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ORIGINAL RESEARCH ARTICLE

Tracking trends in eutrophication based on pigments in recent coastal sediments

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Summary Eutrophication in two different coastal areas — the Gulf of Gdańsk (southern Baltic) and the Oslofjord/Drammensfjord (Norway) — both subject to human pressure and with restricted water exchange with adjacent seas, was investigated and compared. Sediment cores (up to 20 cm long) were collected at 12 stations using a core sampler, 6 in each of the two areas, and divided into sub-samples. The physicochemical parameters characterizing the adjacent water column and near-bottom water, i.e. salinity, oxygen concentration and temperature, were measured during sample collection. Chlorophylls-a, -b and -c, their derivatives and selected carotenoids were determined for all the samples, as were additional parameters characterizing the sediments, i.e. C_{org}, N_{tot}, $\delta^{13}C$ and $\delta^{15}N$, grain size. ^{210}Pb activity was also determined and on that basis sediment mixing and accumulation rates were estimated. The distribution of pigments in sediments was related to environmental conditions, the sampling site location and sediment characteristics. The results are in agreement with other observations that eutrophication in the Gulf of Gdańsk has increased, especially since the 1970s, whereas in the Oslofjord it decreased during the same period. The pigments are better preserved in inner Oslofjord sediments than in those from the Gulf of Gdańsk. The results demonstrate that the sum of chloropigments-a in

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sediments calculated per dry weight of sediments is a valuable measure of eutrophication, providing that the monitoring site is selected properly, i.e. sediments are hypoxic/anoxic and non-mixed. Besides, the results confirm previous observations that the percentages of particular chlorophyll-a derivatives in the sum of chloropigments-a are universal markers of environmental conditions in a basin. The ratios of chloropigments-b and chlorophylls-c to the sum of chloropigments-a (ΣChlns-b/ΣChlns-a; Chls-c/ΣChlns-a) may by applied as complementary markers of freshwater and marine organic matter input, respectively.

1. Introduction

Eutrophication is one of the most important problems affecting many coastal areas worldwide (e.g. Bianchi et al., 2010; Chen et al., 2001; Fleming-Lehtinen et al., 2015; HELCOM, 2007; Li et al., 2013; Orive et al., 2002). It occurs in aquatic basins of high primary production caused by elevated nutrient concentrations (Edlund et al., 2009; Harmon et al., 2014). The intensive blooms of algae and cyanobacteria (including toxin-producing phytoplankton species), followed by high rates of sedimentation and accumulation, in conjunction with restricted water exchange result in eutrophication, which is manifested by hypoxia/anoxia in the sediments and near-bottom water (Conley et al., 2011; HYPOX, 2016). Oxygen depletion inhibits the growth of benthic organisms — this is reflected in the formation of laminar sediments (Reuss et al., 2005; Zhao et al., 2012). Like darkness and low temperatures, anoxia prevents the remineralization of organic matter in sediments (Hedges and Keil, 1995).

Despite the large body of knowledge relating to eutrophication and its imprint on bottom sediments, it is still not easy to evaluate it quantitatively, analyze its trends in a basin and compare it in different locations. Numerous proxies have been applied to this phenomenon, including organic compounds — principally pigments. These are chlorophyll-a, carotenoids and their derivatives. Chlorophyll-a in water is well known as a marker of primary production and has been used for this purpose in oceanography for over 50 years (e.g. Bianchi and Canuel, 2011; Jeffrey and Mantoura, 1997); the same applies to its derivatives (Bianchi et al., 1997, 2002a,b; Carpenter et al., 1988). However, chlorophyll-a concentrations in water change frequently in time and space, whereas chloropigments-a (chlorophyll-a and its derivatives) in sediments have been shown to be good indicators of the average primary production in a basin (Bianchi et al., 2002a,b; Harris et al., 1996; Stephens et al., 1997; Szymczak-Żyła et al., 2011). Particular sedimentary chlorophyll-a derivatives may be taken as markers of syn- and post-depositional environmental conditions (Szymczak-Żyła et al., 2011). Not only chloropigments but also carotenoids are monitored in sediments as chemotaxonomic and biomass markers; indeed, β-carotene is considered an even better proxy for total algal biomass than chlorophyll-a (Dixit et al., 2000; Leavitt, 1993; Schüller et al., 2013). Numerous papers have focused on chloropigments and carotenoids in recent and old sediments, mainly in lakes (e.g. Hodgson et al., 2004; Leavitt et al., 1997; McGowan et al., 2012; Moorhouse et al., 2014; Pienitz et al., 1992). Pigments have also been tracked in shelf areas (Chen et al., 2001; Li et al., 2012, 2013; Louda et al., 2000; Shankle et al., 2002; Sampere et al., 2008), in large river estuaries in America (Canuel et al., 2009; Chen et al., 2005; Edlund et al., 2009; Wysocki et al., 2006) and Asia (Li et al., 2011; Zhao et al., 2012), in New Zealand fjords (Schüller and Savage, 2011) and off the coast of Antarctica (Sañé et al., 2013). In contrast, not many papers have been written on pigments in European coastal zone sediments (Bianchi et al., 1996; Bourgeois et al., 2011; Reuss et al., 2005; Tselepides et al., 2000) and even fewer on Baltic sediments (Bianchi et al., 2002a,b; Kowalewska, 1997; Kowalewska et al., 2004; Reuss et al., 2005; Savage et al., 2010; Szymczak-Żyła and Kowalewska, 2007), despite the fact that eutrophication and hypoxia were identified as problems in this sea already many years ago (Conley et al., 2009; HELCOM, 2007).

Pigment concentrations in sediments depend on different factors, associated with (1) primary production and sedimentation, (2) pigment stability and (3) post-depositional conditions in sediments. Pigment degrade already in the water column and after deposition in the sediments as a result of senescence, oxidation, herbivore grazing or bacterial degradation (e.g. Bianchi et al., 1988; Louda et al., 1998, 2002; Spooner et al., 1994a,b; Szymczak-Żyła et al., 2006; Welschmeyer and Lorenzen, 1985). The influence of particular factors on pigment content may be different at different sites, so it is not an easy task to compare the extent of eutrophication in different areas based on pigment proxies in sediments, or to make judgements about eutrophication trends (Leavitt, 1993; Reuss et al., 2005).

The aim of this work was to compare eutrophication in different water basins, exemplified by the Gulf of Gdańsk (southern Baltic) and the Oslofjord/Drammensfjord (Norway), and its trends in each one. These two water bodies differ in salinity, geomorphology and the extent of water mixing, but both experience limited exchange of water with the adjacent sea and both are subject to human pressure. The aim was realized by analysing the pigment content in recent sediments in relation to environmental conditions in the near-bottom water as well as sediment characteristics, including accumulation rate, sediment mixing, grain size distribution, carbon and nitrogen content, i.e. parameters and factors associated with eutrophication.

2. Material and methods

2.1. Study areas

2.1.1. Gulf of Gdańsk

The Gulf of Gdańsk (Fig. 1, area 4940 km^2) is part of the southern Baltic Sea (Majewski, 1990). The adjacent

