Organic Geochemistry 115 (2018) 166–173

Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

CPPB-aE (13^2,17^3-cyclopheophorbide-a enol) in sediments – A potential proxy of oxygen deficiency in near-bottom water

Małgorzata Szymczak-Żyła

Marine Pollution Laboratory, Institute of Oceanology, Polish Academy of Sciences, ul. Powstańców Warszawy 55, 81-712 Sopot, Poland

ARTICLE INFO

Article history:
Received 31 May 2017
Received in revised form 22 September 2017
Accepted 17 October 2017
Available online 4 November 2017

Keywords:
13^2,17^3-cyclopheophorbide-a enol
CPPB-aE
Chlorophyll-a diagenesis
Chlorophyll-a derivatives
Sediments
Pigments
Baltic Sea
HPLC

ABSTRACT

The labile degradation product of chlorophyll-a – 13^2,17^3-cyclopheophorbide-a enol (CPPB-aE) – has been found in considerable amounts (up to 380 nmol/g d.w.) in marine sediments from the Gdańsk Deep (southern Baltic Sea) and in hypoxic/anoxic sediments from the Oslofjord/Drammensfjord (up to 371 nmol/g d.w.). A modified version of HPLC-DAD analysis with a lower column temperature (10 °C) significantly improved separation of this compound. The results of this work show that the presence of CPPB-aE in sediments, owing to its instability under oxic conditions, may be a biomarker of oxygen deficiency in near-bottom water.

1. Introduction

The early diagenesis of chlorophyll-a in sediments has been studied for many years and the variety of chlorophyll-a derivatives found in marine and/or lacustrine sediments described (e.g. Eckardt et al., 1992; Louda et al., 2000; Leavitt and Hodgson, 2001). Pigments in sediments have aroused interest as possible biomarkers to determine sources and transformation pathways of organic matter, diagenetic processes and/or depositional conditions (e.g. Harris et al., 1996; Chen et al., 2001; Szymczak-Żyła et al., 2011). The best-known chlorophyll-a derivatives in recent sediments, and thought to be the most abundant, are pheophytin-a, pheophorbides-a and their pyro-derivatives. There are also many lesser known chlorophyll-a degradation products: one such example is 13^2,17^3-cyclopheophorbide-a enol (CPPB-aE). This derivative was first recorded in marine sponges and characterised by Karuso et al. (1986). Since then, a few papers have reported the presence of this derivative in different marine organisms such as benthic dinoflagellates (Yamada et al., 2014) or bivalves (Louda et al., 2008). CPPB-aE has also been detected in particulate organic matter collected in sediment traps (Ocampo et al., 1999) and in marine sediments from the Black Sea, Mediterranean Sea, Peru Margin and Florida Bay (Ocampo et al., 1999; Goericke et al., 2000; Louda et al., 2000). The sources of this chlorophyll-a derivative for sediments are not fully known. Goericke et al. (2000) suggested that the major source of CPPB-aE was herbivores feeding on phytoplankton, but those authors did not rule out the possibility that it could also be formed in sediments. This was indeed confirmed by Louda et al. (2000) during studies of chlorophyll-a diagenesis in the carbonate sediments of Florida Bay. The papers addressing the issue of CPPB-aE in sediments began by pointed out the instability of this compound under oxic conditions, but also indicated that it was one of the most abundant chlorophyll-a derivatives in recent sediments. Ocampo et al. (1999) even suggested that the formation of CPPB-aE was a major diagenetic pathway for chlorophyll-a. Therefore, it is quite surprising that many scientists studying pigments in sediments have not observed the occurrence of this derivative.

The aim of this study was to find out whether CPPB-aE is present in Baltic Sea sediments and if so, whether it could be used as a proxy of oxygen deficiency in near-bottom water.

2. Experimental

The study was conducted primarily in the Gdańsk Basin of the southern Baltic Sea (Fig. 1). The samples were collected during

