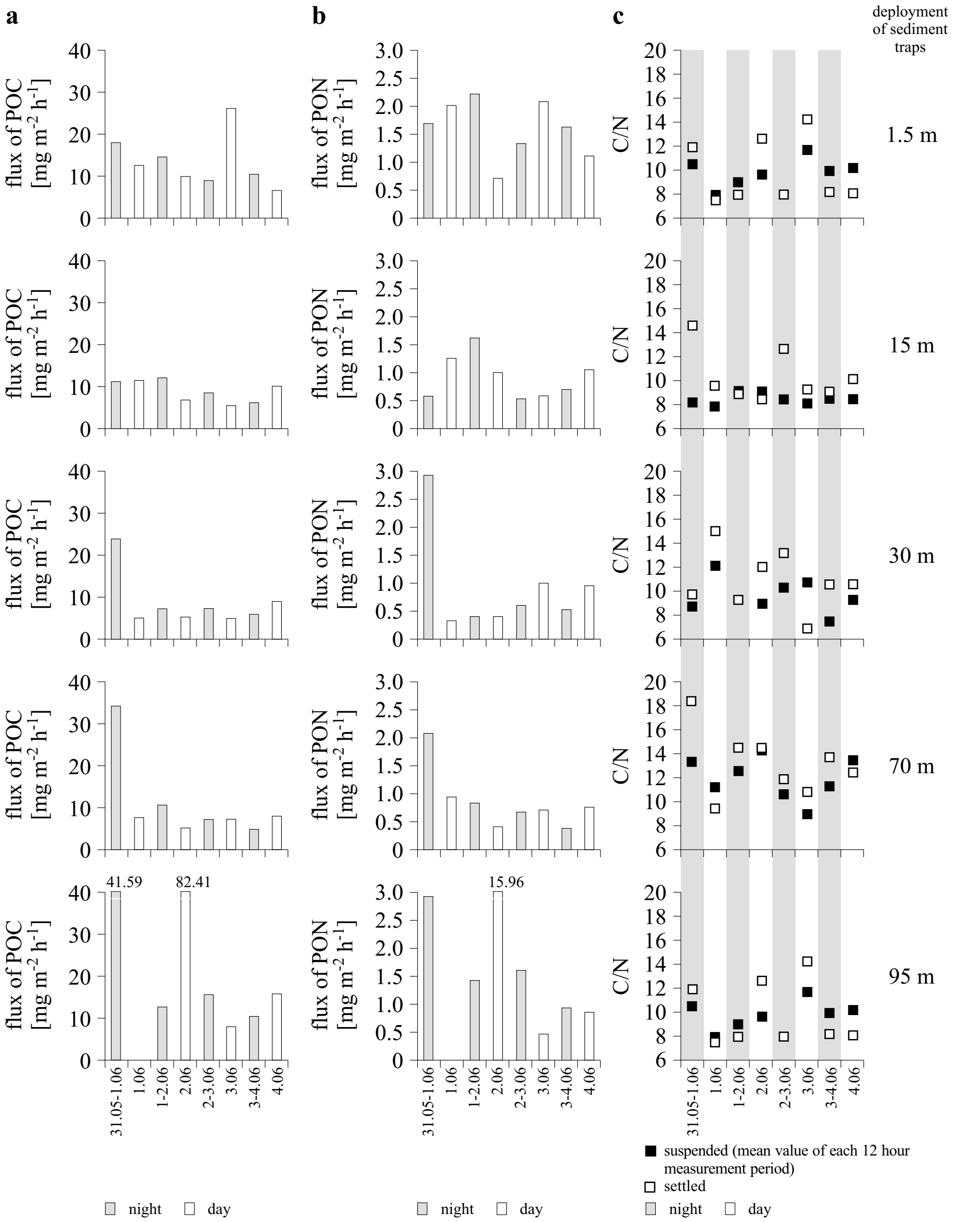

Fig. 6. Fluxes of particulate organic carbon (POC) (a), particulate organic nitrogen (PON) (b) [mg m^{-2} h^{-1}] and C/N molar ratios (c) in the sediment trap and in the overlying waters in the Gdańsk Deep (31.05.–4.06.2001)

Quantitative studies of phytoplankton biomass have been used by several authors as indicators of primary production. The only pigment common to all phytoplankton (Jeffrey 1980) – chlorophyll *a* – has been widely utilised to