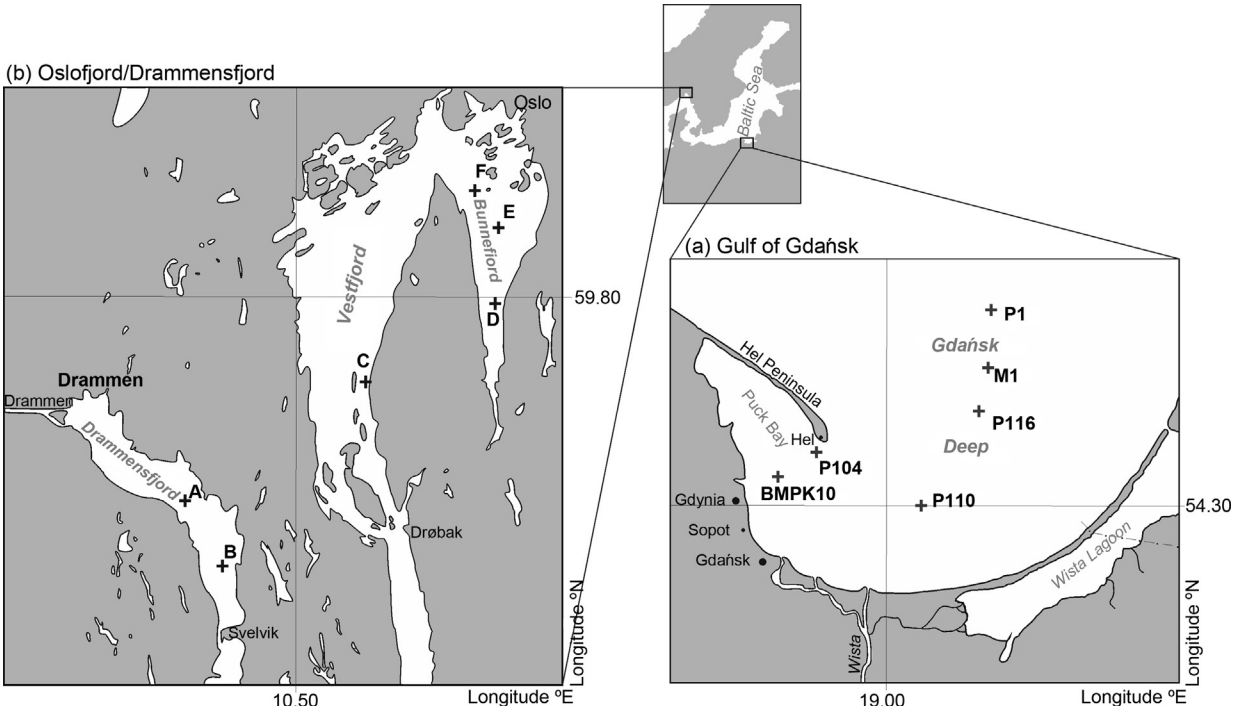

Figure 1 Location of the sampling sites: (a) Gulf of Gdańsk and (b) Oslofjord/Drammensfjord.

Gdańsk-Sopot-Gdynia conurbation (>1.2 million inhabitants) has a considerable anthropogenic influence on the Gulf. In addition, the Gulf of Gdańsk annually receives some 39 km^3 (average flow rate ~1240 $m^3 s^{-1}$) of freshwater from the River Wisła (Vistula) (Pastuszak and Witek, 2012), which corresponds to ~13% of the total volume of Gulf of Gdańsk waters. The catchment area of the River Wisła covers about 54% of the area of Poland (~170 000 km^2) and is inhabited by almost 60% of the country's population (~27% of the Baltic catchment area's population), and the river itself accumulates pollutants from industrial, municipal and agricultural effluents; nutrients are especially important. The nutrients and organic matter entering the Gulf with Wisła waters causes high primary production, which, together with the limited water exchange in the Gulf of Gdańsk, results in eutrophication (IMGW, 2013; Witek et al., 1999).

The depth of the Gulf of Gdańsk (average — 59 m; maximum — 118 m) increases seawards from the shallow coastal zone. The salinity of the Gulf's surface waters varies from ~4.5 near the Wisła mouth to ~8 in the northern, deep part of the basin. In its deeper regions (the Gdańsk Deep), vertical stratification of the water occurs, resulting in a halocline at a depth of 60—80 m that separates the more saline deep water (~12.5) from the less saline water at the surface. As vertical water exchange is limited, the bottom water in the deepest areas is hypoxic/anoxic (Conley et al., 2009; IMGW, 2013). The oxygen conditions improve during intermittent inflow events of cold and well-oxygenated seawater from the North Sea through the Danish Straits. Such strong inflows into the Baltic take place once every few years, usually during late autumn or winter (HELCOM, 2013; Mälkki and Perttilä, 2012; Mohrholz et al., 2015). The hydrological conditions and bottom topography strongly differentiate this shallow basin as far as sediment characteristics are concerned. Thus, the sediments in the Gulf vary from coarse sands near the coast to silty clay in the Gdańsk Deep. This and the lack of tides make the Gulf an exceptional natural model basin for studying eutrophication in a marine environment strongly impacted by freshwater input (IMGW, 2013).

2.1.2. Oslofjord/Drammensfjord

The Oslofjord (southern Norway) is an approximately 100 km long northward extension of the Skagerrak (Fig. 1). It is divided into an inner and outer fjord by a narrow sound with a sill at 19.5 m water depth (Drøbak Sound). The inner Oslofjord consists of two main basins: the Vestfjord and the Bunnefjord, both with a maximum water depth of about 160 m, separated by a sill at about 50 m water depth. Both fjord basins contain a number of smaller, semi-enclosed basins. The bottom topography of the Oslofjord restricts deeper-water exchange and renewal in the inner fjord. The water masses are stratified with brackish surface water and marine bottom water. Deep water renewals take place in winter with strong northerly winds (Hess et al., 2014). The inner microtidal area, which borders the most densely populated and industrialized area in Norway, has received large amounts of waste waters and nutrients, particularly during the last century. As a consequence of that and the limited water-exchange between the different basins, oxygen-depleted bottom water conditions have developed in several basins (Dale et al., 1999). The nutrient load to the inner Oslofjord reached a maximum around 1970; since then it has decreased considerably, and the oxygen conditions are slowly improving in most basins (Hess et al., 2014).

The outer Oslofjord is connected to the Drammensfjord, which has a length of 20 km and a width of 1.6—3.0 km. It is separated from the Greater Oslofjord by a sill at Svelvik, which was dredged from 6 to 8 m depth around 1900, and to

10 m in 1951 (Smittenberg et al., 2005). Since the 1800s, the redoxcline in Drammensfjord has moved to shallower water depths following the increased influx of organic material from the pulp and paper industry, and from an increasing population and more intensive agriculture in the drainage area (Alve, 1991). Oxygen depletion was first detected in 1899, and the presence of H_2S in June 1933 (Öztürk, 1995; Smittenberg et al., 2005). An incursion of oceanic waters currently occurs once every 3–5 years, mainly between November and May, displacing some of the anoxic bottom waters upwards (Alve, 1995a; Richards, 1965). The shallowest position of the redoxcline occurred in the late 1970s to early 1980s, when it lay at 30–35 m water depth (Magnusson and Næs, 1986). In 1988, following the closing down of industry and the implementation of governmental regulations, it was recorded at about 35 m water depth in the north and about 60 m in the south with anoxic sediments in the deeper parts and oxic sediments in the shallower parts (Alve, 1995b). Recent studies conducted by local authorities (Monitoring of Drammensfjord 2008–2011, NGI, 2010) show that the deep-water dissolved oxygen levels increased from anoxic to a period of oxic conditions following the 2004/2005-dredging of the sill to 12 m depth. The mixing of freshwater from the River Drammen (drainage area ~17 000 km^2, average flow rate ~300 $m^3 s^{-1}$), which enters the fjord at its head, gives rise to a brackish surface water layer (salinity 1–10, depending on the season) that is separated from saline bottom water (30.5) below 40 m depth. River regulation has smoothed the annual freshwater supply to the fjord over the last 60 years, reducing the effect of spring flooding and increasing the winter supply. This has shifted the minimum freshwater supply from winter to late summer, thus increasing the residence time of the surface water during summer (Smittenberg et al., 2005).

2.2. Sample collection

Sediments were collected at six stations in the Gulf of Gdańsk and six stations in the Oslofjord/Drammensfjord (Fig. 1; Table 1). The stations in the Gulf of Gdańsk were selected so as to cover a wide range of environmental conditions in the study area, i.e. different water depth, salinity, oxygen concentration, sediment type and distance from the coastline. The four stations selected – P110, P116, M1 and P1 – were positioned along the way of Wisła water inflow in the Gulf as far as the Gdańsk Deep. The other two stations were located in Puck Bay, the shallow, western part of the Gulf (Table 1): station BMPK10 in the middle of the Bay and P104 close to the town of Hel, a recreational and sports centre, near intensively used shipping lanes and strong water currents around the tip of the Hel Peninsula.

The stations in the Oslofjord/Drammensfjord were also selected such as to obtain many different locations concerning distance from the open sea, salinity, oxygen concentration and human pressure (Fig. 1; Table 1). Two stations were located in Drammensfjord: A in the middle of the fjord and B

Table 1 Characteristics of the sampling stations.

