Diurnal variations in nitrogen, phosphorus and iron compounds in the southern Baltic Sea

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Abstract

In order to assess their short-term variability, nutrient concentrations were measured at standard depths at 2 h intervals in the deepest region of the Gdańsk Deep during the first ten days of June 2001. The mean concentrations of nutrients in the euphotic zone were: N_N (NO_2^-, NO_3^-, NH_4^+) – 1.93 μmol dm^{-3}, PO_4^{3-} – 0.12 μmol dm^{-3} and Fe_{tot} – 0.11 μmol dm^{-3}. During daylight hours, when the rate of assimilation was fastest, concentrations of nitrogen, phosphorus and iron compounds were very low. The phosphate concentration fell to a minimum (0.03 μmol dm^{-3}) between 04:00 and 10:00 hrs, while total iron dropped to 0.01 μmol dm^{-3} between 10:00 and 16:00 hrs. Both levels were below the limiting values for phosphorus and iron. At night, concentrations of NO_3^- and PO_4^{3-} rose by 25%, those of NH_4^+ and Fe_{tot} by 35%. The mean molar ratios of N_N:PO_4^{3-} and Fe_{tot}:PO_4^{3-} in the surface layer were subject to significant daily fluctuations. The molar N_N:PO_4^{3-} ratio was higher than the optimum value

The complete text of the paper is available at http://www.iopan.gda.pl/oceanologia/

established for the Baltic Sea. Below the halocline, the concentrations of dissolved iron and phosphorus rose as a result of diffusion from sediments in response to changing redox conditions.

1. Introduction

Nutrients are significant factors limiting phytoplankton growth in the sea. During photosynthesis carbon, nitrogen, phosphorus and iron are incorporated into organic matter in a molar ratio of 106:16:1. According to laboratory Fe uptake studies, phytoplankton need 0.0008 mol of Fe for each 106 mol C to meet minimum growth requirements (Anderson & Morel 1982) and 0.01 mol of Fe for each 106 mol of C for optimum growth (Morel & Hudson 1985). Increasing loads of terrigenous inorganic nitrogen, phosphorus and iron may indirectly stimulate primary production and consequently cause larger amounts of organic matter to be deposited on the sea bed. Mineralisation of organic matter often leads to the total exhaustion of dissolved oxygen and thus to sediment acidification (Jonsson et al. 1990). The spreading of the anoxic zone has resulted in a substantial drop in the concentrations of labile forms of phosphorus and iron in sediments. The release of phosphates and iron(II) into the water means that an additional potential source of nutrients becomes available for primary production (Carman & Jonsson 1991, Jensen et al. 1995).

Jansson et al. (1984), Granéli et al. (1990) and Bianchi et al. (2000) suggested that during the past 200 years nitrogen has been the factor limiting primary production in the Baltic Proper. Granéli et al. (1990) considered the spring diatom bloom in the Baltic to be nitrogen-limited, and other workers in the 1990s found that nitrogen and phosphorus limit primary production in late spring (Kivi et al. 1993, Trzosińska & Łysiak-Pastuszak 1996, Falkowska et al. 1998). In summer, the bioavailability of phosphorus in waters containing very low concentrations of inorganic nitrogen is advantageous to cyanophyta and stimulates their blooms (Larsson et al. 2001). In water bodies where phytoplankton growth is nitrogen-limited, limitation by iron may be concurrent (Entsch et al. 1983). According to Wu et al. (2000), it is P compounds that limit primary production in oceans, even if sufficient Fe is available; this implies that N is not the limiting factor in such waters. Now although these last-mentioned results apply to oligotrophic ocean waters, they may also be of significance to the Baltic.

Stal et al. (1999) observed that iron limited nitrogen fixation and the growth of diazotrophic cyanobacteria in the Baltic (*Synechococcus* spp.) were primarily nitrogen-limited, but iron appeared to be a secondary limiting factor. Their measurements of chl a and of trichome numbers also

showed a marked growth of *Nodularia spumigena* following the addition of iron. Balode et al. (1998) and Hellström (1998), too, suggested that iron was a factor potentially limiting cyanobacterial bloom growth in the Baltic.

Recent work has shown that many coastal phytoplankton species grow far better in the presence of Fe levels much higher than those required by pelagic phytoplankton (Sunda & Huntsman 1995). Observations of Baltic diatoms *Cyclotella meneghiniana* have shown that iron may therefore be an important factor regulating their growth. In an experimental population of diatoms, the effect of iron limitation was clearly manifested by the lower numbers of cells and the smaller concentrations of chl a. At iron concentrations of $\leq 10^{-8}$ mol dm^{-3}, cell numbers increased only half as fast as in the control, where the iron concentration was 1.2×10^{-5} mol dm^{-3}. Cells grown at iron concentrations between $\leq 10^{-8}$ and $\leq 10^{-7}$ mol dm^{-3} reduced the chl a content by about 16–26% as compared to the control cells (Lewandowska & Kosakowska 2004).

Rydin et al. (2002) and Moisander et al. (2003) demonstrated that a lack of iron limited the growth of phytoplankton in the Baltic Sea, e.g. *Aphanizomenon* sp., *Anabaena* spp. and *Nodularia* spp.

The biological response to environmental changes is closely associated with the frequency of such changes. Diurnal variation occurs as a consequence of the assimilation and decomposition of organic matter; in turn, the rates and dynamics of these two processes are influenced by changing physical (insolation, temperature, hydrodynamics and wave action), chemical (availability of nutrients and vitamins) and biological parameters (abundance and species composition of phyto- and zooplankton, and bacteria) (Falkowska 1998). The principal aim of the present work was to describe short-term fluctuations in the concentrations of nitrogen compounds (nitrates, nitrites and ammonium), phosphorus compounds and total iron, as well as the sequence in which these nutrients are consumed in the euphotic layer. The works also aims to identify all the processes taking place in the aphotic zone that could possibly contribute to the enrichment of the productive zone.

2. Material and methods

The investigations of short-term variability of chemical and physical parameters were conducted on 2–6 June 2001 in the Gdańsk Deep ($\varphi = 54°52'$N, $\lambda = 19°10'$E) from on board the ORP 'Kopernik'. The sampling station was located in the open waters of the southern Baltic 30 Nm from the Vistula river mouth. Samples were collected at standard depths at 2-hour intervals. Temperature and salinity were measured with

a CTD PROFILER (FALMOUTH SCIENTIFIC INC.), and seawater samples collected with a 12-bottle rosette were processed immediately in the on-deck laboratory.

