Chlorophyll *a* and its derivatives in recent sediments of the southern Baltic Sea collected in the years 1992–1996*

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> > **KEYWORDS**

Chlorophyll a Chlorophyll a derivatives Chlorins Phytoplankton pigments Sediments Baltic Sea HPLC

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Abstract

Determinations of chlorophyll a and its derivatives (chlorins) as well as chlorophylls b, c and β -carotene in recent sediments (0–10 cm) of the southern Baltic Sea carried out in the years 1992–1996 are compiled. Correlations of the concentrations of chlorins with parameters such as the origin of a sample, oxygen in near-bottom waters (literature data) and organic carbon in sediments were analysed with respect to the chlorins' utility as environmental markers. Comparison of the concentration levels of chlorins in sediments with the literature results proves that these compounds are sensitive environmental markers of primary production in the overlying waters (taking local water currents into account) and of environmental conditions. Moreover, together with other sedimental pigments, they are markers of prevailing plankton classes in the adjacent waters, and are valuable indicators of the average plankton composition supplementary to biological determinations.

1. Introduction

Chlorophyll a is the most abundant plant pigment in nature, also in the sea. Processes such as phytoplankton growth, cell sinking, cellular

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senescence and zooplankton grazing affect the concentration of chlorophyll a in seawater. Moreover, chlorophyll a and other chlorophylls and carotenoids in seawater act as taxonomic markers, since different classes of algae contain these pigments in various proportions (Jeffrey *et al.*, 1996).

Phytoplankton pigments in seawater have been studied for many years; in recent years these studies have gathered in intensity owing to the development of high-performance liquid chromatography (HPLC) (Mantoura *et al.*, 1996). The investigation of chlorophyll *a* derivatives (porphyrins) in sediments gave rise to organic geochemistry and the concept of the 'biological marker' (Treibs, 1936; Eglinton and Calvin, 1967). Since environmental factors exert such a strong influence on the structure of chlorophyll *a* and its diagenetic routes, the type of porphyrin found in a sediment is taken to be a paleoindicator, *i.e.* a compound indicative of its sedimentological history. While that research was performed on prehistoric sediments (Bidigare *et al.*, 1990; Callot *et al.*, 1990), studies of recent marine sediments have focused more on the structural differences between the immediate derivatives of chlorophyll *a* (chlorins) (Fig. 1). No quantitative systematic analysis of chlorophyll *a* transformation in recent marine sediments has so far been carried out.

Eutrophication is a fundamental problem in the southern Baltic, especially in its coastal zone (HELCOM, 1993, 1996). The high primary production rate caused by elevated nutrient ion concentrations and the irregular water exchange with the North Sea and Atlantic makes the Baltic an excellent model basin for following the transformation of chlorophyll in the marine environment. The primary aim of the present work was to compile the results of studies of chlorophyll a and its derivatives carried out in 1992–1996 on recent (0–10 cm layer) Baltic sediments (Kowalewska, 1994; Kowalewska et al., 1996, 1997; Kowalewska and Konat, 1997), and then to correlate them with such parameters as the sediment layer depth, sampling station position, near-bottom water oxygen and organic carbon in sediments in order to examine environmental influence on the abundance and transformation of chlorophyll a. An additional goal was to verify, on the basis of the results and literature phytoplankton data, the relationship between the pigments in sediments and the occurrence of plankton in the adjacent waters.



Fig. 1. Scheme of chlorophyll *a* diagenesis in sediments

2. Experimental

2.1. Sample collection

Samples of recent marine sediments were collected with a Niemistö core sampler in different seasons during cruises of r/v 'Oceania' in 1992–1996, with the exception of samples collected with a box corer during a cruise of



Fig. 2. Location of the sediment sampling stations on the Baltic Sea in 1992–1996

r/v 'Baltica' in April 1994. Fig. 2 shows the location of the sampling stations. The samples cover different sites and types of sediments. The marine stations can be divided into three groups:

- coastal around the Gulf of Gdańsk (92A in Puck Bay, a shallow, eutrophic bay, P110d – near the tip of the Hel Peninsula, where strong, near-bottom currents occur, ZN2 – near the mouth of the Vistula, the largest Polish river discharging into the Baltic, PGd – near the port of Gdynia),
- the open sea (P39, P3, P8, PBW, BCX, AN1, P110) of different water depths and sediment types,
- the Deeps (P5 in the Bornholm Deep and G-2, P116 in the Gdańsk Deep) the deepest, usually anoxic (Tabs. 1 and 2), regions of the Polish economic zone. The Gdańsk Deep is a sink for particulate matter transported by the Vistula (Majewski, 1990). On the other hand, the particulates transported by the river Oder are first trapped in the Oder Estuary (Szczecin Lagoon) and then washed out during seawater inflows and settled again in the Bornholm Basin (Robakiewicz, 1993).