Station	Coordinates	Water depth [m]	Parameters of near-bottom water			Sediment accumulation rate [cm y^{-1}]	Sediment mixing depth [cm]
			Salinity	Temp. [°C]	Oxygen [mg L^{-1}]		
Gulf of Gdańsk							
P1	54°50.042′N 19°19.683′E	112	12.0	6.3	3.4	0.16 ± 0.01	0
M1	54°44.912′N 19°17.662′E	95	11.7	6.4	3.9	0.16 ± 0.01	0
P116	54°39.091′N 19°17.575′E	92	10.8	6.4	0.5	0.14 ± 0.01	0
P110	54°29.986′N 19°06.902′E	72	8.6	5.0	5.4	0.17 ± 0.02	3
BMPK10	54°33.545′N 18°40.950′E	31	7.5	4.9	11.1	No accumulation or max 0.07 ± 0.01	12
P104	54°34.944′N 18°47.370′E	55	7.6	4.5	12.1	No accumulation	12
Oslofjord/Drammensfjord							
A	59°41.276′N 10°22.745′E	113	31.2	8.0	0.3	0.11 ± 0.01	0
B	59°38.862′N 10°24.804′E	122	31.0	8.2	0.5	0.27 ± 0.02	0
C	59°45.066′N 10°34.429′E	154–158	32.3	8.3	9.2	0.20 ± 0.02	4
D	59°47.386′N 10°43.154′E	152	32.6	9.2	1.7	0.10 ± 0.03	5
E	59°50.643′N 10°43.557′E	77	33.2	8.5	0.2	0.18 ± 0.01	0
F	59°51.470′N 10°41.710′E	78	33.6	8.3	1.7	0.05 ± 0.01	3

nearer Svelvik. The other four stations were located in the inner Oslofjord: station C in the deepest, southernmost part of the Vestfjord, and stations D, E and F in the Bunnefjord. Station D was in the deepest and southern-most part of the Bunnefjord, station E in its shallower part, and station F was closest to the port of Oslo.

The sediments were collected during two cruises of r/v 'Oceania': in April 2014 (in the Gulf of Gdańsk) and in June 2014 (in the Norwegian fjords). Sediment samples were taken with a Niemistö core sampler in the Gulf of Gdańsk and with a GEMAX twin-core sampler in the Norwegian fjords; in both cases the core diameter Φ = 10 cm. Eight cores were collected at each station. All the cores were photographed immediately after collection (Appendix 1). After collection the following layers were taken from each sediment core: 0–1, 1–5, 5–10, 10–15 and 15–20 cm; sub-samples from all the cores collected at the same station were pooled. The additional core for ^{210}Pb analysis was divided into thinner, 1 cm thick layers from 0 to 10 cm and 2 cm thick layers from 10 to 30 cm sediment depth. All the sub-samples were frozen on board immediately after collection.

2.3. Physicochemical seawater parameters

The salinity, temperature and oxygen concentration were measured with a SBE19 probe (vertical profiles in the water column) and with a ProfiLine Multi 197i WTW meter (near-bottom water).

2.4. Analyses

2.4.1. Pigment analysis

The concentrations of pigments were determined in all samples with HPLC using a procedure described in detail elsewhere (Kowalewska et al., 1996; Szymczak-Żyła et al., 2008).

2.4.1.1. Pigment extraction from sediments. A frozen sediment sample (3–5 g) was placed in a glass centrifuge tube and left to thaw. After centrifugation (10 min, 2500 rpm) water was removed and the sample flushed with acetone, stirred, sonicated (2–3 min), centrifuged again, and the extract decanted. The extraction was repeated until the supernatant was colourless (max. 3 times). The acetone extracts were transferred to a separate funnel in which liquid–liquid extraction was performed in the acetone extract:benzene:water system. The benzene layer was then transferred to a glass vial and evaporated to dryness in a stream of argon and stored frozen (−20°C) until HPLC analysis. The extracted sediment was dried at 60°C and weighed. The pigment content was calculated per dry sediment weight.

2.4.1.2. HPLC pigment analysis. The sediment extract prepared as above was dissolved in acetone and injected into the HPLC set (Knauer, Germany) with two detectors: diode array (DAD 2800 Knauer) and fluorescence detector (RF-20Axs, Shimadzu, Japan), autosampler (Knauer Optimas, Germany), then into a Lichrospher 100RP-18 endcapped column (250 mm × 4 mm, 5 μm; Merck, Germany) through a guard column (Lichrospher 100RP-18 endcapped, 4 mm × 4 mm; Merck, Germany).

The following pigments were determined: chloropigments-a (chlorophyll-a and its derivatives: pheophorbides-a, pyropheophorbides-a, chlorophyll-a-allomers, chlorophyll-a-epimer, pheophytin-a, pheophytin-a-epimer, pyropheophytin-a and sum of steryl chlorin esters); chloropigments-b (chlorophyll-b and pheophytin-b); sum of chlorophylls-c; carotenoids (fucoxanthin, alloxanthin, diatoxanthin, lutein, zeaxanthin, cantaxanthin, echinenone and β-carotene).

Separations of chloropigments-a and -b were carried out using an HPLC/DAD set, in the A (acetone):B (80:20, acetone: water, v/v) gradient system at a flow rate of 1.0 mL min^{-1}. The mobile phase and gradient system was a modified version of that used by Szymczak-Żyła et al. (2008). Absorption spectra were measured over the 360–750 nm range. Pigment concentrations were determined according to the procedure described by Szymczak-Żyła et al. (2008).

Chlorophylls-c were analyzed using an HPLC/FL set, in the A (acetone):B (80:20, acetone:water, v/v) gradient system at a flow rate of 0.5 mL min^{-1}. The excitation and emission wavelengths were 440 and 630 nm, respectively. Quantitative data of chlorophylls-c content were obtained according to the procedure described by Kowalewska et al. (1996).

Carotenoid separations were carried out using an HPLC/DAD set, in the A (85:15, methanol:0.5 M ammonium acetate, aq. v/v):B (90:10, acetonitrile:water, v/v): C (ethyl acetate) gradient system at a flow rate of 1.0 mL min^{-1}. The mobile phase and gradient system was a modified version of that used by Chen et al. (2001). Carotenoid concentrations in the samples were calculated in the same way as those for chloropigments-a and b (Szymczak-Żyła et al., 2008).

Pigments were identified on the basis of retention time and absorbance spectra compared with pigment standards (DHI, Denmark).

2.4.2. Additional analyses

2.4.2.1. ^{210}Pb analysis – sediment accumulation rate. The ^{210}Pb dating method (Goldberg, 1963) was used to determine the sediment accumulation rate. Sediment samples for ^{210}Pb dating were freeze-dried and ground in the laboratory. Sediment moisture and porosity were calculated. The ^{210}Pb activity concentration was measured indirectly by the alpha spectrometry counting of its daughter nuclide ^{210}Po (Zaborska et al., 2007). In brief, sediment samples were spiked with ^{209}Po (chemical yield tracer) and digested. Polonium isotopes were spontaneously deposited onto silver discs. These were analyzed for ^{210}Po and ^{209}Po activity concentration in a multi-channel analyser (Canberra) equipped with Si/Li detectors. The samples were counted for 1 day. The activity concentration of ^{210}Po in a sample was determined on the basis of chemical recovery by comparing the measured and spiked activity concentration of ^{209}Po. Blanks and standards were measured to verify the efficiency of the separation procedure and detection. Standard reference materials (IAEA-326) were used to verify the measurements. One blank sample (without the sediment) was measured with every 7 sediment samples. The environmental background was negligible. The linear accumulation rate (LAR, cm y^{-1}) was calculated assuming an exponential decrease in ^{210}Pb$_{ex}$ with sediment depth (Zaborska et al., 2007).

2.4.2.2. Grain size analysis. The fine fractions from sampling stations BMPK10 and P104 and the sediment samples from the other stations were analyzed by laser diffraction using a Fritsch Laser Particle Sizer Analysette-22 (Kramarska

et al., 1996) and recorded at a resolution of 1 ϕ. Sodium pyrophosphate was used to prevent aggregates forming during measurement. Because the sediment samples from the Oslofjord contained carbonates, they were pre-treated with 10% HCl. All sediment samples were treated with 30% H_2O_2 before analysis in order to remove organic matter. Sediments from stations BMPK10 and P104 were first passed wet (Myślińska, 1992) through a sieve of mesh diameter of 0.063 mm.

