Short-term variations in the concentrations of suspended particles, chlorophyll *a* and nutrients in the surface seawater layers of the Gdańsk Deep

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Particles
Chlorophyll *a*
Nutrients
Microlayer
Gdańsk Deep

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Abstract

An important interface between the atmosphere and sea, the sea-surface microlayer is a collection phase for many natural and anthropogenic materials, serving both as a source and a recipient of materials from the atmosphere and the water column.

Samples of sea-surface microlayer and subsurface bulk water were collected at short time intervals (every 1 h and every 4 h) in two periods: 2–6.06.1992 and 30.04–4.05.1994 and analysed for particle concentration with a Multisizer II Coulter Counter.

The results present diurnal variations in particle numbers and their distribution functions. The data illustrate the effect of the chlorophyll *a* and nutrient contents on particle concentration.

Both particle concentration and chlorophyll *a* content underwent periodic fluctuations. Maximum values were recorded in the morning and afternoon hours.

1. Introduction

Particles of suspended matter control the physical and chemical processes in the sea. For example, the quantity of such particles in unit volume of seawater affects its optical, acoustic and chemical properties. Furthermore, several elemental biogeochemical cycles are based on the migration of substances suspended in seawater (Simpson, 1982). The higher the concentration of reactive elements and compounds in seawater, the faster their removal from the dissolved to the suspended phase, and subsequently the greater their sedimentation mass. As a result of its sorptive properties, therefore, suspended matter exerts a significant influence on the chemistry and structure of marine sediments.

Suspended matter particles originate from four major sources of varying efficiency, depending on the type of basin and its geographical location:

- riverine input of terrigenic material;
- atmospheric input of material produced by weathering and during volcanic eruptions, and from anthropogenic sources;
- resuspension from sediments as a result of the action of erosive marine currents;
- autogenic biological production.

Several authors (Manjo, 1978; Lambert *et al.*, 1981; Richardson, 1980 cited by Simpson, 1982) suggest that suspended matter particles are composed of biogenic silica and calcium, organic matter, fecal balls and loamy material. Simpson (1982) found that organic matter predominated in large-diameter suspended particles, particularly in the uppermost surface-water layer, where diminutive neuston organisms prevail. Viscosity and atmospheric pressure are responsible for the formation of the surface film, to which the neuston organisms adhere. Consisting of bacteria, fungi and algae (Pliński, 1992; Rheinheimer, 1987; Sieburth, 1971), this surface neuston population has adjusted anatomically and physiologically to the living conditions in the surface film, which include exposure to intensive solar radiation and sudden changes in temperature. This population is from 10 to 10 000 times more numerous than the phytoplankton population found several centimetres deeper (Hardy and Apts, 1984; Norkrans, 1980; Wandschneider, 1979).

This paper presents the results of a study of the distribution and size of suspended particles in relation to the time of day; background analyses of chlorophyll pigment content and nutrient concentrations were done. A description of the diurnal transformations undergone by suspended matter is attempted.

2. Material and methods

The experimental part of the study was carried out during two periods: 2–7 June 1992 and 30 April – 5 May 1994, on board ORP 'Kopernik', anchored at a measuring station over the Gdańsk Deep ($\phi = 55°01'$N, $\lambda = 18°42'$E). In 1992 seawater samples were collected at 4 h intervals; in 1994, every hour. Plate-surface-microlayer samples (PM) 90 ± 16.6 μm in width were collected with a 30×30 cm glass plate (Harvey and Burzell, 1972). Screen-surface-microlayer samples (EM) 242 ± 39.8 μm in width

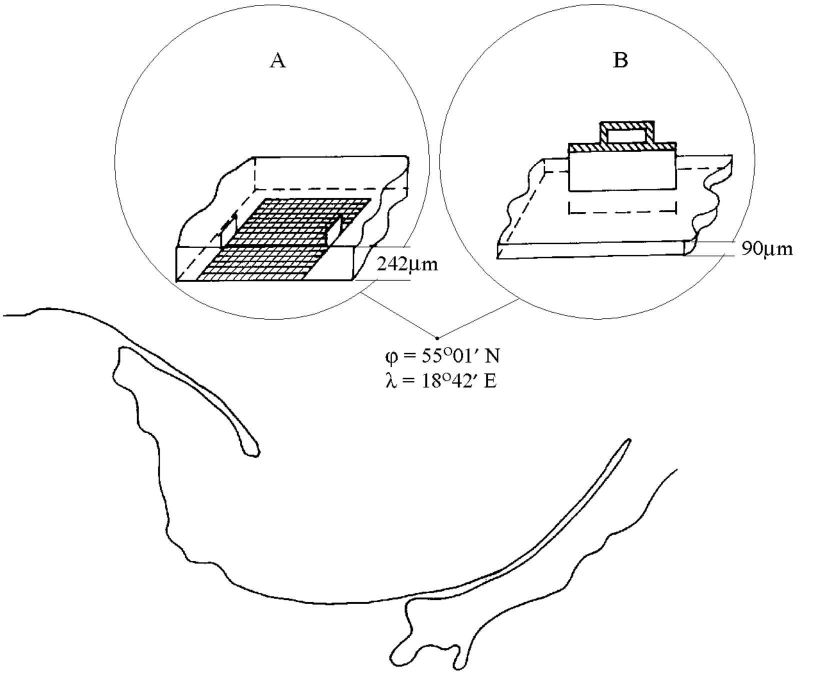


Fig. 1. Location of the sampling station in the Gdańsk Deep (2–6.06.1992; 30.04.–04.05.1994), and the sampling method from the surface microlayer water: screen technique for the EM microlayer (A), glass plate technique for the PM microlayer (B)

were collected with a Garrett net (Garrett, 1965). Water from the subsurface layer was taken by immersing a polyethylene bottle at about 15 cm depth (Fig. 1). Water samples designated for particle analysis were frozen immediately. Simultaneously, water samples for nitrate and phosphate determination were collected from the same water layers. Chlorophyll *a* and ammonia were determined in screen-surface-microlayer and subsurface water. To collect a PM sample of 1 dm^3 volume, the plate was immersed about 60 times; EM samples required 20 immersions. Chemical analyses of chlorophyll *a* and nutrients were carried out on board the ship immediately after sampling. The spectrophotometric methods recommended for Baltic Sea water (UNEP/IOC/IAEA, 1988) were applied. The chlorophyll *a* concentration was determined by measuring the absorption of an acetone extract according to the BMB method (Edler, 1979). After the samples had been thawed in the Marine Plant Laboratory of the Oceanographic Institute of Gdańsk University, particle numbers were analysed using a Multisizer II Coulter

Table 1. Statistical characteristics of suspended particles [N cm^{-3}] in samples from the sea-surface microlayer (EM) and the subsurface water (SUB) of the Gdańsk Deep (2–6.06.1992)

Estimator	EM 242 ± 40 μm	SUB 15 cm
n	19	19
X	12800	8200
D	11200	7900
M	11000	7900
δ	5100	2400
Min.	6800	5100
Max.	26900	12600

Symbols:

n – number of samples,
X – mean,
D – dominant,
M – modal,
δ – standard deviation,
Min. – minimum value,
Max. – maximum value.

Table 2. Statistical characteristics of suspended particles [N cm^{-3}] in samples from the sea-surface microlayer (PM), (EM) and subsurface water (SUB) of the Gdańsk Deep (30.04.–4.05.1994)

Estimator	PM 90 ± 16.6 μm	EM 242 ± 39.8 μm	SUB 15 cm
n	63	80	92
X	28000	27700	19000
D	23900	23600	14900
M	42400	14400	17700
δ	14000	15200	13500
Min.	10800	9600	3700
Max.	66000	83100	74000

Symbols as in Tab. 1.

Counter. Electronic counters of particles are commonly used for the analysis of suspended-particle size distribution in seawater (Eisma and Kalf, 1987; Dera, 1983; Jonasz and Zalewski, 1977; Sheldon *et al.*, 1972). The measurements were carried out according to the guidelines in Coulter (1985), by means of a 200 μm-diameter tube in the 1992 experiment and a 100 μm tube in 1994. The measurements were made using a syphoning method, the particles being counted in water samples of 500 or 1000 μl. The measuring tubes were calibrated using filtered (Sartorius 0.2 μm) seawater from the Baltic Sea with the addition of Latex suspension (calibration standard – E36). In 1992, 19 samples of screen-surface-microlayer (EM) and the same number of subsurface water samples (SUB) were analysed (Tab. 1), and in 1994, 63 samples of plate-surface-microlayer water (PM), 80 samples of screen-surface-microlayer water (EM) and 92 samples of subsurface layer (SUB) were examined (Tab. 2).

The results of particle concentration, in every size class for each sample, represent the average values of 3–10 measurements. The method applied did not render possible the evaluation of actual particle shape, so the results were approximated for a sphere with a diameter corresponding to the particle volume. In 1992, particle size distribution was classified in diameter ranges from 4.02 to 31.00 μm, while in 1994 the diameters ranged from 2.11 to 27.14 μm. The upper diameter limit was defined by particle size characteristics; *i.e.* particles of large diameters (> 30 μm) were found only sporadically. The lower diameter level was defined by the counter sensitivity, which depended on the use of a suitable measuring tube.

3. Results

The statistical characteristics of the numbers of suspended particles in the various size classes determined in the screen-surface microlayer and in the subsurface water layer in June (3–6) 1992 are presented in Tabs. 3 and 4. Analogous characteristics from the period 30 April – 5 May 1994 are shown in Tabs. 5, 6 and 7. During both experimental periods, the fraction containing particles of the smallest diameters was the most abundant and the most highly differentiated. Generally speaking, in late April – early May 1994, particle concentrations in all the water layers examined were higher than in June 1992. There was also a marked differentiation in the hyperbolic pattern of particle size distribution, presented as the cumulative number of particles versus particle diameter (Figs. 2 and 3).

Significant, marked irregularities in the particle size distribution pattern were found in the experiments in late April – early May 1994. Particle concentrations varied considerably between particular water layers.

In June 1992, the particle number in the screen-surface microlayer 250 μm in width was twice as large as that in the subsurface layer (at 15 cm depth).

Only slight differences were found between the particle concentrations in the plate-surface-microlayer (PM) and screen-surface-microlayer samples (EM) in April/May 1994 as regards particles < 10 μm; the suspended particle concentration in the subsurface layer was lower. As far as the pattern of particle distribution functions in diameter classes over 10 μm are concerned, no significant discrepancies were observed between the three water layers analysed. However, there were differences in the 14–17 μm size class.

Table 3. Statistical characteristics of suspended particles in 1 cm^3 of the screen-surface microlayer (EM) (242 $\pm$ 39.8 μm) of the Gdańsk Deep (2–6.06.1992)

Diameter range in the size class [μm]	X	D	M	δ	Min.	Max.
<4.02	8000	4700	4600	12000	3000	56200
4.03 – 5.24	2800	2600	2500	1100	1600	5800
5.25 – 6.47	1400	1200	1200	540	700	2700
6.48 – 7.70	800	600	600	400	400	1770
7.71 – 8.92	530	390	370	330	220	1250
8.93 – 10.15	400	290	270	270	170	970
10.16 – 11.38	320	230	230	220	100	780
11.39 – 12.60	250	200	570	170	76	620
12.61 – 13.83	200	160	160	140	58	480
13.84 – 15.05	140	100	100	98	39	340
15.06 – 16.28	100	65	65	77	26	280
16.29 – 17.51	70	50	46	57	17	210
17.52 – 18.73	54	32	32	43	16	160
18.74 – 19.96	42	28	76	34	11	130
19.97 – 21.19	34	23	23	28	11	110
21.20 – 22.41	29	18	10	24	7	90
22.42 – 23.64	23	14	14	20	6	80
23.65 – 24.86	18	11	8	16	5	70
24.87 – 26.09	15	9	5	13	5	60
26.10 – 27.32	11	6	6	11	3	44
27.33 – 28.54	10	7	5	9	3	38
28.55 – 29.77	9	5	5	7	3	34
29>78– 31.00	7	4	3	6	2	28

Symbols as in Tab. 1.

There are considerable temporal variations throughout a 24 h period in the concentration of particles of all sizes, and of chlorophyll *a*, phosphates, nitrates and ammonia (Figs. 4–8). The increased sampling frequency revealed a greater variability in the parameters analysed (Figs. 9–13). In the plate-surface-microlayer samples, the amplitudes of nitrate and phosphate concentrations and the particle numbers peaked in the microlayers, whereas the subsurface water contained relatively low amounts of these substances. The diurnal variations in the substances analysed seemed to be of a cyclic nature.