The other group of stations includes three in the Szczecin Lagoon, a basin where primary production is high and which is less anoxic than the Deeps (Poleszczuk, 1995); samples were collected at each of these stations in August and October 1996 during boat expeditions of the Biological Oceanography Department of Szczecin University.

2.2. Analytical methods

Pigment extraction

The method of extraction was in part similar to that used routinely in studies of chlorins (Eckardt *et al.*, 1992; Kowalewska, 1994). A pre-weighed frozen sediment sample (1-30 g) was allowed to thaw; it was then centrifuged to remove water and flushed with 20 cm³ of acetone, mixed, sonicated for 5 minutes and centrifuged again. The extraction procedure was usually repeated no more than three times to the visual disappearance of colour. The supernatant fractions were then combined and re-extracted with benzene in a 30:3:27 (v/v/v) acetone:benzene:water system (Kowalewska, 1995). The benzene extract was transferred to a glass vial and evaporated to dryness in a stream of argon. The sample thus prepared was stored in a deep-freeze, usually for no longer than two weeks.

Station	Layers [cm]	Coordin- ates	Depth [m]	$ O_2 \\ \left[ml \ l^{-1} \right] $	$_{\rm Corg}^{\rm Corg}$	Sedi- ment	Time of sampling	chl a^*	$\operatorname{chl} b$	chls c	pheo a	pyro- pheo	phrbs	steryl-s	β -car
open se	38														
P39	$\begin{array}{c} 0-1\\ 1-5\\ 5-10\end{array}$	$54^{\circ}48'N$ $14^{\circ}48'E$	46	2.2	pu pu	silt	1992 October	$\begin{array}{c} 0.866 \\ 0.258 \\ 0.281 \end{array}$	$\begin{array}{c} 0.081 \\ 0.036 \\ 0.07 \end{array}$	$\begin{array}{c} 0.077 \\ 0.047 \\ 0.011 \end{array}$	2.27 1.129 1.88	$\begin{array}{c} 1.473 \\ 0.731 \\ 1.124 \end{array}$	$\begin{array}{c} 0.265\\ 0\\ 0\\ 0 \end{array}$	$ \begin{array}{c} 1.84 \\ 0.53 \\ 0.6 \end{array} $	$2.18 \\ 0.58 \\ 1.05$
P39	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$54^{\circ}44'N$ $15^{\circ}08'E$	63	က	5.86 5.65 5.68	$_{ m clay}$	1995 October	27.71 13.18 6.38	$\begin{array}{c} 0.25 \\ 0.36 \\ 0.28 \end{array}$	1.86 1.16 0.43	$\begin{array}{c} 23.67 \\ 15.03 \\ 5.85 \end{array}$	$10.48 \\ 6.19 \\ 5.89$	14.15 7.58 4.2	nd** nd nd	24.38 23.08 11.42
P3	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$55^{\circ}13'N$ $17^{\circ}04'E$	91	က	$\begin{array}{c} 0.33 \\ 0.75 \\ 0.22 \end{array}$	sand	1995 March	$\begin{array}{c} 0.29 \\ 0.9 \\ 0.04 \end{array}$	$\begin{array}{c} 0.04 \\ 0.02 \\ 0 \end{array}$	$\begin{array}{c}1\\0.07\\0.001\end{array}$	$12.06 \\ 1.04 \\ 0.35$	pu pu	$17.48 \\ 0.57 \\ 0.001$	000	$2.65 \\ 1.1 \\ 0.00$
$\mathbf{P3}$	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$55^{\circ}13'N$ $17^{\circ}04'E$	91	1.62	$1.02 \\ 0.83 \\ 0.47$	sand	1995 October	$\begin{array}{c} 0.6 \\ 0.6 \\ 0.03 \end{array}$	$\begin{array}{c} 0.07 \\ 0.01 \\ 0 \end{array}$	$\begin{array}{c} 1.9\\ 1.4\\ 0\end{array}$	$5.2 \\ 4.7 \\ 0.24$	$\begin{array}{c} 2.89 \\ 0.98 \\ 0.15 \end{array}$	$8.78 \\ 5.7 \\ 0.001$	000	$2.1 \\ 2.8 \\ 0.2$
P8	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$55^{\circ}29'N$ $18^{\circ}12'E$	78	2.7	pu pu	silt	1992 October	$5.15 \\ 0.774 \\ 0.539$	$\begin{array}{c} 0.731 \\ 0.117 \\ 0.102 \end{array}$	0.222 0.043 0.013	$\begin{array}{c} 14.428 \\ 0.102 \\ 0.117 \end{array}$	$\begin{array}{c} 12.854 \\ 3.176 \\ 2.191 \end{array}$	7.04 0 0	$\begin{array}{c} 10.62 \\ 0.83 \\ 2.32 \end{array}$	$\begin{array}{c} \cdot \ 3.15 \\ 3.13 \\ 3.21 \\ 3.21 \end{array}$
PBW	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$55^{\circ}29'N$ $18^{\circ}14'E$	80	$\stackrel{7}{\scriptstyle \sim}$	3.85 3.36 3.58	silt	1995 October	$5\\3.77\\1.6$	$\begin{array}{c} 0.59 \\ 0.41 \\ 0.79 \end{array}$	$1.52 \\ 0.62 \\ 0.006$	$12.36 \\ 9.19 \\ 10.74$	6.55 5.22 5.39	9.61 7.07 3.9	pu pu	0.49 7.38 9.28
P69	$\begin{array}{c} 0-5 \\ 5-10 \end{array}$	$55^{\circ}20'N$ $18^{\circ}20'E$	78	9	pu	sand/ gravel	1994 August	$0.207 \\ 0.013$	$0.014 \\ 0.001$	$0.019 \\ 0.001$	$0.38 \\ 0.04$	$0.22 \\ 0.03$	$0.72 \\ 0.09$	$0.08 \\ 0.03$	pu