2.4.2.3. Carbon and nitrogen analyses. Organic carbon (C_{org}), total nitrogen (N_{tot}), stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope analyses were done in a Flash EA 1112 Series Elemental Analyzer combined with an IRMS Delta V Advantage Isotopic Ratio Mass Spectrometer (Thermo Electron Corp., Germany). Dry, homogeneous samples of the sediments were weighed (2–4 mg for the Baltic Sea sediment samples, 20–25 mg for the Oslofjord/Drammensfjord sediment samples) into silver vials and acidified with 2 M HCl (Chang et al., 1991; Hedges and Stern, 1984). The C_{org} and N_{tot} concentrations are stated as percentages of the bulk of the dry sample after removal of carbonates. Quality control of the organic carbon measurements was carried out with standards (Thermo Electron Corp.). The accuracy and precision (average recovery 99.1 ± 2.0%) of the methodology were satisfactory. Isotopic ratios $\delta^{13}C$ and $\delta^{15}N$ were calculated using laboratory working pure reference gases CO_2 and N_2 calibrated against IAEA standards: CO-8 and USGS40 for $\delta^{13}C$ and N-1 and USGS40 for $\delta^{15}N$. The $\delta^{13}C$ results are given in the conventional delta notation, i.e. versus PDB for $\delta^{13}C$ and versus air for $\delta^{15}N$.

2.5. Statistical analysis

The results were statistically processed using STATISTICA 12.5 software (StatSoft, Poland): correlation analysis, cluster analysis and principal component analysis (PCA) were used. Non-parametric methods (e.g. R-Spearman correlation analysis) were applied to cases where the basic conditions necessary for using parametric methods were not fulfilled (tested with the Shapiro–Wilk and Brown-Forsyth tests). Correlation analysis was used to evaluate the relationships between the pigment contents, pigment ratios in the sediment and the environmental parameters. A correlation of $p < 0.05$ was regarded as significant. Cluster analysis (Ward's method, Euclidean distance) was used to produce a classification of the sampling stations taking into account sediment characteristics (pigment content, grain size, organic carbon and nitrogen content) and near-bottom water parameters. Relationships between the content of pigments, ratio of particular pigments in the sediment samples and other measured parameters were also checked using PCA.

3. Results

3.1. Pigment distribution

The highest pigment concentrations were found in sediments collected from the Gdańsk Deep, where the concentration of e.g. ΣChlns-a in the surface (0–1 cm) layer of sediments ranged from ~350 nmol g^{-1} d.w. (dry weight of sediment) at station P110 to ~800 nmol g^{-1} d.w. at station P1 (Fig. 2). Relative to the Gdańsk Deep area, the sediments from Puck Bay (stations BMPK10, P104) contained much lower amounts of pigments (e.g. ΣChlns-a in 0–1 cm layer ~80 nmol g^{-1} d.w.). From the Oslofjord/Drammensfjord, only the sediments from the Bunnefjord were rich in pigments, where the concentration of ΣChlns-a in the surface (0–1 cm) layer of sediments ranged from ~130 nmol g^{-1} d.w. at station F to ~320 nmol g^{-1} d.w. at station E (Fig. 2). A considerably lower pigment content was determined in Drammensfjord (~35 nmol g^{-1} d.w. at station A and ~60 nmol g^{-1} d.w. at station B) and in Vestfjord (station C ~35 nmol g^{-1} d.w.).

The concentration ranges of parent chloropigments and carotenoids in the surface (0–1 cm) sediment layer were as follows: 4–227 nmol g^{-1} d.w. (chl-a), 0.2–15 nmol g^{-1} d.w. (chl-b), 0.2–8.5 nmol g^{-1} d.w. (chls-c), 3.5–387 nmol g^{-1} d.w. (fuco), 0.5–45 nmol g^{-1} d.w. (diato), 1–82 nmol g^{-1} d.w. (lut) and 0–256 nmol g^{-1} d.w. (β-car) (Table 2). The profiles of all pigment concentrations resembled that of the sum of chloropigments-a.

Pigment concentrations were distinctly higher in the surface (0–1 cm) layer than in the deeper sediment layers of the Gulf of Gdańsk (Fig. 2). This was not observed in the samples from the Oslofjord/Drammensfjords, where the surface layer pigment concentrations are comparable to or even lower than in the deeper layers.

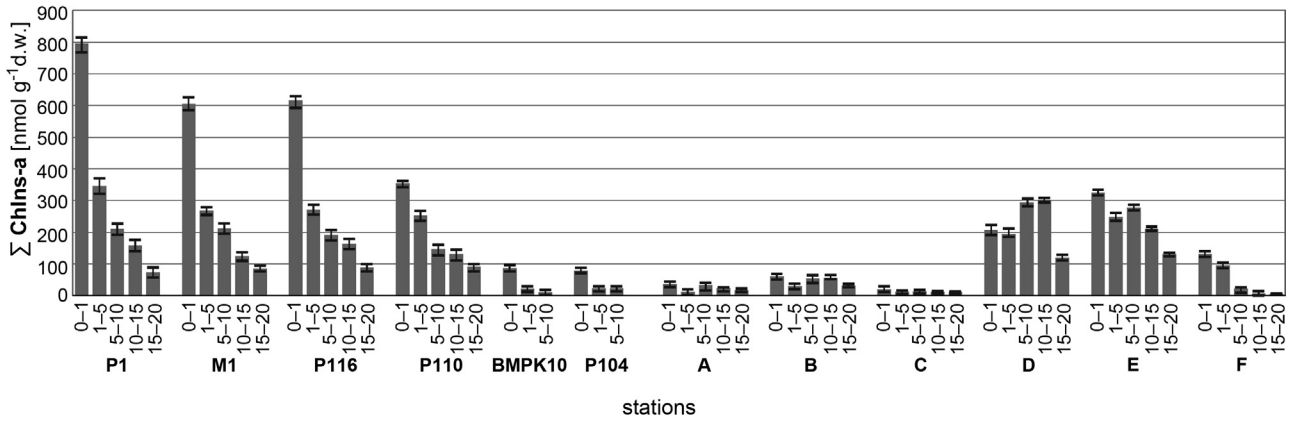

Figure 2 Average contents [nmol g^{-1} d.w.] of the sum of chloropigments-a (ΣChlns-a); $n = 2$.

Table 2 Average contents of selected pigments [nmol g^{-1} d.w.] in the surface (0–1 cm) sediment layer; $n = 2$.

Station	Chl-*a*	Chl-*b*	Chls-*c*	Fuco	Diato	Lut	β-car
Gulf of Gdańsk							
P1	227.4	14.8	8.5	386.6	45.0	81.7	255.8
M1	164.3	12.3	5.7	204.1	36.2	76.2	207.9
P116	194.3	13.1	6.7	268.3	34.9	67.3	184.7
P110	176.9	7.4	6.5	144.4	12.8	29.1	67.6
BMPK10	35.3	1.4	1.8	27.6	1.4	4.3	14.3
P104	32.9	1.4	1.8	41.1	4.4	3.4	13.1
Oslofjord/Drammensfjord							
A	9.3	1.1	0.2	3.5	0.5	4.6	8.0
B	22.3	1.6	0.5	12.6	3.5	10.0	19.5
C	4.3	0.2	0.3	8.9	0.9	1.3	0.0
D	83.9	5.1	3.1	79.3	23.0	24.5	89.0
E	79.4	5.3	5.1	90.8	34.3	27.2	119.6
F	32.5	1.5	2.3	23.5	18.3	21.3	104.1

3.2. Physicochemical parameters of seawater

All the stations in the Oslofjord/Drammensfjord were characterized by a much higher salinity both in the water column and in the near-bottom water, and the halocline was at a shallower depth, than in the Gulf of Gdańsk (Table 1, Appendix 2). The temperature of the near-bottom water was higher and more evenly distributed in the Norwegian fjords than in the Gulf of Gdańsk. In the Gulf of Gdańsk higher temperatures were recorded at the stations in the Gdańsk Deep than at the shallower stations, in Puck Bay. There was anoxia in the near-bottom water at one station (P116, oxygen concentration – 0.5 mg L^{-1}) in the Gdańsk Deep, while three other stations in the Gdańsk Deep (P1, M1 and P110) had low oxygen concentration (3.5–5.4 mg L^{-1}). Only two shallow-water stations (BMPK10 and P104) had a high oxygen concentration. All but one of the stations in the Norwegian fjords exhibited anoxia/hypoxia. The exception was station C (Vestfjord) with the higher oxygen concentration (9.2 mg L^{-1}) (Table 1).

3.3. Sediment characteristics

3.3.1. ^{210}Pb – sediment accumulation rates

$^{210}Pb_{tot}$ in the surface (0–1 cm) layer varied significantly depending on sampling region – from ~82 to ~650 Bq kg^{-1} in the Gulf of Gdańsk and from ~120 to ~280 Bq kg^{-1} in the Oslofjord (Appendix 3). The $^{210}Pb_{tot}$ values for the Gulf of Gdańsk cores concur with those recently reported by several authors (Suplińska and Pietrzak-Flis, 2008; Zaborska et al., 2014; Zalewska et al., 2015). The $^{210}Pb_{tot}$ results for Norwegian fjord sediments are also comparable to those obtained by other authors (Dolven and Alve, 2010; Smittenberg et al., 2005; Zegers et al., 2003).