Table 4. Statistical characteristics of suspended particles in 1 cm^3 of the subsurface water (15 cm depth) of the Gdańsk Deep (2–6.06.1992)

Diameter range in the size class [μm]	X	D	M	δ	Min.	Max.
<4.02	3500	3200	3000	1200	2320	6400
4.03 – 5.24	1800	1600	1600	560	1180	3130
5.25 – 6.47	800	670	690	280	510	1430
6.48 – 7.70	420	360	350	130	230	680
7.71 – 8.92	266	260	200	70	170	420
8.93 – 10.15	190	180	150	44	120	290
10.16 – 11.38	150	130	200	38	98	230
11.39 – 12.60	120	100	170	46	68	230
12.61 – 13.83	80	70	60	33	46	190
13.84 – 15.05	54	45	42	23	32	120
15.06 – 16.28	34	31	31	11	21	60
16.29 – 17.51	23	24	28	7	12	40
17.52 – 18.73	18	19	12	5	9	30
18.73 – 19.96	14	14	12	5	5	22
19.97 – 21.19	11	12	13	3	7	19
21.20 – 22.41	9	9	8	3	4	15
22.42 – 23.64	7	7	5	2	3	12
23.65 – 24.86	6	5	5	2	3	11
24.87 – 26.09	4	5	6	1	2	8
26.10 – 27.32	4	4	4	1	2	7
27.33 – 28.54	3	3	3	1	2	6
28.55 – 29.77	2	2	2	1	1	5
29.78 – 31.00	2	2	1	1	1	4

Symbols as in Tab. 1.

Table 5. Statistical characteristics of suspended particles in 1 cm^3 of the plate-surface microlayer water PM (90 $\pm$ 16.6 μm) of the Gdańsk Deep (30.04.–4.05.1994)

Diameter range in the size class [μm]	X	D	M	δ	Min.	Max.
<2.11	12800	10900	10400	6190	4620	27900
2.12 – 2.86	5800	5200	3260	2850	2310	13300
2.87 – 3.60	2960	2500	1370	1590	1400	7370
3.61 – 4.35	1680	1370	2140	970	510	4620
4.36 – 5.09	990	790	590	570	310	2640
5.10 – 5.83	650	500	350	380	180	1720
5.84 – 6.58	440	360	280	250	120	1110
6.59 – 7.32	320	280	290	180	88	870
7.33 – 8.07	230	200	250	120	66	590
8.08 – 8.81	180	150	130	99	44	470
8.82 – 9.55	140	120	120	81	34	370
9.56 – 10.30	120	100	100	68	30	320
10.31 – 11.04	105	99	110	57	20	320
11.05 – 11.79	95	80	70	53	20	290
11.80 – 12.53	93	84	90	51	18	280
12.54 – 13.27	97	90	90	52	14	270
13.28 – 14.02	100	85	60	61	10	340
14.03 – 14.76	99	84	90	60	10	340
14.77 – 15.51	96	84	90	55	10	260
15.52 – 16.25	92	78	90	65	10	320
16.26 – 16.99	82	60	50	66	10	330
17.00 – 17.74	71	54	60	60	10	280
17.75 – 18.48	67	50	50	55	8	250
18.49 – 19.23	50	36	20	41	8	160
19.24 – 19.97	40	30	40	32	8	150
19.98 – 20.71	28	20	10	25	4	120
20.72 – 21.46	22	12	10	18	6	80
21.47 – 22.20	18	12	10	14	2	70
22.21 – 22.94	14	10	10	11	1	60
22.95 – 23.69	12	10	10	7	2	30
23.70 – 24.43	10	8	10	7	2	30
24.44 – 25.18	10	8	10	7	1	40
25.19 – 25.92	10	8	10	12	1	80
25.93 – 26.66	7	7	10	4	1	20
26.67 – 27.14	6	6	2	5	1	30

Symbols as in Tab. 1.

Table 6. Statistical characteristics of suspended particles in 1 cm^3 of the screen-surface microlayer water EM (224 $\pm$ 36 μm) of the Gdańsk Deep (30.04.–4.05.1994)

Diameter range in the size class [μm]	X	D	M	δ	Min.	Max.
<2.11	14100	11400	11000	7900	5850	47280
2.12 – 2.86	5700	5200	3200	2500	1410	13680
2.87 – 3.60	2740	2410	1460	1300	800	7200
3.61 – 4.35	1530	1220	860	900	380	4590
4.36 – 5.09	900	720	590	580	220	3040
5.10 – 5.83	560	460	390	360	130	1620
5.84 – 6.58	390	300	200	250	98	1150
6.59 – 7.32	270	210	140	180	76	910
7.33 – 8.07	210	140	130	140	50	660
8.08 – 8.81	150	120	60	110	40	560
8.82 – 9.55	120	90	90	94	32	540
9.56 – 10.30	100	70	90	96	26	640
10.31 – 11.04	79	59	44	65	22	400
11.05 – 11.79	75	56	56	64	20	420
11.80 – 12.53	75	55	44	55	18	300
12.54 – 13.27	80	59	70	57	12	260
13.28 – 14.02	87	70	60	63	18	330
14.03 – 14.76	100	81	90	83	18	450
14.77 – 15.51	103	74	60	100	10	550
15.52 – 16.25	110	75	68	110	10	620
16.26 – 16.99	104	70	70	114	8	630
17.00 – 17.74	91	60	60	101	8	600
17.75 – 18.48	73	52	40	67	6	290
18.49 – 19.23	58	40	40	61	8	380
19.24 – 19.97	46	31	24	44	4	260
19.98 – 20.71	32	22	20	32	1	190
20.72 – 21.46	24	19	20	22	2	130
21.47 – 22.20	18	12	8	15	1	82
22.21 – 22.94	14	10	6	13	1	66
22.95 – 23.69	10	8	10	9	1	44
23>70– 24.43	8	6	6	7	1	38
24.44 – 25.18	7	5	4	7	1	40
25.19 – 25.92	7	4	2	10	2	60
25.93 – 26.66	5	4	4	8	1	62
26.67 – 27.14	4	2	2	8	1	64

Symbols as in Tab. 1.

Table 7. Statistical characteristics of suspended particles in 1 cm^3 of the subsurface water SUB (15 cm depth) of the Gdańsk Deep (30.04.–4.05.1994)

Diameter range in the size class [μm]	X	D	M	δ	Min.	Max.
<2.11	9800	8000	9900	6200	1700	34000
2.12 – 2.86	4100	3400	3400	2400	900	12200
2.87 – 3.60	1900	1480	1400	1200	350	5000
3.61 – 4.35	1000	740	600	720	200	2900
4.36 – 5.09	580	400	340	440	140	1900
5.10 – 5.83	350	250	150	270	70	1430
5.84 – 6.58	240	170	90	200	50	1100
6.59 – 7.32	180	130	100	150	50	820
7.33 – 8.07	130	90	82	100	30	610
8.08 – 8.81	93	70	44	70	24	440
8.82 – 9.55	72	53	42	60	14	360
9.56 – 10.30	57	42	20	45	14	260
10.31 – 11.04	50	43	18	33	10	180
11.05 – 11.79	47	38	20	33	12	160
11.80 – 12.53	50	41	42	34	8	140
12.54 – 13.27	57	45	28	41	10	190
13.28 – 14.02	68	50	26	56	8	240
14.03 – 14.76	81	55	46	78	10	360
14.77 – 15.51	92	54	50	96	14	430
15.52 – 16.25	101	60	60	111	10	510
16.26 – 16.99	100	55	28	118	10	570
17.00 – 17.04	94	53	30	114	8	560
17.75 – 18.48	81	52	80	92	7	470
18.49 – 19.23	65	39	10	68	8	300
19.24 – 19.97	52	32	20	54	4	240
19.98 – 20.71	40	24	14	36	6	140
20.72 – 21.46	29	20	10	26	6	100
21.47 – 22.20	21	14	6	19	2	72
22.21 – 22.94	16	10	4	13	2	52
22.95 – 23.69	12	8	4	11	2	49
23.70 – 24.43	9	7	2	10	2	63
24.44 – 25.18	7	4	2	10	1	74
25.19 – 25.92	6	4	4	10	1	77
25.93 – 26.66	5	3	2	11	1	80
26.67 – 27.14	4	2	2	9	1	71

Symbols as in Tab. 1.

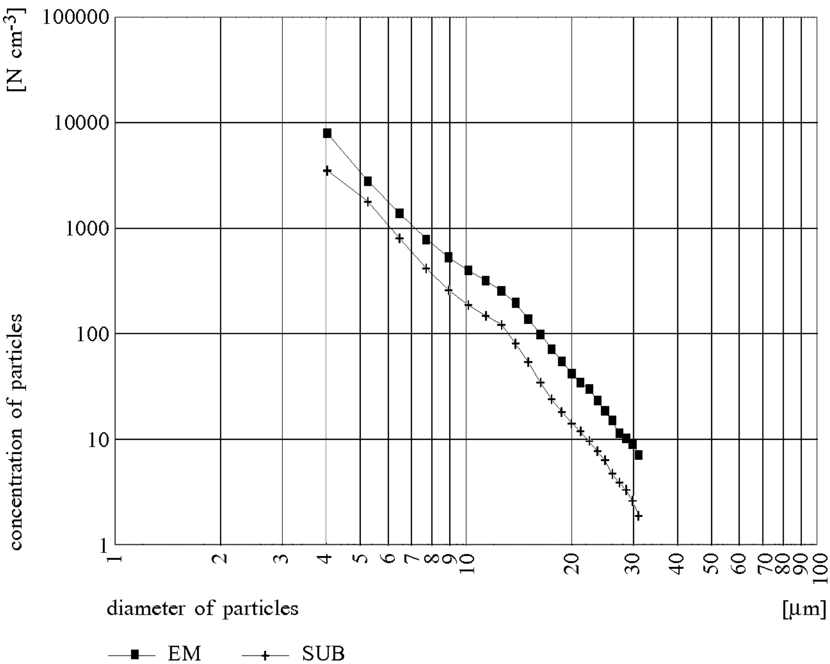


Fig. 2. Mean cumulative particle-size distribution (log-log) in the surface water of the Gdańsk Deep (2–6.06.1992)

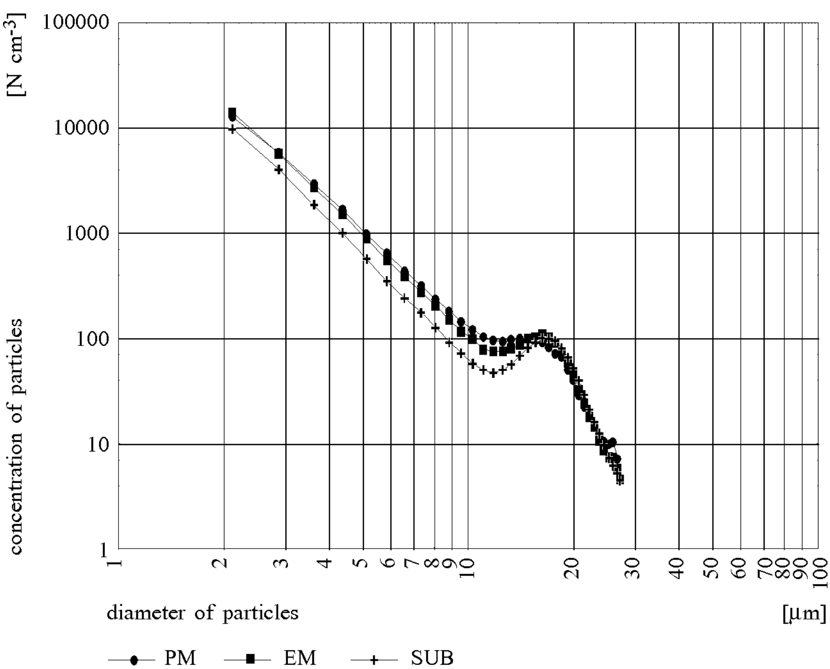


Fig. 3. Mean cumulative particle-size distribution (log-log) in the surface water of the Gdańsk Deep (30.04.–4.05.1994)