---

E-mail address: szymczak@iopan.gda.pl

https://doi.org/10.1016/j.orggeochem.2017.10.011
0146-6380/

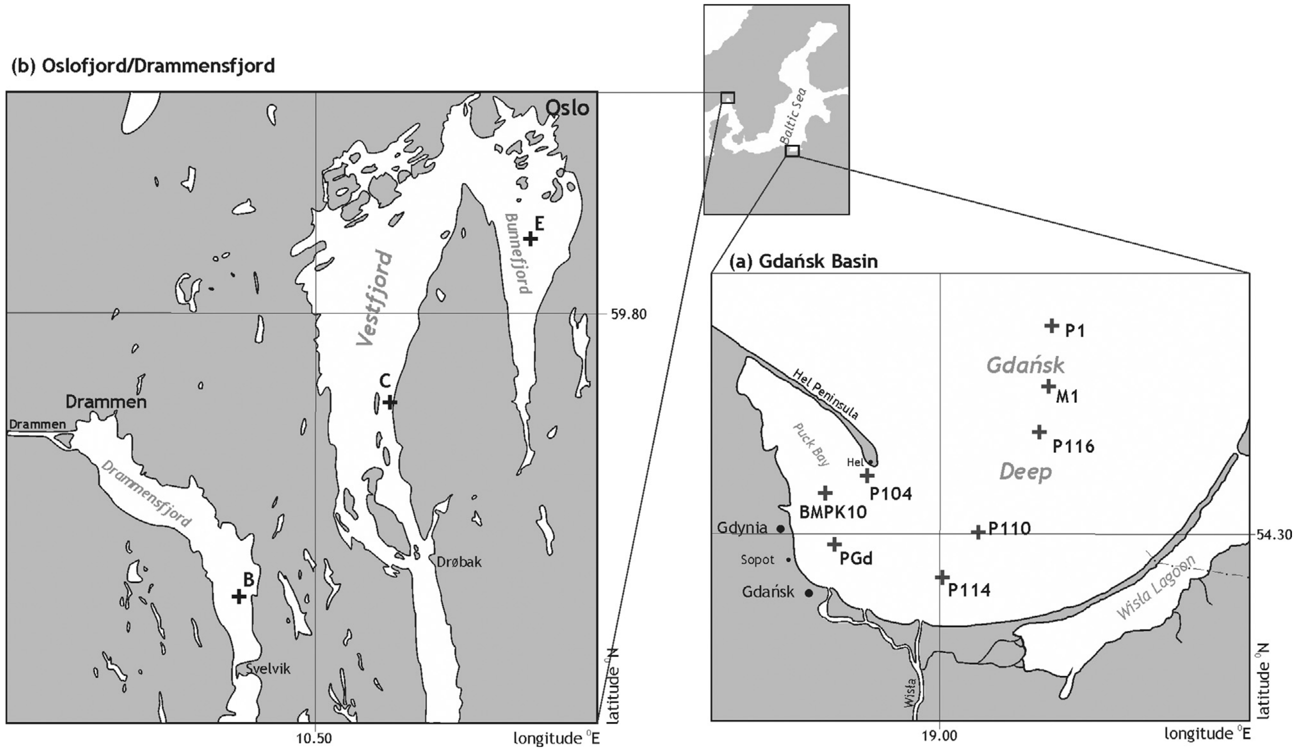

Fig. 1. Location maps showing sampled areas.

two cruises: in April 2014 and April 2015, at eight stations in total, twice at three of them (during both cruises). The stations were selected in order to represent different near-bottom oxygen conditions (Table 1). The stations were located in the shallow, well-oxygenated part of the Gulf of Gdańsk and also in the deeper part of the study area (Gdańsk Deep), where the waters are stratified and the strong halocline prevents vertical mixing in the water column, resulting in hypoxia/anoxia in the near-bottom water (IMGW, 2013). To confirm the relationships observed in the Gdańsk Basin, results for sediment samples taken in June 2014 from another area – Oslofjord/Drammensfjord (southern Norway) – at two hypoxic/anoxic stations and one with a higher oxygen content in the near-bottom water (Fig. 1; Table 1), were also included. Recent sediments (up to 10 cm) were collected with a Niemistö core sampler. After collection, the cores were divided into layers: 0–1 cm, 1–5 cm, 5–10 cm. In addition, a 50-cm long core was taken in April 2015 at the Gdańsk Deep station with a low oxygen content in the near-bottom water (P116). This core was divided into 2 cm thick layers. Sediment sub-samples were placed into tight sealed polyethylene bags and stored in a deep-freeze (−20 °C) until further analysis. Sediment handling was done under nitrogen protective atmosphere. The water depth and near-bottom water oxygen concentration were measured during sediment sampling.

Pigment analyses and quantifications were carried out according to procedures described in detail elsewhere (Szymczak-Żyła et al., 2008), slightly modified. In brief, ultrasound-assisted extraction of sediments with acetone was applied, followed by separation and identification using a high-performance liquid chromatography system equipped with a diode-array detector (HPLC-DAD). The pigments were separated on a Lichrospher 100RP-18e column (250 × 4 mm, 5 μm; Merck, Germany). The only modification of the method was the lower column temperature (10 °C) during analysis.

To assess the stability of CPPB-aE in the sediments stored frozen (−20 °C), a long-term (8 months) 'storage experiment' was performed. Samples (in triplicate, n = 3) kept in tight sealed polyethylene bags were analysed after 0 (initial), 1, 2, 4, 6 and 8 months of storage.

To assess the influence of oxygen on CPPB-aE stability, a short-term (4 weeks) 'incubation experiment' was performed. Sediment samples (in triplicate, n = 3) kept in different conditions (A – darkness, room temperature (~25 °C); B – darkness, refrigerator (~5 °C); C – darkness, room temperature, inert gas (argon); D – darkness, refrigerator, inert gas) were analysed after 0 (initial), 1, 3, 7, 14, 21 and 28 days of incubation. Both experiments were carried out on sediments with a high CPPB-aE content.

The data were analysed statistically using STATISTICA 12.5 software (StatSoft, Poland). Repeated measures of analysis of variance (rANOVA) was used to reveal differences between the mean chloropigment content in samples during the laboratory experiments. Correlation analysis was used to evaluate the relationships between the CPPB-aE/ΣChlns-a ratio in the sediment and the environmental parameters. Since the basic conditions necessary for using the parametric linear correlation (tested using the Shapiro-Wilk and Brown-Forsyth tests) were not fulfilled, its non-parametric equivalent was applied.

