Short-term changes in the hydrochemical constituents in the water column of the Gdańsk Deep (Baltic Sea) in spring. Part 1. Nutrient and oxygen concentrations in relation to the density stratification*

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Lucyna Falkowska, Dorota Burska,
Jerzy Bolałek
Institute of Oceanography,
Gdańsk University,
Gdynia

Dorota Roguszczak
Pedagogical University,
Słupsk

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Abstract

Both the seasonal thermocline in the uppermost layer of the sea and the halocline in the near-bottom layer were found to constrain transport of chemical compounds to the productive layer of the Gdańsk Deep. The occasional disappearance of the halocline resulted on the one hand in the flow of nitrogen and phosphorus compounds through the intermediate layer towards the surface, and on the other in a considerable improvement in oxygen conditions in the near-bottom layer, this usually being either poorly oxygenated or anoxic. A statistically significant negative correlation between nitrate and oxygen concentrations was found in the isohaline layer. The N:P ratio was usually low during the day but increased at night. During

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spring this ratio increased in the euphotic layer. The large number of high N:P ratios may attest to the shortage of phosphates and to the change in the limiting factor – from nitrogen compounds in early spring to phosphates in late spring.

1. Introduction

Being components of proteins, nitrogen and phosphorus are essential elements in plant and animal growth, and every organism derives them from external sources. However, the shortage of assimilable forms of nitrogen and phosphorus in the biosphere sets a limit to the growth of organisms on land and in water. Although some plants are capable of taking up organic compounds of phosphorus, or organic nitrogen compounds like urea or amino-acids, most of them incorporate these elements in the form of ammonia, nitrites, nitrates and phosphates. Nutrients are the most important factors limiting phytoplankton growth. In seawater, photosynthesis converts carbon, nitrogen and phosphorus into organic matter, these elements being taken up in the molar ratio of 106:16:1.

As the concentrations of organic nitrogen and phosphorus compounds in seawater depend on photosynthetic intensity and biomass mineralisation, they are subject to both diel and seasonal variability. Processes such as vertical diffusion, advection, upwelling or sedimentation of dead organisms and their microbial destruction contribute to a considerable extent to the redistribution of nitrogen and phosphorus compounds in the water column (Nausch and Nehring, 1997).

The objective of this work is to determine the relationship between nitrogen (nitrites, nitrates and ammonia) and phosphorus (phosphates and organic phosphorus) compounds on the one hand, and the oxygen content and the variable density stratification in the water column of the Gdańsk Deep on the other. The factors controlling the nitrogen and phosphorus cycles are considered extremely significant in existing and updated nutrient dynamic models of the Baltic Sea, which is why they have been accorded so much attention in these investigations. Studies of both long- and short-term biogeochemical cycles that take the hydrodynamic aspects of the region into account are necessary if the effects of eutrophication are to be predicted and counteracted.

2. Material and methods

The studies of short-term variability in chemical and physical parameters were carried out at a single station in the Gdańsk Deep ($\varphi = 54°52'$, $\lambda = 19°07'$) in 1989–1996 (Fig. 1). Nine cruises on board the naval craft 'Kopernik' were undertaken, each covering only the spring growing season

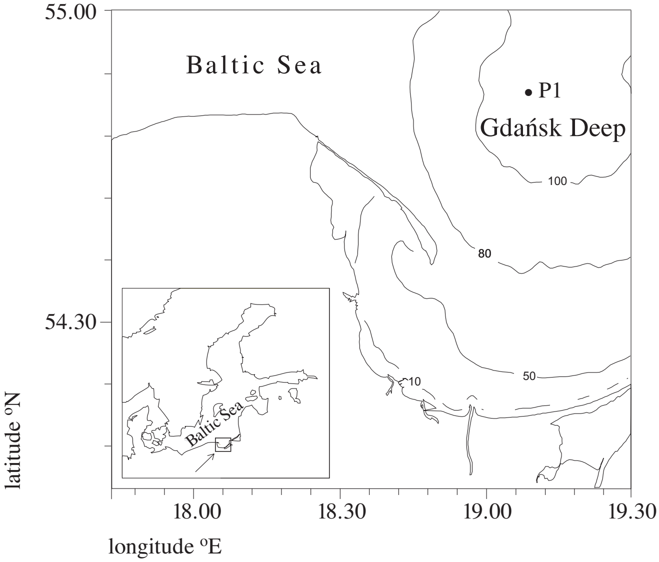


Fig. 1. Location of the sampling station P1 in the Gdańsk Deep

(May or June). During each cruise, measurements were made on board the stationary vessel and samples were collected from standard depths (0, 5, 10, 15, 20, 30... down to 100 m depth) over a period of 3–5 days, the time intervals between particular casts being 4, 2 and 1 h. Tab. 1 shows the number of vertical profiles done during each cruise and also gives the time intervals between consecutive profiles. Temperature and salinity *vs* depth were measured with an STD probe (MC 5 Hydro-Bios Salinity Temperature Bridge, Apparatebau, Kiel–Holtenau, Germany), while the water samples were collected in Niskin bottles. Nutrients were determined using the standard methods, dissolved oxygen by the Winkler method (Grasshoff *et al.*, 1983; UNEP/IOC/IAEA, 1988). The analytical precision

Table 1. Materials collected during each cruise in the Gdańsk Deep

Time intervals between consecutive profiles	22–24 May 1989	14–18 May 1990	28–31 May 1991	3–7 June 1991	2–6 June 1992	19–26 June 1993	29 April –5 May 1994	9–12 May 1995	18–24 June 1996
	Number of vertical profiles								
4 h	9	25	23	24	23	24	26	19	35
2 h								12	32
1 h						24	33		

in the medium concentration range of the inorganic nitrogen, phosphate and total phosphorus determinations ranged from 1 to 5%. The accuracy of the determinations was 0.03 μmol dm^{-3} at low phosphate concentrations < 0.2 μmol dm^{-3}, and 0.02 μmol dm^{-3} at low nitrate and nitrite concentrations < 0.15 μmol dm^{-3}. The detection limit of the phosphate, nitrate and nitrite concentrations was 0.01 μmol dm^{-3}, of ammonia 0.05 μmol dm^{-3}. Organic phosphorus was calculated by subtracting the phosphate concentration from the total phosphorus concentration. The relative density was calculated according to the international equation for the state of marine water by Dera (1992). The temperature and salinity measurements for 1994 are missing owing to the failure of the STD system.

3. Results

Considerable diel variability in the nutrient and oxygen concentration of the water column has been recorded over the last 8 years. During the spring, when nutrients were in greatest demand, their total removal from the euphotic layer (0–15 m) occurred only infrequently (Tab. 2). Concentrations of nitrates, nitrites and phosphates below the detection limit were noted a few times; ammonia was entirely absent only in June 1996. The greatest variability and the highest concentrations of organic phosphorus occurred in this layer. Mean nutrient concentrations were generally higher below the euphotic layer. Maximum nutrient concentrations occurred below the isohaline layer, where the amplitudes were also greatest. In spring the waters of the Gdańsk Deep were well aerated. Only in the near-bottom layer was a significant fall in oxygen content recorded. Values below 1 cm^3 dm^{-3} were noted in May of 1989 and 1995 and June of 1992 and 1993.

In spring nitrites made up the smallest proportion (1–6%) of the inorganic components of dissolved nitrogen in each of the layers examined. The proportions of nitrates and ammonia varied depending on depth and aeration. Nitrates made up 19–64% (mean 30%) and ammonia 30–90% (mean 65%) in the euphotic layer. In the deep-water part of the basin nitrates were dominant (60–75%), but when the oxygen content was low, the proportion of ammonia was the highest of all the inorganic compounds of nitrogen.

