

**Temporal variability in
the chemical composition
of bottom sediments
in the Pomeranian Bay
(southern Baltic)***

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KEYWORDS

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Abstract

Seasonal changes in the chemical composition of sediments from four stations located in the Pomeranian Bay were analysed. The investigations were carried out in four periods (March and July 1996, and May and October 1997). The following parameters were investigated: organic carbon and nitrogen, total phosphorus and organic phosphorus, loss on ignition and redox potential.

On the basis of these results the influence of the following processes and phenomena was noted: the early spring phytoplankton bloom dominated by diatoms (March 1996); the intense inflow of allochthonous matter brought into the Bay with the waters of the Świna (May 1997); the summer bloom of blue-green algae and dinoflagellates (July 1996); the consequences of the summer 1997 flood which occurred in southern Poland (October 1997).

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1. Introduction

The seasonal variability in the chemical composition of sediments in estuarine zones depends on numerous coexisting factors, of which the following are the most important:

- seasonal variability in riverine water inflows (Grelowski *et al.* in press),
- seasonal variability in the productivity of the region, which is related to variable light and thermal conditions (Witek *et al.* 1993, Ochocki *et al.* 1995, Witek 1995, Ochocki *et al.* 1999), and which consequently results in different seasonal rates of organic matter deposition,
- variable hydrodynamic conditions in the region (Siegel *et al.* 1994a,b),
- seasonal variability in the activity of microorganisms and benthic organisms (Martynova 1984, Graca 1997).

The C/N ratio is one of the most often used parameters in analyses of the origin and degree of mineralisation of organic matter in the water column and sediments (Romankevich 1984, Maksymowska 1998). This parameter varies over quite a considerable range, depending on the type of living organisms and degree of degradation. It is widely accepted that the chemical formula of a newly formed particle of marine organic matter is $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4$, and that the molar C:N:P ratio is equal to 106:16:1 (Redfield 1958). Decomposition of organic compounds begins directly after the decay of living organisms and is a selective process consisting primarily in the removal of labile organic compounds (Deming & Baross 1993). Carbon is removed from organic compounds with greater difficulty than nitrogen during mineralisation, which is due to the greater C–C than C–N chemically bound energy (Posedel & Faganeli 1991). The molar C/N ratio in organic matter can therefore be an indicator of both the origin of organic matter and its degree of mineralisation.

Maksymowska (1998) states that the C/N ratios for the Gulf of Gdańsk do not allow one to distinguish allochthonous organic matter from that produced there. Her studies indicated that for the greater part of the year, the C/N ratio in Wisła river suspensions was close to values characteristic of marine phytoplankton. For that reason, this index only gave an idea of the proportion of phytoplanktonic organic matter to overall organic matter in the waters or sediments of the Gulf of Gdańsk, without differentiating between marine and riverine phytoplankton.

It must be stressed that a direct comparison between the Gulf of Gdańsk and the Pomeranian Bay is not possible, as Wisła waters flow directly into the Gulf, whereas Odra (Oder) waters flow through a very complex estuarine system, the large but shallow Szczecin Lagoon being its most important part. The average retention time in the Lagoon is two months

(Grelowski *et al.* in press); during the 1997 flood this was reduced to eight days in the eastern part of the Lagoon and to 24 days in its western sector (Mohrholz *et al.* 1998). The average retention time is usually sufficient for the preliminary degradation processes of riverine organic matter to occur, which leads to elevated C/N ratios in the waters flowing into the Pomeranian Bay.

The aim of the present paper was to examine the changes taking place in the sediments of the Pomeranian Bay in particular seasons. The temporal variability of the parameters analysed (content of organic and total phosphorus, content of organic carbon and organic nitrogen, loss on ignition, redox potential) was based on material collected in March and July 1996, and in May and October 1997.