3. Results and discussion

The HPLC-DAD chromatogram of the pigment extract from Gdańsk Basin sediments registered at 660 nm shows pyropheophorbides-a, pheophytin-a and pyropheophytin-a as major chlorophyll-a derivatives (Fig. 2A). These pigments are commonly found in sediments (e.g. Bianchi et al., 2002; Szymczak-Żyła et al., 2011). Moreover, another chlorophyll-a derivative – $13^2,17^3$-cyclopheophorbide-a enol (CPPB-aE) – was identified in the

Table 1
Characteristics of the sampling stations and average contents of chloropigments-a in recent sediments (0–10 cm).

Station	Date of collection	Oxygen in near-bottom water [mg/l]	Chloropigments-a in sediments [nmol/g d.w.]			CPPB-aE/ΣChlns-a
			Layer [cm]	CPPB-aE [*]	ΣChlns-a [**]	
Gdańsk Basin						
P1	04.2014	3.4	0–1	380 ± 13[***]	795 ± 10	**0.48**
			1–5	295 ± 15	346 ± 8	**0.85**
			5–10	254 ± 8	210 ± 6	**1.21**
M1	04.2014	3.9	0–1	301 ± 15	604 ± 28	**0.50**
			1–5	201 ± 10	267 ± 8	**0.75**
			5–10	271 ± 8	211 ± 10	**1.28**
P116	04.2014	0.5	0–1	370 ± 5	616 ± 9	**0.60**
			1–5	220 ± 10	272 ± 12	**0.81**
			5–10	275 ± 4	190 ± 2	**1.45**
	04.2015	2.7	0–1	303 ± 8	550 ± 1	**0.55**
			1–5	208 ± 11	260 ± 10	**0.80**
			5–10	270 ± 12	200 ± 8	**1.35**
P110	04.2014	5.4	0–1	180 ± 7	354 ± 1	**0.51**
			1–5	192 ± 1	253 ± 9	**0.76**
			5–10	145 ± 5	147 ± 4	**0.99**
	04.2015	11.3	0–1	108 ± 9	300 ± 14	**0.36**
			1–5	198 ± 12	260 ± 2	**0.76**
			5–10	168 ± 10	165 ± 5	**1.02**
BMPK10	04.2014	11.1	0–1	31 ± 1	86 ± 4	**0.36**
			1–5	6 ± 0.4	21 ± 1	**0.29**
			5–10	<0.6	10 ± 0.5	**<0.06**
	04.2015	12.4	0–1	23 ± 1	65 ± 2	**0.35**
			1–5	<1.2	35 ± 0.7	**<0.03**
			5–10	<0.6	16 ± 0.4	**<0.04**
P104	04.2014	12.1	0–1	30 ± 0.8	78 ± 5	**0.38**
			1–5	<0.7	23 ± 1	**<0.03**
			5–10	<0.7	22 ± 0.5	**<0.03**
PGd	04.2015	12.5	0–1	15 ± 0.6	50 ± 1	**0.30**
			1–5	<1.5	48 ± 2	**<0.03**
			5–10	<1.0	23 ± 1	**<0.04**
P114	04.2015	13.1	0–1	15 ± 1	58 ± 0.5	**0.26**
			1–5	<0.5	40 ± 1	**<0.01**
			5–10	<0.5	44 ± 2	**<0.01**
Oslofjord/Drammensfjord						
B	06.2014	0.5	0–1	36 ± 1	60 ± 0.7	**0.60**
			1–5	24 ± 0.5	28 ± 1	**0.86**
			5–10	60 ± 2	51 ± 1	**1.18**
C	06.2014	9.2	0–1	13 ± 10	35 ± 1	**0.37**
			1–5	<0.8	10 ± 0.2	**<0.08**
			5–10	<0.8	10 ± 0.5	**<0.08**
E	06.2014	0.2	0–1	199 ± 9	321 ± 10	**0.62**
			1–5	238 ± 10	264 ± 7	**0.90**
			5–10	371 ± 15	285 ± 12	**1.30**

[*] $13^2,17^3$-cyclopheophorbide-a enol.

[**] Sum of other chloropigments-a (pheophorbides-a, pyropheophorbides-a, chlorophyll-a-allomers, chlorophyll-a-epimer, pheophytin-a, pheophytin-a-epimer, pyropheophytin-a and steryl chlorin esters.

[***] Mean value ± $R/2$ ($R = |x_1 - x_2|$); $n = 2$.

sediments on the basis of its characteristic spectrum: it has absorption maxima at 360, 425 and 686 nm (Fig. 2B). Only a few authors have previously found CPPB-aE in marine sediments (Ocampo et al., 1999; Goericke et al., 2000; Louda et al., 2000). This may be because the analysis of this compound can be difficult, an aspect mentioned by other authors. Aydin et al. (2003) pointed out that the method traditionally used in their laboratory for other chlorophyll-a derivatives did not allow CPPB-aE to be clearly distinguished from the baseline. If C-18 columns were used, better separation of this peak would require a different solvent system and gradient (Aydin et al., 2003); failing this, another type of column, e.g. a C-30, would have to be applied (Goericke et al., 2000). The method described here used a C-18 column, but a lower column temperature (10 °C) improved separation of CPPB-aE from other chlorophyll-a derivatives (Fig. 2C). Another reason for this derivative not being detected in sediments may be because it is unstable in the presence of oxygen, which may cause it to decompose after sediment collection. The 'storage experiment' showed that, compared with the initial value, storage for 4 months at −20 °C still yielded a high percentage CPPB-aE recovery (89%; Fig. 3). A statistically significantly ($p < 0.05$) lower percentage of this compound was recorded after 6 months of storage, but the percentage of chlorophyll-a and other major chlorophyll-a derivatives did not change significantly (Fig. 3).