Table 2. Statistical characteristics of nitrogen and phosphorus compound concentrations [μmol dm^{-3}] and oxygen content [cm^3 dm^{-3}] in the water column of the Gdańsk Deep

Layer	Data	n	$X_a \pm SD$	Min	Max	n	$X_a \pm SD$	Min	Max	n	$X_a \pm SD$	Min	Max
		Nitrate				Nitrite				Ammonium			
	May 1989*	36	0.75 ± 0.35	0.23	2.02					19	1.41 ± 0.81	0.56	4.03
	May 1990	100	0.81 ± 0.21	0.34	1.65	100	0.10 ± 0.07	<LD	0.69	48	0.79 ± 0.31	0.30	1.51
	May 1991	91	0.26 ± 0.20	0.01	1.03	95	0.07 ± 0.07	0.01	0.40	54	0.97 ± 0.52	0.05	1.85
euphotic	June 1991	95	0.30 ± 0.87	0.01	1.76	94	0.05 ± 0.04	0.01	0.23	79	1.08 ± 0.47	0.05	2.54
	June 1992	92	0.30 ± 0.21	0.01	1.21	92	0.11 ± 0.10	<LD	0.38	86	0.86 ± 0.57	0.22	3.71
0–15	June 1993	94	0.59 ± 0.23	0.19	1.78	96	0.09 ± 0.07	0.01	0.43	67	1.50 ± 1.10	0.08	3.95
[m]	May 1994	123	0.67 ± 0.42	0.03	2.19	129	0.15 ± 0.11	0.01	0.62	133	1.32 ± 1.14	0.11	5.89
	May 1995	101	0.76 ± 0.74	0.02	2.94	108	0.28 ± 0.20	0.02	1.30	104	1.23 ± 0.92	0.12	2.65
	June 1996	197	0.33 ± 0.28	<LD	1.67	202	0.09 ± 0.11	<LD	0.57	200	1.15 ± 0.88	<LD	5.39
	May 1989*	29	0.79 ± 0.32	0.27	2.17					16	1.36 ± 0.59	0.56	2.42
	May 1990	124	2.30 ± 1.18	0.68	5.23	124	0.16 ± 0.14	0.02	1.20	60	0.95 ± 0.77	0.40	5.40
	May 1991	66	0.24 ± 0.20	0.01	1.24	72	0.08 ± 0.09	0.01	0.50	46	1.03 ± 0.61	0.05	2.37
isohaline	June 1991	71	0.18 ± 0.17	0.01	0.76	72	0.08 ± 0.13	0.01	1.14	64	1.04 ± 0.35	0.37	1.88
	June 1992	69	0.30 ± 0.25	0.01	1.70	69	0.09 ± 0.11	<LD	0.38	62	0.81 ± 0.54	0.11	3.21
	June 1993	72	0.61 ± 0.31	0.08	1.59	72	0.07 ± 0.05	0.01	0.21	49	1.03 ± 0.71	0.14	3.21
	May 1994	88	0.62 ± 0.57	0.03	5.05	97	0.16 ± 0.11	0.01	0.61	101	1.50 ± 1.23	0.11	6.92
	May 1995	73	0.93 ± 0.66	0.06	2.86	81	0.28 ± 0.19	0.02	0.91	77	1.11 ± 0.80	0.10	5.07
	June 1996	143	0.27 ± 0.24	<LD	1.62	148	0.09 ± 0.12	<LD	0.59	153	1.05 ± 0.82	0.05	5.07
	May 1989*	23	6.13 ± 3.43	1.05	9.96					15	1.37 ± 0.67	0.54	2.84
	May 1990	72	5.10 ± 1.27	3.04	7.72	72	0.17 ± 0.06	0.07	0.55	30	0.93 ± 0.84	0.43	5.40
	May 1991	47	2.85 ± 2.60	0.01	7.86	48	0.14 ± 0.26	0.01	1.83	35	1.58 ± 1.17	0.23	5.40
heterohaline	June 1991	68	4.03 ± 2.73	0.01	9.42	69	0.05 ± 0.05	0.01	0.37	66	1.33 ± 0.59	0.35	3.72
	June 1992	56	4.04 ± 3.07	0.11	9.89	56	0.13 ± 0.12	0.01	0.44	54	1.11 ± 0.90	0.23	4.69
	June 1993	72	4.15 ± 2.41	0.10	9.98	72	0.90 ± 0.88	0.04	3.10	51	1.33 ± 1.25	0.18	8.79
	May 1994	91	4.06 ± 1.87	0.05	8.29	99	0.20 ± 0.12	0.04	0.73	101	1.25 ± 1.28	0.17	8.27
	May 1995	74	1.93 ± 1.58	0.07	7.22	81	0.36 ± 0.21	0.01	1.05	77	2.40 ± 2.23	0.10	11.57
	June 1996	145	0.89 ± 0.45	0.02	2.24	149	0.12 ± 0.11	0.01	0.56	152	1.22 ± 1.22	0.08	7.40

Table 2. (continued)