2. Materials and methods

The Pomeranian Bay is located at the western end of the Polish coast. The bottom of the Bay is mostly covered with fine grey sand. White sand, as well as streaked and red sand is present on the northern slopes of the Odra Bank. The sediments at the mouth of the Świna are also little diversified. Fine sands with admixtures of coarser fractions and a certain amount of organic matter can be found there. The finest fractions with admixtures of silts occur in the vicinity of the Świna estuary and off the coast of the Bay east of the estuary. The north-western part of the Bay, the Sassnitz Deep, also contains areas covered with fine fractions (Kramarska & Jurowska 1991, Majewski & Lauer 1994).

Sediment samples from four stations (Fig. 1) were collected from on board r/v 'Baltica' in March and July 1996 and in May and October 1997 using a Reineck box sampler. All sediment cores were divided into 2.5 cm segments, placed in plastic containers and frozen at -20°C until analysis. The redox potential (Eh) of the sediments was measured immediately after sampling using a pHmeter (Eijkelpamp). The organic matter content was estimated from losses on ignition of dry sediments to constant mass (about 6 hours) at 550°C . Total phosphorus in the sediments was determined using a method developed by Gericke & Kurmies (1952), and modified by Golachowska (1977a). In this method, the sediment sample is dissolved in a mixture of perchloric and sulphuric acids. After filtration of the mineralised sample, total phosphorus was determined by the molybdenum yellow method. Total inorganic phosphorus was determined using a method developed for soils by Mehta *et al.* (1955), also modified by Golachowska (1977b). Organic phosphorus was determined as the difference between total phosphorus and total inorganic phosphorus.

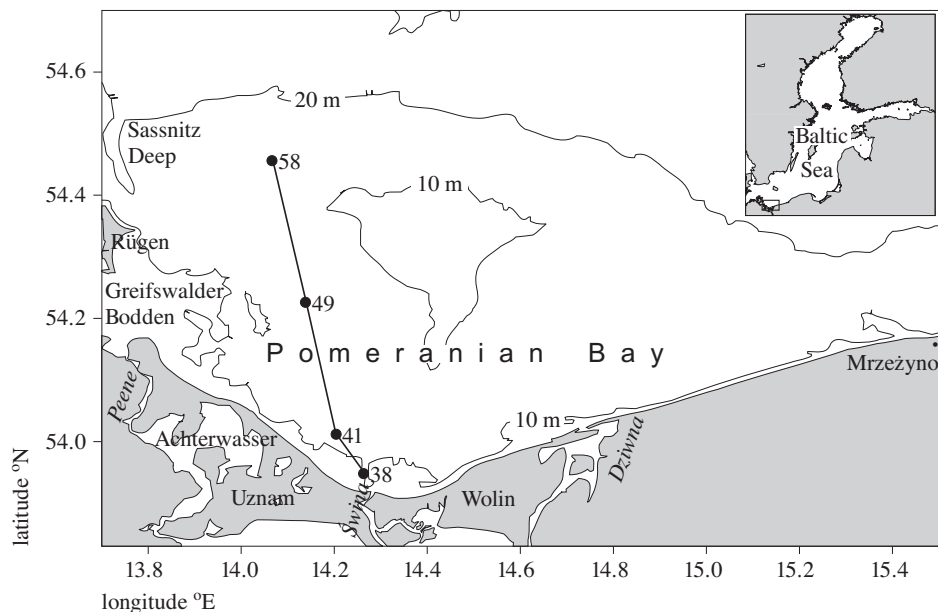


Fig. 1. Study area and location of sampling stations (These stations are not located in the fairway)

The contents of organic carbon and organic nitrogen in sediments were determined by means of a CHN autoanalyser (PERKIN ELMER 2400 series). The samples were dried to constant mass and homogenised, after which calcium carbonate was removed (Hedges & Stern 1984).