CPPB-aE was detected in surface sediments (0–1 cm) at all stations (13–380 mnol/g d.w) both in the Gdańsk Basin and the Oslofjord/Drammensfjord (Table 1). In the deeper sediments (layers: 1–5 and 5–10 cm) this compound occurs in considerable amounts only in cores sampled at stations where the near-bottom water is oxygen-deficient. Goericke et al. (2000) suggested that the major source of CPPB-aE in sediments was herbivores feeding on phytoplankton, which would explain the presence of

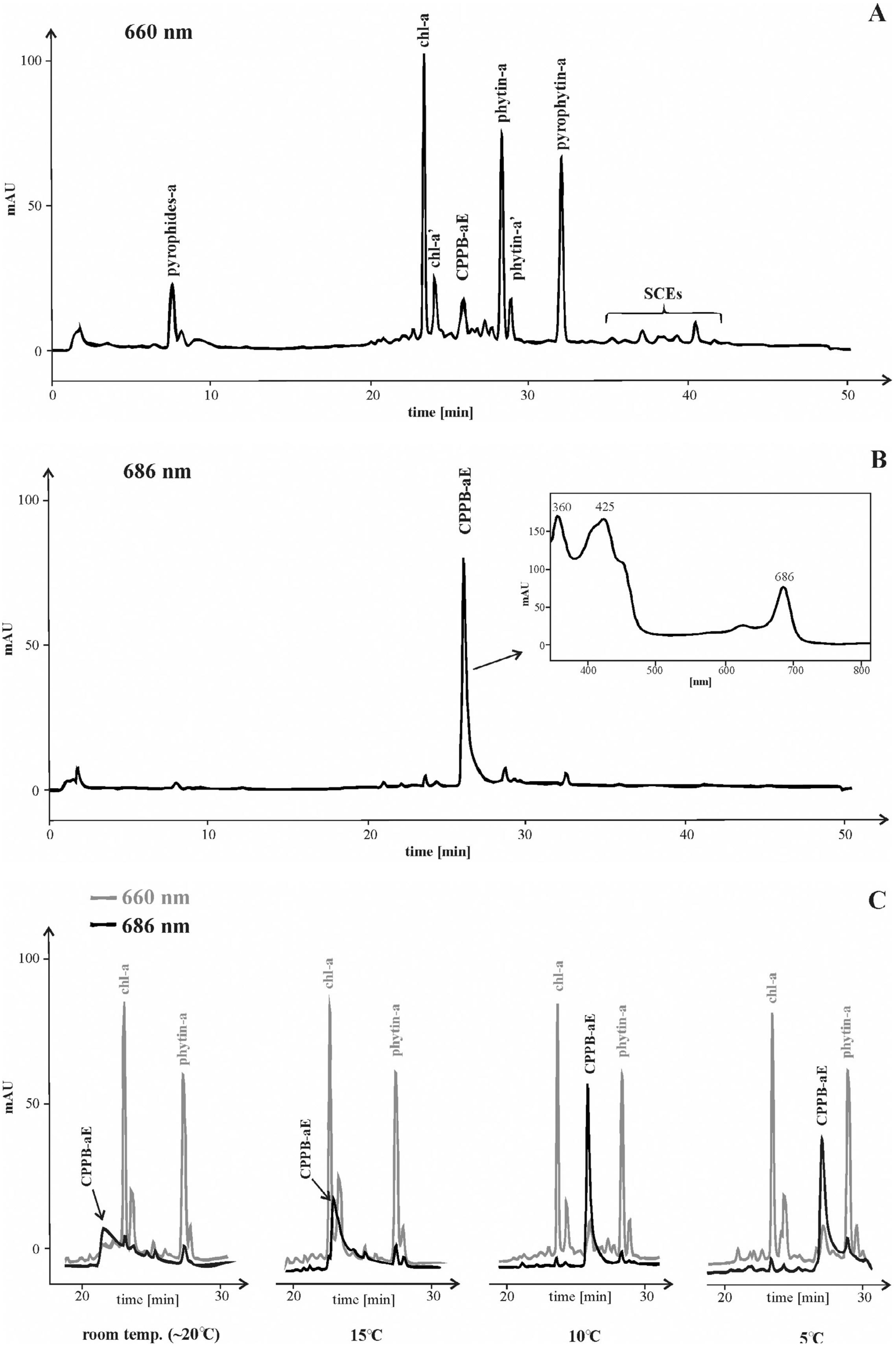

Fig. 2. HPLC-DAD chromatograms of pigments extracted from Gdańsk Basin sediments: (A) recorded at 660 nm; (B) recorded at 686 nm showing the spectrum of CPPB-aE (the spectrum was collected on-line – in the eluent); (C) influence of column temperature on the separation of CPPB-aE (grey line – 660 nm; black line – 686 nm).