Layer	Data	n	$X_a \pm SD$	Min	Max	n	$X_a \pm SD$	Min	Max	n	$X_a \pm SD$	Min	Max
		Phosphate				Organic phosphorus				Oxygen			
	May 1989	36	0.13 ± 0.05	0.02	0.29	20	0.28 ± 0.16	0.05	0.72	35	8.01 ± 0.97	4.97	9.11
	May 1990	100	0.34 ± 0.13	0.12	0.68	77	0.38 ± 0.23	0.01	1.05	100	7.60 ± 0.35	6.38	8.52
	May 1991	94	0.20 ± 0.18	0.01	0.61	93	0.75 ± 0.89	0.03	2.90	95	8.73 ± 0.78	6.32	10.00
euphotic	June 1991	95	0.11 ± 0.07	0.01	0.30	89	1.00 ± 0.42	0.09	2.05	95	7.76 ± 1.15	4.94	9.76
	June 1992	87	0.22 ± 0.14	0.01	0.60	65	0.18 ± 0.17	0.01	0.82	87	8.62 ± 0.63	6.40	10.12
0–15	June 1993	168	0.21 ± 0.30	0.02	3.28	69	0.31 ± 0.58	0.02	3.96	95	6.88 ± 0.29	5.67	7.90
[m]	May 1994	208	0.59 ± 0.44	0.04	2.94	100	0.75 ± 0.77	0.05	6.93	132	9.46 ± 1.35	5.44	12.30
	May 1995	106	0.49 ± 0.40	0.01	1.89	91	0.26 ± 0.27	0.01	1.64	103	9.42 ± 0.67	5.42	11.37
	June 1996	205	0.11 ± 0.13	<LD	0.97	86	0.27 ± 0.47	0.01	2.95	196	10.70 ± 0.9	6.49	11.91
	May 1989	29	0.15 ± 0.07	0.06	0.29	16	0.15 ± 0.07	0.02	0.31	29	7.34 ± 1.18	4.87	9.20
	May 1990	124	0.57 ± 0.21	0.08	1.36	95	0.30 ± 0.20	0.01	0.97	123	7.18 ± 0.54	4.76	8.38
	May 1991	72	0.22 ± 0.13	0.01	0.70	70	0.53 ± 0.22	0.05	0.93	72	8.22 ± 0.64	6.31	9.30
isohaline	June 1991	72	0.17 ± 0.09	0.02	0.38	66	0.62 ± 0.29	0.22	1.63	72	7.11 ± 1.22	4.72	8.71
	June 1992	67	0.33 ± 0.21	0.01	0.98	48	0.17 ± 0.15	0.01	1.09	66	8.44 ± 0.43	7.31	9.69
	June 1993	126	0.25 ± 0.22	0.02	1.98	51	0.25 ± 0.30	0.02	1.58	72	7.20 ± 0.83	4.88	8.55
	May 1994	156	0.66 ± 0.44	0.09	2.16	72	0.55 ± 0.41	0.10	2.37	99	8.38 ± 1.36	5.11	11.19
	May 1995	80	0.57 ± 0.41	0.03	1.92	71	0.23 ± 0.25	0.03	1.01	76	8.48 ± 0.83	4.82	9.99
	June 1996	154	0.14 ± 0.18	0.01	1.35	64	0.27 ± 0.36	0.01	1.91	144	10.99 ± 0.6	7.01	11.97
	May 1989	24	0.66 ± 0.48	0.17	1.88	12	0.09 ± 0.23	0.17	0.82	24	4.31 ± 2.60	0.83	7.96
	May 1990	71	1.12 ± 0.44	0.08	2.53	55	0.27 ± 0.24	0.02	1.19	71	5.53 ± 1.28	2.73	7.72
	May 1991	48	0.85 ± 0.51	0.06	1.91	43	0.84 ± 0.52	0.10	2.63	48	5.76 ± 1.93	1.79	8.62
heterohaline	June 1991	71	1.02 ± 0.55	0.08	2.17	66	0.84 ± 0.46	0.08	3.15	71	4.20 ± 2.22	1.26	8.68
	June 1992	55	0.95 ± 0.48	0.10	1.91	41	0.16 ± 0.21	0.10	1.14	55	5.03 ± 2.87	0.97	8.69
	June 1993	126	3.20 ± 3.03	0.08	13.40	41	0.68 ± 1.16	0.08	5.97	72	4.02 ± 2.50	0.71	7.88
	May 1994	155	2.45 ± 0.83	0.14	4.63	56	0.48 ± 0.52	0.03	2.35	98	4.61 ± 1.20	2.01	9.57
	May 1995	78	2.25 ± 1.63	0.05	5.68	57	0.45 ± 0.63	0.05	3.46	78	3.71 ± 3.00	0.38	9.43
	June 1996	155	0.85 ± 0.46	0.01	1.93	63	0.43 ± 0.59	0.01	2.86	143	6.69 ± 0.82	2.54	10.46

* sum of nitrate and nitrite concentrations

n – number of data, X – mean value, SD – standard deviation; Min – minimum value, Max – maximum value, LD – limit of detection

4. Discussion

4.1. Temperature, salinity, nutrients and oxygen

Nutrient concentrations in seawater are the resultant of numerous overlapping processes. Some of these are of a periodic nature related to the variability in the diurnal rate of primary production or to periodic dynamic phenomena in the sea (seiches, internal waves). Others, such as erosion of the sea bottom or shore due to the action of currents or storms, the discharge of dissolved and suspended matter from the land or the atmospheric precipitation of aerosols on to the sea surface are not diurnal in nature; they depend on the speed and direction of the wind. The diversity and complex nature of the physical, chemical and biological processes occurring in the water column affect the concentrations and the transformation rates of the substances in question.

During the nine cruises in 1989–1996 the earliest studies in the spring were carried out in April–May 1994 (the temperature and salinity measurements for this period are missing, however) and in early May 1995. At this time the water temperature was still rather low (6–6.5°C) and no distinct thermocline had yet developed; the isohaline layer stretched down to 70 m. Below that level and practically down to the bottom there was a pronounced rise in salinity to > 11 PSU (Fig. 2 – profile A). Similar temperatures and salinities were recorded in 1991 when at the end of May and the beginning of June the temperature was 8–9° without a distinct thermocline being present. At that time, however, the situation at 70 m was different – there was a distinctly rising salinity gradient (max *ca* 10 PSU) separating the two water masses (Fig. 2 – profiles D1 and D2). As the Gdańsk Deep lies some way off the main route of oceanic water flow, it is not always replenished by it. Even so, high salinities of the order of 11–12 PSU should be ascribed to the intense exchange of water through the Danish Straits. Winter inflows of oceanic waters reach the Gdańsk Deep in spring, reinforcing the density structure of the waters there. Such advection events were observed with varying intensity in 1991, 1992, 1993, 1994, 1995 (Cyberska 1991, 1992, 1993, 1995, 1996; Łysiak-Pastuszak, 1994). The 1990 studies were also conducted in the second half of May, when there was thermal layering from the surface down to 20 m (Fig. 2 – profile B). Above the weak thermocline, the water temperature was in excess of 10°C, while below the thermocline it was *ca* 6°C and the isothermal layer extended down to the bottom. The studies conducted in May 1990 were exceptional, as in that period there was no salinity gradient in the near-bottom layer