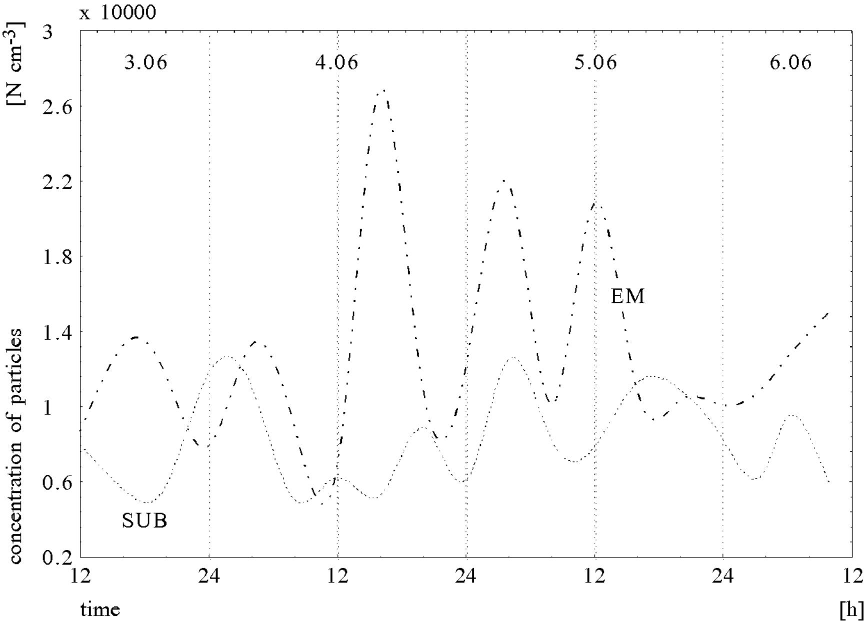


Fig. 4. Diurnal fluctuations in particle concentration at selected sea surface water layers of the Gdańsk Deep (1992); EM – screen-surface microlayer, SUB – subsurface layer

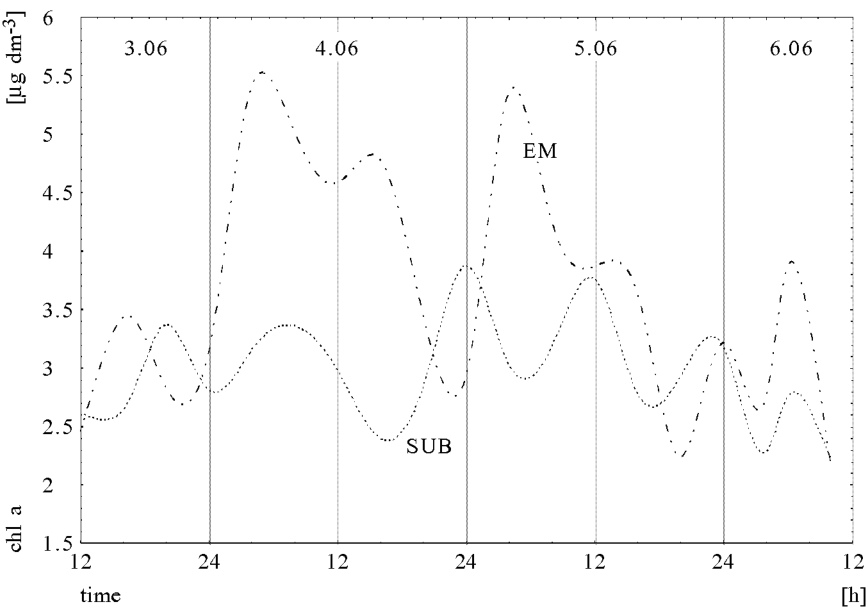


Fig. 5. Diurnal fluctuations in chlorophyll *a* concentration at selected sea surface water layers of the Gdańsk Deep (1992); EM – screen-surface microlayer, SUB – subsurface layer

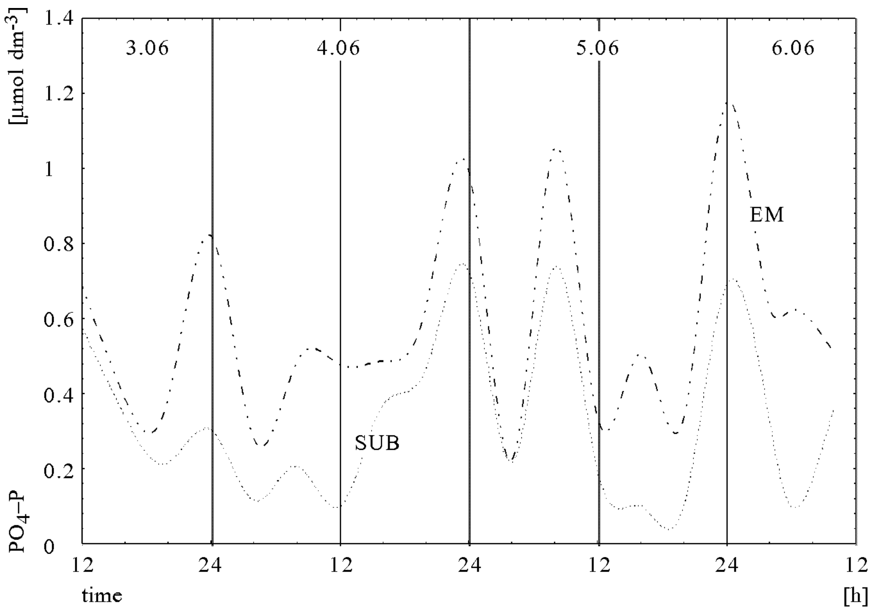


Fig. 6. Diurnal fluctuations in phosphate concentration at selected sea surface water layers of the Gdańsk Deep (1992); EM – screen-surface microlayer, SUB – subsurface layer

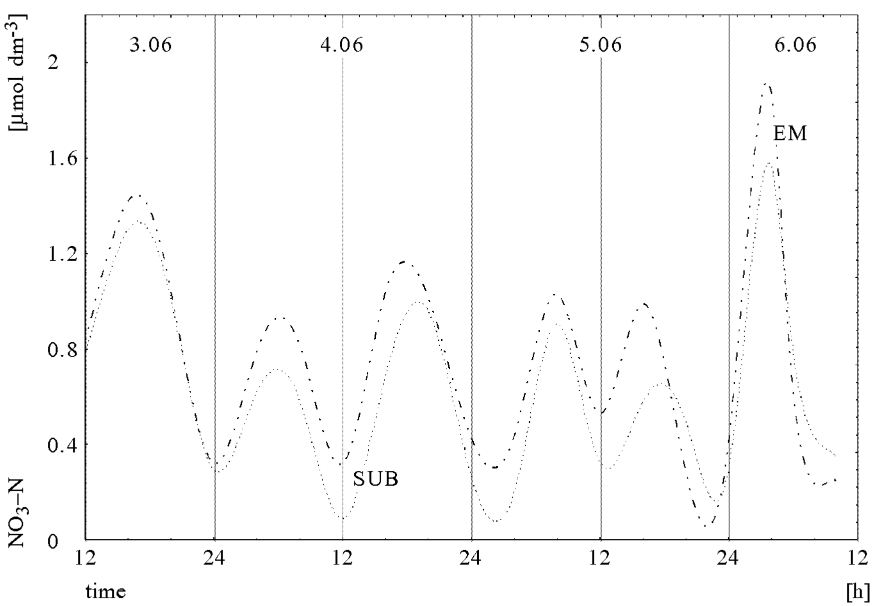


Fig. 7. Diurnal fluctuations in nitrate concentration at selected sea surface water layers of the Gdańsk Deep (1992); EM – screen-surface microlayer, SUB – subsurface layer

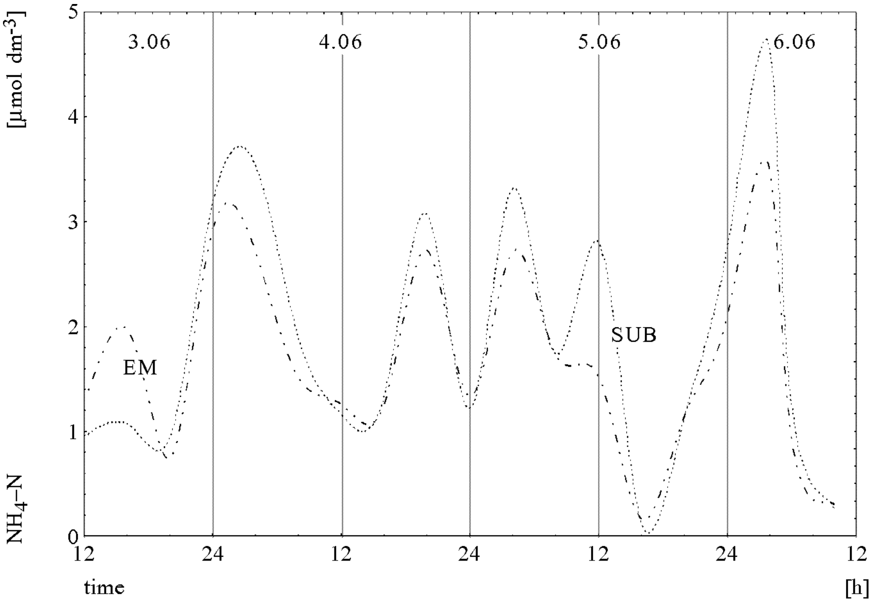


Fig. 8. Diurnal fluctuations in ammonium concentration at selected sea surface water layers of the Gdańsk Deep (1992); EM – screen-surface microlayer, SUB – subsurface layer

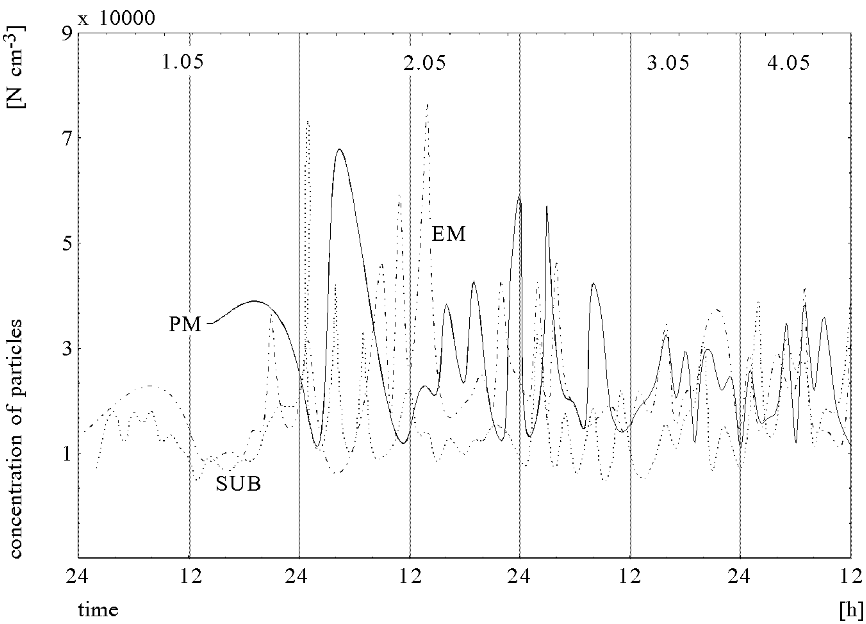


Fig. 9. Diurnal fluctuations in particle concentration at selected sea surface water layers of the Gdańsk Deep (1994); PM – plate-surface microlayer, EM – screen-surface microlayer, SUB – subsurface layer

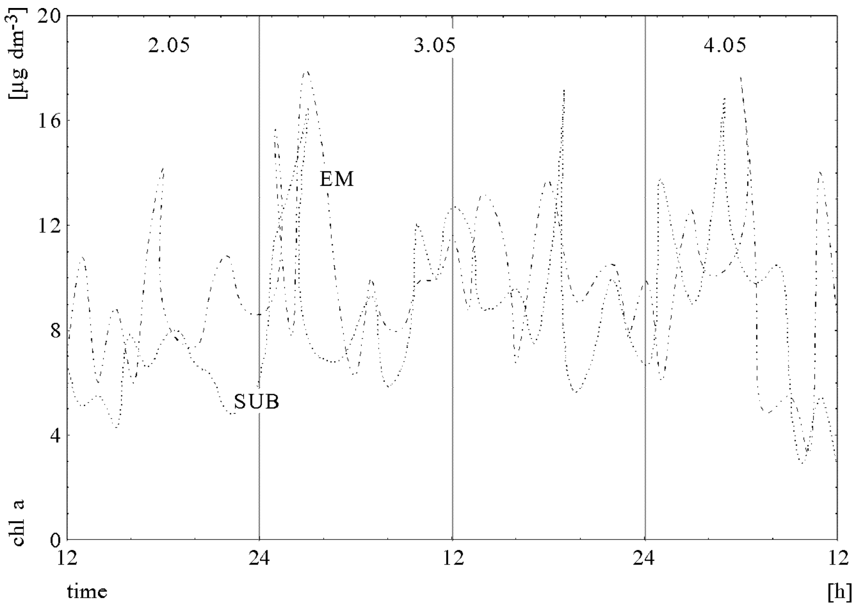


Fig. 10. Diurnal fluctuations in chlorophyll *a* concentration at selected sea surface water layers of the Gdańsk Deep (1994); EM – screen-surface microlayer, SUB – subsurface layer