eta-car	$1.33 \\ 0.46 \\ 0.52$	2.41 2.52 0.85	3.35	$\begin{array}{c} 41.75\\ 22.72\\ 26.01\end{array}$		$15.09 \\ 0.75 \\ 0.8 \\ 0.8$	14.13	pu	$17.76 \\ 5.22 \\ 1.83$
steryl-s	$3.64 \\ 0.36 \\ 0.81$	$2.94 \\ 0.49 \\ 0.34$	pu	$\begin{array}{c} 0.56 \\ 0.44 \\ 0.96 \end{array}$		$16.02 \\ 5.57 \\ 10.79$	pu	$11.48 \\ 4.23$	$1.17 \\ 0.07 \\ 0.23$
phrbs	6.212 0.895 0.918	5.153 0.45 0.244	3.88	35.42 7.08 3.07		$\begin{array}{c} 4.275 \\ 0.763 \\ 0 \end{array}$	7.57	$25.31 \\ 25.54$	2.42 2.89 1.81
pyro- pheo	$\begin{array}{c} 4.865 \\ 0.406 \\ 0.861 \end{array}$	$\begin{array}{c} 4.054 \\ 1.906 \\ 1.385 \end{array}$	5.47	22.91 8.8 8.8		$\begin{array}{c} 12.635 \\ 9.857 \\ 7.789 \end{array}$	21.78	$22.3 \\ 11.59$	$9.41 \\ 4.25 \\ 1.61$
pheo a	$5 \\ 0.258 \\ 0.422$	5.221 3.462 2.117	6.52	$\frac{107.2}{16.7}\\13.25$		15.475 9.428 7.26	27.63	45.38 20.32	11.17 5.07 2.14
chls c	$\begin{array}{c} 0.113 \\ 0.0005 \\ 0.0004 \end{array}$	$\begin{array}{c} 0.526 \\ 0.129 \\ 0.013 \end{array}$	0.84	$\begin{array}{c} 25.34\\ 0\\ 0 \end{array}$		$\begin{array}{c} 0.116 \\ 0.411 \\ 0.319 \end{array}$	0.001	$1.12 \\ 0.41$	$\begin{array}{c} 0 \\ 0.41 \\ 0.425 \end{array}$
chl b	$\begin{array}{c} 0.271 \\ 0 \\ 0 \end{array}$	$\begin{array}{c} 0.285 \\ 0.25 \\ 0 \end{array}$	0.16	$\begin{array}{c} 2.15 \\ 0.85 \\ 0.45 \end{array}$		$\begin{array}{c} 0.627 \\ 0.429 \\ 0.343 \end{array}$	0.43	$0.498 \\ 0.27$	$\begin{array}{c} 0.41 \\ 0.3 \\ 0.17 \end{array}$
chl a^*	$3.034 \\ 0 \\ 0$	$\begin{array}{c} 4.091 \\ 0.698 \\ 0.281 \end{array}$	2.37	47.44 25.33 8.28		$7.504 \\ 4.78 \\ 4.349$	12.66	20.953 7.9	9.05 3.78 1.67
Time of sampling	1992 October	1992 October	1994 April	1996 May		1992 October	1994 April	1994 August	1996 May
Sedi- ment	silt	$\operatorname{silt}/\operatorname{clay}$	silt	$\operatorname{silt}/\operatorname{clay}$		clay	clay	clay	clay
Corg [%]	$\bigg\}_{1.14}$	pu pu	1.23	5.52 5.19 3.35		$\bigg\}_{4.48}$	4.64	hu	4.82 4.73 4.93
$\underset{\left[\mathrm{ml}\ l^{-1}\right]}{\mathrm{O}_{2}}$	2.7	5.2	3.5	9.1		$\stackrel{\checkmark}{\sim}$	2.7	< 2	0.68
Depth [m]	83	20	85	71		89	89	89	89
Coordin- ates	$55^{\circ}22'$ N $18^{\circ}23'$ E	56° 25' N 18° 36' E	$55^{\circ}21'N$ $19^{\circ}04'E$	$54^{\circ}30'N$ $19^{\circ}06'E$		$55^{\circ}15'N$ $15^{\circ}59'E$	55°15′N 15°59′E	55°15′N 15°59′E	$55^{\circ}15'N$ $15^{\circ}59'E$
Layers [cm]	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	0 - 3	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	eps	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	0 - 3	$\begin{array}{c} 0-5 \\ 5-10 \end{array}$	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$
Station	BCX	AN1	P63	P110	the De	P5	P5	P5	P5