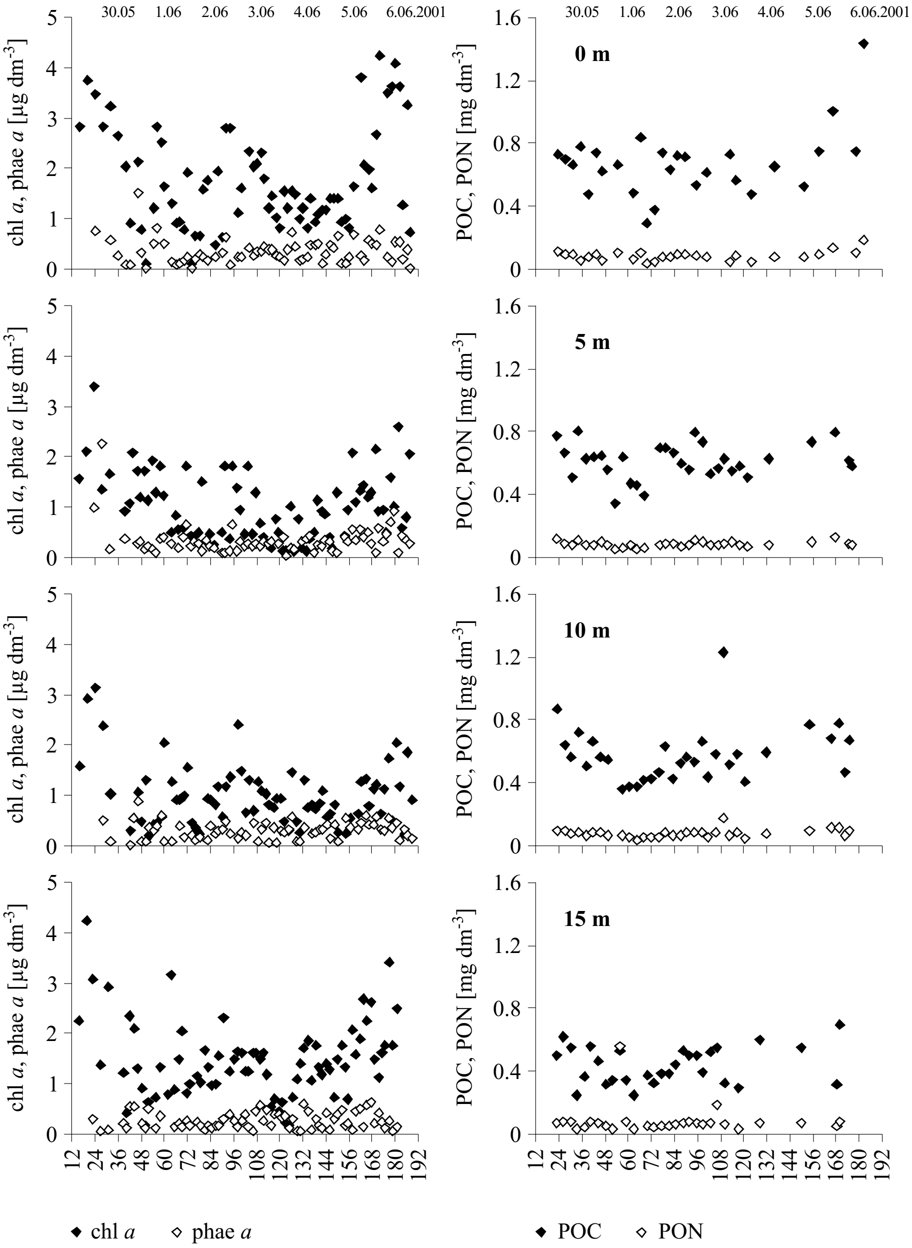

Fig. 7. Temporal fluctuations of particulate organic carbon (POC), particulate organic nitrogen (PON) [mg dm^{-3}], chlorophyll *a* (chl *a*) and phaeophytin *a* (phae *a*) [μg dm^{-3}] concentrations in the euphotic layer (30.05.–6.06.2001)