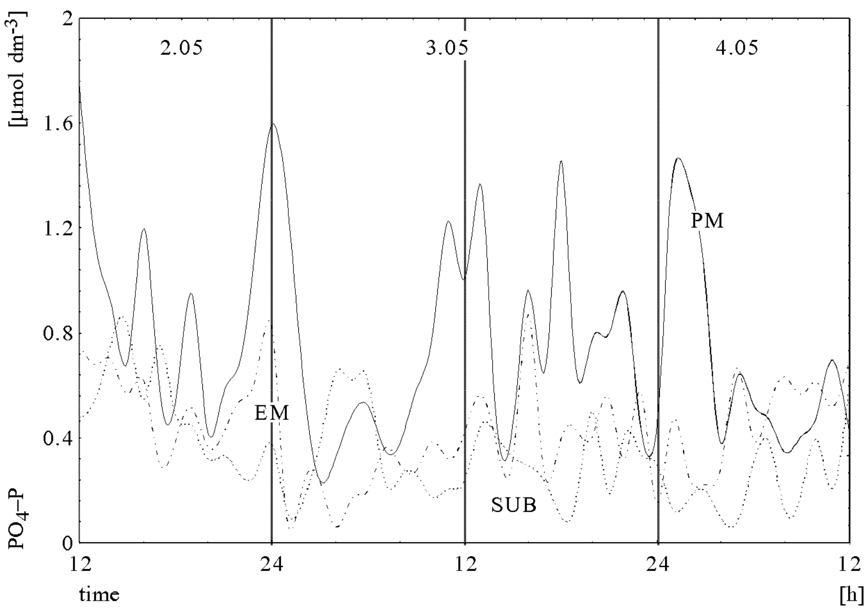


Fig. 11. Diurnal fluctuations in phosphate concentration at selected sea surface water layers of the Gdańsk Deep (1994); PM – plate-surface microlayer, EM – screen-surface microlayer, SUB – subsurface layer

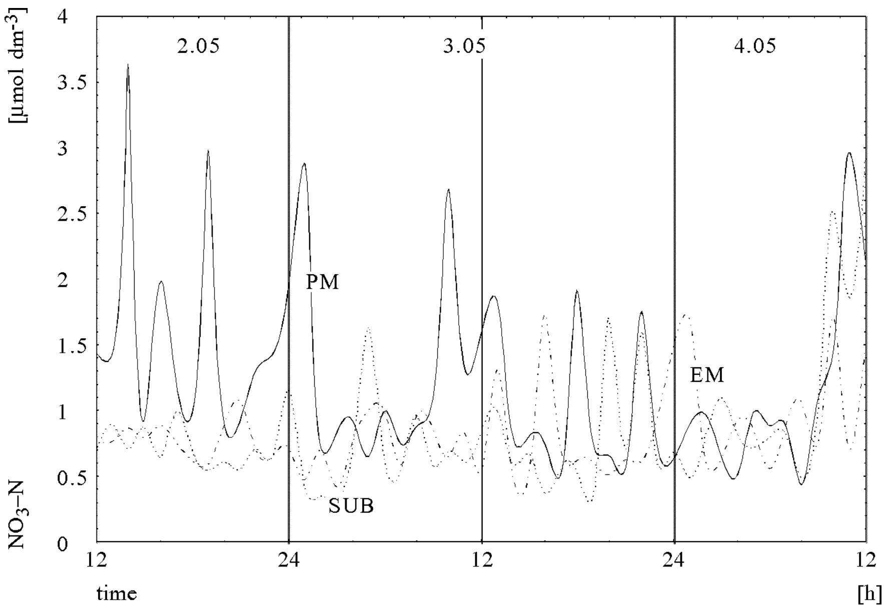


Fig. 12. Diurnal fluctuations in nitrate concentraation at selected sea surface water layers of the Gdańsk Deep (1994); PM – plate-surface microlayer, EM – screen-surface microlayer, SUB – subsurface layer

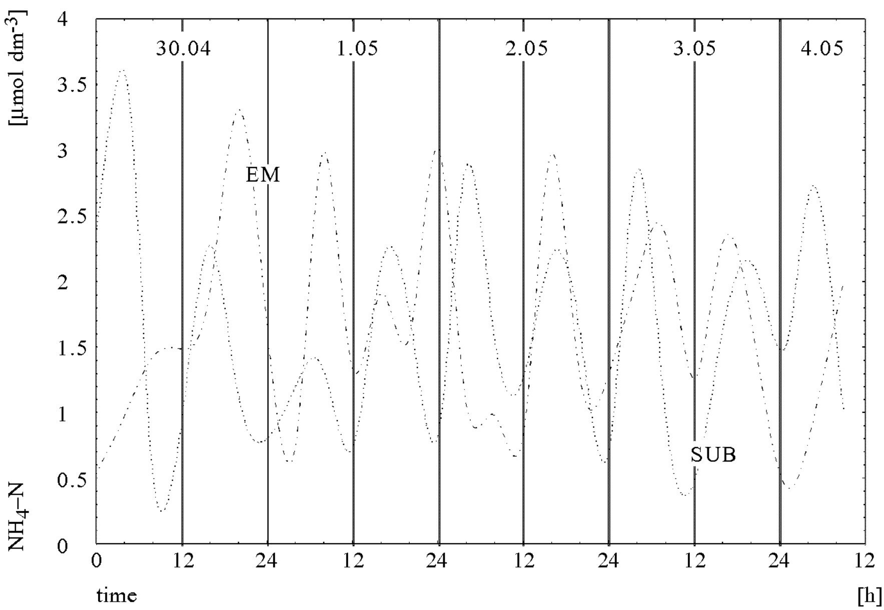


Fig. 13. Diurnal fluctuations in ammonium concentration at selected sea surface water layers of the Gdańsk Deep (1994); EM – screen-surface microlayer, SUB – subsurface layer

4. Discussion

Diurnal variations in the concentrations of suspended particles, chlorophyll *a* and nutrients

The concentration and size distribution of suspended particles in seawater depend on a number of complementary processes. Some of these are evidently cyclic in nature, owing to diurnal fluctuations in the primary production rate or to cyclic dynamic processes in the marine environment. Other processes, *e.g.* bottom and shoreline erosion due to the impact of marine currents and storms, suspended matter input from land run-off, or atmospheric input of aerosols at the sea surface, are subject not to the diurnal cycle but to the direction and strength of the wind. The number of particles of various sizes found in unit volume at the seawater-atmosphere interface is thus the resultant of a variety of complicated physical, chemical and biological processes.

From the biological standpoint, it would be interesting to assess the contribution of plankton organisms to the total number of suspended particles. However, because the phyto- and zooplankton populations were not analysed simultaneously, the figures presented here are only approximate. Chlorophyll *a* is often used as a phytoplankton biomass indicator; our results of chlorophyll *a* determinations in the screen-surface microlayer and in the subsurface layer indicated that the particles were mostly phytoplankton cells, because their concentration showed a statistically significant correlation with the chlorophyll *a* content in both water microlayers (Figs. 14–15). In the surface microlayer and in the subsurface layer, bacterioneuston (Marumo *et al.*, 1971; Norkrans, 1980; Rheinheimer, 1987; Sieburth, 1968, 1971; Tsyban, 1975) and nanoplankton (Hardy, 1982; Hardy and Apts, 1984; Wandschneider, 1979) contributed to some extent to the $\phi < 10$ μm particle class. In the Norwegian Sea and the Barents Sea similar correlations were found between the concentrations of particles in the 2.24–43.82 μm class and the chlorophyll *a* content (Bralewska and Kuliński, 1993).

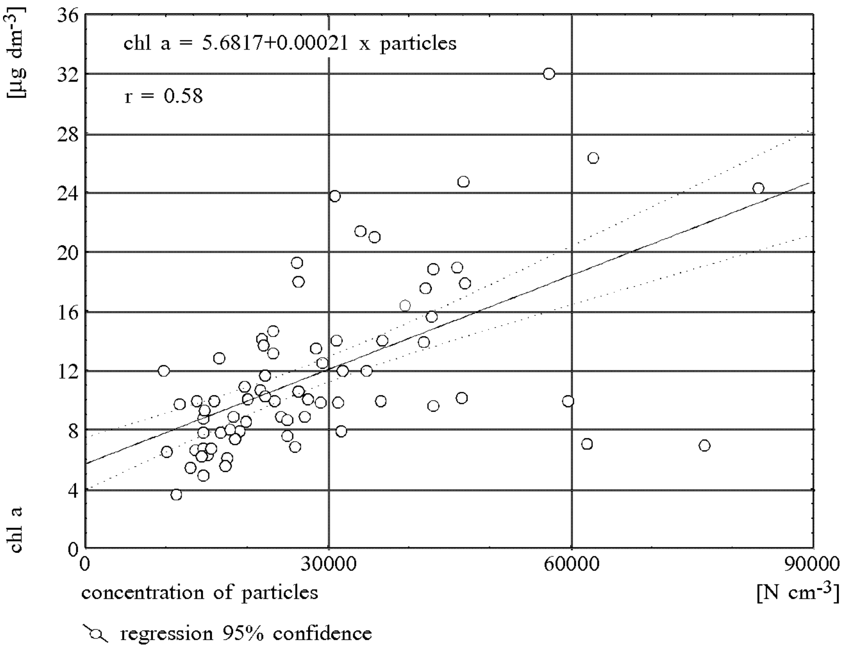
Analysis of the particle size distributions in the different water layers revealed the differences they underwent during the two periods of the growing season examined (Fig. 16):

I – late April – early May,

II – beginning of June.

During the first experimental period, primary production was still proceeding at a considerably elevated rate, and the zooplankton biomass was increasing continually following the April phytoplankton bloom typical of the southern Baltic Sea. The spring bloom population in the Gulf of Gdańsk

a



b

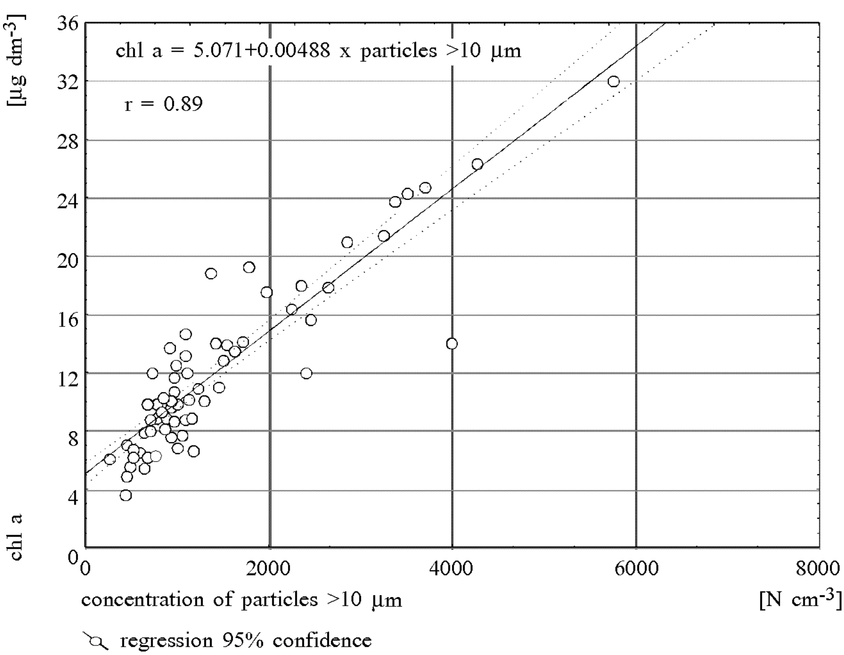


Fig. 14. Linear regression of chlorophyll *a* and particle concentration in the screen-surface microlayer of the Gdańsk Deep; total number of particles (a), particles of diameter > 10 μm (b)