Total nitrogen and total phosphorus were measured by the simultaneous oxidation method of Raimbault et al. (1999); the respective relative standard errors were 3.6% and 3.4%. Total dissolved iron was measured by the bathophenanthroline method, while other dissolved nutrients and the oxygen content were determined by standard methods (Grasshoff et al. 1983). Absorbance was measured with a Perkin-Elmer two-beam Lambda 3b spectrophotometer. The detection limits were 0.01 μmol dm^{-3} for phosphate, nitrate and nitrite, and 0.05 μmol dm^{-3} for ammonium. The relative analytical error for total iron determinations was 8.4%. In addition, chlorophyll a and phaeophytin a were measured in samples of seawater collected concurrently. A meteorological record was also kept.

3. Results

The vertical stratification of the water column is an important factor determining the spatial distribution of nutrients. In June 2001, measurements were carried out in unstable hydrodynamic conditions, during the formation of the thermocline. In the first few hours of sampling, a 20-metre-thick thermocline oscillated between 20 and 40 m depth (Fig. 1). At the end of the first day, a fivefold increase in wind velocity, from 1.2 to 6.2 m s^{-1}, caused the thermocline to dissipate. At the end of the second sampling day, the thermocline began to re-form (Kullenberg 1982). The mean temperature of the surface water ranged from 9 to 10.4°C, that of the intermediate layer hovered around 4°C. The near-bottom temperature rose to > 6°C. The salinity down to 70 m varied little (7.1–7.3 PSU), but increased below this depth (av. 7.85 ± 0.31 PSU). The salinity gradient was steepest at 80 m, whereas the near-bottom salinity varied only slightly (11.5 –11.7 PSU).

Affected by both thermal and salinity stratification, the oxygen content in the euphotic layer varied widely during the daytime (Table 1). Its amplitude in surface waters was extremely high on occasion (> 4.5 cm^3 dm^{-3}). Below the halocline, the oxygen content fell sharply to 0.52 cm^3 dm^{-3}. Furthermore, in seawater samples collected from the near-bottom layer, the presence of hydrogen sulphide was always detectable by its smell.

The nutrient distribution varied significantly. In the euphotic layer, the mean values of chemical parameters were relatively stable (Table 1), though point values were widely scattered. Particularly high ranges were recorded for total iron, nitrite and ammonium. About 60% of the total
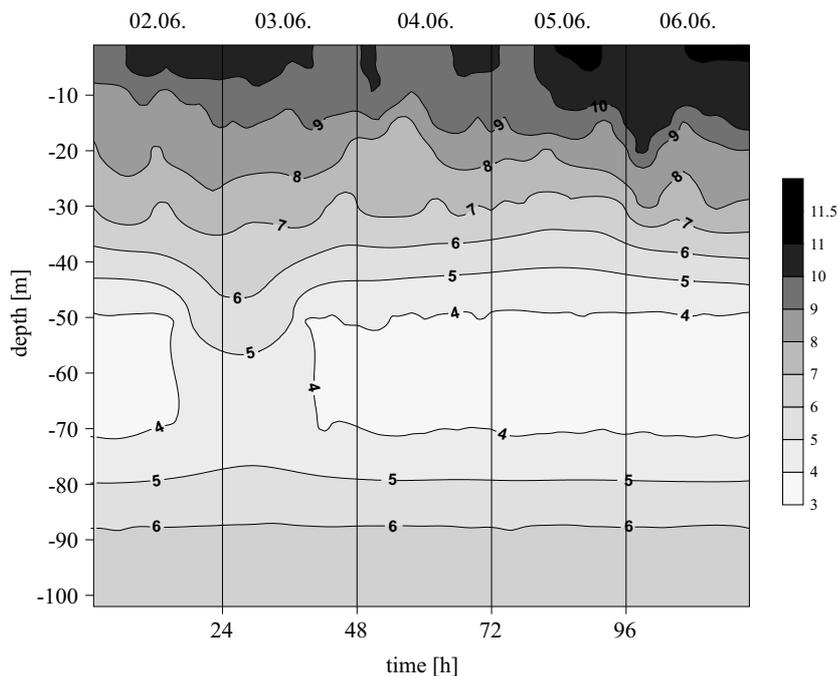
Fig. 1. Vertical temperature profile [°C] in the Gdańsk Deep, June 2001

iron and about 65% of phosphate determinations were < 0.2 μmol dm^{-3} (Fig. 2). 83 and 86% of ammonium and nitrate measurements respectively gave concentrations of < 1.2 μmol dm^{-3}.

The mean molar ratios of particular parameters were stable in the euphotic layer, but the DIN:P ratio there remained at a higher than optimum level. This was indicative either of a deficit of phosphate or a surplus of inorganic nitrogen compounds (Table 2).

In the aphotic zone, the mean concentrations of nitrite, ammonium and phosphate, and the total concentrations of phosphorus and iron increased from a depth of 30 m down to the sea bed (Table 1). The mean ammonium concentration dropped to 0.84 μmol dm^{-3} at 90 m, but rose again near the bottom. Phosphate displayed the highest variability in the aphotic layer (range: 43.14–87.50%), and its near-bottom concentrations decreased with falling oxygen content. Total iron (range: 12–23.52%) and total nitrogen concentrations (7.68–27.46%) were the least variable and increased with depth (Table 1). The mean molar ratios of nitrogen to phosphorus compounds decreased in near-bottom waters, as did the Fe$_{\text{tot}}$:PO$_4$ ratio. Molar ratios of iron to nitrogen compounds increased with depth, reaching maximum values below the halocline (Table 2).

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Table 1. Statistical characteristics of changes in nutrient concentrations [μmol dm^{-3}] and oxygen content [cm^3 dm^{-3}] in the Gdańsk Deep, based on 59 vertical profiles