3. Results and discussion

The organic carbon (C_{org}) and nitrogen (N_{org}) contents in the sediments of the Pomeranian Bay were related to the organic matter content calculated as loss on ignition (LOI). The statistical analyses done for all the periods studied showed a high, statistically significant correlation between these parameters, and the dependence was described by the following linear regression equations:

$$C_{org}(\%) = 0.235 \text{ LOI}(\%) - 0.014, \quad r = 0.93, \quad (1)$$

$$N_{org}(\%) = 0.030 \text{ LOI}(\%) + 0.001, \quad r = 0.92. \quad (2)$$

The equation coefficients, calculated for particular seasons, were not stable and their variability is shown in Fig. 2. The lowest C_{org} in organic matter was recorded in the sediments collected in March 1996; these were also characterised by the highest percentage of N_{org} in organic matter. These results speak in favour of an early spring phytoplankton bloom, which is

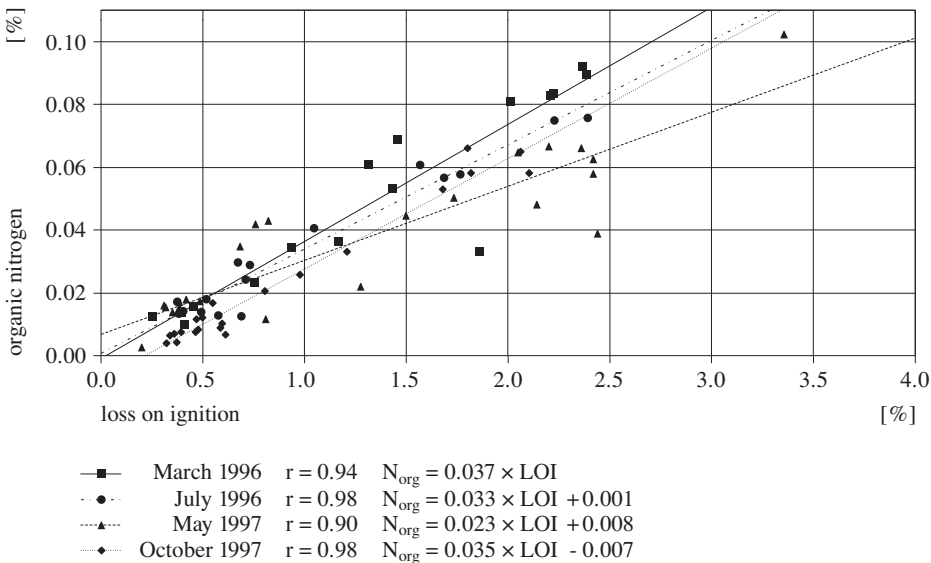
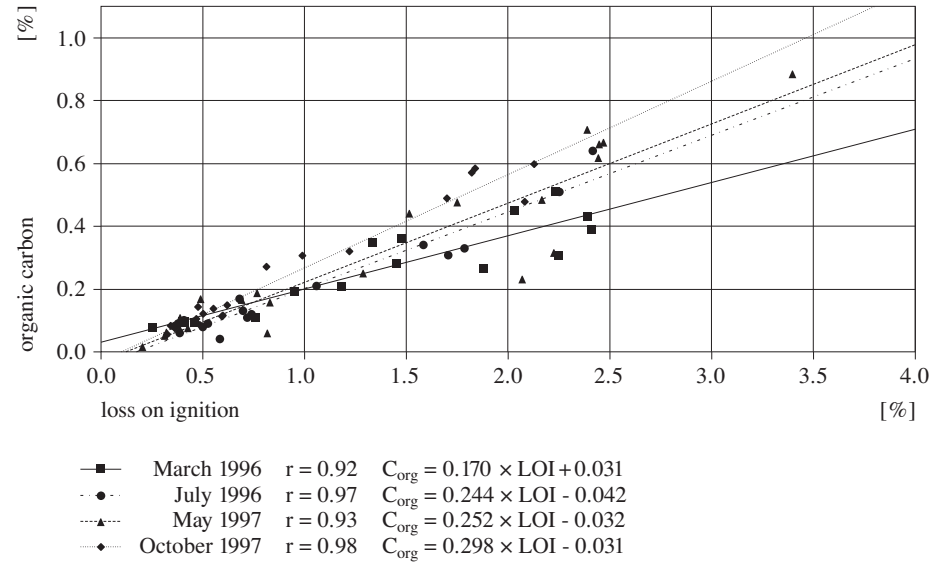
Table 1. Selected parameters of sediments from 4 stations (38, 41, 49 and 58) in the Pomeranian Bay during 4 seasons