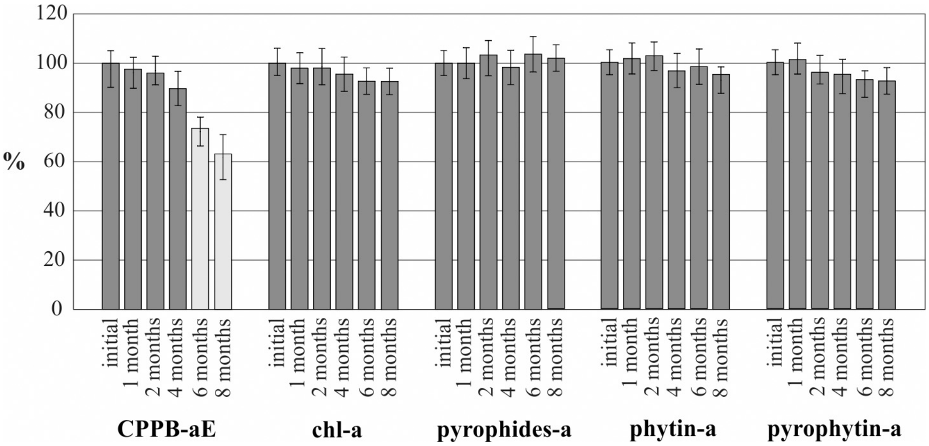

Fig. 3. Chloropigments-a recoveries (%) from sediments stored in a freezer (−20 °C); light bars – values statistically different from the initial one, $p < 0.05$; $n = 3$. Pigment concentration-initial values [nmol/g d.w.]: CPPB-aE – 225, chl-a – 96, pyrophides-a – 70, phytin-a – 83, pyrophytin-a – 85.

this compound in all surface (0–1 cm) sediments. Under oxic conditions in near-bottom water, surface sediments are also well-oxygenated and CPPB-aE is decomposed – converted to other derivatives such as chlorophyllones (Goericke et al., 2000; Louda et al., 2008). Although all chloropigments-a are decomposed under the influence of physico-chemical factors such as oxygen, the 'incubation experiment' showed that incubation of sediments in the presence of oxygen caused a faster decomposition of CPPB-aE than of other chloropigments-a. The four-week incubation of sediments at room temperature resulted in a decrease in CPPB-aE concentration of approximately 70% compared to initial value (from 185 nmol/g to 56 nmol/g d.w.), but the change was statistically significant ($p < 0.05$) after two weeks (Fig. 4A). Decomposition of chlorophyll-a was also observed but the change became significant only after 3 weeks. Lowering the temperature to 5 °C, i.e. to the conditions similar to those in the near-bottom water, inhibited decomposition of chlorophyll-a, but only slightly reduced decomposition of CPPB-aE (Fig. 4B). Only by flushing the sediments with inert gas (argon), which produced anaerobic conditions, could the decomposition of this compound be significantly inhibited (Fig. 4C and D). Incubation of sediments under anaerobic conditions resulted in an increase of CPPB-aE concentration and a decrease of pyropheophorbide-a by 22% and 30%, respectively. This corroborates the observation of Louda et al. (2000) that this chlorophyll-a derivative can also be formed in hypoxic/anoxic sediments: those authors reported that sedimentary pyropheophorbide-a from Florida Bay was readily converted to CPPB-aE within the first 20 cm of burial.

The sediments differed not only in the total contents of CPPB-aE but also in the molar ratio of CPPB-aE to the sum of other chloropigments-a (CPPB-aE/ΣChlns-a) (Table 1). The ratio of CPPB-aE/ΣChlns-a in surface sediments (0–1 cm) was higher in the samples from the Gdańsk Deep stations and hypoxic/anoxic sediments from the Oslofjord/Drammensfjord (0.48–0.62) than in the well-oxygenated ones (0.26 –0.38). The analysis of variance indicated that these differences are statistically significant (Kruskal-Wallis ANOVA, $p < 0.01$). Analysis of correlation revealed a statistically significant negative correlation between the CPPB-aE/ΣChlns-a ratio and the oxygen content in the near-bottom water (Spearman R, $r = -0.9$, $p < 0.05$). An interesting case is station P110, where the oxygen content in the near-bottom water was higher in April 2015 than in April 2014, but the CPPB-aE/ΣChlns-a ratio in the surface sediments from this station was lower in April 2015 than in April 2014 (Table 1). This indicated that oxygen may be a factor affecting this ratio in surface sediments. The ratio of CPPB-aE to the sum of other chloropigments-a (CPPB-aE/ΣChlns-a) was higher in the deeper sediment layers (up to 1.44 at station P116) than in the surface layer. This confirmed the observation of other authors (Louda et al., 2000) and the results of 'incubation experiments' (Fig. 4C and D) that CPPB-aE can also be formed in sediments.