H	X ± (Min − Max)	RSD	X ± (Min − Max)	RSD	X ± (Min − Max)	RSD	X ± (Min − Max)	RSD
	nitrite		nitrite		ammonium		total nitrogen	
0	0.36 ± (0.02 − 0.81)	41.67	0.81 ± (0.23 − 2.15)	54.32	0.96 ± (LD − 3.72)	70.83	39.29 ± (16.44 − 90.74)	30.29
5	0.34 ± (0.05 − 0.78)	44.12	0.67 ± (0.14 − 1.91)	55.22	0.87 ± (0.08 − 5.34)	103.45	38.24 ± (16.44 − 66.95)	28.14
10	0.38 ± (0.05 − 1.51)	60.37	0.67 ± (0.25 − 1.30)	41.79	0.75 ± (0.09 − 2.46)	65.33	36.54 ± (18.52 − 76.55)	30.49
15	0.33 ± (0.02 − 3.30)	132.53	0.66 ± (0.18 − 1.66)	45.45	0.78 ± (0.08 − 4.09)	83.33	32.62 ± (19.36 − 50.67)	25.07
20	0.27 ± (0.01 − 0.58)	48.69	0.66 ± (0.13 − 2.01)	53.03	0.87 ± (0.06 − 5.37)	106.90	37.22 ± (23.53 − 71.12)	29.45
30	0.24 ± (0.02 − 0.65)	62.50	0.87 ± (0.24 − 2.51)	54.02	0.80 ± (010 − 3.48)	73.75	39.19 ± (17.69 − 76.55)	26.46
50	0.24 ± (0.05 − 1.95)	111.57	1.28 ± (0.46 − 2.76)	47.66	0.89 ± (0.17 − 2.93)	59.55	40.38 ± (24.37 − 76.55)	27.41
70	0.40 ± (0.05 − 0.87)	40.00	0.40 ± (LD − 1.18)	87.50	0.97 ± (0.21 − 5.27)	74.23	62.62 ± (40.23 − 76.13)	12.10
90	0.68 ± (0.27 − 1.63)	36.60	0.78 ± (0.07 − 1.29)	39.74	0.84 ± (0.17 − 3.38)	54.76	95.87 ± (76.96 − 114.12)	7.68
100	1.27 ± (0.36 − 3.49)	44.09	0.51 ± (0.12 − 1.05)	43.14	1.26 ± (0.13 − 5.93)	64.29	85.47 ± (59.85 − 98.67)	9.34
	phosphate		total phosphorus		total iron		oxygen	
0	0.12 ± (0.03 − 0.34)	56.67	0.32 ± (0.12 − 0.54)	34.38	0.15 ± (0.08 − 0.25)	26.67	8.35 ± (6.34 − 11.04)	9.58
5	0.12 ± (0.04 − 0.40)	52.59	0.33 ± (0.14 − 0.93)	39.39	0.08 ± (0.01 − 0.20)	71.45	8.48 ± (4.66 − 9.23)	10.38
10	0.12 ± (0.04 − 0.45)	63.20	0.34 ± (0.16 − 0.71)	35.29	0.10 ± (0.01 − 0.21)	50.00	8.14 ± (4.97 − 9.49)	9.46
15	0.11 ± (0.02 − 0.38)	59.82	0.29 ± (0.11 − 0.56)	31.03	0.13 ± (0.02 − 0.23)	38.46	7.88 ± (6.05 − 8.94)	12.18
20	0.13 ± (0.02 − 0.43)	65.91	0.32 ± (0.07 − 0.71)	37.50	0.19 ± (0.10 − 0.31)	26.31	8.26 ± (7.10 − 9.02)	4.72
30	0.15 ± (0.03 − 0.38)	51.30	0.35 ± (0.16 − 0.73)	31.43	0.17 ± (0.10 − 0.30)	23.53	7.54 ± (5.13 − 8.63)	9.02
50	0.27 ± (0.09 − 1.25)	71.80	0.47 ± (0.21 − 1.43)	42.55	0.24 ± (0.15 − 0.35)	16.67	8.87 ± (4.44 − 10.52)	7.92
70	0.65 ± (0.08 − 1.58)	40.76	0.93 ± (0.48 − 2.01)	33.33	0.36 ± (0.23 − 0.45)	16.67	5.46 ± (2.88 − 7.56)	17.76
90	1.67 ± (0.98 − 2.36)	13.17	2.09 ± (1.63 − 2.87)	13.40	0.50 ± (0.37 − 0.64)	12.00	1.21 ± (0.45 − 5.57)	55.37
100	2.04 ± (0.02 − 2.47)	17.65	2.62 ± (2.00 − 3.22)	12.21	0.70 ± (0.53 − 1.02)	17.14	0.52 ± (0.17 − 1.18)	44.23

Symbol description: H – depth [m], X – mean value, Min – minimum concentration of a parameter, Max – maximum concentration of a parameter, RSD – variability coefficient for a parameter [(SD × X^{-1}) 100%].
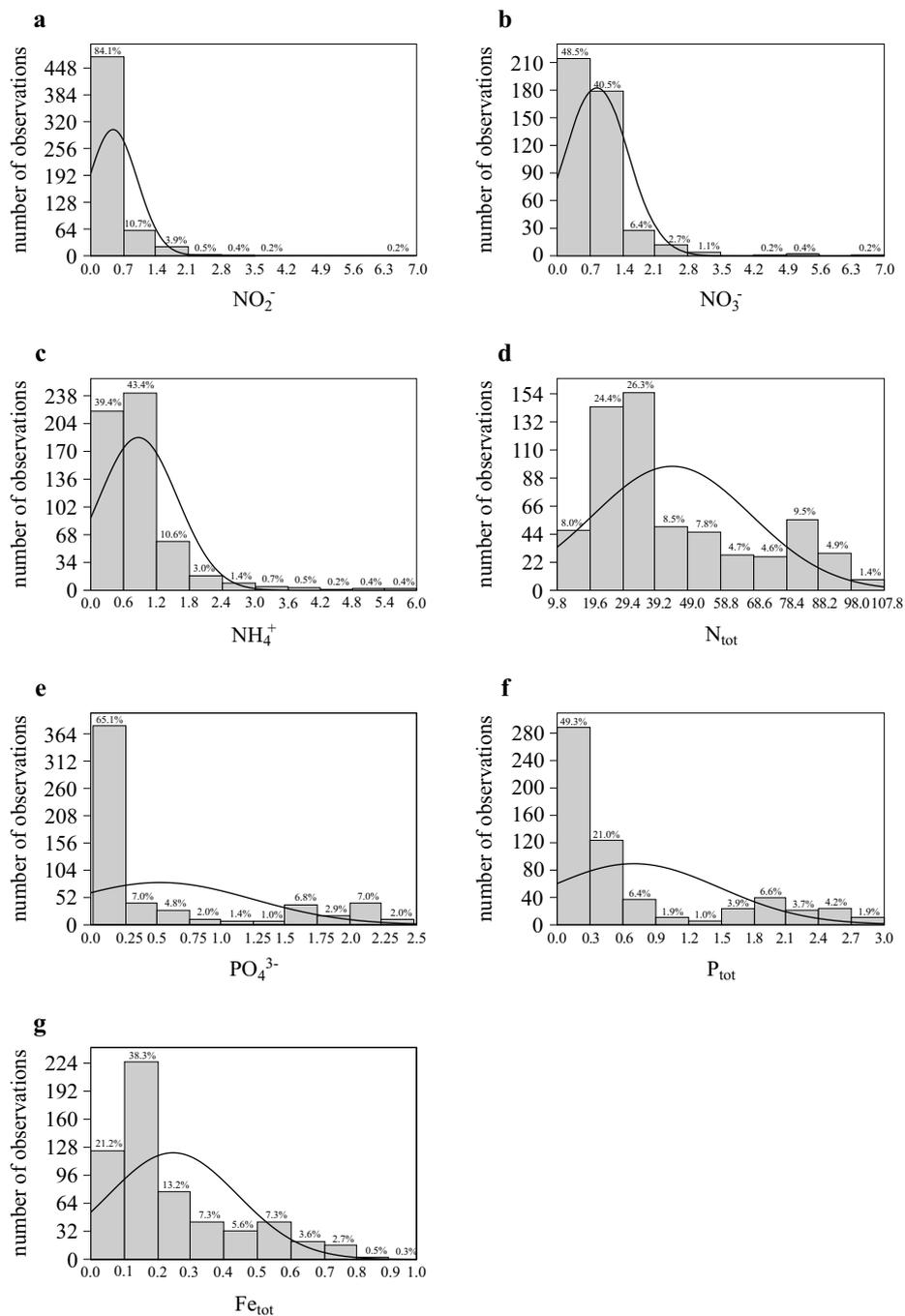
Fig. 2. A frequency histogram of chemical parameter concentrations in the entire water column in the Gdańsk Deep in June 2001: nitrite (a), nitrate (b), ammonium (c), total nitrogen (d), phosphate (e), total phosphorus (f), total iron (g)