Table 1. (continued)

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Table 1	(conti	nued)													
Station	Layers [cm]	Coordin- ates	Depth [m]	$\operatorname{O_2}_{[\mathrm{ml}\ l^{-1}]}$	Corg [%]	Sedi- ment	Time of sampling	chl a^*	chl b	chls c	pheo a	pyro- pheo	phrbs	steryl-s	β -car
P27	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$55^{\circ}00'$ N $16^{\circ}00'$ E	78	$\stackrel{<}{\sim}$	5.37 5.08 5.18	clay	1995 March	$\begin{array}{c} 14.8\\ 15.1\\ 11.4\end{array}$	$\begin{array}{c} 0.93 \\ 1.83 \\ 1.14 \end{array}$	$3.8 \\ 4.75 \\ 0.001$	34.3 32.3 20	23.8 27.42 15.03	75.78 36.02 9.4	pu pu	$23.4 \\ 40.9 \\ 19.9$
G^{-2}	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$54^{\circ}50'$ N $19^{\circ}20'$ E	108	$\overline{\nabla}$	$\left. ight\} 5.19$	clay	1992 October	$\begin{array}{c} 22.739 \\ 18.32 \\ 6.242 \end{array}$	$\begin{array}{c} 0\\ 1.467\\ 0.532\end{array}$	$\begin{array}{c} 0.856 \\ 1.117 \\ 0.067 \end{array}$	$\begin{array}{c} 44.287\\ 31.759\\ 15.381\end{array}$	$\begin{array}{c} 45.7 \\ 37.26 \\ 16.907 \end{array}$	$19.873 \\ 6.903 \\ 1.076$	$\frac{18.77}{26.19}$ 18.04	59.08 52.87 20.89
G^{-2}	0 - 3	$54^{\circ}50'N$ $19^{\circ}20'E$	108	2.4	6.02	clay	1994 April	36.86	0	2.9	68.53	49.68	21.43	nd	99.55
G^{-2}	$\begin{array}{c} 0-5 \\ 5-10 \end{array}$	$54^{\circ}50'N$ $19^{\circ}20'E$	108	$\stackrel{\scriptstyle \checkmark}{\sim}$	nd	clay	1994 August	46.656 11.41	$2.36 \\ 0.467$	$1.028 \\ 0.218$	$\frac{115.4}{35}$	$62.04 \\ 19.03$	37.78 38.79	$20.14 \\ 8.22$	168.72 nd
G^{-2}	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$54^{\circ}50'$ N $19^{\circ}20'$ E	108	-1	$5.82 \\ 5.8 \\ 5.46 $	clay	1995 November	66.07 53.8 50.1	$\begin{array}{c} 0 \\ 0.26 \\ 0.2 \end{array}$	5.95 3.16 1.78	58.82 57.81 56.19	24.9 54.45 44.26	24.35 18.87 11.48	nd nd	51.04 144.04 137.13
$G^{-2'}$	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$54^{\circ}50'$ N $19^{\circ}19'$ E	112	0.99	7.1 6.48 6.1	clay	1996 May	$\begin{array}{c} 9.03 \\ 27.36 \\ 14.01 \end{array}$	$1.54 \\ 1.35 \\ 0.47$	$10.01 \\ 7.55 \\ 0.001$	$\frac{118.56}{38.84}$ $\frac{38.84}{37.47}$	$\begin{array}{c} 42.22 \\ 35.71 \\ 17.72 \end{array}$	23.44 18.46 13.46	nd nd	52.99 47.89 23.1
P116	0^{-3}	$54^{\circ}39'N$ $19^{\circ}18'E$	88	en en	5.2	clay	1994 April	14.78	1.21	0	30.91	13.33	10.67	nd	11.95
P116	$\begin{array}{c} 0-1 \\ 1-5 \\ 5-10 \end{array}$	$54^{\circ}39'$ N $19^{\circ}17'$ E	89	<4	6.65 5.45 5.65	clay	1995 March	35.9 12.9 21.9	$4.8 \\ 1.5 \\ 1.8 $	$\begin{array}{c} 33\\1\\0\end{array}$	100.5 30.6 39.1	57.92 21.25 40.19	$102 \\ 4.6 \\ 19.21$	nd nd	94.8 43 88.6