In addition, a 50-cm long sediment core, taken from an area with a known history regarding oxic conditions in near-bottom water (Gdańsk Deep, station P116), was examined. According to the accumulation rate determined for the sediments collected at the same station (Szymczak-Żyła et al., 2017), these sediments were deposited over the last 360 years. The oxygen concentration in the water of the Gdańsk Deep has been decreasing since the beginning of the 20th century (Cyberska and Lauer, 1990). This is in accordance with the profile of CPPB-aE contents in this core (Fig. 5). During good oxygen conditions in near-bottom water, CPPB-aE was either absent or present in low quantities (layers from 50 to 14 cm) and CPPB-aE/ΣChlns-a ratio lower than 0.28. In the layer 12–14 cm (formed around the 1920s), the concentration of this compound increased. The highest value of CPPB-aE was found in the 8–10 cm layer (350 mnol/g d.w.; Fig. 5), which was formed around the 1950s (between 1944 and 1958); this was even higher than the sum of other chloropigments-a (CPPB-aE/ΣChlns-a = 1.4). According to the literature, hydrogen sulphide was first recorded in the Gdańsk Deep in the 1963, although a critical situation had been observed earlier (Piechura et al., 1963; SHMI, 1968–1970). The near-bottom water of the Gdańsk Deep subsequently became deficient in oxygen.

This study of recent sediments shows that regardless of the sources of CPPB-aE for sediments, the high content of this derivative in deeper sediment (high CPPB-aE/ΣChlns-a ratio) may be a biomarker indicating oxygen deficiency in near-bottom water. Future analyses of a longer sediment core (formed over the past millennia) will show whether the method indicating the presence of hypoxic periods, outlined in this work, is also suitable for much older sediments. Identification of past hypoxic periods is very important, especially in the context of climate change studies, especially since the methods currently used for this purpose, i.e. the presence of laminar layers in the sediment record or trace element distribution, do not always yield conclusive results.

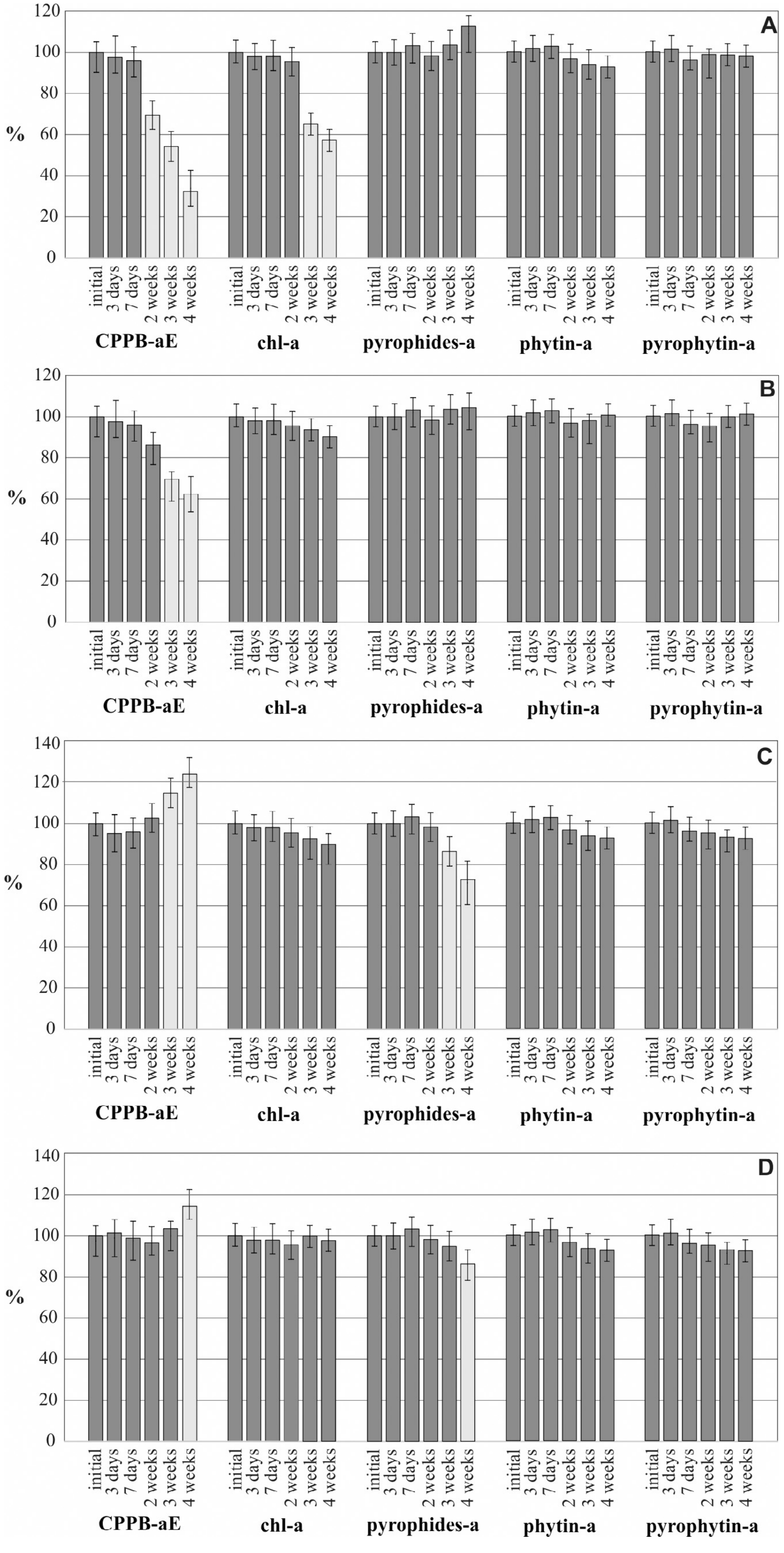

Fig. 4. Chloropigments-a recoveries (%) from sediments incubated in different conditions: (A) darkness, room temperature (~25 °C); (B) darkness, refrigerator (~5 °C); (C) darkness, room temperature, inert gas; (D) darkness, refrigerator, inert gas; light bars – values statistically different from the initial one, $p < 0.05$; n = 3. Pigment concentration -initial values [nmol/g d.w.]: CPPB-aE – 185, chl-a – 79, pyrophides-a – 80, phytin-a – 85, pyrophytin-a – 98.