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Table 2. Statistical characteristics of changes in molar ratios of nutrients in the Gdańsk Deep in June 2001, based on 59 vertical profiles

H	X ± (Min − Max)	RSD	X ± (Min − Max)	RSD	X ± (Min − Max)	RSD
	$DIN:PO_4^{3-}$		$NO_3^-:PO_3^{3-}$		$Fe_{tot}:NO_3^-$	
0	$20.83 \pm (6.00 - 73.41)$	57.13	$8.12 \pm (1.63 - 32.98)$	72.17	$0.23 \pm (0.04 - 0.73)$	65.22
5	$18.00 \pm (6.27 - 61.35)$	64.94	$6.51 \pm (1.51 - 29.19)$	79.11	$0.14 \pm (0.01 - 0.57)$	71.42
10	$16.00 \pm (3.73 - 46.60)$	49.94	$6.11 \pm (0.16 - 22.63)$	63.17	$0.31 \pm (0.02 - 0.53)$	35.48
15	$18.13 \pm (5.73 - 77.84)$	71.92	$7.92 \pm (1.07 - 44.34)$	91.16	$0.23 \pm (0.01 - 0.79)$	60.87
20	$17.99 \pm (4.02 - 101.04)$	99.98	$6.94 \pm (0.33 - 43.76)$	102.59	$0.40 \pm (0.04 - 1.82)$	82.50
30	$15.31 \pm (3.63 - 76.29)$	79.36	$7.55 \pm (0.66 - 51.33)$	100.13	$0.24 \pm (0.04 - 0.81)$	58.33
50	$11.15 \pm (2.21 - 37.61)$	52.38	$6.24 \pm (1.24 - 29.28)$	73.24	$0.22 \pm (0.03 - 0.57)$	50.00
70	$2.78 \pm (1.18 - 14.61)$	107.91	$0.56 \pm (0.01 - 2.82)$	107.14	$1.86 \pm (0.29 - 5.67)$	73.34
90	$1.39 \pm (0.60 - 3.12)$	31.65	$0.49 \pm (0.03 - 1.32)$	44.90	$0.99 \pm (0.20 - 3.86)$	76.77
100	$1.27 \pm (0.83 - 1.91)$	22.05	$0.26 \pm (0.06 - 0.51)$	42.31	$1.16 \pm (0.56 - 4.40)$	77.59
	$Fe_{tot}:PO_4^{3-}$		$Fe_{tot}:DIN$			
0	$1.45 \pm (0.24 - 3.82)$	18.62	$0.09 \pm (0.02 - 0.33)$	66.67		
5	$0.74 \pm (0.03 - 1.97)$	21.62	$0.05 \pm (0.04 - 0.26)$	80.00		
10	$0.96 \pm (0.05 - 3.07)$	16.67	$0.07 \pm (0.01 - 0.29)$	71.43		
15	$1.52 \pm (0.06 - 7.27)$	17.63	$0.09 \pm (0.00 - 0.23)$	55.55		
20	$1.99 \pm (0.26 - 12.52)$	21.10	$0.16 \pm (0.02 - 1.40)$	106.25		
30	$1.37 \pm (0.26 - 6.71)$	16.79	$0.13 \pm (0.26 - 1.19)$	115.38		
50	$1.13 \pm (0.16 - 2.41)$	20.35	$0.14 \pm (0.03 - 0.88)$	92.86		
70	$0.66 \pm (0.22 - 4.27)$	21.21	$0.33 \pm (0.06 - 3.64)$	136.36		
90	$0.30 \pm (0.21 - 0.56)$	16.67	$0.26 \pm (0.06 - 1.15)$	46.15		
100	$0.35 \pm (0.22 - 0.60)$	14.28	$0.31 \pm (0.01 - 1.21)$	51.61		

Symbols and abbreviations as in Table 1.

4. Discussion

Playing a crucial role in the eutrophication of the sea, the spatial distribution of nutrients is the upshot of a variety of processes, such as the seasonal and diurnal cycle of nutrient assimilation and mineralisation. The incorporation of nitrogen and phosphorus compounds and their regeneration in the euphotic zone may occur as short-term events, e.g. diurnally (Brockmann et al. 1990). Hutchins et al. (1993) showed that iron enters a short cycle associated with phytoplankton growth and that iron concentrations depend on assimilation and mineralisation.

Euphotic layer

In open Baltic waters, primary production is sustained mainly through nutrient recycling. In early June 2001, the respective mean concentrations of DIN:(NO_2^- + NO_3^- + NH_4^+), phosphate and Fe_{tot} in the euphotic layer were close to 1.9, 0.12 and 0.11 μmol dm^{-3}, values typical for the time period covered by the present study (Trzosińska 1990).

During daylight, PO_4^{3-} and Fe_{tot} concentrations decreased in the euphotic layer (Fig. 3), and N_N did likewise as a result of phytoplankton assimilation. The levels of nutrients limiting marine phytoplankton growth, as estimated from the saturation constant Ks, were 0.1–0.5 for phosphate and 1–2 μmol dm^{-3} for inorganic nitrogen (Fisher et al. 1988), and 0.0084 μmol dm^{-3} for iron (for the coastal diatom *Thalassiosira weissflogii*) (Anderson & Morel 1982). Coale et al. (1996) estimated a saturation constant for Fe of 0.00012 μmol dm^{-3} for diatoms in equatorial Pacific waters.