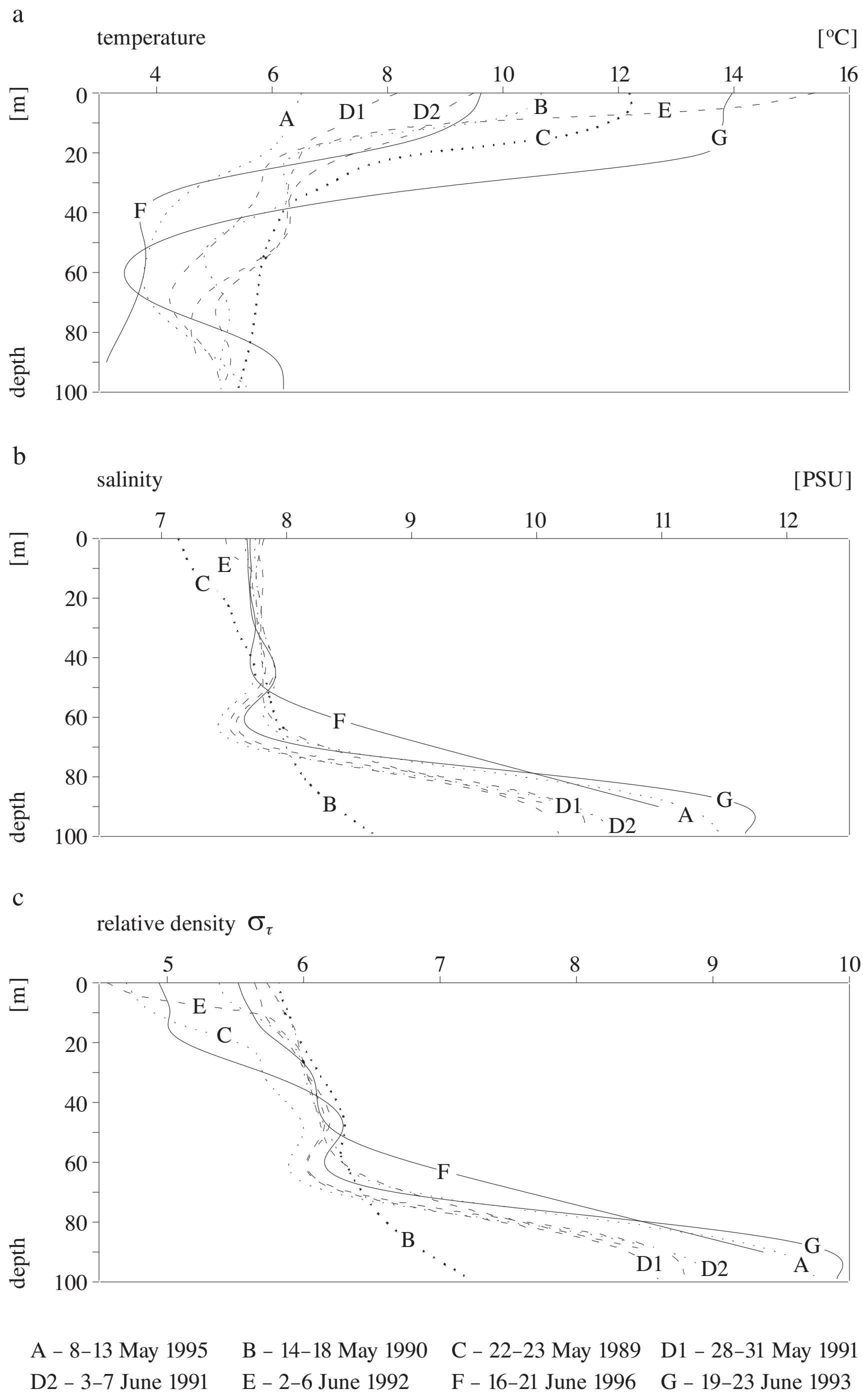


Fig. 2. Vertical profiles of mean temperature (a), salinity (b) and density (c) in the study periods in the Gdańsk Deep

and the density σ_T there was close to 7. This situation was recorded in monitoring studies carried out in the southern Baltic Sea. According to Cyberska (1991), the fact that the water layer down to the bottom was isohaline was due to prolonged stagnation in the southern Baltic, including the Gdańsk Deep.

The June 1992 studies showed the temperature in the surface layer of the Gdańsk Deep to be relatively high (*ca* 15°C), but from 5 m downwards the temperature dropped markedly (Fig. 2 – profile E), reaching a maximum gradient of 0.7°C m^{-1} at 5–20 m. In the deep layer, from 70 m downwards, the salinity increased to a maximum of 10 PSU. Comparison of temperature measurements in 1992 and 1993 indicates that the thermocline recorded in the second half of June 1993 was much better pronounced as compared to the one in 1992. Located at *ca* 20 m, it had a single 20-metre-thick isothermal water layer above it (Fig. 2 – profile G). Like the year before, there was a distinct halocline and the near-bottom σ_T reached a value of 10.

These highly variable vertical distributions of physical parameters must have affected the vertical distributions of nutrients and oxygen. The salinity gradients at 70 m recorded in May 1991, June 1993 and May 1995 set up a natural barrier, causing nitrates, nitrites and phosphates to be stratified, so that they accumulated in the near-bottom layer (Fig. 3). The strong salinity gradient in the halocline coincided with the considerable nitrate and phosphate gradients of 0.5 and 0.35 μmol dm^{-3} m^{-1} respectively.

The absence of a halocline in May 1990 resulted in the lack of distinct layers in the near-bottom waters, as occurred in early June 1992 (Fig. 4). This favoured turbulent water mixing, and consequently, the much easier transport of nutrients from the deeper layers towards the euphotic zone. In 1990 the 1 μmol dm^{-3} isoline of nitrates and 7.5 isohaline were located at *ca* 20 m, whereas in June 1992, as a result of strong density stratification, they were found at a depth of *ca* 70 m. The weakening of the halocline resulted in good aeration of the near-bottom waters, which are usually either poorly oxygenated or even anoxic. The 6 cm^3 dm^{-3} oxygen isoline reached almost to the bottom. The lack of oceanic inflows from the Danish Straits region led to stagnation in 1990, even though the water was fairly well aerated (Cyberska, 1991). The halocline must therefore be considered a natural barrier to the unconstrained transport of substances. Since the halocline strongly restricts vertical mixing, changes in nutrients and oxygen concentrations in the deep water are mainly caused by advection and convection, vertical diffusion, microbial destruction of organic matter and exchange with the sediment (Nausch and Nehring, 1997; Falkowska, 1998).

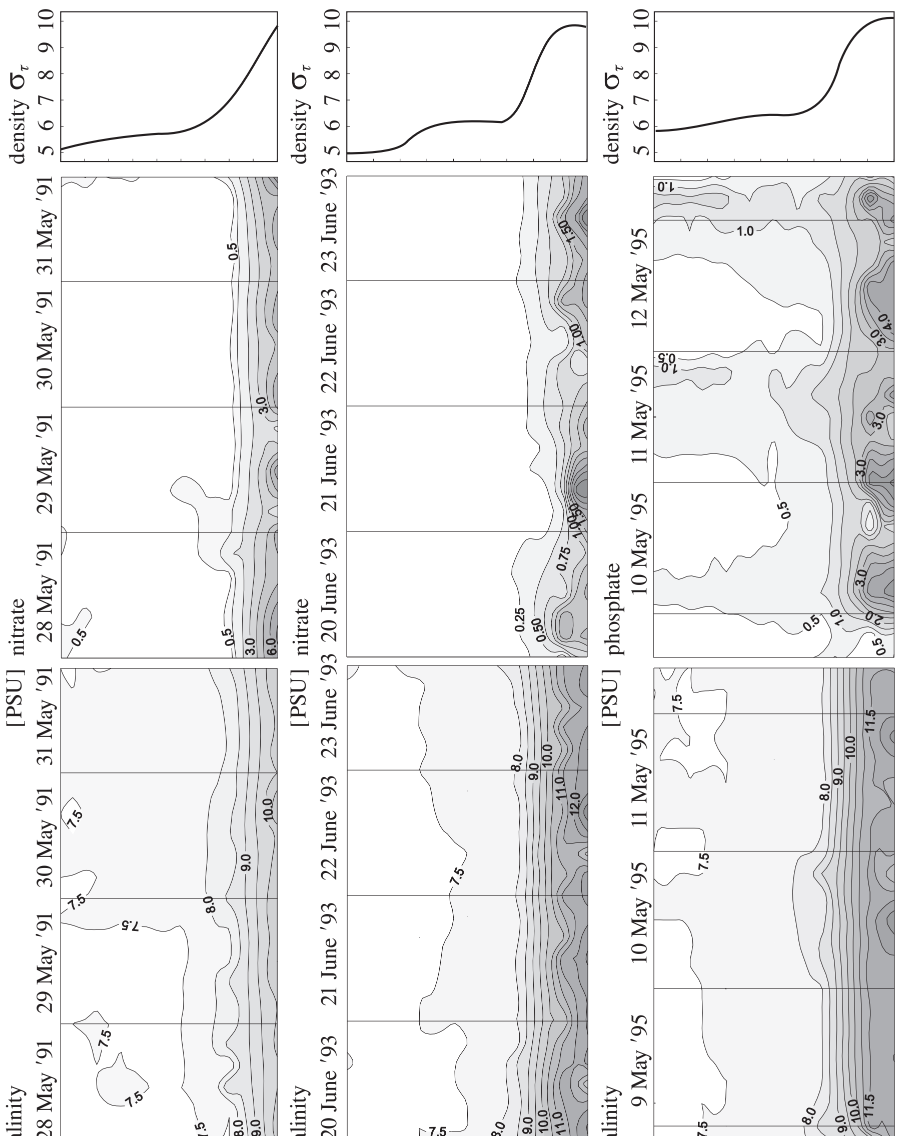


Fig. 3. Temporal changes in nitrate and phosphate concentrations [mmol m^{-3}] and salinity in the water column of the Gdańsk Deep