Most of the $^{210}Pb_{tot}$ activity concentration profiles showed an exponential decrease along the core, although sediment mixing and/or extremely low net sedimentation was apparent at some stations. The $^{210}Pb_{tot}$ profiles of Norwegian fjord sediments (C, D, F) indicated disturbances in the surface sediments (3–5 cm) caused by human or animal activity and/or by currents (Table 1; Appendix 3). Similar $^{210}Pb_{tot}$ profiles were reported by Dolven and Alve (2010) and Smittenberg et al. (2005) for the Oslofjord sediments. According to those authors these sediments exhibited numerous disturbances as well as mixing in both the upper and lower parts of the cores. In the fjords (this work) there was no mixing at three stations: A, B and E. In the Gdańsk Deep no sediment mixing was found to have occurred at three stations (P1, M1, P116), while there was slight (3 cm) mixing at station P110 and intensive mixing at the shallow-water stations BMPK10 and P104 down to 12 cm depth (Table 1).

The stations in the Gdańsk Deep were characterized by intermediate linear accumulation rates (LARs) ranging from 0.14 cm y^{-1} (station P116) to 0.17 cm y^{-1} (station P110) (Table 1). The LAR was not calculated for station P104 in Puck Bay, since the $^{210}Pb_{tot}$ activity concentration profile did not decrease with depth there. At station BMPK10, the $^{210}Pb_{tot}$ profile showed very little decrease with depth, and it was difficult to calculate the LAR (no accumulation at all or no more than 0.07 cm y^{-1}). The last two stations were located in relatively shallow areas (30–50 m), where the coarser sediment fraction prevailed as a result of local currents transferring fine particulate matter to deeper areas. LARs ranging from 0.05 cm y^{-1} (station F) to 0.18 cm y^{-1} (station E) were measured for eastern Oslofjord (Bunnefjord) sediments. Station C in the western Oslofjord (Vestfjord) displayed the second highest LAR of 0.20 cm y^{-1}. In the Drammensfjord, the LARs were 0.11 cm y^{-1} (station A) and 0.27 cm y^{-1} (station B) (Table 1).

The LARs obtained in this study for the Gdańsk Deep stations (0.14–0.17 cm y^{-1}) agree with the values reported for this region (0.1–0.24 cm y^{-1}, Pempkowiak, 1991; Suplińska and Pietrzak-Flis, 2008; Zaborska et al., 2014; Zalewska et al., 2015). Few data on sediment accumulation rates in the Oslofjord have been reported. Pau and Hammer (2013) estimated accumulation rates in the northern part of the Vestfjord. They report LARs from 0.04 to 0.18 cm y^{-1}, depending on the bottom depth (with higher rates in deeper areas). Their results generally agree well with the LARs obtained in this work (from 0.5 to 0.20 cm y^{-1}). Dolven and Alve (2010) and Dolven et al. (2013) studied both parts of the Oslofjord. They found very large and variable accumulation rates of 0.1–0.3 cm y^{-1} in the northern Bunnefjord and even larger rates of *ca* 0.4 cm y^{-1} in its southern part. Extremely large LARs of 1.3–2.5 cm y^{-1} and very high fluxes of ^{210}Pb have been reported for the southern Vestfjord (Dolven and Alve, 2010). In the Drammensfjord, sediment accumulation rates from 0.15 to 0.25 cm y^{-1} were measured by Smittenberg et al. (2005) and Huguet et al. (2007), which is in agreement with the results of this work.

3.3.2. Grain size

The grain size fractions are presented as the sum of sand (>0.063 mm), silt (from 0.063 to 0.004 mm) and clay (<0.004 mm). The sediments richest in sand were at stations P104 and BMPK10 (Table 3; Appendix 4). The silt fractions were the largest at the stations in the Gdańsk Deep and the eastern Oslofjord (Bunnefjord). The content of the smallest grain size (<0.004 mm) fraction was the highest in the Drammensfjord and the Vestfjord (station C).

3.3.3. Carbon and nitrogen

Organic carbon concentrations in sediments of the Gdańsk Deep were by far the highest of all the samples studied

(5–8%) (Table 3; Appendix 4). The lowest concentrations were in Puck Bay (BMPK10, P104) (1–3.4%). The organic carbon content in the samples from the Norwegian fjords were in between those values: the highest content was for stations in the Bunnefjord – from 1.5 to 4.5% at D and E, and 7% in the 1–5 cm layer of sediments at F. The values were lower in the Drammensfjord (1.4–2.5%). The $\delta^{13}C$ values measured for sediment cores ranged from −26.9‰ to −20.5‰. The distinctly higher values were measured for four (C, D, E, F) sediment cores collected from the Oslofjords (from −22.3‰ to −20.5‰). The $\delta^{15}N$ values measured for the Baltic Sea sediments ranged from ~2‰ to 3.7‰, while for the Norwegian fjord sediments from ~1.6‰ to 3.5‰ (Appendix 4).

4. Discussion

4.1. Environmental conditions and the pigment record in sediments

Chloropigments-a content in recent sediments is a good, well-documented indicator of productivity in both lacustrine and marine sediments (e.g. Kowalewska et al., 2004; Leavitt and Hodgson, 2001; Louda et al., 2000; Szymczak-Żyła and Kowalewska, 2007; Villanueva and Hastings, 2000). The method based on determining chloropigments-a in sediments (calculated per dry weight of sediment, not normalized to organic carbon) yields the average eutrophication picture for an area. The pigment contents in the sediments discussed in this paper (Fig. 2, Table 2) are in accordance with previous studies of the Gulf of Gdańsk. Szymczak-Żyła et al. (2011) reported that the average sum of chloropigments-a (ΣChlns-a) in the Gdańsk Deep sediments was ~400 nmol g^{-1} d.w. (in 0–1 cm). In that work the highest value (~900 nmol g^{-1} d.w.) was recorded in May 2003. This was a consequence of the intense algal bloom (Chl-a ~20 mg m^{-3}) that had taken place in April 2003 (IMGW, 2009). The high value of pigments determined in the surface (0–1 cm) sediment layer (ΣChlns-a ~800 nmol g^{-1} d.w.) of the Gdańsk Deep in April 2014 (this paper) indicates that productivity in this area is still high. The concentration of pigments in sediments depends not only on primary production but also other factors influencing sedimentation, hydrological and depositional conditions. Taking into account the concentration of pigments (ΣChlns-a) in the surface (0–1 cm) sediment layer and sediment characteristics, including organic carbon and total nitrogen content, grain size distribution and near-bottom water parameters (salinity, temperature and oxygen concentration), hierarchical cluster analysis (dendrogram of the sampling stations – Fig. 3a) showed that sediments in the Gdańsk Deep (stations P1 and P110, M1 and P116) differ from those at the other Gulf of Gdańsk stations, i.e. those in Puck Bay (BMPK10, P104). Furthermore, the Gulf of Gdańsk stations differ significantly from those in the Oslofjord/Drammensfjord area (Fig. 3a). Principal Component Analysis (PCA) was applied to check these results and to find the most significant factor affecting the pigment concentration in the sediments of the study areas (Fig. 3b and c). The PCA data matrix model explains over 90% of the total variations with the first two principal components. The considerably lower pigment content in the Puck Bay sediments corresponds with the good oxic conditions in the near-bottom water and the high content of sand fraction (Fig. 3b and c), which is due to the strong water currents in this area. A high positive and significant correlation of ΣChlns-a with the percentage of organic carbon ($r = 0.92$, $p < 0.05$) and the percentage of the fine sediment fraction <0.063 mm ($r = 0.88$, $p < 0.05$) was obtained for all the samples from the Gulf of Gdańsk. Shankle et al. (2002) has observed that sediment grain size is an important factor affecting pigment content in sediments. The pigment-rich Gdańsk Deep sediments contain large quantities of organic carbon, total nitrogen and silt fraction (Fig. 3b and c). Anoxia in the near-bottom water and sediments prevents the decomposition of organic matter and preserves pigments in the Gdańsk Deep sediments. The pigment concentration correlates negatively with the oxygen content in the near-bottom water ($r = -0.9$, $p < 0.05$), which

Table 3 Sediment characteristics: grain size, organic carbon (C_{org}), total nitrogen (N_{tot}), stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) content in the surface (0–1 cm) sediment layer.