estimate primary production (Shulenberger & Ried 1981, Gowen et al. 1992). The increase in the proportion of phae *a* in the photosynthetic pigments suggests that the phytoplankton community is in a senescent phase or has been degraded as a result of grazing (Vernet & Lorenzen 1987, Heiskanen & Keck 1996). The present studies were conducted during a period of low primary production, indicated by low chlorophyll a concentrations (Figs 5 and 7) in the euphotic zone (usually < 2 μg dm^{-3}). Several authors have noted a similar situation in the Gdańsk Deep region in late spring (Witek 1995, Burska et al. 1997, Falkowska et al. 1998, Renk 2000, Pryputniewicz et al. 2002). The POC and PON concentrations were also generally in accordance with the ranges reported by Maksymowska (1996) in the Gulf of Gdańsk during this season. The variability of POC, PON, chl a and phae a at several levels of the euphotic layer reached 48% (Fig. 7). Chl a concentrations peaked twice: between 08:00 and 10:00 hrs and between 18:00 and 20:00 hrs. Phae a made up a considerable part of the total photosynthetic pigment content at night and around noon (70% and 48 % respectively), when the C/N molar ratio in suspended matter was also the highest (C/N = 17.1 and 15.3 respectively). Given stable hydrodynamic conditions, changes in the concentration of photosynthetic pigments during the daytime were driven by intensive irradiance, while at night, the steering factor was the presence of heterotrophic organisms (Falkowska & Latała 1995, Falkowska 2001, Neale 2001, Pryputniewicz et al. 2002, Magulski et al. 2004). Our observations indicated the stratified occurrence of autotrophic and heterotrophic organisms. Both types of organisms were dominant in different water layers: autotrophic organisms at 0.5 m and 15 m depth, heterotrophic organisms at 5 m and 10 m. The dominance of autotrophic organisms was indicated by the lowest mean POC/chl a values noted at the surface (328) and at 15 m (280). The lowest C/N molar ratio (8.5) with simultaneous maximum carbon and nitrogen content in suspended matter was noted in the 5–10 m layer and indicated the dominance of heterotrophic organisms (Table 2, Fig. 3). In the Gdańsk Basin, Witek (1995) described the laminar occurrence of plankton.

As a result of organic matter degradation, the C/N molar ratio increased with depth, reaching its maximum at the upper halocline boundary (11.8). The chlorophyll content in the total amount of organic matter decreased with depth (POC/chl $a > 4500$). However, in the bottom layer, organic matter was rich in nitrogen (C/N molar = 8.9) and the POC/chl a ratio increased further (mean value 7568). The nitrogen enrichment of the bottom layer was caused by the high density of bacteria (Rheinheimer et al. 1989, Czerwińska & Krzywobłodzka 1994), in which the C/N ratio reached a mean value of 5.5 (Kemp 1999).

On the first day of measurements, the amount of organic matter collected from the entire water column in the sediment traps was very high, probably because of the relatively high primary production during the preceding days. This view is endorsed by the higher chl a concentrations measured on 30 May 2001 (from 1.54 to 4.16 μg dm^{-3} in the euphotic layer). As a result of the steep density gradients, organic matter accumulated above and within the thermocline layer during that day. As a result, the highest 'load' of organic matter, as compared to the previous days, accumulated at 30 m (Figs 6a and 6b).

On 3 June 2001 the influence of the steep density gradient on the amount of organic matter collected in the sediment trap was also evident. A secondary thermocline forming at 5 m reduced suspended matter transport below the thermocline layer. The reduction of sedimentation and even the trapping of suspended particles within the surface layer resulted in an increase in the flux into the trap located at 1.5 m depth (POC = 25.90, PON = 2.05 mg m^{-2} h^{-1}). As a consequence, lower fluxes were measured in other sediment traps (Figs 6a and 6b) and loss rates (1.5 m) of SPM were overestimated by 46.5%.

Fluxes of organic matter down to 1.5 m seem to reflect the rate of phytoplankton production and mortality in the surface layer (POC = 12.54 mg m^{-2} h^{-1}, PON = 1.53 mg m^{-2} h^{-1}). Removal of organic matter was most effective from that layer (from 8.8% to 46.5% of carbon and from 6.5% to 36.9% of nitrogen within the measurement period) (Table 3). The mass of organic matter from 0–15 m layer was several times lower than the value indicated by the sediment trap located at 1.5 m. The difference between the material fluxes from the traps at 15 m and 1.5 m indicated that, on average, about 28% of the carbon and 40% of the nitrogen were retained in this layer during the 24 h period. These values indicated that nitrogen was retained 12% more effectively than carbon. On the basis of the C/N molar ratio inside the sediment trap and outside it ($C/N_{settled}$:$C/N_{suspended}$), it was observed that nitrogen was removed preferentially from the entire water column (Fig. 8). However, the highest intensity of this process was noted directly above and below the thermocline (mean diurnal value 1.22 and 1.15 respectively). Similar rates of carbon and nitrogen removal were recorded at 1.5 and 90 m (mean values 1.02 and 1.03 respectively). There were also distinct differences in the diurnal effectiveness of nitrogen removal as compared to carbon removal (Fig. 8). The highest rate of nitrogen removal was observed at night, the maximum rate being at the border of the euphotic zone (1.31 times higher than the average rate). Recorded in the surface and bottom layers, the $C/N_{settled}$:$C/N_{suspended}$ ratio indicated that the organic matter was rich in nitrogen. This was probably caused by a high concentration of heterotrophic organisms (Czerwińska & Krzywobłodzka 1994, Rheinheimer