On the basis of saturation constants and interspecific values, i.e. KN = 1.5 μmol dm^{-3}, KP = 0.3 μmol dm^{-3} and KFe = 0.0084 μmol dm^{-3} (for coastal diatoms), we can calculate the following ratios: KN/KP = 5, KFe/KP = 0.028. These values suggest that phosphorus is the element limiting primary production in the whole euphotic zone (Figs 4a and 4b). However, Brand et al. (1983) reported a value of 0.1 μmol dm^{-3} as significantly limiting the rate of primary production in neritic waters. These authors also observed that the growth of oceanic cyanobacteria was limited by iron at concentrations < 0.01 μmol dm^{-3}, but that the growth of other oceanic phytoplankton species was limited only slightly or not at all by iron concentrations < 0.001 μmol dm^{-3}. Experiments have shown that the demands of oceanic and coastal species reflect a difference between neritic and oceanic species. The latter species grow at substantially lower iron concentrations than their neritic equivalents: previous experiments with diatoms – *Thalassiosira oceania* (oceanic) and *Thalassiosira pseudonana* (neritic) – have shown that oceanic species require less iron for cell growth
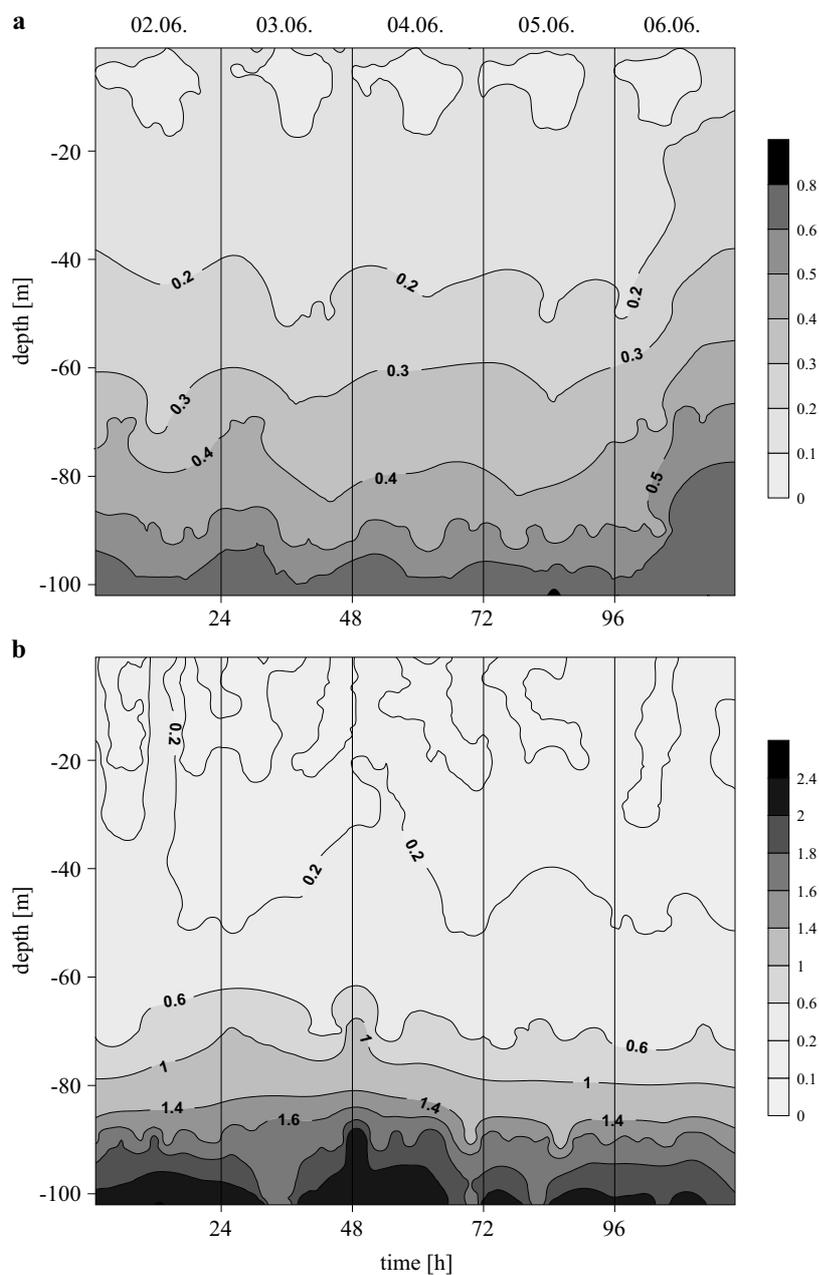
Fig. 3. Vertical concentration profile for Fe_{tot} [μmol dm^{-3}] (a) and PO_4^{3-} [μmol dm^{-3}] (b) in the Gdańsk Deep in June 2001

than neritic ones, even though the rates of iron assimilation are similar (Sunda & Huntsman 1995). Wells & Trick (2004) have indicated that the demand for iron is to a great extent species-dependent.
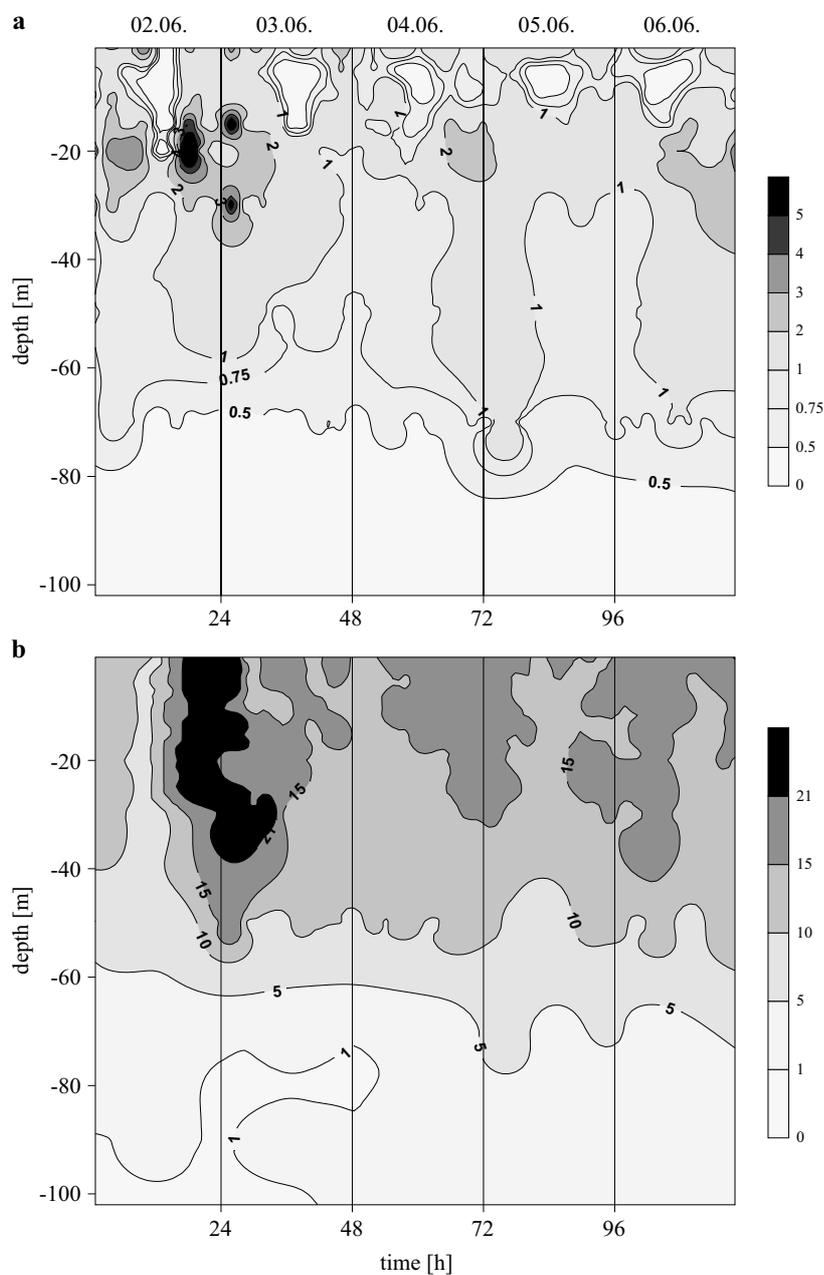
Fig. 4. Vertical profile of molar ratios for $Fe_{tot}:PO_4{}^{3-}$ (a), $DIN:PO_4{}^{3-}$ (b) in the Gdańsk Deep in June 2001