Station	Layers [cm]	Coordin- ates	Depth [m]	$ \substack{\mathrm{O}_2 \\ [\mathrm{ml}\ \mathrm{l}^{-1}] }$	Corg [%]	Sedi- ment	Time of sampling	chl a^*	$\operatorname{chl} b$	chls c	pheo a	pyro- pheo	phrbs	steryl-s	eta-car
P116	$\begin{array}{c} 0-1\\ 1-5\\ 5-10\end{array}$	$54^{\circ}39'N$ $19^{\circ}17'E$	06	5.38	$\begin{array}{c} 6.95 \\ 6.83 \\ 5.61 \end{array}$	clay	1996 May	$\begin{array}{c} 49.47\\92.23\\7.04\end{array}$	$\begin{array}{c} 2.17 \\ 2.94 \\ 0.62 \end{array}$	$25.25 \\ 5.13 \\ 0$	299.07 68.23 8.36	33.98 56.03 0.71	$53.98 \\ 17.74 \\ 8.89$	0 0	$130.04 \\ 156 \\ 9.2$
coastal															
92A	$\begin{array}{c} 0-1\\ 1-5\\ 5-10\end{array}$	$54^{\circ}35'$ N $18^{\circ}41'$ E	40	-1	$\bigg\}_{1.01}$	silt	1992 October	$7.239 \\ 5.345 \\ 1.047$	$\begin{array}{c} 0\\ 0.895\\ 0\end{array}$	$\begin{array}{c} 0.484 \\ 0.013 \\ 0.003 \end{array}$	$\begin{array}{c} 14.392 \\ 15.269 \\ 6.175 \end{array}$	$12.192 \\ 14.185 \\ 5$	$\begin{array}{c} 4.172 \\ 3.527 \\ 0.272 \end{array}$	15.87 7.23 2.77	14.43 4.93 2.85
92A'	$\begin{array}{c} 0 - 1 \\ 1 - 5 \\ 5 - 10 \end{array}$	$54^{\circ}35'$ N $18^{\circ}40'$ E	35	8.5	4.48 4.26 3.34	silt /clay	1995 March	31.7 18.8 6.4	$2.62 \\ 3.2 \\ 0.99$	$\begin{array}{c}1\\0.9\\0.001\end{array}$	44.9 32.1 16.8	27.37 20.47 9.3	$16.4 \\ 12.6 \\ 5.03$	pu pu	51.7 43.9 16
P110d	$\begin{array}{c} 0-1 \\ 1-5 \end{array}$	$54^{\circ} 30' \mathrm{N}$ $18^{\circ} 49' \mathrm{E}$	33	11	$0.27 \\ 0.3$	sand	1996 May	$0.14 \\ 1.92$	$\begin{array}{c} 0.002 \\ 0.167 \end{array}$	$0.14 \\ 0$	$1.07 \\ 1.81$	$0.11 \\ 1.17$	$0.93 \\ 0.91$	$0.01 \\ 0.26$	$0 \\ 3.65$
ZN2	$\begin{array}{c} 0-1 \\ 1-5 \end{array}$	$54^{\circ}22'$ N $18^{\circ}57'$ E	17	7.16	$0.47 \\ 0.26$		1995 October	$5.03 \\ 1.59$	$0.62 \\ 0.44$	$0.79 \\ 0.05$	$6.2 \\ 5.72$	4.26 3.3	$18.15 \\ 5.95$	pu	$8.16 \\ 2.93$
PGd	$\begin{array}{c} 0 - 1 \\ 1 - 5 \\ 5 - 10 \end{array}$	$54^{\circ}31'N$ $18^{\circ}41'E$	28	10.6	$3.42\ 3.1\ 2.78$	silt	1996 May	$15.71 \\ 10.95 \\ 6.22$	$\begin{array}{c} 0.6\\ 1.79\\ 1.43\end{array}$	$5.92 \\ 1.62 \\ 0.29$	$37.16 \\ 15.95 \\ 10.93$	$9.25 \\ 6.83 \\ 3.64$	$10.26 \\ 4.15 \\ 1.83$	$2.78 \\ 2.02 \\ 1.22$	$\begin{array}{c} 19.72 \\ 23.05 \\ 16.03 \end{array}$
$\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	b, c - chi s - sum of detern	lorophylls <i>a</i> of steryl ch nined	$b, b, and for ins, \beta$	c, pheo a . -car – β -ca	– phaec arotene	phytin	a, pyrophe	o – pyro	phaeop	hytin <i>a</i> ,	phrbs –	- phaeoph	lorbides	a,	