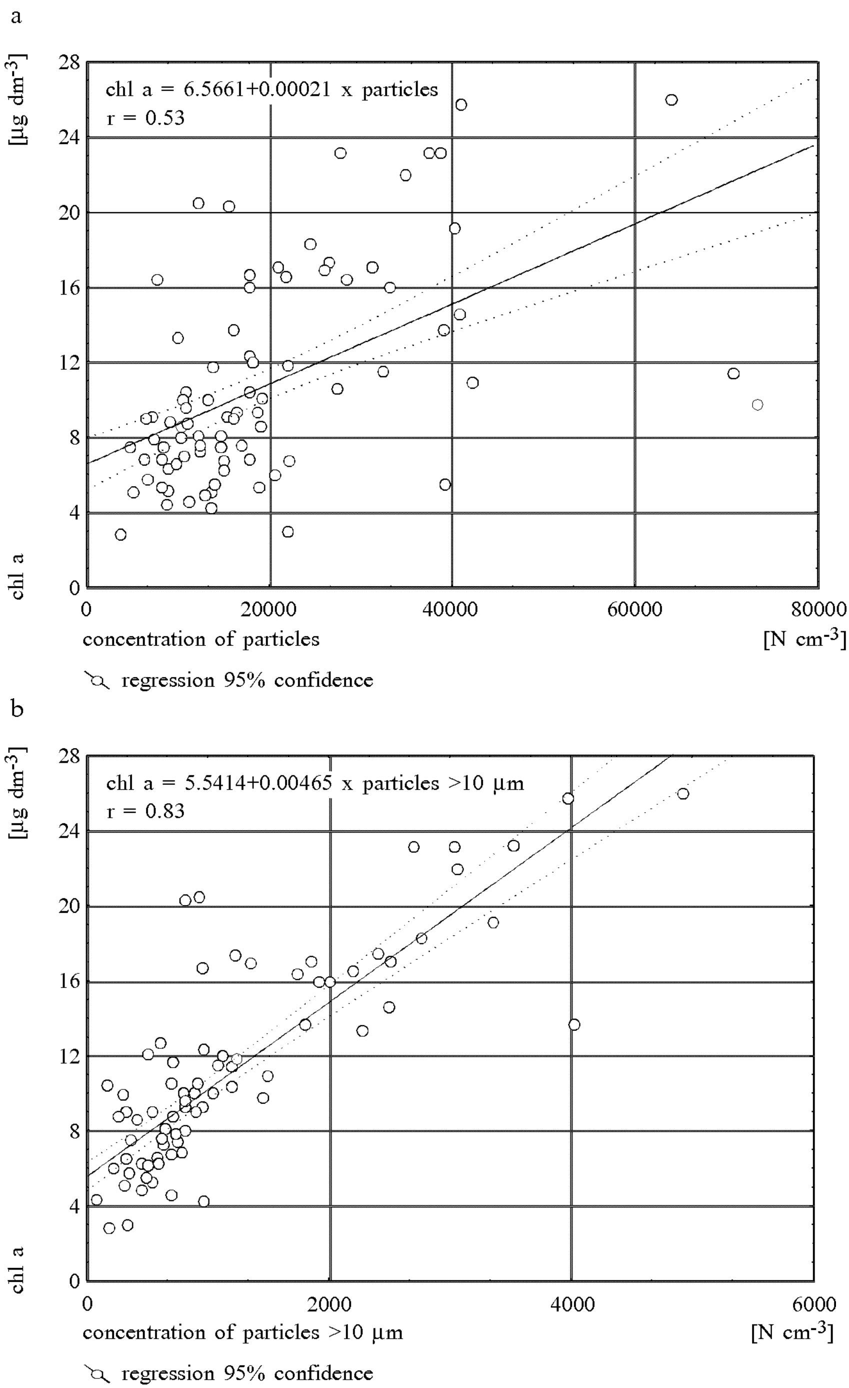


Fig. 15. Linear regression of chlorophyll *a* and particle concentration in the subsurface water of the Gdańsk Deep; total number of particles (a), particles of diameter $> 10\ \mu$m (b)

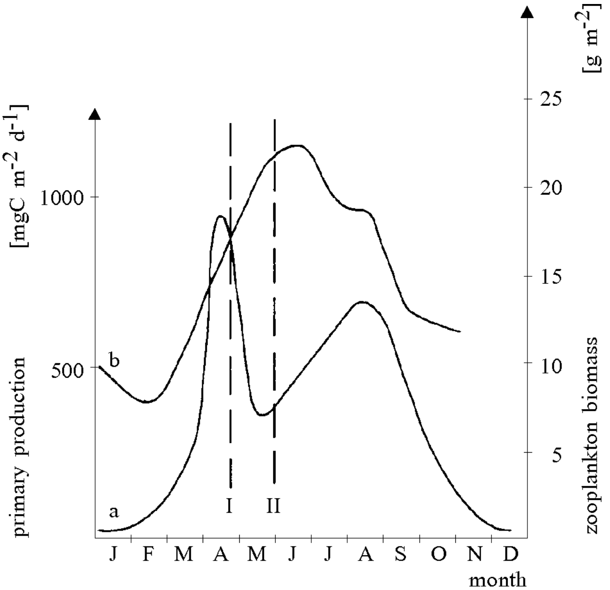


Fig. 16. Seasonal variations in biological variables in the Gdańsk Deep; I – first experimental period, II – second experimental period, a – mean primary production in 1965–84 (Renk, 1990), b – mean zooplankton biomass in 1951–74 (Wiktor, 1990)

is composed mainly of diatoms, although *Euglenophyta* specimens are also frequently encountered. At the height of the spring bloom, the algal biomass is larger than at any other period during the growing season (Pliński *et al.*, 1985); chlorophyll *a* concentrations peak at the same time (Latała, 1994).

In the western Baltic Rheinheimer (1987) found that the population of saprophytic bacteria reached a maximum in April–May, subsequent to the phytoplankton production peak, by which time a large proportion of the phytoplankton had already died.

The second set of experiments were carried out at a time when primary production was declining and the growth of the zooplankton population was accelerating (Renk, 1990; Wiktor, 1990). These observations were substantiated by the chlorophyll *a* concentrations then recorded: during the first experimental period they were more than three times as high as during the second (Figs. 5, 10). Furthermore, the number of particles recorded in the first period was decidedly higher than in the second, even though particles of small size range predominated. The number of particles within the larger diameter range increased only in the second period of experiments (Tabs. 3–7). This observation led to the assumption that primary production and phytoplankton biomass during the experimental periods in 1992 and 1994 did not differ from the mean levels found in the upper water layers of the

Gdańsk Deep region in the long-term studies of Wiktor (1990), Renk (1990) and Renk *et al.* (1992).

The cyclic variations in particle concentration, chlorophyll pigment content and nutrient concentration recorded during these two different periods of the growing season were further influenced by diurnal fluctuations clearly related to the intensity of photosynthesis, the mineralisation of organic matter, and the migration of organisms between different surface-water layers (Figs. 4–13).

Another factor influencing the sea-surface film is the dry atmospheric deposition of aerosols onto it; this is because they contain nitrogen and phosphorus compounds (Falkowska and Bolałek, 1991). In daylight, these compounds can be utilised directly for primary production purposes; at night, however, their atmospheric input adds to the nutrient pool produced during the mineralisation of organic matter.

The sea-surface microlayer is additionally affected by irradiation. This interface receives doses of irradiation varying from hour to hour and even from minute to minute as a result of the natural fluctuations of the solar radiation during the day. The cloud sequence can cause the instantaneous irradiation of the sea surface to change by a factor of up to 5, thereby affecting photosynthesis (Dera, 1983). The concurrent action of several processes is thus responsible for the maximum concentrations of nutrients and their considerable dynamics during the day in the plate-surface microlayer (Figs. 11, 12).

The maximum concentrations of particles and chlorophyll *a* were measured in the early morning hours and in the afternoons. Both chlorophyll *a* concentrations and particle numbers were found to decrease around noon (Figs. 4, 5, 9 and 10). When the measurements were carried out at hourly intervals, the variations in particular water microlayers were superimposed onto this general pattern of fluctuations. At night (between 23.00 and 3.00), the particle concentration and chlorophyll *a* content in the subsurface layer and in the screen-surface microlayer (EM) increased more than in the plate-surface microlayer (PM). Phosphate and ammonia concentrations also clearly increased in these layers at night (Figs. 6, 8, 11 and 13). Because photosynthesis does not occur at night, the mineralisation of organic matter evidently predominates over nutrient assimilation.

The particle size distribution at midnight (Figs. 17a and b) differed depending on the period of the growing season. In late April – early May (Fig. 17a), the number of particles in the $\phi < 10$ μm diameter class was greater in the subsurface layer than in the plate-surface or screen-surface microlayers; even though the particle-size distribution functions were exponential in all layers. The particle-size distribution curves were inflected in the vicinity of

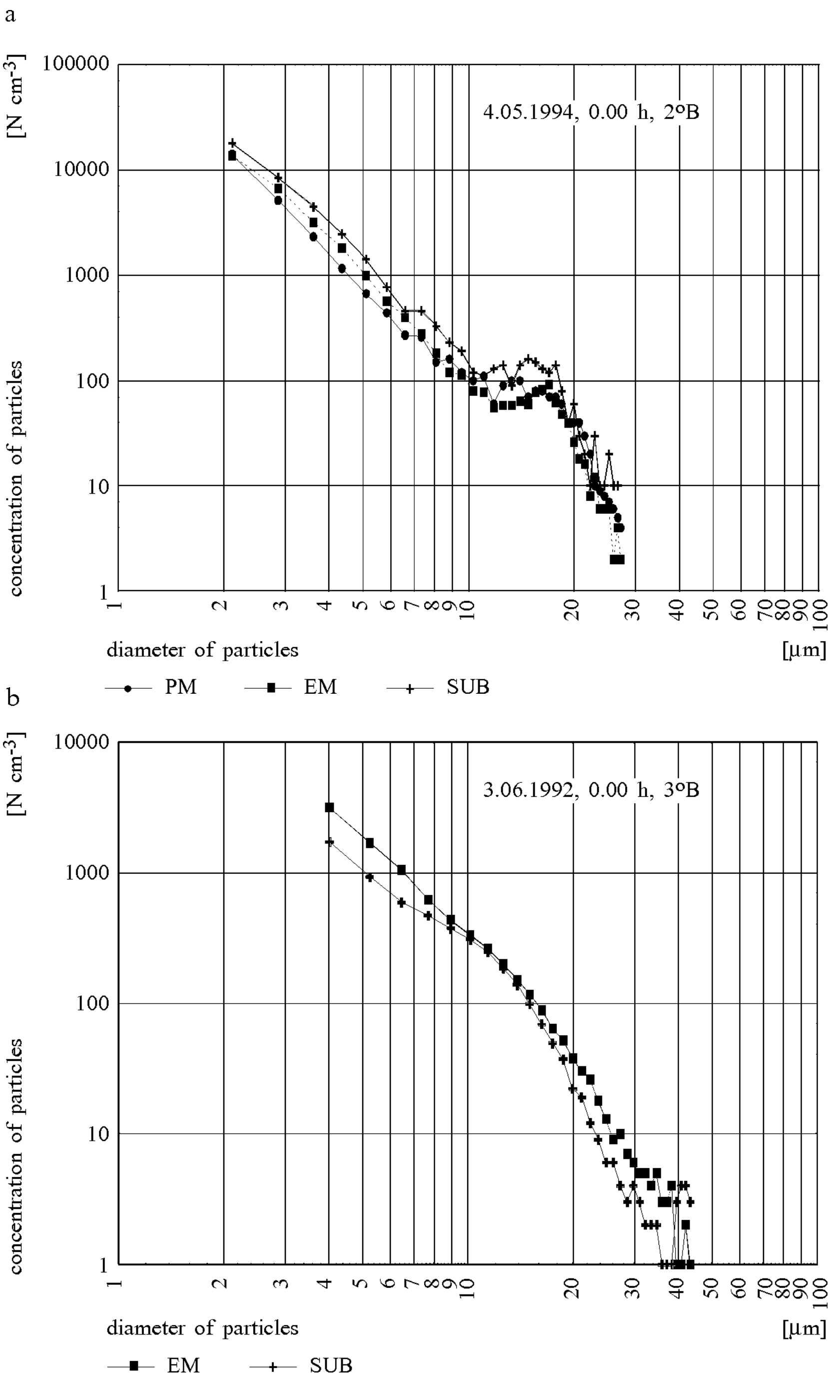


Fig. 17. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log); first experimental period (a), second experimental period (b)

the 10 μm diameter and a marked increase was noted among particles of the $\phi > 10$ μm size class, particularly in the subsurface layer. It seems that the respective positions of the distribution curves illustrate the migration of plankton organisms between the different microlayers. Whereas algae occupying the microlayer move horizontally or dive into deeper water layers, zooplankton, usually inhabiting deeper water, migrates upwards (Hardy, 1982; Rudiakov, 1988). Hence the number of zooplankton specimens and the mass of their excreta increase in the upper water layer. During the second experimental period (early June 1992, Fig. 17b), the distribution curve was inflected for particles of diameter > 20 μm, and the number of particles of this size increased.