In the Gdańsk Deep, the mean total iron concentrations in the euphotic zone in June 2001 were lower than the values stated in the previous paragraph, which suggests that besides nitrogen and phosphorus, iron can

be regarded as another factor limiting primary production in late spring (Table 1). Moreover, the determinations of iron concentrations also included all the other dissolved forms; hence, the concentration of iron assimilated by phytoplankton was at an even lower level. Experiments have shown that the dissolved forms of Fe(II) and Fe(III) and some hydrated Fe(II) complexes are the only forms that are transported through cellular membranes within the cell (Hudson & Morel 1993, Sunda & Huntsman 1995). Previous measurements conducted in the surface waters of the Gulf of Gdańsk have indicated a wide range of variability in iron concentrations. Pohl et al. (1998) determined Fe(III) concentrations from $< \mathrm{LoD}$ to 6.27×10^{-7} mol dm^{-3}. Pempkowiak et al. (2000) reported an iron concentration of 1.79×10^{-9} mol dm^{-3} in the Gdańsk Basin.

In June 2001, the respective concentrations of NO_3^-, NH_4^+, PO_4^{3-} and Fe_{tot} in the productive layer of the Gdańsk Deep during the daylight period fell to 0.15, 0.08, 0.03 and 0.01 μmol dm^{-3}. The lowest concentrations of phosphorus, nitrogen and iron compounds occurred most frequently between 04:00 and 10:00 hrs (PO_4^{3-}), 04:00 and 08:00 hrs (NH_4^+), 06:00 and 12:00 hrs (NO_3^-), 10:00 and 16:00 hrs (Fe_{tot}) (Fig. 5). A comparable share of NO_3^- and NH_4^+ in the total N_N content (Fig. 6) with a simultaneous greater decrease in NH_4^+ as compared to the NO_3^- concentrations suggested a change in phytoplankton preferences. The succession from nitrate to ammonium followed the succession of phytoplankton species (Tamminen 1990, Falkowska et al. 1998). Such a scenario was recorded in 1989–96, when in spring ammonium made up 58% of the total nitrogen compounds in the euphotic layer during the day, and up to 90% at night (Falkowska et al. 1998). A high percentage of ammonium in the sum of inorganic nitrogen compounds may indicate a high rate of mineralisation (Tamminen 1990). This process can take place in warmed-up surface waters within less than an hour (Falkowska & Latała 1995). An evident increase in nutrient concentrations occurred at night; in the case of NO_3^- and PO_4^{3-},
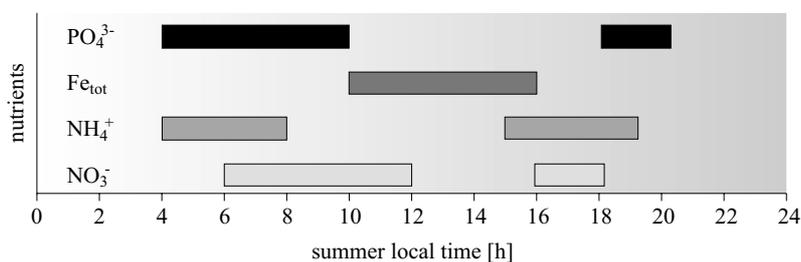
Fig. 5. Periods of the most intensive nutrient incorporation during the diurnal cycle
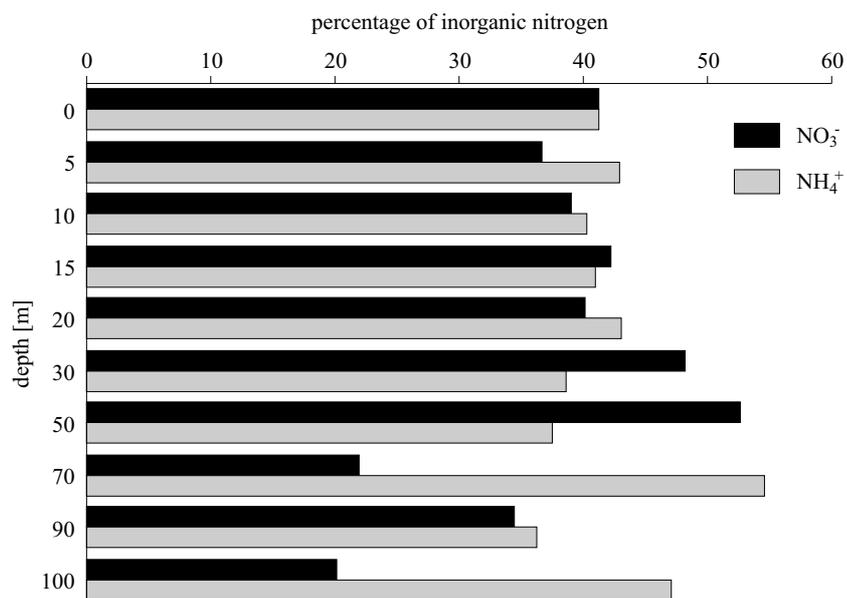
Fig. 6. Nitrate and ammonium as a percentage of inorganic nitrogen in the Gdańsk Deep in June 2001

concentrations rose by 25%, and in the case of NH_4^+ and Fe_{tot} by 35% (Fig. 7). In the decomposition of organic matter, a process lasting 24 hours, it is PO_4^{3-} and later NH_4^+ that are released first as a result of hydrolysis. Due to the fact that nitrification is light-inhibited, the increases in NO_3^- concentrations in the euphotic layer were recorded at night (Olson 1981, Falkowska et al. 1998).