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Oder Estua	CIII]	[III]	8	sampling					pheo			
	ury											
К 0- 1- 0-	$^{-1}_{-5}$	5.5 5.5 5.5	6.27 7.32 6.2	1996 August	$\begin{array}{c} 44.4\\ 17.8\\ 21\end{array}$	5.45 2.51 1.4	$2.88 \\ 0.2 \\ 0.24$	86.9 50.4 38.2	$\begin{array}{c} 91.7\\51.4\\36.9\end{array}$	$125.3 \\ 117.5 \\ 14.1$	7.7 8.4 9.4	57.9 53.5 57.6
L 5-0-	$^{-1}_{-5}$	4.6 4.6 4.6	6.56 7.58 3.82	1996 August	148.8 54.1 23.2	8.5 4.24 2.58	$11.48\\1.44\\0.06$	132.7 51.3 54.2	92.7 51.9 56.7	88.9 30.8 13.3	16.9 21.3 10.1	32.7 102.6 67.1
M 1- 5-	$^{-1}_{-5}$	പറവ	$4.9 \\ 2.97 \\ 3.62$	1996 August	19.7 18 9.8	$2.86 \\ 0.85 \\ 1.03$	$\begin{array}{c} 3.9\\ 1.71\\ 0.19\end{array}$	41.6 15.3 14.1	$22.2 \\ 18.7 \\ 15.1$	$6.7 \\ 9.4 \\ 3.6$	4.1 4.1 3.5	$38.4 \\ 38.4 \\ 25.2$
K 0- 1- 5-	$^{-1}_{-5}$	7.6 7.6 7.6	7.14 8.24 8.17	1996 October	36.6 46.2 55.5	4.55 3.52 7.4	$2.32 \\ 1.17 \\ 5.56$	$64.9 \\ 67.5 \\ 102.4$	70 54.2 65.9	85.7 44.8 83.3	$\begin{array}{c} 11\\ 9.2\\ 5.2 \end{array}$	$\begin{array}{c} 0.84\\ 50\\ 76.4 \end{array}$
L 5-0-	$^{-1}_{-5}$	ບ ບ ບ ບ ບ ບ	$6.15 \\ 6.75 \\ 7.9$	1996 October	$\begin{array}{c} 43.1 \\ 41.1 \\ 33.8 \end{array}$	$1.71 \\ 2.95 \\ 2.57$	$1.95 \\ 0.08 \\ 0.16$	39.6 47.3 47.8	36.9 47.5 54.2	$10.8 \\ 11 \\ 40.1$	$6.8 \\ 12.6 \\ 14.9$	61.3 71.8 86.5
M 1- -0-	$^{-1}_{-5}$	9.3 9.3 9.3	$\begin{array}{c} 3.2\\2\\3.46\end{array}$	1996 October	$4.4 \\ 14.9 \\ 6.4$	$1.87 \\ 0.42 \\ 0.53$	$\begin{array}{c} 2.62 \\ 0 \\ 0 \end{array}$	61.3 10.1 12.1	23 10.8 12.6	$\begin{array}{c} 45.5 \\ 8.3 \\ 3.9 \end{array}$	4.7 2.9 3.3	$\begin{array}{c} 0.21 \\ 16.4 \\ 17.6 \end{array}$

High-performance liquid chromatography (HPLC)

The detailed procedure has been described previously (Kowalewska, 1993, 1994, 1995; Kowalewska et al., 1996; Kowalewska and Konat, 1997). The sediment extract prepared as above was dissolved in a small amount of acetone (100–1500 μ l) and injected (20 μ l) into a chromatograph system (Knauer, Germany) equipped with a diode-array detector (Chrom-a-Scope) or a fluorimetric detector (Shimadzu, type RF–551). A Merck Lichrospher 100RP18e column (250×4 mm, 5 μ m) was used with the same precolumn $(4 \times 4 \text{ mm}, 5 \mu \text{m})$. Separations were carried out in an acetone-water gradient system, usually as follows: 0 min 80:20, 10 min 85:15, 20 min 95:5, 40-55 min 100% acetone, 65 min 80:20, at an elution rate of 0.5 ml min⁻¹ for chlorophylls c or 1.0 ml min⁻¹ for the other pigments. Fluorescence analyses were carried out at Ex/Em wavelengths 440/630 nm for detecting chlorophylls c and at Ex/Em 430/660 nm for detecting chlorins at very low concentrations of these pigments; in other cases the diode-array detector was used. The pigments in the diode-array HPLC measurements were quantified on the basis of both the HPLC and UV–VIS absorption spectrophotometric measurements (Shimadzu, UV-VIS spectrophotometer, UV 1202), using the following equation:

$$c = E_{\lambda_{\max}} \ \% A_{\lambda_{\max}} \ v \ D \ 1000/\varepsilon \ l \ w,$$

where

c – pigment concentration in the dried sediment ($\mu g g^{-1}$ or nmol g^{-1}),

 $E_{\lambda_{\max}}$ – extinction measured at the maximum wavelength (for chlorins the long maximum),

- $%A_{\lambda_{\max}} \%$ of the peak area in the total area of all the integrated peaks (ΣA) of the HPLC_{d-a} chromatogram registered at the maximum wavelength,
- v
- volume of the acetone solution prepared for HPLC measurements (ml),
- D dilution factor (dilution of the HPLC solution for the spectrophotometric measurement),
- ε literature extinction coefficient for the maximum wavelength (ml/(mg cm) or ml/(nmol cm)),
- l optical path length (cm),

w – weight of dried sediment (g).