One hour before sunrise (SR 4.05) the layout of particle-size distribution curves (Fig. 18) changed markedly as compared to the situation of three hours earlier (Fig. 17a); the number of smaller particles had diminished considerably in the subsurface layer. It is most likely that a certain portion of the organic matter had undergone mineralisation by the ever-present bacteria and fungi, and at the same time zooplankton had been grazing on phytoplankton cells (Rheinheimer, 1987). For these reasons, the particle-size distribution curves reveal two points of inflection, the first located within the 5–10 μm diameter range, and the second in the > 20 μm range. There was a noticeable increase in the number of particles within the largest size ranges. This pattern of particle-size distribution was probably determined by size-dependent zooplankton migration as well as by selective zooplankton feeding, *i.e.* zooplankton grazing on selected phytoplankton species. It could be assumed that during this experimental period the larger phytoplankton cells were consumed at a different rate than the tiny nanoplankton organisms. Feeding selectivity is a specific phenomenon and not well understood. Investigations into this problem have shown that some zooplankton species either translocate in the direction of specific phytoplankton or bacterial colonies, or else are not attracted by any particular species at all (Fronczak and Styczyńska-Jurewicz, 1985; Pliński, 1994; Rudiakov, 1988; Sifford, 1979).

Many authors (Alcaraz, 1984; Marumo *et al.*, 1971; Rudiakov, 1988; Sifford, 1979; Wandschneider, 1979) share the opinion that the majority of marine organisms migrate on a daily or seasonal basis. Thus, their distribution in the water column depends on the proportions between the proliferation rate, the rate of zooplankton grazing and the number of proteolytic bacteria, as well as on physical factors facilitating migration in water, *e.g.* turbulent exchange, absorption and transportation on sedimenting particles or on rising gas bubbles, to either of which organic matter or suspensions can adhere.

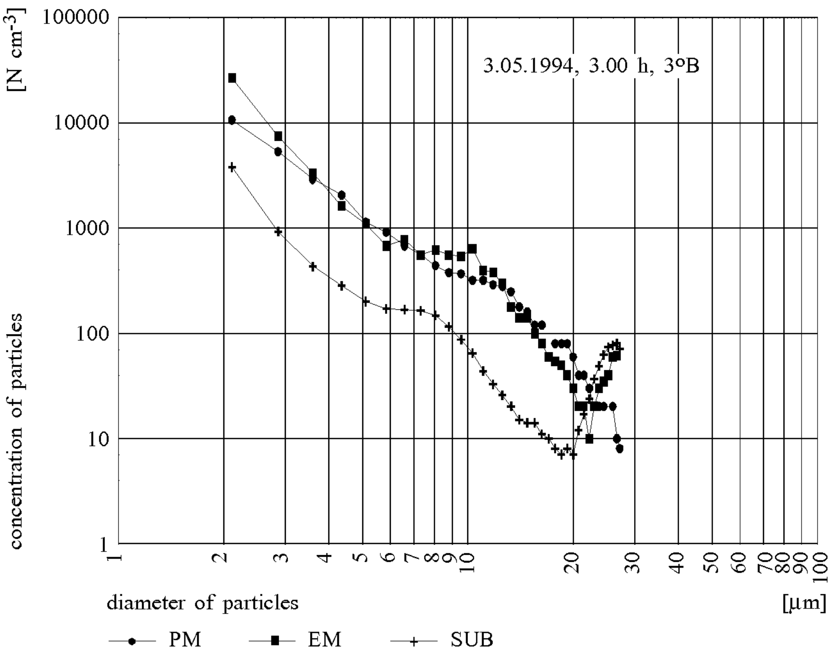


Fig. 18. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log) in the first experimental period

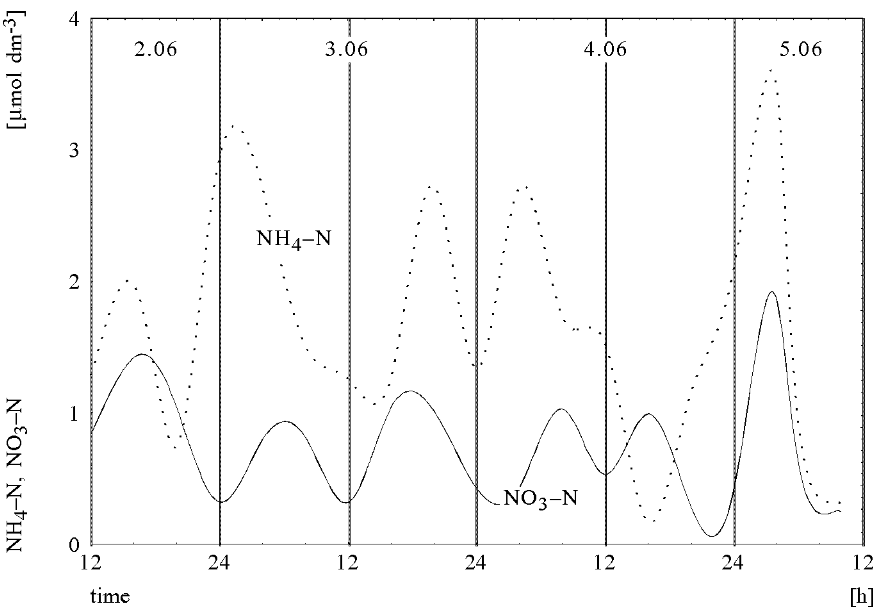


Fig. 19. Diurnal fluctuations in ammonium and nitrate concentrations in the subsurface water of the Gdańsk Deep (1992)

It seems very probable that ammonia concentrations are closely related to migrations of organisms. In both experimental periods, analyses carried out after midnight showed that the ammonia concentration in water from the subsurface layer increased much more than in the screen-surface microlayer; where ammonia was the first of the nitrogen compounds to attain maximum concentrations (Fig. 19). Ammoniphication seems to be responsible for these fluctuations, as it is the initial phase of organic matter mineralisation by bacteria and fungi (*e.g. Pseudomonas*, *Bacilius*, *Vibrio*, *Acinobacter*). In the course of this process, proteins are hydrolysed by appropriate enzymes. The resulting compounds are assimilated by bacteria, and then decomposed by peptidases into simple amino-acids. The deamination of these causes more ammonia to be evolved. The enzymatic hydrolysis of proteins is also characteristic of zooplankton organisms, hence the presence of ammonia, besides uric acid, in zooplankton excreta. In a study carried out on the composition of bacterial populations in the screen-surface microlayer and the subsurface water of the Gdańsk Deep in May 1989, Mudryk *et al.* (1991) found multiple colonies of DNA-hydrolysing bacteria distinctly predominating in the subsurface water, while bacteria responsible for ammoniphication were more abundant in the screen-surface microlayer. The nightly migrations of zooplankton into the subsurface water led to an increase in ammonia concentration in this layer. Harison *et al.* (1983) pointed out that ammonia contributes 50–80% of the total nitrogen-compound pool formed during organic matter mineralisation; this pool consists of zooplankton excreta (30%), microplankton and its bacterial regeneration (63%), and ammoniacal nitrogen diffusing up from deeper water (7%).

At sunrise, the particle-size distribution during the first experimental period (Fig. 20a) was approximately exponential for diameter sizes $< 10\ \mu$m, then the number of larger particles rose, especially in the subsurface layer. In the second experimental period (Fig. 20b), one hour after sunrise, the particle-size distribution became clearly differentiated. The particle numbers suggest that productive processes were more intensive in the screen-surface microlayer than in the subsurface layer. Many authors (Hardy and Apts, 1984; Harvey, 1966; Norkrans, 1980; Sieburth, 1968, 1971; Wandschneider, 1979) point out that the organisms living in the sea surface microlayer are far more active than those in the subsurface layer, a fact manifested by the higher amounts of suspended organic matter found in the former layer. A similar situation was observed in the second experimental period around 8.00 a.m. in direct sunlight; however, in early May the concentrations of particles of diameters $> 10\ \mu$m tended to rise (Fig. 21 a,b).

The pattern of particle-size distribution varied with increasing solar radiation: the numbers of particles decreased in the PM and EM microlayers,

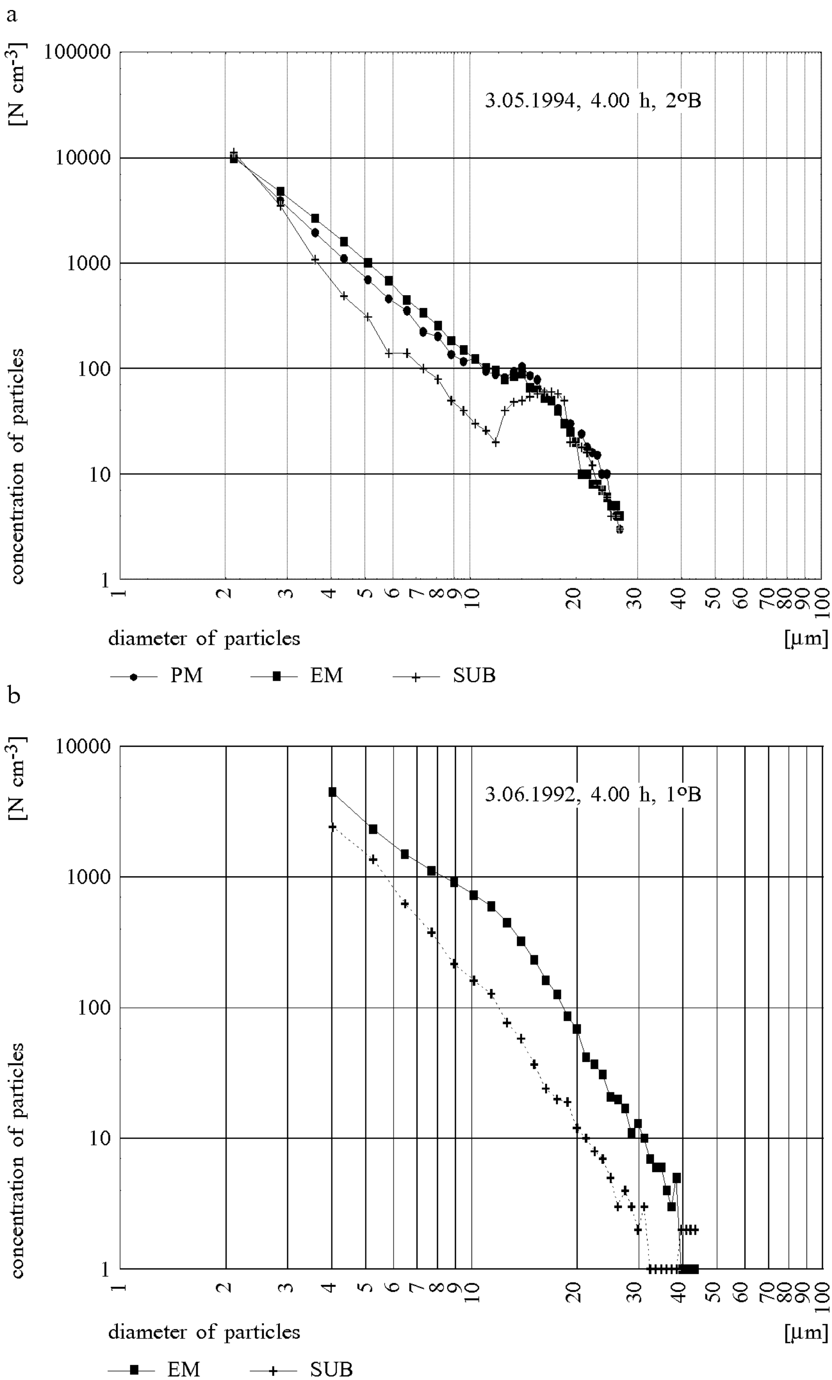
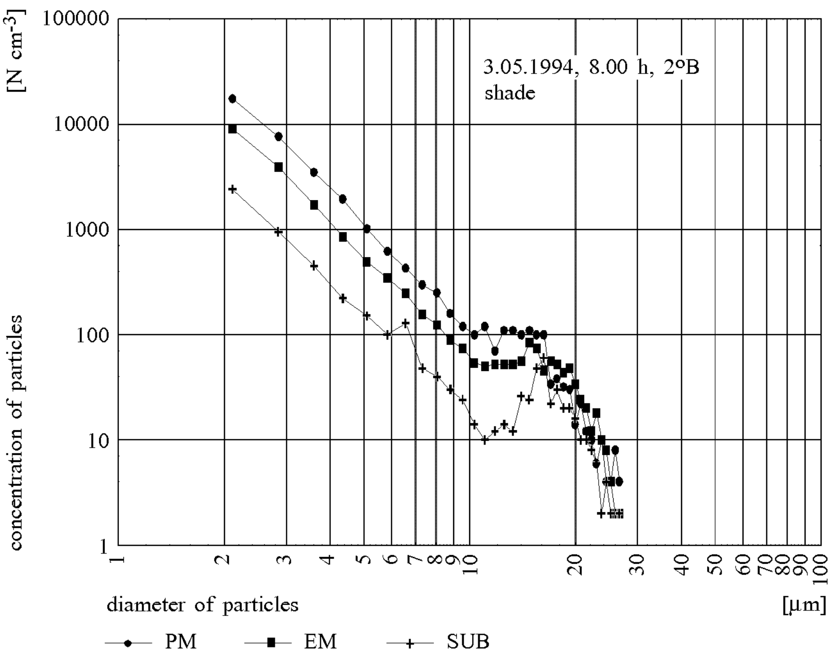