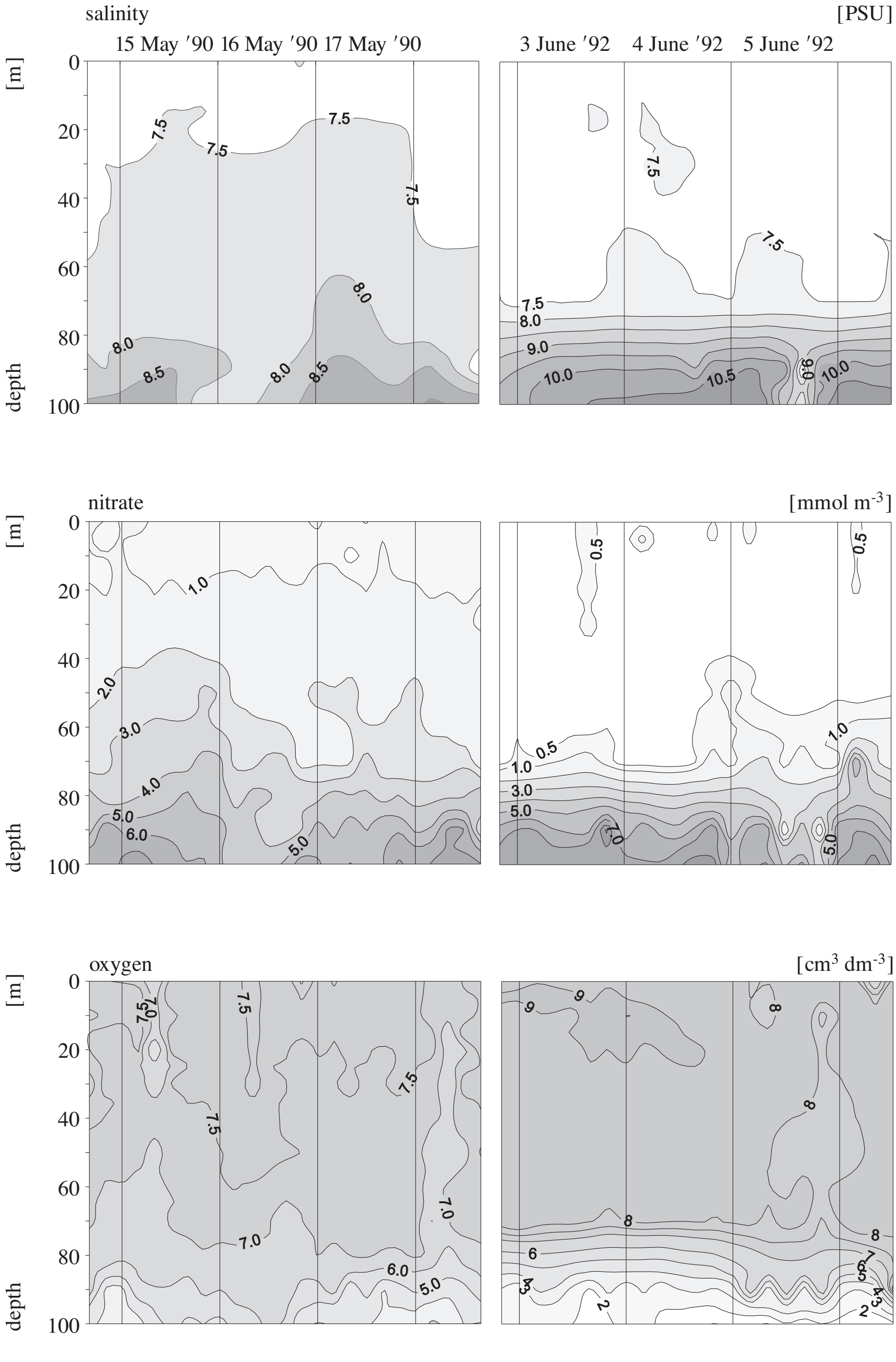


Fig. 4. Temporal changes in nitrate and oxygen concentrations and salinity in the water column of the Gdańsk Deep

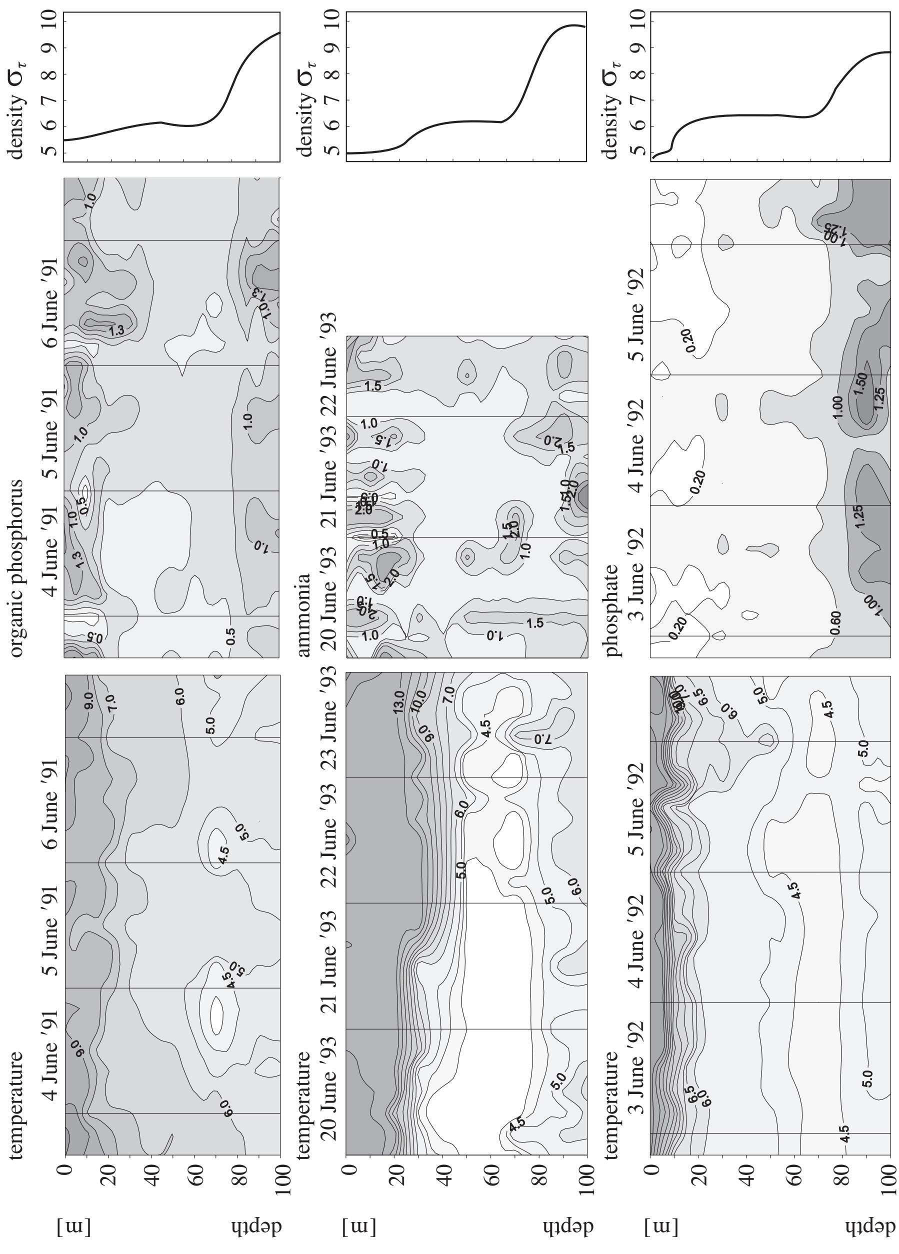


Fig. 5. Temporal changes in nitrogen and phosphorus compounds [mmol m^{-3}] and temperature [°C] in the water column of the Gdańsk Deep