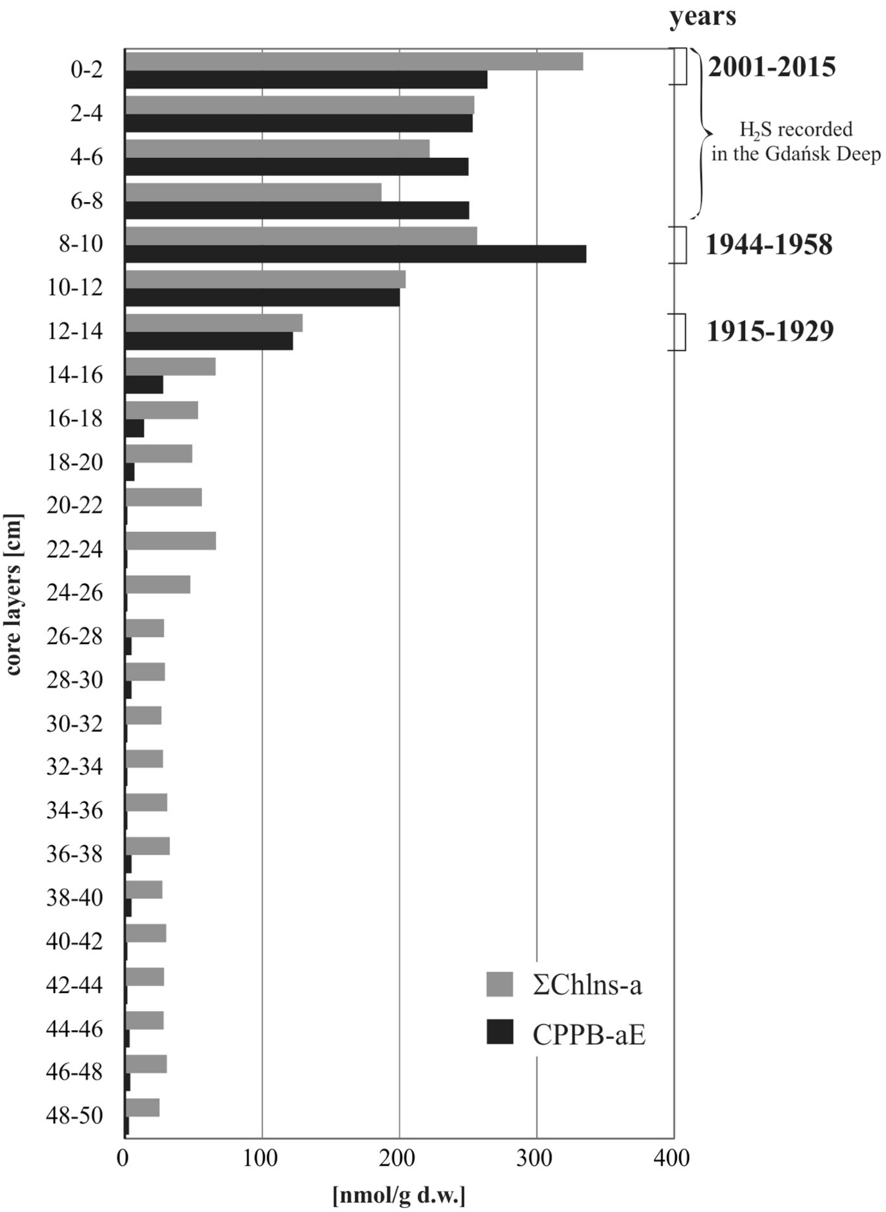

Fig. 5. Downhole profile of chloropigment-a contents [nmol/g d.w.] in the 50-cm long sediment core (Gdańsk Deep, station P116).

4. Conclusions

The results show that especially high quantities (up to 380 nmol/g d.w.) of $13^2,17^3$-cyclopheophorbide-a enol (CPPB-aE), the labile degradation product of chlorophyll-a, are present in Gdańsk Basin sediments in samples from the Gdańsk Deep, where the near-bottom water is deficient in oxygen. This derivative was also detected in hypoxic/anoxic sediments from the Oslofjord/Drammensfjord (up to 371 nmol/g d.w.). The ‘storage experiment’ showed that sediment samples can be stored in a freezer (−20 °C) for up to 4 months without risking the degradation of this compound. Owing to its instability under oxic conditions, as confirmed by the ‘incubation experiment’, CPPB-aE may be a biomarker of oxygen deficiency in near-bottom water. The four-week incubation of sediments at room temperature and in the presence of oxygen resulted in a decrease in CPPB-aE concentration of approximately 70% compared to the initial value. Flushing sediments with inert gas (argon), which produced anaerobic conditions, significantly inhibited decomposition of this compound.