Fig. 20. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log); first experimental period (a), second experimental period (b)

a



b

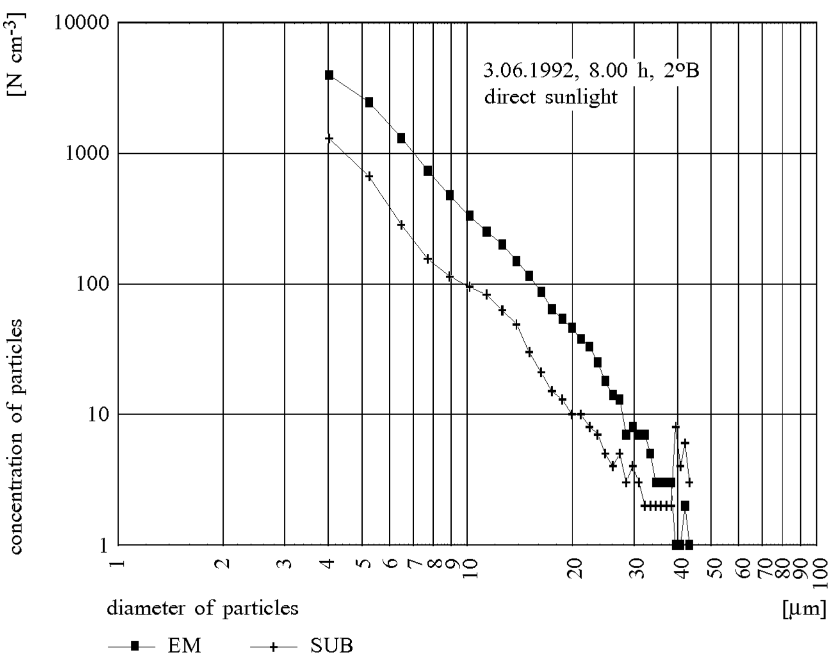


Fig. 21. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log); first experimental period (a), second experimental period (b)

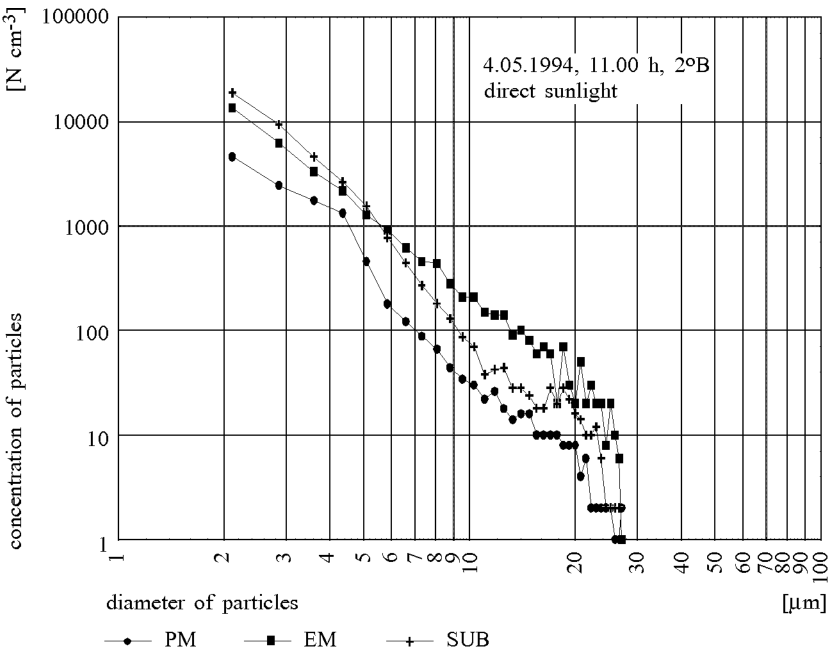
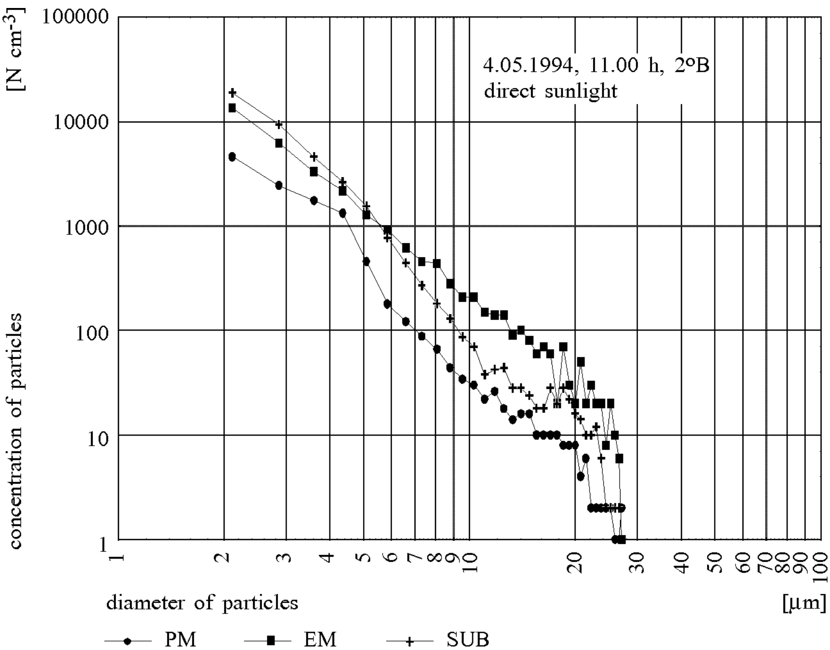


Fig. 22. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log) in the first experimental period

but increased in the subsurface layer (Figs. 22 and 23a). In direct sunlight, the concentration of small particles ($< 5\ \mu$m) was highest in the subsurface layer, and lowest in the PM layer. The characteristic peak corresponding to the concentration increase of particles $> 10\ \mu$m was not detected. Thus the strong solar radiation seems to be the most probable factor inhibiting photosynthesis in the surface film. Renk *et al.* (1985) also observed a 'fading' effect of chlorophyll, *i.e.* a decrease in its concentration under extreme solar radiation in the surface water layers of the Gdańsk Deep. Similar effects of short-term fluctuations in chlorophyll *a* concentrations were found in Puck Bay (Latała and Dąbrowska, 1980). Bacterioneuston species display individual sensitivity to solar radiation. For example, Sieburth (1968) noticed that the Narragansett Bay *Flavobacterium* sp., which contains orange pigment, reached maximum concentration levels under the strongest solar radiation. In general, bacteria containing carotenoids are very tolerant to strong radiation. Solar radiation has harmful effects on bacteria devoid of protective pigments (Rheinheimer, 1987).

At noon under a heavily overcast sky (Fig. 23b), typical particle size distribution curves were observed during the first experimental period. During the second period (Fig. 24), even though the number of particles rose due to increased insolation, the discrepancies between the screen-surface microlayer



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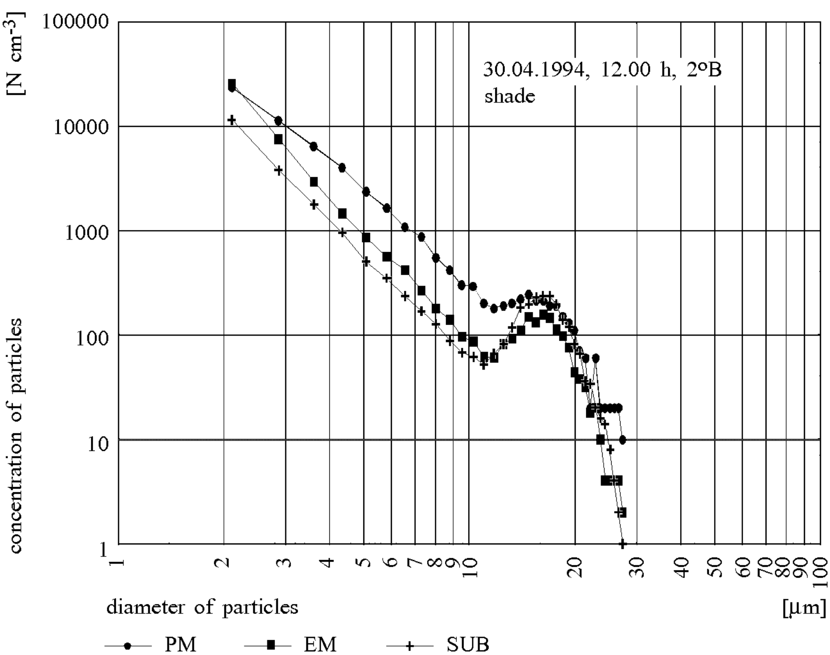
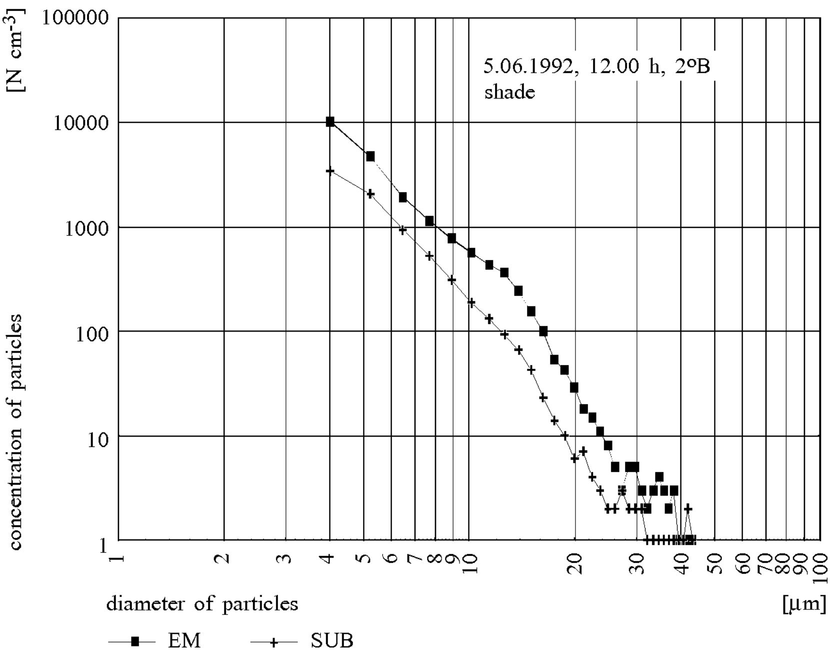