In the surface layer there is another natural barrier hindering the free transport of chemical substances – the thermocline (Fig. 5). The Gdańsk Deep in early spring (April, May) is characterised by either the lack of a density gradient due to thermal layering, or a weak thermocline. A relatively stable thermal gradient is present at 20 m at the end of spring (June). The seasonal thermocline can, however, be disrupted by cool and windy weather (Wulff *et al.*, 1990). Under such conditions phytoplankton can take up nutrients present down to the pycnocline, even though they are beyond the euphotic layer. The lack of thermal layering in the Gdańsk Deep at the end of April and the beginning of May 1994 (Fig. 6) could have resulted from unfavourable weather conditions. A clear density gradient was

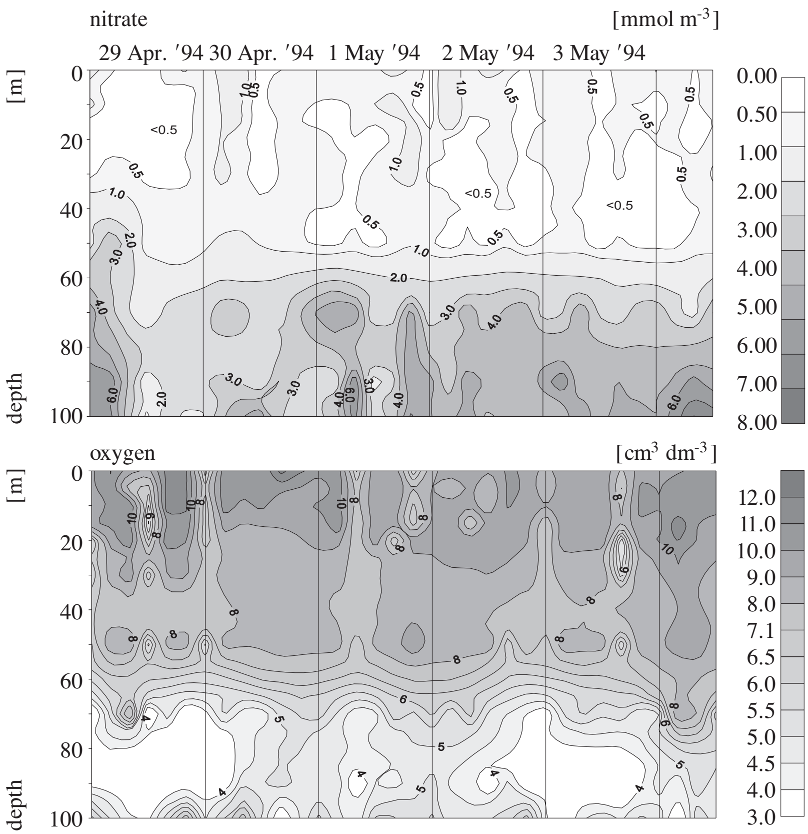


Fig. 6. Temporal changes in nitrate and oxygen concentrations in the water column of the Gdańsk Deep

then found as deep as 60 m; this finding concurred with monitoring studies (Cyberska, 1995) showing that by the end of April 1994 a halocline had also formed at 60 m (isohaline 7.5 PSU). Winter inflows of oceanic water

(December 1993, March 1994) reinforced the density structure and raised the deep-water layer. At that time the productive layer of the sea (down to 15 m) and below the euphotic layer were characterised by a high oxygen content (> 9 cm^3 dm^{-3}). This suggests that nitrogen and phosphorus compounds penetrating from the entire water column above the halocline were sustaining intensive primary production. The additional source of the nitrates, which intensify primary production, was the outflow of the River Vistula (Niemirycz and Borkowski, 1995).

The thermal-salinity stratification greatly affects the oxygen content. The oxygen concentrations in the surface layer are usually high, while those in the near-bottom layer drop to *ca* 1–2 cm^3 dm^{-3} (Tab. 2). In May 1995 there were some short periods of a few hours, when the oxygen content dropped to 0.2–0.5 cm^3 dm^{-3}. An exceptional situation was encountered in May 1990 when the lack of a halocline gave rise to an oxygen content of 6 cm^3 dm^{-3} in the deep water layers (Fig. 4).

4.2. Short-term aspects of the nitrogen and phosphorus cycles

In the open Baltic Sea primary production is maintained primarily by nutrient recycling, so production and destruction of organic matter play a key role in the nitrogen and phosphorus cycles. In the sea these cycles differ from those on land, and bacteria are regarded as playing an important role in the decomposition of organic matter. In the case of phosphorus, this entails the conversion of organic phosphorus into phosphates, and the cycling time is usually short – from a few minutes to a few days at summer water temperatures. The nitrogen cycle is more complicated, and nitrification, occurring in two phases in the presence of oxygen, is decisive. Whereas light inhibits the activity of nitrite and nitrate bacteria, it stimulates the assimilation of nitrogen compounds by phytoplankton. Olson (1981) demonstrated that the first phase of nitrification begins when the minimum light dose is *ca* 0.2–2% of that reaching the surface. For this reason, nitrite bacteria are incapable of competing with phytoplankton for ammonia, which leads to accumulation of nitrites below the thermocline.

This susceptibility to radiation in the euphotic layer means that nitrification can take place there only at night. It is thus an additional process enriching this layer with nitrates. By contrast, bacterial nitrification in the aphotic layer may continue throughout the 24 h period (Fig. 7), since it lies beyond the range of the radiation.

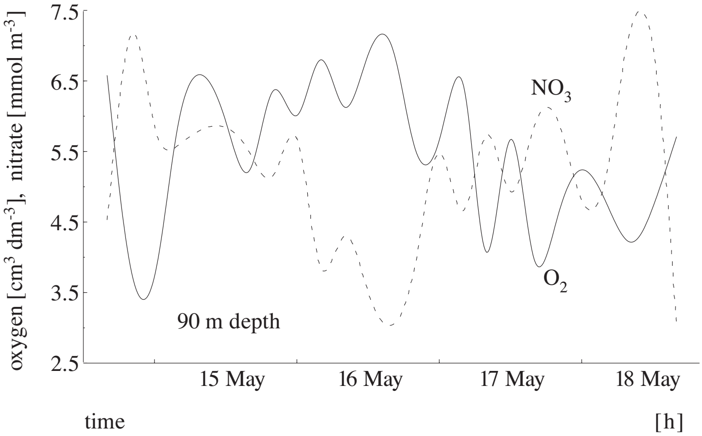


Fig. 7. Diurnal changes of oxygen and nitrogen concentrations measured in 14–18 May 1990

During the springs of the 9-year study period, a statistically significant negative correlation was found between the nitrate and oxygen concentrations in the aphotic part of the isohaline layer at 70 m depth:
NO_3 (μmol dm^{-3}) = $5.75 - 0.53$ O_2 (cm^3 dm^{-3}) (r = –0.55, p < 1%, n = 371). It seems that the diminishing oxygen concentrations are partly connected with the rising nitrate concentrations due to nitrification.