Acknowledgements

This work was partially carried out within the framework of the Polish-Norwegian Research Programme operated by the National Centre for Research and Development under the Norwegian Financial Mechanism 2009–2014, grant CLISED (No. 196128/88/2014). I would like to thank Prof. G. Kowalewska, the head of the MPL IOPAN, for her valuable comments and support; also Dr. A. Filipkowska, Dr. L. Lubecki, of the IOPAN, Sopot, Poland and Dr. T.M. Ciesielski from NTNU, Trondheim, Norway for their assistance with the sample collection; the crews of r.v. ‘Oceania’ and ‘IMOR’ for their help during the cruises; the Associate Editor and two anonymous Reviewers for their constructive comments, which helped improve the manuscript.

Associate Editor—**Elizabeth Ann Canuel**

References

Aydin, N., Daher, S., Gulacar, F.O., 2003. On the sedimentary occurrence of chlorophyllone a. Chemosphere 52, 937–942.

Bianchi, T.S., Rolff, C., Widbom, B., Elmgren, R., 2002. Phytoplankton pigments in Baltic Sea seston and sediments: seasonal variability, fluxes and transformations. Estuarine Coastal and Shelf Sciences 55, 369–383.

Chen, N., Bianchi, T.S., McKee, B.A., Bland, J.M., 2001. Historical trends of hypoxia on the Louisiana shelf: application of pigments as biomarkers. Organic Geochemistry 32, 543–561.

Cyberska, B., Lauer, Z., 1990. Oxygen and thermohaline conditions in the Polish fishing zone in 1979–1983. Oceanologia 29, 3–25.

Eckardt, C.B., Pearce, G.E.S., Keely, B.J., Kowalewska, G., Maxwell, J.R., Maxwell, J.R., 1992. A widespread chlorophyll transformation pathway in the aquatic environment. Organic Geochemistry 19 (1–3), 217–227.

Goericke, R., Storm, S.L., Bell, M.A., 2000. Distribution and sources of cyclic pheophorbides in the marine environment. Limnology and Oceanography 45 (1), 200–211.

Harris, P.G., Zhao, M., Rosell-Melé, A., Tiedemann, R., Sarnthein, M., Maxwell, J.R., 1996. Chlorin accumulation rate as a proxy for Quaternary marine primary productivity. Nature 383, 63–65.

IMGW, 2013. Bałtyk Południowy w 2012 roku. Charakterystyka wybranych elementów środowiska, IMGW, BIP, Warszawa (in Polish).

Karuso, P., Bergquist, P.R., Buckleton, J.S., Cambie, R.C., Clark, G.R., Rickard, C.E.F., 1986. 132,173-Cyclopheophorbide enol, the first porphyrin isolated from a sponge. Tetrahedron Letters 27 (19), 2177–2178.

Leavitt, P.R., Hodgson, D.A., 2001. Sedimentary Pigments. Tracking Environmental Change Using Lake Sediments. In: Smol, J.P., Birks, H.J.B., Last, W.M. (Eds.), Terrestrial, Algal and Siliceous Indicators, vol. 3. Kluwer, Dordrecht, pp. 1–31.

Louda, J.W., Loitz, J.W., Rudnick, D.T., Baker, E.W., 2000. Early diagenetic alteration of chlorophyll-a and bacteriochlorophyll-a in a contemporaneous marl ecosystem. Organic Geochemistry 31, 1561–1580.

Louda, J.W., Neto, R.R., Magalhaes, A.R.M., Schneider, V.F., 2008. Pigment alterations in the brown mussel *Parna Parna*. Comparative Biochemistry and Physiology, Part B 150, 385–394.

Ocampo, R., Sachs, J.P., Repeta, D.J., 1999. Isolation and structure determination of unstabile 13^2,17^3-Cyclopheophorbide a enol from recent sediments. Geochimica et Cosmochimica Acta 63 (22), 3743–3749.

Piechura, J., Wojnich, B., Kowalewski, J., 1963. Hydrological and meteorological studies in the Baltic in 1959–1960. WKiŁ, Warszawa (in Polish).

SHMI, 1968–1970. The Baltic Sea Hydrology annual bulletins 1964–1966; WKiŁ, Warszawa (in Polish).

Szymczak-Żyła, M., Louda, J.W., Kowalewska, G., 2008. Comparison of extraction and HPLC methods for marine sedimentary chloropigment-a determinations. Journal of Liquid Chromatography and Related Technologies 31, 1162–1180.

Szymczak-Żyła, M., Kowalewska, G., Louda, J.W., 2011. Chlorophyll-a and derivatives in recent sediments as indicators of productivity and depositional conditions. Marine Chemistry 125, 39–48.

Szymczak-Żyła, M., Krajewska, M., Winogradow, A., Zaborska, A., Breedveld, G.D., Kowalewska, G., 2017. Tracking trends in eutrophication based on pigments in recent coastal sediments. Oceanologia 59, 1–17.

Yamada, N., Tanaka, A., Horiguchi, T., 2014. CPPB-aE is discovered from phytosynthetic benthic dinoflagellates. Journal of Phycology 50, 101–107.