Parameter	March 1996			July 1996			May 1997			October 1997		
	<i>n</i>	min-max <i>x</i> ± SD	<i>n</i>	min-max <i>x</i> ± SD	<i>n</i>	min-max <i>x</i> ± SD	<i>n</i>	min-max <i>x</i> ± SD	<i>n</i>	min-max <i>x</i> ± SD	<i>n</i>	min-max <i>x</i> ± SD
loss on ignition [%]	19	0.25–2.41 1.35 ± 0.76	20	0.38–3.47 1.28 ± 0.98	21	0.20–3.40 1.20 ± 0.93	20	0.33–2.13 0.84 ± 0.60				
Eh [mV]		no data	19	(–367)–236 (–1) ± 195	20	(–317)–149 (–85) ± 169	20	(–367)–136 (–22) ± 172				
P _{tot} [mg g ^{–1} s.m.]	21	0.082–0.470 0.210 ± 0.121	20	0.118–0.415 0.202 ± 0.100	21	0.052–0.650 0.218 ± 0.197	20	0.114–0.305 0.209 ± 0.063				
P _{org} [mg g ^{–1} s.m.]	21	0.000–0.080 0.014 ± 0.028	20	0.000–0.068 0.009 ± 0.020	21	0.000–0.228 0.032 ± 0.064	20	0.000–0.157 0.063 ± 0.042				
C _{org} [mg g ^{–1} s.m.]	17	0.80–5.11 2.54 ± 1.45	16	0.40–6.40 2.08 ± 1.73	23	0.15–8.81 3.00 ± 2.59	21	0.56–5.97 2.36 ± 1.92				
N _{org} [mg g ^{–1} s.m.]	17	0.11–0.92 0.48 ± 0.31	16	0.13–0.76 0.35 ± 0.23	23	0.03–1.02 0.38 ± 0.25	21	0.04–0.66 0.24 ± 0.22				
C/N ratio	17	4.3–10.5 6.8 ± 1.5	16	3.5–11.6 6.6 ± 2.0	23	3.6–19.9 8.4 ± 4.2	21	8.5–24.0 13.3 ± 3.6				

min – minimum value, max – maximum value, *x* – average value, SD – standard deviation, *n* – number of observations

usually dominated by diatoms containing up to 6 times less carbon than, for example, dinoflagellates (Witek 1995). The linear regression coefficients calculated for the dependence between C_{org} and LOI showed a rising trend in July and May, reaching maximum values in October.

The highest C_{org} and N_{org} were reported in the surface sediments in March 1996 and May 1997 (Table 1). Comparison of C_{org} and N_{org} , as well as molar the C/N ratio, suggest that the organic matter during the



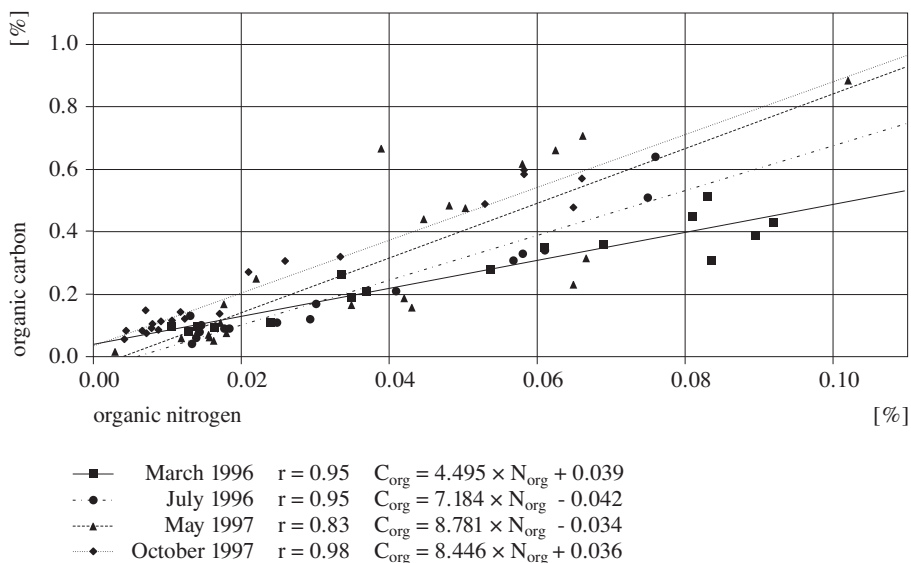


Fig. 2. Correlations between C_{org} , N_{org} and loss on ignition in the sediments of the Pomeranian Bay during the four periods analysed