Table 3. Rates of particulate organic carbon (POC) and nitrogen (PON) loss [% 12 h^{-1}] in the waters of the Gdańsk Deep (31.05.–4.06.2001). Loss rates of suspended C and N were calculated according to the equation L = 100% × f s^{-1} where f is the vertical flux of particulate C and N [mg m^{-2} 12 h^{-1}], and s is the suspended concentration integrated for the water column above the sediment trap [mg m^{-2}] (Reigstad et al. 1999)

depth [m]	Rate of POC loss [% 12 h^{-1}]							
	31.05.–1.06. night	1.06. day	1–2.06. night	2.06. day	2–3.06. night	3.06. day	3–4.06. night	4.06. day
1.5	20.7	17.2	22.6	11.1	11.1	46.5	19.8	8.8
15	2.0	2.3	3.2	1.5	1.4	0.9	0.7	1.6
30	4.1	0.6	1.3	0.6	1.1	0.6	0.9	1.3
70	1.8	0.5	0.7	0.3	0.4	0.5	0.4	0.6
95	2.0	–	0.7	4.5	0.6	0.4	0.6	0.9
depth [m]	Rate of PON loss [% 12 h^{-1}]							
	31.05.–1.06. night	1.06. day	1–2.06. night	2.06. day	2–3.06. night	3.06. day	3–4.06. night	4.06. day
1.5	17.5	18.8	26.6	6.5	11.3	36.9	25.9	13.3
15	0.7	1.6	3.4	1.7	0.6	0.7	0.6	1.2
30	3.7	0.2	0.2	0.4	0.7	1.2	0.5	1.1
70	1.2	0.7	0.6	0.3	0.3	0.4	0.3	0.6
95	1.6	–	0.7	8.2	0.6	0.2	0.5	0.6

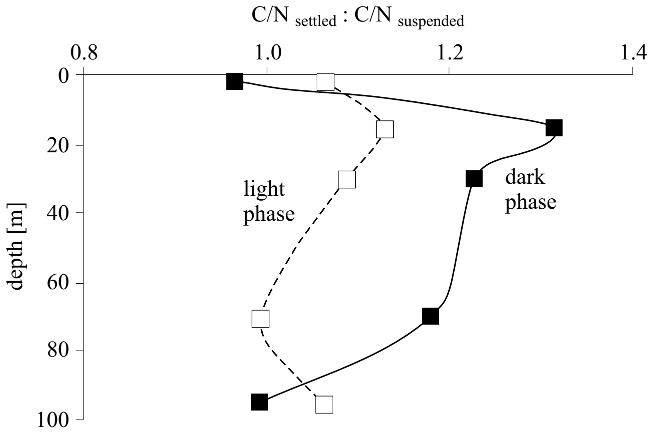

Fig. 8. Vertical profile of C/N$_{settled}$:C/N$_{suspended}$ during different phases of the day in the waters of the Gdańsk Deep (31.05.–4.06.2001) (dark phase from 19:00 to 07:00 hrs, light phase from 07:00 to 19:00 hrs; data points show the mean value of 4 measurement periods, variability from 9 to 26%)

et al. 1989). Reigstad et al. (1999) also noted the presence of heterotrophic organisms in material falling to the bottom of the Gulf of Riga during summer.

5. Conclusions

- The highest POC and PON concentrations in the euphotic layer and their gradual decrease with depth were characteristic features of the short-term variability of suspended matter concentrations in the water column of the Gdańsk Deep. The concentration of suspended matter increased in the bottom layer. This typical profile of the variability of suspended matter concentrations was overlain by organic matter degradation, which increased with depth, resulting in a rise in both the C/N molar ratio and the POC/chl a ratio.
- During late spring, when thermal stratification was unstable, even short-term temperature gradients affected fluxes of matter transported towards deeper regions of the water body. A transient secondary thermocline at 5 m depth – it persisted for one day – caused the POC and PON fluxes in the surface water layer to double.
- Between the new spring production and regenerating system in summer, more particulate organic carbon than nitrogen was lost from the euphotic layer by sedimentation. Nitrogen was removed more effectively than carbon from suspended matter within the entire water column, the maximum rate being recorded directly above and below the thermocline. In the diurnal cycle the rate of removal was highest at night.

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