Ronner (1983) states that in the deep waters of the Baltic Sea denitrification takes place when the oxygen content is *ca* 0.2 cm^3 dm^{-3}. In fact, in June 1993 and May 1995, when oxygen conditions at the bottom of the Gdańsk Deep were poor, a significant positive correlation between the nitrate and oxygen concentrations was found at 100 m depth:
NO_3 (μmol dm^{-3}) = –0.28 + 1.06 O_2 (cm^3 dm^{-3}) (r = 0.69, p < 5%, n = 36). At the same time concentrations of phosphate versus oxygen were negatively correlated:
PO_4 (μmol dm^{-3}) = –3.67 – 0.36 O_2 (cm^3 dm^{-3}) (r = –0.56, p < 1%, n = 736).

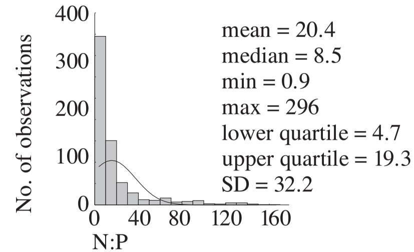
Trzosińska (1990) obtained a similar regression equation for the abyssal waters of the Gdańsk Deep, based on year-round data from 1961–1983. There are, however, some differences between the coefficients published earlier and nowadays. Most probably, they are due to the different, seasonal approach to the calculations, as well as to long-term trends in the variations of oxygen and nutrient concentrations (Trzosińska and Łysiak-Pastuszak, 1996a) and in the primary production recorded in the Gdańsk Basin (Renk, 1997).

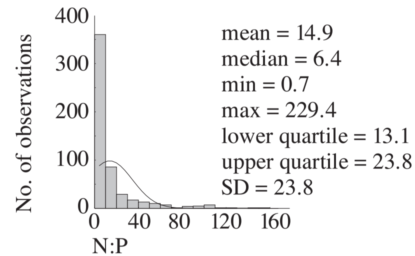
The N:P ratio is often considered to be a measure of potential productivity in seawater. Although nitrogen and phosphorus compounds are not the only factors controlling the growth of planktonic organisms, they are often regarded as limiting primary production. The optimum molar ratio $N(NH_4{}^+ + NO_3{}^- + NO_2{}^-):P(PO_4{}^{3-})$ in the isohaline layer of the Baltic varies from 14 to 16, depending on the species composition of the phytoplankton population (Graneli *et al.*, 1990; Trzosińska 1990, 1992; Wulff *et al.*, 1990).

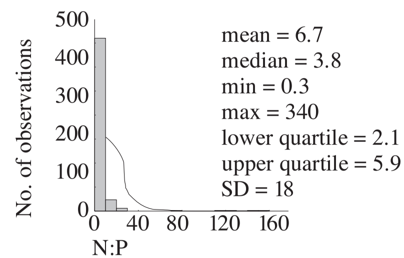
In the springs of 1989–1996, the mean N:P ratio in the euphotic layer approached the optimum level, except in May 1990, 1994 and 1995 when it was distinctly lower (Tab. 3). 75% of the data showed a value lower than 7, which indicates that the level of nitrogen compounds is insignificant. At the end of May and June in 1989, 1991, 1992, 1993 and 1996, the N:P ratio rose as a consequence of a decrease in phosphate concentration. Although high N:P ratios were recorded in April and May, they were not as numerous as in June when 25% of these ratios had values above 25. Such a large number of high N:P ratios may be evidence for a phosphate deficit and a change in the limiting factor – from nitrogen compounds in early spring to phosphates in late spring.

According to Trzosińska and Łysiak-Pastuszak (1996b), the average seasonal cycle of assimilable nitrogen and phosphorus compounds in the eutrophic zone of the Gdańsk Deep were subject to marked changes in 1989–1993 as compared with the previous decade. The minimum concentrations of total nitrate and nitrite had shifted from July to May, that of phosphate from July to June. The results of these studies could explain the changes in the limiting factor during recent springs. High mean N:P ratios of 89 were earlier recorded in spring in strongly eutrophicated regions like the Pomeranian Bay (Trzosińska, 1992). The negative trend in phosphate concentration in the surface layer of the Gdańsk Deep in 1978–1988 was still in evidence throughout the Gulf of Gdańsk, except in the Vistula estuary, where the variations were statistically insignificant (Nehring *et al.*, 1990). Long-term measurement cycles (1979–1993) indicate a statistically significant negative trend in phosphate contents during the winter accumulation in the Gdańsk Deep and a positive trend in the N:P ratio (Trzosińska and Łysiak-Pastuszak, 1996a,b). In the light of the data given here and information about trends, it seems highly questionable whether only nitrogen is indeed a limiting factor in spring.

Layer	Date	Min	Max	Lower quartile 25%	Upper quartile 75%
euphotic 0–15 [m]	22–24 May 1989	6.6	69.00	13.2	26.2
	14–18 May 1990	2.0	17.9	3.4	8.1
	28–31 May 1991	1.2	142.0	5.7	16.7
	3–7 June 1991	1.5	103.7	7.9	26.5
	2–6 June 1992	1.1	108.5	3.7	9.7
	19–26 June 1993	0.9	80.0	6.5	18.4
	29 April–5 May 1994	1.3	48.8	3.1	7.2
	9–12 May 1995	0.9	244.0	3.4	8.7
	18–24 June 1996	1.1	296.0	8.1	63.9
isohaline	22–24 May 1989	5.1	48.7	10.4	24.3
	14–18 May 1990	2.3	50.8	4.7	8.2
	18–31 May 1991	0.7	106.0	3.4	12.3
	3–7 June 1991	1.8	57.0	5.8	14.5
	2–6 June 1992	1.3	101.0	2.2	5.9
	19–26 June 1993	1.8	40.4	4.5	10.6
	29 April–5 May 1994	14	64.4	2.8	6.8
	9–12 May 1995	1.0	33.3	2.7	6.9
	18–24 June 1996	0.8	229.4	7.1	45.1
heterohaline	22–24 May 1989	5.8	31.0	10.7	16.7
	14–18 May 1990	3.4	340.0	4.8	7.8
	18–31 May 1991	0.6	80.3	3.7	6.9
	3–7 June 1991	1.9	27.6	4.3	6.2
	2–6 June 1992	1.5	26.7	3.4	6.4
	19–26 June 1993	0.5	91.0	1.4	4.6
	25 April–5 May 1994	0.7	15.3	1.7	2.9
	9–12 May 1995	0.3	142.0	1.2	5.6
	18–24 June 1996	0.5	82.2	1.5	4.1







symbols as in Tab. 2

Table 3. $NO_3 + NO_2 + NH_4 : PO_4$ ratio in the water column of the Gdańsk Deep

Early spring was notable for frequent low concentrations of nitrogen compounds, particularly during the daytime in the euphotic layer. Thus, the N:P ratio dropped to < 2 (Tab. 3). This ratio usually increased distinctly once in every 24 h, more often at night between 10 and 30 m. At the end of May and the beginning of June there is usually a short-lived late-spring bloom in the southern Baltic. This period (May 1991) was characterised by a permanent low concentration of assimilable nitrogen, but from the beginning of June 1991, a low N:P ratio noted only sporadically. The beginning of June 1992 was, however, somewhat different as compared to June 1991: for a few consecutive days the concentration of nitrogen was low, after which the N:P ratio abruptly rose to a very high level (> 60) at the thermocline depth (Fig. 8).