periods in question originated from two different sources. In March 1996 the relation between carbon and nitrogen in the organic compounds contained in the sediments showed the following linear regression (Fig. 2):

$$C_{org} = 4.495 N_{org} + 0.039. \quad (3)$$

The slope of the curve, the lowest in the entire study period, indicates with a high probability that the organic matter reaching the sediments originated mainly from fresh autochthonous phytoplankton. Diatoms, *e.g.* *Thalassiosira* spp., *Skeletonema costatum*, *Melosira arctica*, *Chaetoceros* spp. (Gromisz *et al.* 1999) dominate the early spring bloom; these have characteristically large cells, up to 120 μm in size (Pliński 1988, Witek 1995). As a result of the high deposition rate, the molar C/N ratio of the organic matter in the sediments is low and remains at nearly the same level during the entire sedimentation process. These findings are in agreement with those of the studies by Enoksson *et al.* (1990) and Savchuk & Wulff (1996) in other parts of the Baltic Sea. These researchers observed an increased sedimentation rate in spring and autumn in comparison with summer and winter values. This finding is connected with the fact that diatoms readily sediment onto the bottom as they do not have mechanisms slowing down or preventing their sedimentation. A high rate of spring sedimentation was also reported from the Gulf of Gdańsk (Maksymowska 1998); this was attributed to the lack of thermal stratification and slow growth of organic matter

consumers at that time of year. A further cause of the rapid sedimentation of organic matter in the Pomeranian Bay is that the basin is shallow.

The relatively high average LOI, as well as the high C_{org} and N_{org} in the sediments collected in March 1996, were probably due to high phosphate discharges from the Szczecin Lagoon to the Pomeranian Bay in February and March 1996 (Table 2). As much as 320 tonnes of inorganic phosphorus entered the Bay in these two months, which amount must in consequence have intensified primary production and affected the composition of the sediments.

Table 2. Estimated inorganic and total phosphorus inflows from the Szczecin Lagoon to the Pomeranian Bay before, during and after the periods analysed

Month	PO_4^{3-} [tonnes P month ⁻¹]	P_{tot} [tonnes P month ⁻¹]
February 1996	180	no data
March 1996	140	no data
June 1996	10	no data
July 1996	50	no data
April 1997	50	300
May 1997	30	270
August 1997	500	1300
September 1997	130	300
October 1997	80	210

Source: Grelowski *et al.* (in press).

In May 1997 the average C_{org} and N_{org} contents were also relatively high, but the relation between carbon and nitrogen in organic compounds in the sediments was of an entirely different nature (Fig. 2):