The fluorescence HPLC measurements were quantified by means of the A_{d-a} vs. A_F calibration curve (A – integrated area of the chlorophylls c peak in the diode-array and fluorescence chromatograms respectively)

determined for extracts of algal laboratory cultures of the diatom *Cyclotella* meneghiniana (Kowalewska, 1995).

Organic carbon

Organic carbon was determined by the wet chromic acid titration method (Goudette *et al.*, 1974).

Oxygen in near-bottom waters

Data were taken from Cyberska, 1993; Łysiak-Pastuszak, 1995; Trzosińska, 1996; *Environmental...*, (in preparation); Kowalewska *et al.*, 1997. In all these cases oxygen was determined 1–2 m above the bottom.

3. Results and discussion

3.1. Content of chlorins a

The characteristics of the sampling stations and the results of pigment analyses are given in Tabs. 1 and 2. The contents of chlorins were highest in the Oder Estuary sediments (total chlorins $a - \Sigma$ Chln a up to 380 nmol g⁻¹), lower in the Deeps, especially in the Gdańsk Deep (Σ Chln a up to 300 nmol g⁻¹) and in the coastal (Σ Chln a up to 120 nmol g⁻¹) and lowest in the open sea sediments (Σ Chln a up to 75 nmol g⁻¹ with the exception of P110 (0–1 cm)). In general, there were large differences between the pigment concentrations, especially in the 0–1 cm layer of sediments from the Gulf of Gdańsk, most probably caused by sudden changes in primary production (Wrzołek, 1995, 1996).

The proportion of chlorophyll a in the total content of chlorins a was highest in the Oder Estuary sediments (20%), lower near the coast (18%)and in the Deeps (16%), and lowest in the open sea (12%) (Fig. 3). This indicates that the primary production is higher in the coastal zone than in the open sea. This inference is confirmed by the fact that the proportion of phaeophytin a, the immediate transformation product of chlorophyll a, is also highest in the coastal sediments ($\sim 34\%$) and the same level in other sediments ($\sim 30\%$). The corresponding phaeophorbide content (the general view is that these are chlorins originating mainly from zooplankton grazing (Welschmeyer and Lorentzen, 1985)) was higher in the open sea (19%) and in the Oder Estuary (18-20%) than near the coast and in the Deeps (13%). The proportion of further chlorophyll a transformation products, *i.e.* pyrophaeophytin a and the steryl chlorin esters is about the same $(\sim 25\%)$ in the case of the former compound and lowest near the coast (8%) and in the Oder Estuary (5-6%) and highest in the Deeps (14%) and open sea (13%) in the case of the latter. Such a distribution



Fig. 3. Proportions of particular chlorins in the total content of chlorins a in the sediment samples (%); legend as in Tab. 1

of chlorins in the sediments is in agreement with the available chlorophyll a data for the overlying waters. The highest chlorophyll a concentrations in seawater were measured near the shore, particularly at the mouth of the Oder and Vistula, and in the Gulf of Gdańsk, from where the phytoplankton detritus is transported to the Gdańsk Deep (Renk, 1992; Kaczmarek *et al.*, 1997; DATA BASE; HELCOM, 1996). The highest percentage of phaeophorbides in the total chlorins a in the open sea sediments and the Oder Estuary is consistent with the literature results that zooplankton is more abundant relative to chlorophyll a in the open sea than near the coast (HELCOM, 1996), and that the zooplankton grazing in the Szczecin Lagoon corresponds to extremly high densities of phytoplankton in the Estuary, so that the basin is still capable of self-purification (Chojnacki, 1991).

3.2. Correlation of chlorophyll *a* with other pigments

The correlation coefficient of chlorophyll a with other pigments (Figs. 4a and 4b) in the open sea sediments was the most even, except for that with steryl chlorins. The highest correlation there was for the pigment almost always accompanying chlorophyll a, *i.e.* β -carotene, and with phaeophytin a, especially in the 0–1 cm layer (r = 0.94 and 0.99 respectively). Similarly, in the coastal sediments the highest correlation was with β -carotene and phaeophytin a (r = 0.95); the value was even higher in the 0–1 cm layer where fresh algal material occurred (r = 0.96–0.98). The correlation coefficient with chlorophylls c and b, which do not occur in all phytoplankton species, was highest in the Oder Estuary and in



Fig. 4. Correlation coefficients (r) of chlorophyll a with other pigments in Baltic Sea sediments: all samples (a), in the 0–1 cm layer (b)