The diel fluctuations in the N:P ratio displayed precisely the opposite pattern to that of the diurnal fluctuations in chlorophyll *a* concentration and primary production (Renk, 1997; Renk *et al.*, 1985). The N:P ratio was generally low during the day, but increased at night. This regularity was not usually observed in June.

The increase in nitrogen concentrations and the consequent increase in the N:P ratio, the latter to a level exceeding the optimum, may have been due to the nitrification of organic matter and/or to the ammonification of phyto- and zooplankton excreta; the latter process intensifies during the night (Corner and Davies, 1971; Harrison *et al.*, 1983). The nitrogen compounds in the euphotic layer consisted principally of ammonia, with an average 24 h contribution to the entire nitrogen pool of 58%, increasing to as much as 90% during the night. In all the study periods, ammonia was often predominant down to the halocline (except in May 1990). This prevalence could also have been due to a preference for nitrate among the vernal phytoplankton species. The situation in spring therefore differs from that at other seasons, when the uptake preference is as follows: ammonia > urea > nitrates (Sahlsten *et al.*, 1988). Below the isohaline layer N:P was low; according to Tamminen (1990), this is typical of the subhalocline water masses in the Baltic Sea and displayed only slight seasonal variations, corresponding to the seasonal changes in the oxygen supply in deep water (Trzosińska, 1992). Here the nitrate concentration reached *ca* 75% and ammonia accounted for *ca* 20% of the total inorganic nitrogen. Statistically significant nitrate accumulation in the near-bottom layer occurred only during the oxic period. Trzosińska (1992) states that during 1979–1988 its rate in the subhaline water of the Gdańsk Deep was 2–3 times greater than in the upper water layers. Earlier, Nehring (1989) had made a similar observation in the Bornholm Deep. This author pointed

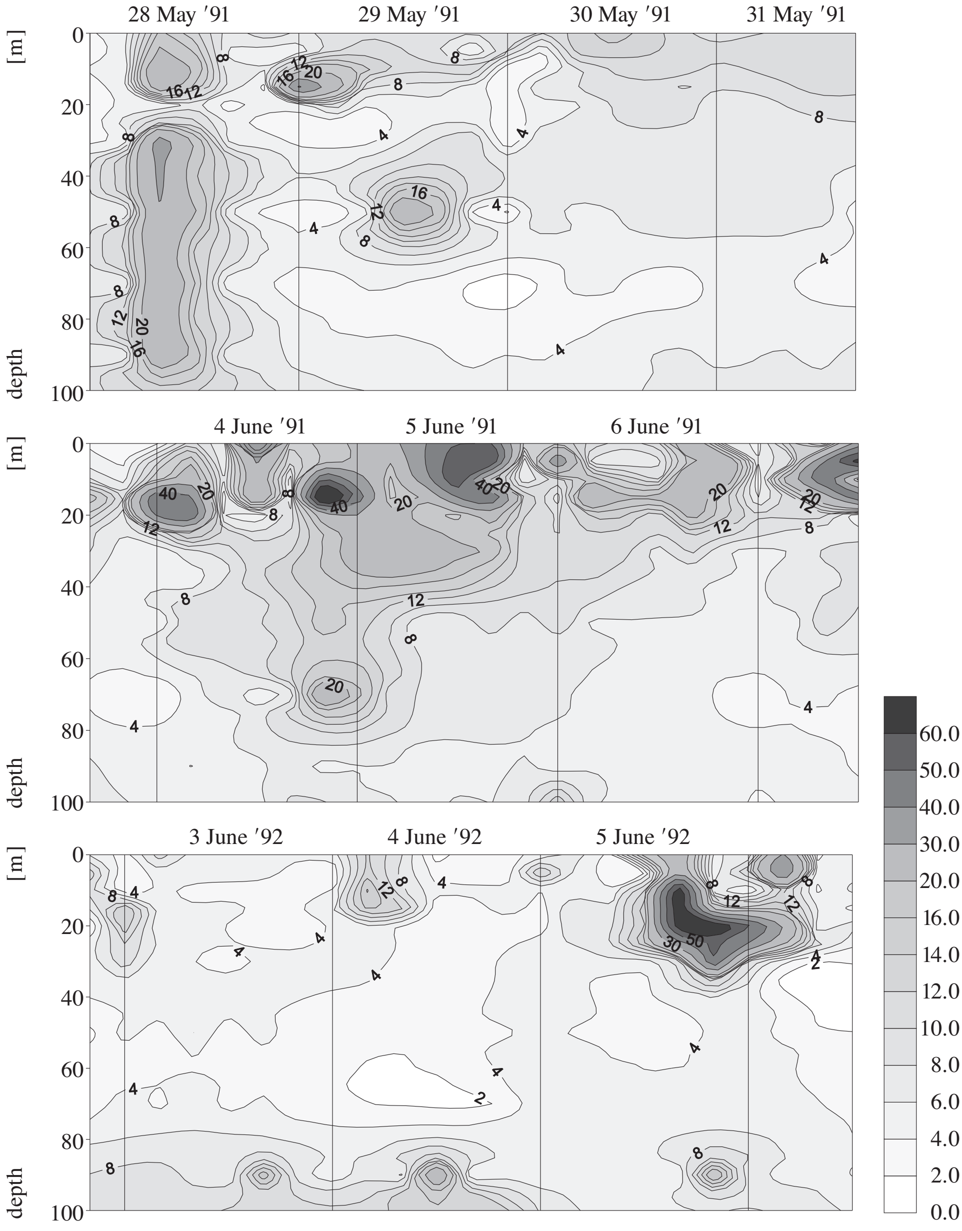


Fig. 8. Temporal changes in the N:P ratio in the water column of the Gdańsk Deep during the late-spring growing season

out that the trend coefficient in oxygenated waters could be regarded as an approximate measure of anthropogenic influences on nitrate and phosphate concentrations in the deep waters of the Baltic Sea.

5. Conclusions

- Favourable oxygen conditions in the springs of 1989–1996 were found throughout the water column of the Gdańsk Deep. The weak stratification of water density (recorded in May 1990) favours the transport of nutrients from deep layers into the euphotic layer. The turbulent mixing of water aerated the near-bottom waters, which are usually either poorly oxygenated or periodically anoxic.
- The reinforcement of the halocline after oceanic inflows suppressed cross-halocline mixing and impeded vertical transport of oxygen and nutrients. In the heterohaline water, the oxygen content decreased to < 6 cm^3 dm^{-3}. Only in the near-bottom layer (100 m depth) was a significant fall in oxygen content recorded. At the same time the concentration of nitrogen and phosphorus compounds increased compared to the isohaline layer.
- During the springs of the nine-year study period, a statistically significant negative correlation was found between the nitrate and oxygen concentrations in the isohaline water at 70 m depth.
- When the oxygen conditions at the near-bottom water (100 m depth) were poor a significant positive correlation between nitrate and oxygen concentrations was found. At the same time concentrations of phosphate versus oxygen were negatively correlated.
- In the surface layer, the thermocline sets up an additional seasonal natural barrier to the transport of chemical substances towards the productive surface layer.
- The N:P ratio varied with respect to the diel fluctuations of nutrient concentrations in the euphotic layer. It was generally low during the day, sometimes < 2, and increased at night.
- In the euphotic layer the mean N:P ratio approached the Redfield number. In early May the N:P ratio was distinctly lower – 75% of them were < 7 in value. This ratio rose at the end of May and June (upper quartile = 25). This seems to be in accordance the average seasonal cycle of nutrients observed in recent years and reflects the change in limiting factor from nitrogen compounds in early spring to phosphates in late spring.

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