$$C_{org} = 8.781 N_{org} - 0.034. \quad (4)$$

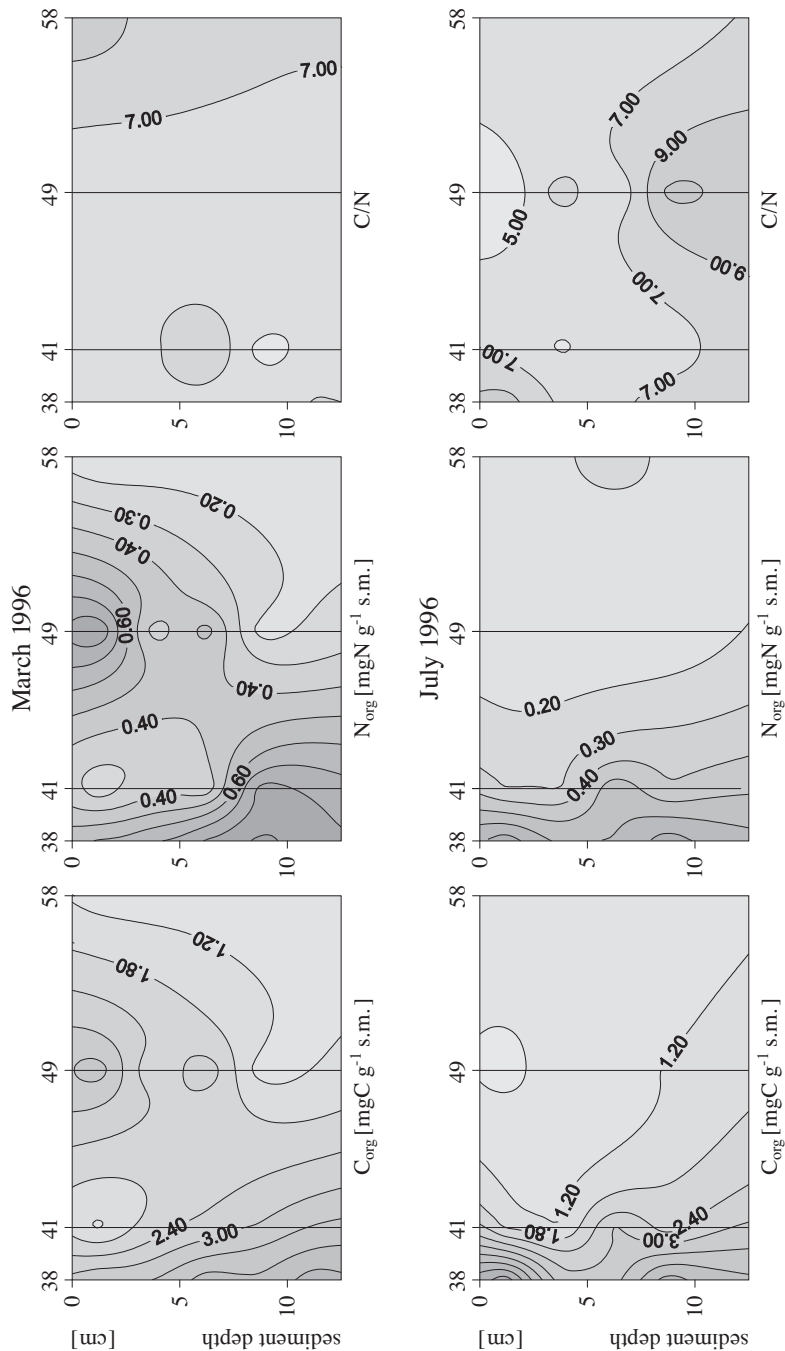
From May until the end of summer the degradation of organic matter intensifies. This is related to the increase in biomass of degrading heterotrophic organisms and grazing on organic matter in the water column (Maksymowska 1998). During that time of year zooplankton (Wiktor 1990) and bacterioplankton (Witek 1995) are thought to be abundant in re-suspended matter. Consequently, fluxes of autochthonous organic matter reaching the sediments are reduced, while the C/N ratio in this matter remains relatively low, as, like phytoplankton, both bacteria and zooplankton have a low C/N ratio.

The relatively high C/N ratio in the sediments of the Pomeranian Bay in May 1997 can therefore be explained by the inflow of allochthonous matter

brought into the Bay with the waters of the Świna. In April and May 1997 loads of total phosphorus for exceeded the loads of mineral phosphorus discharged into the Bay (Table 2). About 490 tonnes of phosphorus in the form of particulate and dissolved organic matter entered the Bay in this period. Most of this was probably deposited in the bottom sediments, thus contributing to the increased C/N ratio, as was recorded even at a distant station (No. 49) (Fig. 3). A similar phenomenon was observed in spring in the sediments of the Gulf of Gdańsk (Maksymowska 1996), where the C/N ratio was highest in the surface sediments directly affected by Wisła waters.