the open sea (r = 0.86, ~0.8 respectively); near the coast it was similar for chlorophyll b (r = 0.83, in the 0–1 cm layer a little higher, r~0.9) and lower for chlorophylls c (r = 0.51, in the 0–1 cm layer r = 0.53). The correlation was much lower in the Deeps, both for chlorophylls c, occurring mainly in diatoms and dinoflagellates (r = 0.36, in 0–1 cm layer r = 0.39) and for chlorophyll *b*, which occurs *e.g.* in green algae (r = 0.35, in 0–1 cm layer r = 0.2). The correlation coefficients for pyrophaeophytin *a* were higher under good oxygen conditions (open sea, coast, $r \sim 0.87$, in 0–1 cm layer r = 0.9–0.95) than in the Oder Estuary (r = 0.8, in 0–1 cm layer r = 0.72) and the Deeps (r = 0.72, in 0–1 cm layer r = 0.47). The phaeophorbides correlate with chlorophyll *a* best in the open sea sediments (r = 0.8, in 0–1 cm layer r = 0.84), which confirms the higher abundance of zooplankton relative to phytoplankton in open sea waters than in coastal waters. In the Oder Estuary this correlation is evidently lower (r = 0.39, in 0–1 cm layer 0.42), which means that the transformation of chlorophyll *a* takes place there in another way than in the open sea. The steryl esters had the highest positive correlation coefficient in the Oder Estuary sediments (r = 0.93), the highest negative correlation being for the 0–1 cm layer of the Deeps' sediments (r = -0.95); for other sediments, the correlation was close to zero.

3.3. Correlation of pigments in the 0–1 cm sediment layer with oxygen in the near-bottom waters

Only in the Oder Estuary sediments was the correlation negative for all the pigments studied (Fig. 5), as might be expected in accordance with the rule that the more anoxic the conditions at a high primary production rate, the better preserved are the pigments in the sediments.



Fig. 5. Correlation coefficients (r) of pigments in the 0–1 cm sediment layer with oxygen in near-bottom water (1–2 m above bottom)

In the open sea sediments and in the Deeps the correlation was positive. Near the coast the highest positive correlation was with chlorophylls c(r = 0.48) and with chlorophyll a (r = 0.18); the correlation with β -carotene, which is more sensitive to oxygen, was negative. The only explanation for these relationships is that the occurrence of chlorins in the bottom sediments is controlled by several different parameters, and that an increase in the oxygen content in the near-bottom waters (2 m above the bottom) directly or indirectly influences the primary production more intensively than the deterioration of chlorophyll a. In the Oder Estuary other parameters were more even than in the marine samples collected at different times and sites, so the effect of oxygen on chlorophyll adecomposition was all the more apparent. Here under oxic conditions phaeophytin a and phaeophorbides a were the most abundant, β -carotene less so. As can be concluded from the correlation of the pigment concentrations in sediments with oxygen, algae containing chlorophylls c (e.g. diatoms) are more abundant in oxygen-rich waters than chlorophyll b containing algae (e.q. green algae).

3.4. Correlation of pigments with organic carbon

Chlorophyll *a*, β -carotene and phaeophytin *a*, the immediate transformation product of chlorophyll *a*, correlate best with C_{org} near the coast (Fig. 6a), especially in the 0–1 cm sediment layer (Fig. 6b) (r = 0.96, 0.98, respectively). This means that the main stock of organic matter in that





Fig. 6. Correlation coefficients (r) of pigments with organic carbon (C_{org}) in sediments: all samples (a), in the 0–1 cm layer (b)

area is composed of phytoplankton. In the Oder Estuary this correlation is distinctly lower, as is the case with all the other compounds studied, with the exception of pyrophaeophytin a and steryl chlorins, further products of chlorophyll a transformation. This may be due to the fact that there are sources of organic matter for these sediments other than phytoplankton detritus and/or that chlorophyll a decomposition is very rapid there. In the Deeps the correlation with most of the pigments is generally lower than near the coast; that with phaeophytin a, transported from the near-shore waters and with chlorophylls c and β -carotene, is higher. Correlation coefficients with pyrophaeophytin are more even, despite the location of the sampling stations.

4. Conclusions

Chlorin contents were highest in Oder Estuary sediments (ΣChln a up to 380 nmol g⁻¹), lower in the Deeps, especially in the Gdańsk Deep (ΣChln a up to 300 nmol g⁻¹) and in coastal sediments (ΣChln a up to 120 nmol g⁻¹) and lowest in the open sea sediments (ΣChln a up to 75 nmol g⁻¹).

- Chlorophyll *a* diagenesis in the southern Baltic Sea is very rapid. The immediate transformation products of chlorophyll *a* in this environment are phaeophytin *a* and phaeophorbides, then pyrophaeophytin *a* and steryl chlorin esters.
- Primary production is highest near the seashore, especially at the mouth of the Vistula, in the coastal zone of the Gulf of Gdańsk and in the Oder Estuary. Zooplankton is more abundant relative to phytoplankton in open sea waters and in the Oder Estuary the intensity of its grazing activity corresponds to the extremely high phytoplankton biomass.
- Chlorophyll *c*-containing algae (diatoms and dinoflagellates) are deficient in relation to the chlorophyll *b*-containing algae (green algae) and blue-green algae in the coastal area of the Gulf of Gdańsk.
- Chlorins in sediments are sensitive environmental markers of both the average primary production in the overlying waters (taking local water currents into account) and the environmental conditions. Together with other pigments in the sediments, they are valuable taxonomic indicators supplementary to biological determinations.

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