Not only the *in situ* values of nutrient concentrations, but also the ratios of nutrients in plant tissues play an important part in limiting primary production. The ecological status of a water body can result in nutrients not being assimilated in accordance with the Redfield ratio (Trzosińska & Łysiak-Pastuszak 1996). The molar DIN:P ratio for oceanic waters is 16:1, but in the Baltic its value is lower – from 14:1 to 16:1 (Renk 1997). According to Trzosińska (1990), the molar DIN:P ratio for the Gdańsk Deep lies between 12:1 and 14:1. The considerable variability of DIN:P ratios in the Baltic Sea is due to the selective assimilation of nutrients by the mixed phytoplankton population (Rhee & Gotham 1980), as well as to the proportion of nutrients supplied by riverine inflow (Brockmann et al. 1990, Trzosińska & Łysiak-Pastuszak 1996). In the past few years in the Gulf of Gdańsk, a c. 5% decrease in phosphate concentrations and an accelerating fall in nitrate concentrations have been observed as compared to the 1990s (Łysiak-Pastuszak & Drgas 2001a, b).
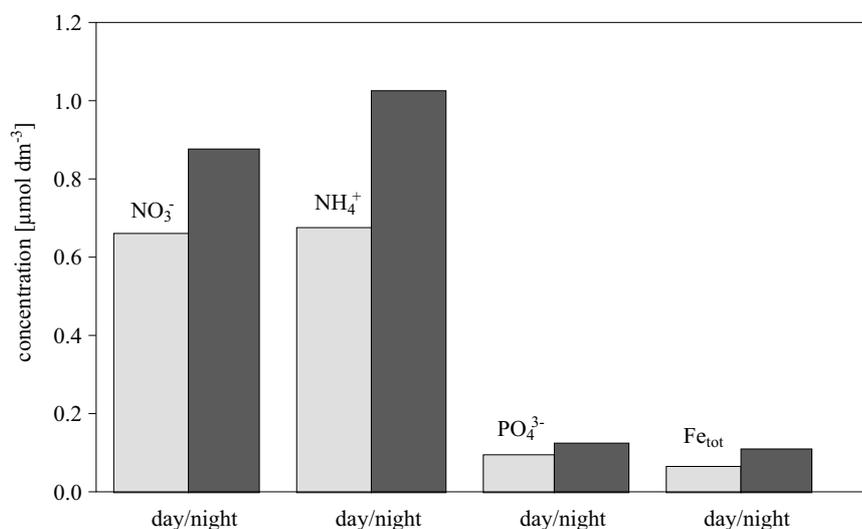
Fig. 7. The concentrations of NO_3^-, NH_4^+, PO_4^{3-} and Fe_{tot} during the light and dark periods

In June 2001, the ratios of $DIN(NO_2^- + NO_3^- + NH_4^+):PO_4^{3-}$ as well as $Fe_{tot}:PO_4^{3-}$ and $Fe_{tot}:N_N$ displayed a significant variability that was very probably generated by the activities of the planktonic organisms themselves and mixing processes in the water column (Table 2, page 250). Falkowska et al. (1998) obtained similar values for the molar ratios of $DIN:PO_4^{3-}$ in the Gdańsk Deep, which exceeded the optimum level for the Baltic, particularly in the 0–5 m layer. The large number of high $DIN:PO_4^{3-}$ values determined in the euphotic layer was put down to the PO_4^{3-} deficit that usually occurs in late spring, thereby limiting plant growth (Falkowska et al. 1998). The molar ratios for $Fe_{tot}:PO_4^{3-}$ and $Fe_{tot}:NO_3^-$ measured in June 2001 were significantly higher than those obtained by Sunda & Huntsman (1995) for oceanic waters (Table 3). Nevertheless, Brand et al. (1983), Sunda & Huntsman (1995), and Wells & Trick (2004) stressed that coastal phytoplankton has a much greater need for iron than its oceanic counterpart. The concentration of Fe can be 100–1000 times higher

Table 3. Molar ratios for $Fe_{tot}:PO_4^{3-}$ and $Fe_{tot}:NO_3^-$

Zone	$Fe_{tot}:PO_4^{3-}$	$Fe_{tot}:NO_3^-$	Source
North Pacific	0.00024–0.0003	0.000035–0.000042	Sunda & Huntsman 1995
North Atlantic	0.00042	0.000064	Sunda & Huntsman 1995
Gulf of Gdańsk (open sea)	1.37	0.26	this paper

in coastal waters than oceans (Sunda & Huntsman 1995). In the case of the Baltic we have a highly eutrophic, semi-enclosed sea with a significant input of terrigenous Fe. This can widen the differences between the molar ratios N:P:Fe in oceans and the Baltic.

Aphotic layer

The elevated concentrations of particular nutrients in the aphotic zone may have been due to biochemical (organic matter degradation) and physical processes (diffusion, advection and convection). The unstable thermocline was a significant factor stimulating the exchange of nutrients between the euphotic and aphotic layers. The dissipation of the thermocline at the end of the first sampling day (see Fig. 1, data for June 2) caused phosphate to diffuse from the water overlying the halocline, thereby enriching the euphotic layer (Fig. 3). As a consequence of this additional phosphate input to the surface waters, the $DIN:PO_4^{-3}$ ratio fell to < 10 (Fig. 4).

High phosphate concentrations and oxygen depletion in the aphotic layer were related principally to ongoing mineralisation. This process can be described by using Apparent Oxygen Utilisation (AOU) and its correlation with the elements that make up living tissue. The statistically significant correlation between AOU and phosphate concentration demonstrates the validity of this assumption (Table 4).

Table 4. Empirical relationship between Apparent Oxygen Utilisation (AOU) and phosphate concentration [μmol dm^{-3}]

Zone	Saturation [%]	$PO_4^{3-} = aAOU + b$	r	$AUO:PO_4^{3-}$	Source
Ocean	–	0.00724 AOU	–	138	Redfield et al. 1963
Ocean	–	0.00571 AOU	–	175–183	Pilson 1998
Baltic Sea	–	0.00641 AOU	–	180	Sen Gupta & Koroleff 1973
Baltic Sea	–	0.00629 AOU	–	159	Shaffer 1987
Baltic Sea (Gdańsk Deep)	100–10	0.0055–0.0762 AOU	0.93	181	this paper

r – significant positive correlation.