The sediments collected in May also displayed a considerable decrease in redox potential as compared with the other months studied (Table 1). This fact may indicate intensified organic matter mineralisation in the sediments over that period. Eh is a frequently used indicator in the analysis of organic matter transformations during mineralisation (Pempkowiak 1994, Bolałek & Kowalewska 1997). The mineralisation of organic matter in the water column of the Pomeranian Bay occurs mainly by means of aerobic processes, while in the sediments both aerobic and anaerobic conditions are encountered, this latter fact being confirmed by variations in the Eh potential from -367 mV to $+236$ mV (Table 1). Over that range of Eh, organic matter is mineralised by the successive reduction of oxygen, nitrates, manganese compounds (IV), and sulphate (VI). When all these oxidisers are no longer present in sediments, disproportionation reactions occur (Martens 1976).

In July 1996 the average C_{org} and P_{org} were the lowest, while the average N_{org} was among the lowest (Table 1). At the same time the molar ratio in this profile was very low: 5 in the central Bay and 9 in the vicinity of the Świna mouth (Fig. 3). These findings may indicate the appearance of summer blue-green algae and an intensive dinoflagellate bloom (Gromisz *et al.* 1999, Ochocki *et al.* 1999), giving rise to changes in the chemical composition of the bottom sediments of the Bay. The low sedimentation rate (excluding station 38) over that period is caused not only by a lower bloom intensity (due to the reduced phosphate discharge from the Szczecin Lagoon – Table 2), but also by the smaller sizes of cells, the diameters of which do not exceed $60\ \mu\text{m}$ (Witek 1995). Thus, during summer, despite ongoing primary production, the organic matter flow from the water column to the Pomeranian Bay sediments is insignificant. Similar findings were made by Hagström *et al.* (1989) and Wassmann *et al.* (1990) for other parts of the Baltic Sea, and also for the Barents and Norwegian Seas. The low C/N ratios during that period of time may also be due to the large biomass of bacteria and zooplankton in the sediments (Martynova 1984, Maksymowska 1998).