Station	Grain size [%]			C_{org} [%]	N_{tot} [%]	$\delta^{13}C$ [‰]	$\delta^{15}N$ [‰]
	Sand >0.063 mm	Silt 0.063–0.004 mm	Clay <0.004 mm				
Gulf of Gdańsk							
P1	0.8	75.8	23.4	8.13	1.14	−25.3	3.72
M1	0	73.5	26.5	6.90	0.94	−25.4	2.51
P116	0	73.2	26.8	7.22	1.02	−25.2	2.21
P110	1.4	76.5	22.1	6.65	0.98	−25.2	2.52
BMPK10	53.9	35.4	10.7	3.36	0.37	−25.2	2.46
P104	64.1	28.7	7.2	1.62	0.22	−25.2	3.52
Oslofjord/Drammensfjord							
A	0	51.9	48.1	2.03	0.15	−25.9	2.75
B	0	54.8	45.2	1.60	0.15	−25.2	1.23
C	0	54.1	45.9	2.97	0.23	−21.7	1.02
D	0	67.5	32.5	2.58	0.33	−22.0	2.29
E	0	63.8	36.2	1.58	0.19	−22.0	2.99
F	0	63.9	36.1	3.74	0.33	−21.5	2.32

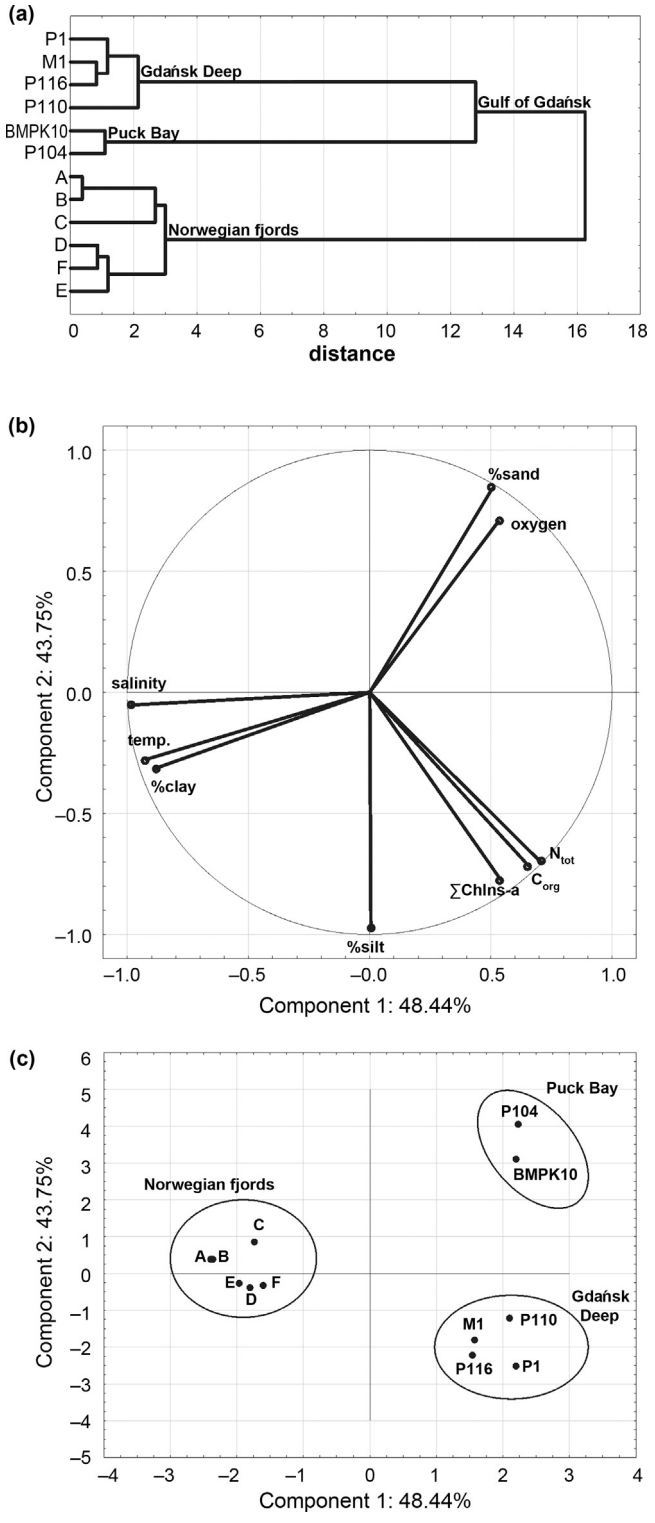

Figure 3 Results of the statistical analysis: (a) hierarchical dendrogram of sampling stations (cluster analysis — Ward's method, Euclidean distance) based on characteristics of the surface (0—1 cm) sediment layer: chloropigments-a content (∑Chlns-a), organic carbon (C_{org}) and total nitrogen (N_{tot}) content, grain size (%sand, %silt, %clay) and near-bottom water parameters (salinity, temperature and oxygen concentration); (b) scatter plot of principal component loading by individual variables; (c) scatter plot of principal component object scores by sampling sites.

is in agreement with the observations of other authors that oxygen is one of the most significant factors affecting the pigment concentration in sediments (Bianchi et al., 2000; Reuss et al., 2005; Villanueva and Hastings, 2000). Gulf of Gdańsk sediments differ significantly from the Oslofjord/Drammensfjord sediments (Fig. 3a and c), which have a higher clay fraction content and higher near-bottom water salinity and temperature. The near-bottom waters of most of the Norwegian fjord areas studied here, except Vestfjord, were anoxic/hypoxic (Table 1). In the Oslofjord/Drammensfjord areas studied, only the sediments of the Bunnefjord were rich in pigments, while in the Drammensfjord, despite the anoxic/hypoxic conditions, there were far fewer pigments in the sediments (Fig. 2, Table 2). This is indicative of this area's low productivity, or that a large proportion of pigments is degraded to colourless products in the water column. All this demonstrates that chloropigments-a in surface sediments are a reflection of the eutrophication of the basin.

Pigment concentrations are distinctly higher in the surface (0—1 cm) layer, which might have been formed in the past 5—7 years, than in deeper sediment layers of the Gulf of Gdańsk (Fig. 2). This tallies with our previous observations (Szymczak-Żyła and Kowalewska, 2007) and those of other authors (Stephens et al., 1997; Villanueva and Hastings, 2000) that the pigment content decreases the fastest in the surface sediment layer. In the deeper layers pigment transformation proceeds much more slowly, especially in anoxic basins. However, this was not observed in the samples from the Oslofjord/Drammensfjord, where pigment concentrations in the surface layer are comparable to or even lower than in the deeper layers (Fig. 2). This suggests decreasing primary production and that conditions in the Norwegian fjords are more propitious to pigment preservation in sediments. The topography of the fjords being what it is (see Section 2.1.2), the pigments remain undecomposed for many years. In the Gulf of Gdańsk vertical mixing and bottom-water exchange is limited but not within the same range as in the fjords.

Sediments differed not only in the content of pigments but also in the percentage of particular chlorophyll-a derivatives in their sum. Our previous observations from Gulf of Gdańsk studies showed that the percentage of particular sedimentary chlorophyll-a derivatives may be taken to be markers of syn- and post-depositional environmental conditions (Szymczak-Żyła et al., 2011). Chlorophyll-a allomers are characteristic of sediments originating from an oxygenated coastal zone. Chlorophyll-a and pheophorbides-a indicate the presence of comparatively fresh material (Louda et al., 1998, 2002). Pyropheophorbides-a are mainly a marker for grazing by zooplankton and/or zoobenthos (Bianchi et al., 1998, 2002a, b; Head and Harris, 1996; Szymczak-Żyła et al., 2006). Finally, pyropheophytin-a and the steryl derivatives occur mainly in anoxic sediments (Chen et al., 2001; Louda et al., 2000; Shankle et al., 2002; Szymczak-Żyła et al., 2011; Villanueva and Hastings, 2000). Based on these observations, we named indicators of processes ('grazing') and environmental conditions ('oxic' and 'anoxic') (Fig. 4a—c). There was a high (almost 20%) percentage of 'grazing' chlorophyll-a derivatives (pyropheophorbides-a) in the Puck Bay sediments (stations BMPK10 and P104), which corresponds with the sediment mixing results. The $^{210}Pb_{tot}$ profile in the sediments indicated intensive mixing at the shallow-water Puck Bay stations down to 12 cm depth (Table 1). The pigment results

presented in this paper suggest that the sediments there were probably disturbed by animal activity. In the Norwegian fjords the sediments at stations C, D, F were also mixed. The high percentage of 'grazing' derivatives at stations C and F suggests that benthic activity is responsible for sediment mixing in these areas. Indeed, a large biomass of benthic animals (Polychaetes) was observed already during sampling at station F (Appendix 1). However, at station A, where the sediments were not mixed, the high percentage of 'grazing' derivatives suggests intense zooplankton activity in the water column. Two stations with mixed sediments (P110 and D) did not have a high proportion of 'grazing' indicators. This can be explained by mixing by abiotic factors (e.g. currents) at these sampling sites.