Fig. 23. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log); first experimental period (a), second experimental period (b)

a



b

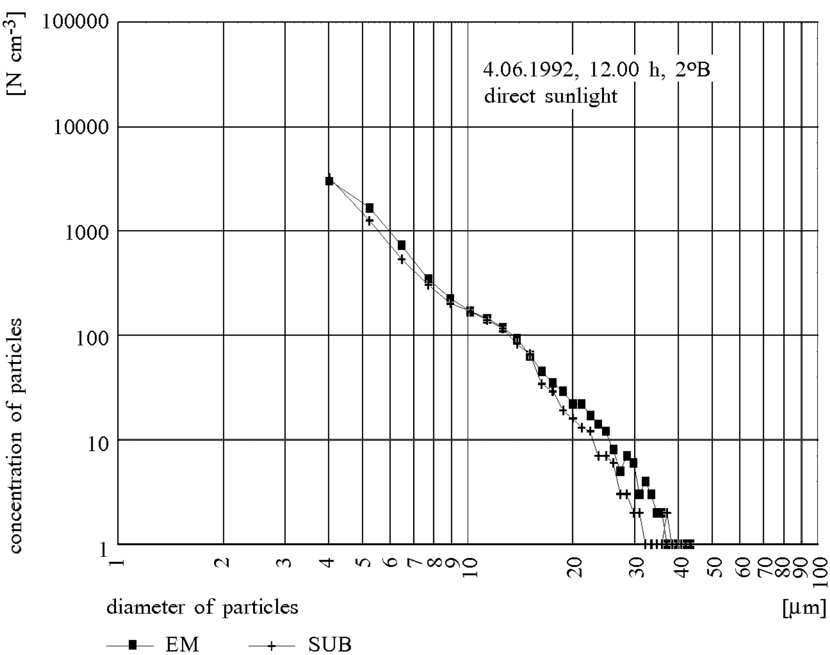
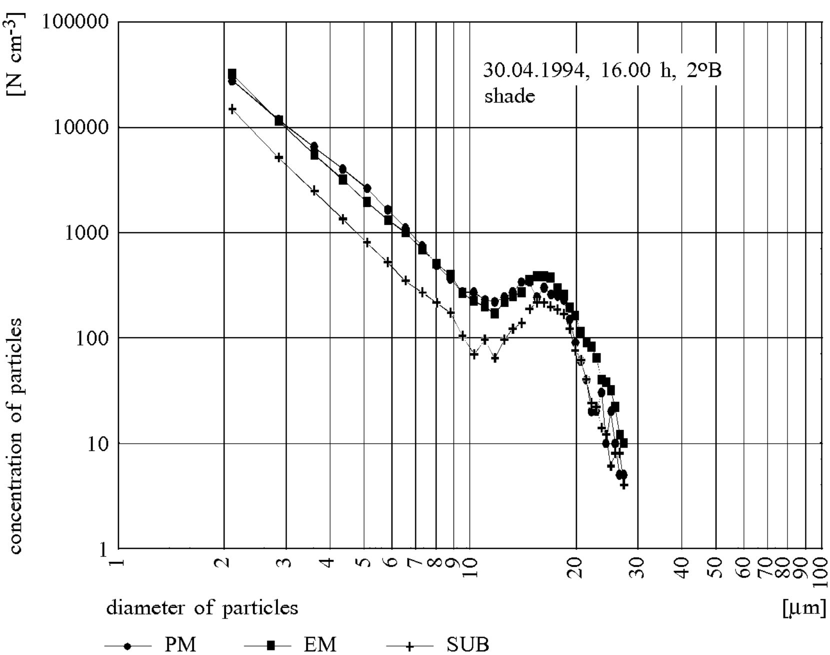


Fig. 24. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log) in the second experimental period; Sun screened by clouds (a), direct sunlight (b)

a



b

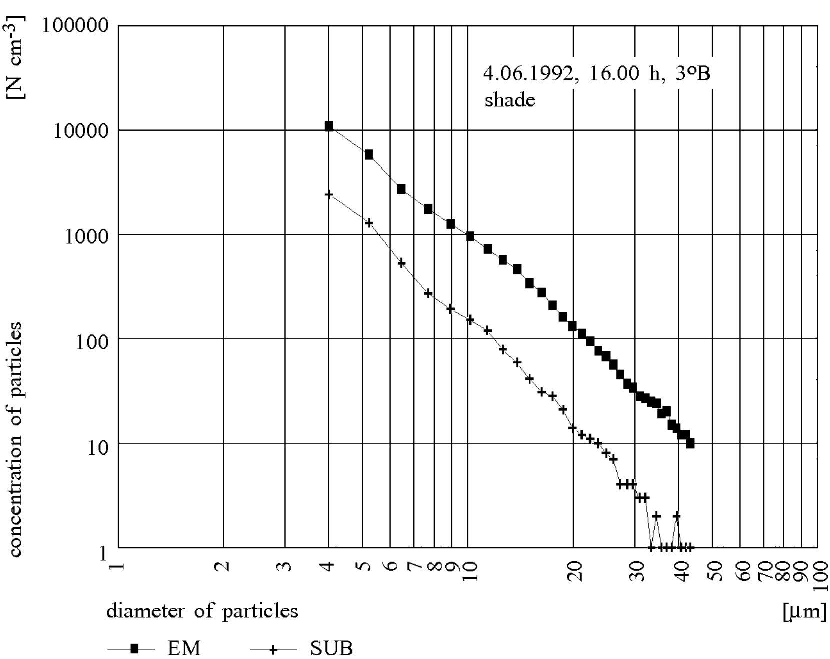


Fig. 25. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log); first experimental period (a), second experimental period (b)

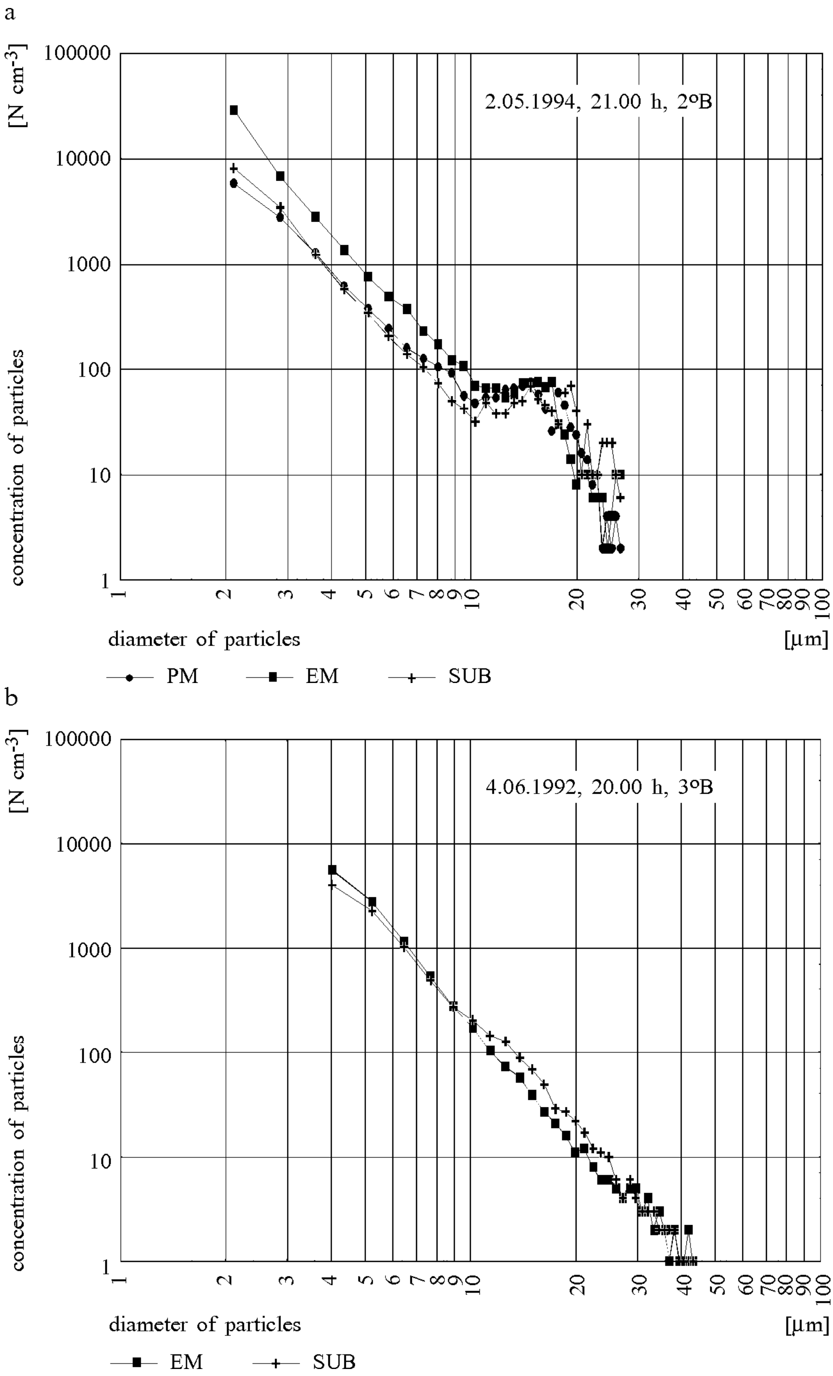


Fig. 26. Cumulative particle-size distribution at selected sea surface water layers of the Gdańsk Deep (log-log); first experimental period (a), second experimental period (b)

and the subsurface layer diminshed. During this period photosynthesis was not as intensive as during the first one, because in June the algal biomass and chlorophyll pigment concentrations usually decline following the early spring maximum (Latała, 1994).

The number of particles within the $> 10\ \mu$m diameter range increased significantly in the afternoon hours, as indicated by the experiments in late April – early May 1994 (Fig. 25a). Particle distribution characteristics was analogous to those recorded earlier (12.00, Fig. 23b). With the Sun screened by clouds and a sea state of 2°B, the numbers of particles in the PM and EM microlayers were approximately the same as in the subsurface layer. In June 1992 at this time of the day (Fig. 25b), the greatest discrepancies in particle concentrations were recorded between the EM microlayer and the subsurface layer in all size classes.

Towards the end of the day, there was a clear shift of particles from the plate-surface to the screen-surface microlayer and farther down to the subsurface layer, especially the particles of the smallest diameters (Fig. 26a and b). Furthermore, the concentrations of large particles decreased markedly in these layers. This observation indicates that as production slowed down during the afternoon hours, migration, grazing, and mineralisation of organic matter became the dominant processes.

5. Conclusions

The interface between sea and atmosphere constitutes a medium of chemically and biologically complex variables as compared to the subsurface water. Analysis of the diurnal cycles of suspended particle, chlorophyll *a* and nutrient concentrations have shown that the most pronounced fluctuations occurred in the plate-surface microlayer rather than in the screen-surface microlayer and the subsurface layer. Increased sampling frequency revealed a greater variability in the substances analysed.

The cycles of suspended particle, chlorophyll pigment and nutrient concentrations investigated at different times of the growing season overlapped the distinct fluctuations in these substances resulting from the intensity of production, organic matter mineralisation and migrations of organisms between the various surface water layers.

The significant correlation between the number of particles (especially with diameters $> 10\ \mu$m) and the chlorophyll *a* concentration suggests that phytoplankton cells make a considerable contribution to the total suspended matter content.

The concentrations of suspended particles and chlorophyll *a* in the surface water layers of the Gdańsk Deep was found to be higher in late April – early May than at the beginning of June.

The hyperbolic distribution functions obtained in late April – early May turned out to be more complex than those obtained at the beginning of June, and were indicative of a greater differentiation of plankton species in the first period. Judging from the deviation of the distribution curves from the exponential pattern, this differentiation occurred in the order of magnitude subsurface > screen-surface microlayer > plate-surface microlayer, despite the fact that the plate-surface microlayer contained the greatest number of particles.

Organisms smaller than 15 μm were the most sensitive to solar radiation in the PM microlayer. At noon some of them migrated down to subsurface layer, and it was in this water layer that the highest concentration of small particles was recorded at that time of the day. Microorganisms from the $\phi > 7$ μm size classes were the most abundant in the sea-surface microlayer, despite the intense irradiation.

Two clear maxima were distinguished in the diurnal cycles of particle and chlorophyll pigment concentrations in both the PM and the EM microlayers during the two experimental periods in the growing season: a stronger maximum in the mornings of the first period, and in the afternoons during the second. The maxima were accompanied by two minima: around midnight and at noon. For smaller particles in the subsurface layer, the cycle was reversed.

The distribution of the various phytoplankton and nanoplankton species among the submicrolayers of the sea-surface water is the resultant of many factors, *e.g.* the relationship between the rate of species proliferation and the rate of zooplankton grazing on the one hand, and the number of bacteria hydrolysing DNA on the other; the physical factors facilitating their migration in seawater are also of importance.

The diurnal variations of particle concentrations resulting from the fluctuations of productive processes and the migration of organisms were also closely related to nutrient concentrations. In both experimental periods, the ammonia concentration increment recorded after midnight was much greater in the subsurface water layer than in the screen-surface microlayer; ammonia was usually the first of the nitrogen compounds to reach maximum concentrations. The process responsible for the increase in ammonia concentration in this layer was ammoniphication, the initial step in the mineralisation of organic matter by bacteria and fungi. As a result of the enzymatic hydrolysis of proteins, ammonia appeared as a component of zooplankton excreta.

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