In June 2001, the $AOU:PO_4^{3-}$ ratio was equal to 181, which can be interpreted as 181 moles of oxygen needed to oxidise 1 mole of phosphorus.

The above value falls within the range of measurements published by Pilson (1998) for the ocean, and is also close to the values established by Sen Gupta & Koroleff (1973) for the Baltic. The differences between the $AOU:PO_4{}^{3-}$ ratios obtained by various authors may be due to the different hydrological and hydro-chemical conditions in the Gdańsk Deep.

Organic matter mineralisation in the aphotic zone (70 m) has been confirmed by a statistically significant negative correlation between oxygen content and nitrate concentration:

$$NO_3{}^- \ (\mu mol \ dm^{-3}) = 1.2214 - 0.1557 \, O_2 \ (cm^3 \ dm^{-3}) \ (r = -0.57, p < 1\%).$$

The equation shows that the decreasing oxygen content is related to an increase in nitrate concentration as a result of nitrification. Falkowska et al. (1998) obtained a regression equation with a much steeper slope for the data collected in the spring seasons of the years 1989–95:

$$NO_3{}^- \ (\mu mol \ dm^{-3}) = 5.5 - 0.53 \, O_2 \ (cm^3 \ dm^{-3}) \ (r = -0.55, p < 1\%).$$

This could be evidence for the unstable environmental conditions that are thought to occur in the heterohaline water layer of the Gdańsk Deep in spring.

In June 2001, oxygen conditions in the water column were good; however, in the near-bottom layer in the Gdańsk Deep there was an oxygen deficit ($< 1 \ cm^3 \ dm^{-3}$) that retarded the mineralisation of organic matter. Organic nitrogen therefore increased. The statistically significant positive correlation between nitrate concentration and oxygen content could indicate that denitrification had just started (Table 5).

Table 5. Empirical relationship between nitrate concentration [$\mu mol \ dm^{-3}$] and oxygen content [$cm^3 \ dm^{-3}$] in the near-bottom waters of the Gdańsk Deep

Regression equation	Year	Season	H	r	Source
$NO_3{}^- = 2.70 + 1.77 \, O_2$	1969–1983	year	100	0.57	Trzosińska 1990
$NO_3{}^- = -0.28 + 1.06 \, O_2$	1989–1995	May–June	100	0.69	Falkowska et al. 1998
$NO_3{}^- = 0.61 + 0.66 \, O_2$	1995	May	100	0.58	Burska 2000
$NO_3 = 0.19 + 0.45 \, O_2$	2001	June	100	0.83	this paper

H – depth [m], r – significant positive correlation.

This hypothesis has been confirmed by the increasing concentrations of nitrite and ammonium at the bottom (Table 1, page 248); nevertheless, the much higher concentrations of the latter point to the prevalence of ammonification over denitrification.

The effect of the oxygen deficit was reflected in the drop in nitrate concentrations, whereas the elevated phosphate and iron levels were due to diffusion from the sediments (Carman & Jonsson 1991, Jensen et al. 1995). This resulted in the lowest molar ratios for $DIN:PO_4^{3-}$, $NO_3^-:PO_4^{3-}$ and $NH_4^+:PO_4^{3-}$; the decrease was smaller in the case of the $Fe_{tot}:PO_4^{3-}$ ratio (Table 2, page 250).

In June 2001, a negative correlation was found between the oxygen content and phosphate concentration that was statistically highly significant (Table 6). This correlation was comparable to those obtained by Trzosińska (1990) and Falkowska et al. (1998).

Table 6. Empirical relationship between phosphate concentration [μmol dm^{-3}] and oxygen content [cm^3 dm^{-3}] in the near-bottom layer of the Gdańsk Deep

Regression equation	Year	Season	H	r	Source
$PO_4^{3-} = 2.55 - 0.27\ O_2$	1967–1983	year	80	–0.50	Trzosińska 1990
$PO_4^{3-} = 3.67 - 0.36\ O_2$	1989–1995	May–June	100	–0.56	Falkowska et al. 1998
$PO_4^{3-} = 2.06 - 0.25\ O_2$	2001	June	100	–0.89	this paper

H – depth [m], r – significant negative correlation.

Low levels of oxygen, but also the presence of hydrogen sulphide, were detected in the Gdańsk Deep in June. This is much earlier in the season than the dates given by Trzosińska & Łysiak-Pastuszak (1996): on the basis of their data from 1989–93, these authors concluded that hydrogen sulphide only begins to form in late summer or early autumn. On the basis of environmental measurements in 1989–96, Falkowska et al. (1998) drew attention to a sharp drop in oxygen content, particularly in May 1995. An oxygen depletion so early in the year may be compelling evidence of on-going eutrophication associated with an earlier start to the growing season. It could also indicate changing hydrological conditions (the inflow of oceanic waters in autumn and a temperature rise in the near-bottom layer) resulting from global climate change.

5. Conclusions

The maximum and minimum concentrations of nitrogen, phosphorus and iron compounds during the diurnal cycle of matter transformation appear to be governed by biotic and abiotic factors controlling the rates of assimilation and degradation of organic matter. Phosphate and iron concentrations in the euphotic layer dropped below the values considered

to be limiting. Expressed as the sum of nitrogen compounds, inorganic nitrogen concentrations lay close to the limiting value. The sequence of nutrient depletion during the day was as follows:
$PO_4{}^{3-}$ (04:00–10:00 hrs), $NH_4{}^+$ (04:00–08:00 hrs), $NO_3{}^-$ (06:00–12:00 hrs), Fe_{tot} (10:00–16:00 hrs). Despite a significant depletion of all nutrients, phosphorus appears to play the most important part in limiting primary production.

The concentrations of iron compounds in the euphotic layer are very low: this implies that some other compound is responsible for limiting primary production over a short time-scale and in a small area.

Molar ratios of $DIN:PO_4{}^{3-}$ in the euphotic layer were greater than the Redfield ratio; therefore, these are values indicating not only that phosphate concentrations are very low, but also that in late spring phosphorus replaces nitrates as the factor limiting primary production.

The release of phosphates and iron from sediments and the mineralisation of organic matter in the aphotic layer are a potential source of nutrients and an important link in their short-term recycling.

The oxygen deficit in the near-bottom waters of the Gdańsk Deep so early in the season could indicate faster rates of organic matter deposition and its mineralisation under the influence of higher temperatures in near-bottom waters when hydrological conditions are stable.

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