The maximum percentage of chlorophyll-*a*-allomers, which form under oxic conditions, ('oxic' indicator) was in the sediments from the Puck Bay stations and in Vestfjord (station C), while derivatives characteristic of anoxic conditions (pyropheophytin-a and the steryl chlorin esters – 'anoxic' indicator) were found in sediments from the Gdańsk Deep and the remaining Norwegian fjord stations (A, B, D, E, F) (Fig. 4b and c). This is indicative of oxic/anoxic conditions in the near-bottom water (Table 1).

4.2. Freshwater and seawater influences

Eutrophication occurs in coastal areas impacted by inorganic nutrient loads, by nutrients bound to organic matter and restricted water exchange. The traditional proxies used for determining organic matter sources are the carbon-to-nitrogen ratio (C N^{-1}) and the stable isotopes of these two elements ($\delta^{13}C$, $\delta^{15}N$) (Fontugne and Jouanneau, 1987; Maksymowska et al., 2000; Szczepańska et al., 2012), but the ranges characteristic of different organic matter sources are broad and frequently overlap (Cravotta, 1997; Schulz and Zabel, 2006). The use of these three proxies for sediments often yields different information, so that determining the origin of organic matter is difficult. The use of $\delta^{15}N$ as an indicator for sediments is particularly ambiguous, because nitrogen is fractionated in the trophic network rather than during photosynthesis. The typical nitrogen isotopic composition ($\delta^{15}N$) of marine phytoplankton in temperate seas varies from 3.0‰ to 12.0‰. Freshwater phytoplankton isotopic signatures mentioned in the literature have $\delta^{15}N$ around 5‰ (Schulz and Zabel, 2006).

The C N^{-1} results for five (P1, M1, P116, P110, P104) of the six sediment cores from the Gulf of Gdańsk (range from ~8 to ~10) indicate a mixed marine and terrigenous origin of the sedimentary organic matter (Szczepańska et al., 2012). The exception is station BMPK10, for which the measured values are higher (from 10.5 to 13.4), indicating a more terrigenous origin. The $\delta^{13}C$ values (from −25.7‰ to −25‰) indicate that the organic matter in all the cores consists of a mixture of terrestrial and marine matter. This is in agreement with the conclusion drawn from the C N^{-1} ratio and data published earlier for this area (Szczepańska et al., 2012; Voss et al., 2000). The $\delta^{15}N$ values measured for the Baltic Sea sediments ranged from ~2‰ to 3.7‰. The stable nitrogen signature recorded in this study is similar to that of Voss et al. (2000), who noted that this signature is indicative of marine phytoplankton. This observation thus contradicts the C N^{-1} ratio and $\delta^{13}C$ results.

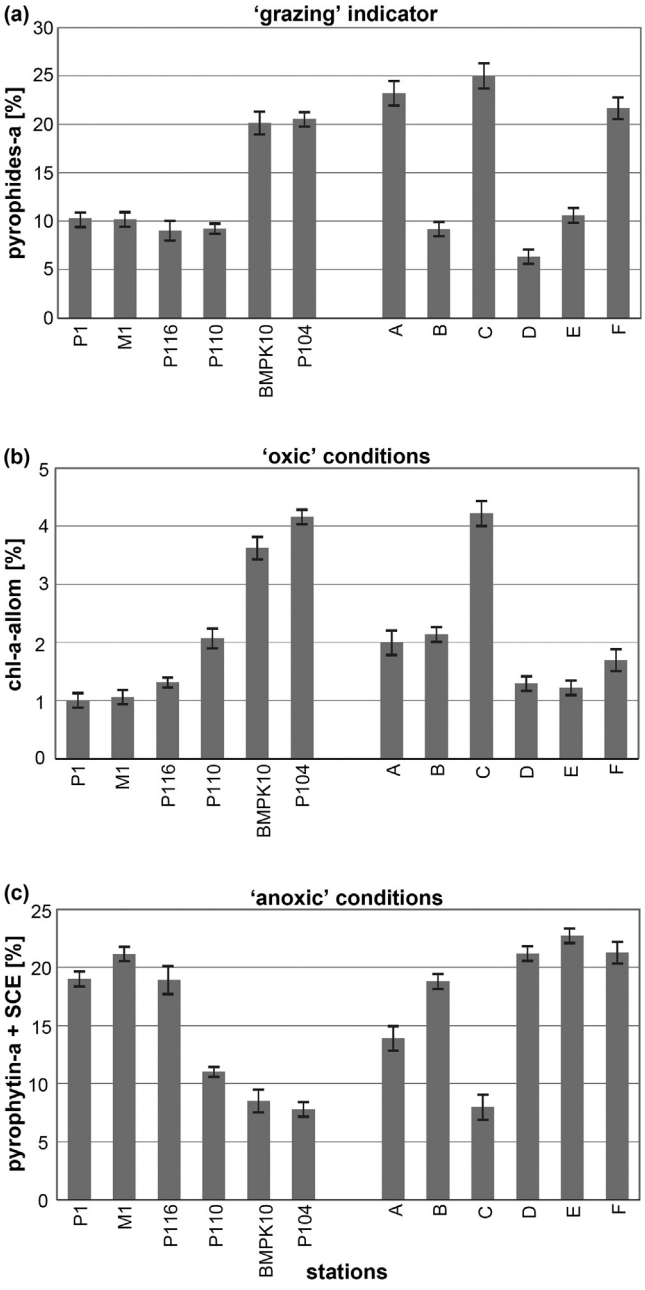

Figure 4 Average percentage of particular chlorophyll-*a* derivatives in the sum of chloropigments-a: (a) pyropheophorbides-a ('grazing' indicator); (b) chlorophyll-*a*-allomers ('oxic' indicator); (c) sum of pyropheophytin-a and steryl chlorin esters ('anoxic' indicator); $n = 2$.

The C N^{-1} ratios encountered in the cores from the Norwegian fjords ranged from ~9 to ~19. These values were close to those obtained by other authors for the same area (Smittenberg et al., 2005). The highest values were measured for the sediment core collected from station A and are indicative of the terrigenous provenance of the organic matter. The C N^{-1} ratio for the sediment cores from stations B and C ranges from 12.6 to 14.8, indicating that the organic matter is a mixture of terrestrial and marine material. The lowest ratios (from 9 to 12) were for sediments at stations D and E and was closer to the values for freshly deposited marine phytoplankton (Kenney et al., 2010). The $\delta^{13}C$ values measured for

sediment cores collected from the Oslofjord (Stations C, D, E, F) (from −22.3‰ to −20.5‰; Appendix 4) point to the marine provenance of the organic matter. The values for the sediment cores from Drammensfjord (A and B) are lower, from −26.9‰ to −25.0‰, which indicates that the organic matter in those sediments is a mixture of terrestrial and marine materials. The results for sediment cores A and B are similar to the results obtained by other authors (Huguet et al., 2007; Smittenberg et al., 2005), but differ from the conclusion for station A based on the C N^{-1} ratio. The $\delta^{15}N$ values measured for the Norwegian fjord sediments ranged from 1.6‰ to 3.5‰ (Appendix 4), indicating that the organic matter there originated from phytoplankton or terrestrial organisms (Schulz and Zabel, 2006). All the cores display a great variation of $\delta^{15}N$ with depth, demonstrating the varying origin and fate of organic matter, especially in the Norwegian fjord. Generally, in our work $\delta^{15}N$ values are smaller in the fjord sediments, especially in the Drammensfjord, than in the Gulf of Gdańsk sediments; this can be explained by the different main sources of organic matter for these two water areas, maybe because of the higher input of sewage (Cravotta, 1997) or undecomposed macrophyta (Bucholc et al., 2014; Kenney et al., 2010) which characterize the higher $\delta^{15}N$, in the Gulf of Gdańsk.