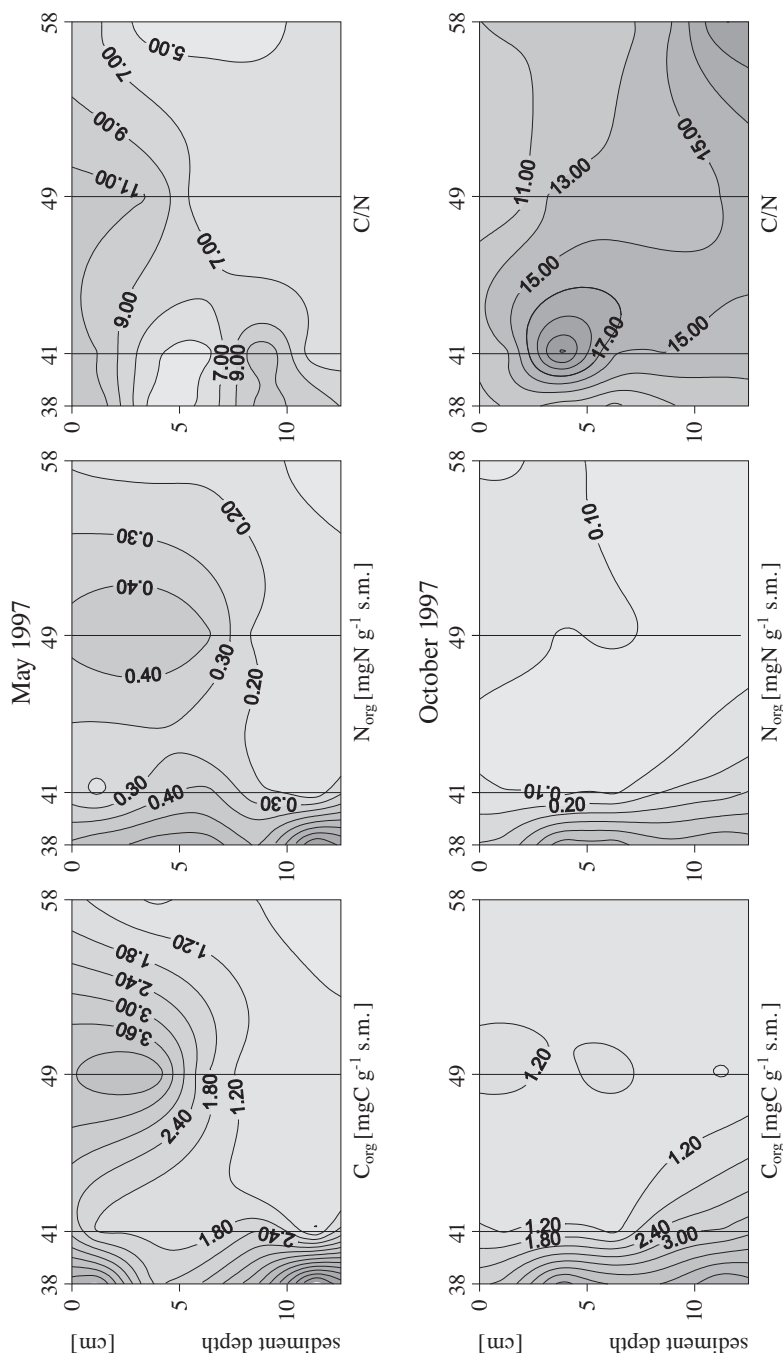


Fig. 3. Organic carbon and organic nitrogen content and molar C/N ratio in the sediments of profiles in the Pomeranian Bay in March and July 1996, May and October 1997

Autumn blooms in the southern Baltic are usually less intense than spring ones; they are characterised by very large diatom cells, *e.g.* *Actinocyclus octonarius*, *Coscinodiscus* sp.+*granii* (Gromisz *et al.* 1999), up to 300 μm in diameter (Pliński 1988, Witek 1995). The chemical composition of sediments in the Pomeranian Bay in October 1997 was additionally influenced by a considerable discharge of terrigenous organic matter with the post-flood waters.

During that period both C_{org} and N_{org} were very low, their respective values amounting only to 2.36 mgC g^{-1} d.w. and 0.24 mgN g^{-1} d.w. The molar C/N ratio was clearly the highest in the entire profile down to 12.5 cm depth in this period (Fig. 3). What was intriguing was that at the same time there occurred a considerable increase in organic phosphorus content (Table 1). It is known that phosphorus compounds in organic matter usually degrade rapidly (Deming & Baross 1993). In the case of the sediments analysed in the Pomeranian Bay in October 1997, the organic phosphorus was resistant to degradation, so must have originated from land. Terrigenous organic matter is much richer in phosphorus than the fresh matter produced during primary production in the sea (Waleńczak 1987).

The unusual situation encountered in the Pomeranian Bay sediments in October 1997 may be explained by the consequences of the flood that occurred in southern Poland in July and August 1997. The two separate flood crests which built up in the upper reaches of the Odra catchment area combined in the lower reaches and resulted in a long-lasting (22 June – mid August) outflow of great volumes of water (Dziadziuszko 1998). Phosphate and total phosphorus loads were 2–3 times higher than in comparable periods in previous years (Mohrholz *et al.* 1998, Pastuszek *et al.* 1998, Grelowski *et al.* 1999). The inflowing waters spread mainly north-eastwards from and north-westwards the Świna Strait (Grelowski 1998), significantly influencing the chemical composition of Pomeranian Bay sediments.

4. Conclusions

The investigations carried out in four periods (in March and July 1996, and in May and October 1997) show that the processes taking place in the water column and in the river waters significantly affect the chemical composition of the Pomeranian Bay sediments. The influence of the following processes was noted in these sediments:

- the early spring phytoplankton bloom is dominated by diatoms (March 1996),
- the intense inflow of allochthonous matter brought into the Bay with the waters of the Świna (May 1997),

- the summer bloom of blue-green algae and dinoflagellates is less intensive than the spring or autumn blooms (July 1996),
- the consequences of the flood which occurred in southern Poland in the summer of 1997 (October 1997).

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