Having the above in mind, the chlorophyll-b and chlorophylls-c to sum of chloropigments-a ratios (Chl-b/ΣChlns-a; Chls-c/ΣChlns-a) were validated as markers of riverine and marine provenance of organic matter, respectively. These ratios depend on the initial concentrations of the parent (Chl-b and Chls-c) pigments in the matter undergoing sedimentation and their stability. Even though chlorophyll-*b* and -*c* are less stable than chlorophyll-*a* (Leavitt and Hodgson, 2001), these markers can enrich our knowledge about the origin of organic matter. Previous studies of southern Baltic Sea sediments have shown that the ratios of chlorophylls-c and -b to chlorophyll-a depends on the proportions of diatoms and green algae in the total Baltic phytoplankton. Chlorophyll-c/chlorophyll-a ratios were higher in samples from marine areas (Kowalewska et al., 1996). The authors suggested that the above ratios in the sediment can be used as an indicator for fresh and marine organic matter in the adjacent waters.

The results of this work indicate that the Chl-b/ΣChlns-a ratio was higher in the Gdańsk Deep (stations P1–P116) and Drammensfjord (stations A and B) than in the other sediments studied (Fig. 5a). Both areas are strongly influenced by riverine water. The Gdańsk Deep is a sink for organic matter carried by the River Wisła into the Gulf of Gdańsk (Jankowski

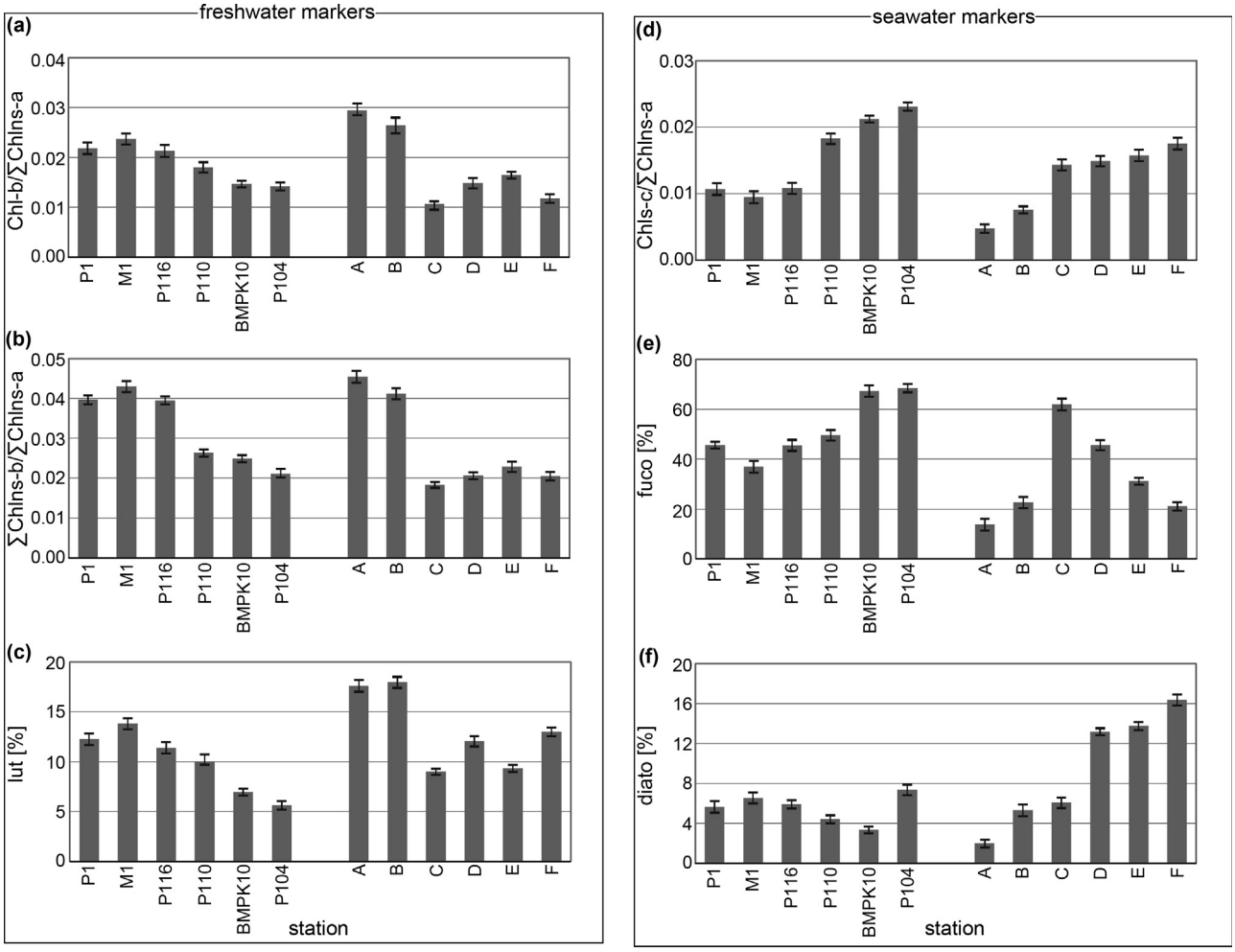

Figure 5 Pigment ratios: (a) chlorophyll-b to chloropigments-a ratio (Chl-b/ΣChlns-a); (b) sum of chloropigments-b to chloropigments-a ratio (ΣChlns-b/ΣChlns-a); (c) percentage of lutein in the sum of carotenoids (%lut); (d) chlorophylls-c to chloropigments-a ratio (Chls-c/ΣChlns-a); (e) percentage of fucoxanthin in the sum of carotenoids (%fuco); (f) percentage of diatoxanthin in the sum of carotenoids (%diato).

and Staśkiewicz, 1994), while Drammensfjord accumulates in sediments freshwater organic matter from the River Drammen (Fig. 1). The highest chl-b/ΣChlns-a ratio was recorded in sediments at station A (Drammensfjord), located close to the mouth of the river, where blooms of green algae *Botryococcus brauni* (Kützing) were observed (Smittenberg et al., 2005). The high correlation between the percentage of lutein in the sum of carotenoids (%lut) and chl-b/ΣChlns-a ($r = 0.7$ and 0.87, $p < 0.05$) for the Gulf of Gdańsk and the Norwegian fjords, respectively, showed that even though lutein is more stable than chlorophyll-b and is recognized as a marker of green algae (Leavitt and Hodgson, 2001), the Chl-b/ΣChlns-a ratio is also a good marker of green algal biomass, which is more abundant in freshwater environments than that of diatoms and dinoflagellates (Bellinger and Sigee, 2010). In sediment samples with a large proportion of chlorophyll-b derivatives, such as the Gulf of Gdańsk (Fig. 5b and c), the higher correlation between %lut and the ΣChlns-b/ΣChlns-a (the sum of chlorophyll-b and its derivatives to the sum of chloropigments-a) ratio ($r = 0.98$, $p < 0.05$) suggests that it is an even better marker than chl-b/ΣChlns-a.

The highest Chls-c/ΣChlns-a ratio was recorded at stations BMPK10 and P104 in the Gulf of Gdańsk and in the Oslofjord samples (stations C–F) (Fig. 5d). There is a high correlation between Chls-c/ΣChlns-a and the percentage of fucoxanthin (the pigment occurring mainly in diatoms (Jeffrey and Vesk, 1997)) in the sum of carotenoids (%fuco) for the Gulf of Gdańsk sediments ($r = 0.92$, $p < 0.05$) and a high correlation with the percentage of diatoxanthin (%diato) for the Oslofjord ($r = 0.87$, $p < 0.05$) (Fig. 5e and f). This suggests that the diatoms are the main source of chlorophylls-*c* in the Gulf of Gdańsk sediments, while in the Oslofjord, besides diatoms, also other marine species containing diatoxanthin such as dinoflagellates. The exception there was station C (Vestfjord) with the high percentage of fucoxanthin (~60%, Fig. 5e). Both phytoplankton groups (diatoms and dinoflagellates) contain not only chlorophyll-a but also chlorophylls-c (Jeffrey and Vesk, 1997). These groups of phytoplankton, though present in both sea- and freshwater, occur in the greatest proportions in waters of seas and oceans, especially in the temperate zones (Sverdrup and Armbrust, 2008). The Chls-c/ΣChlns-a ratio in sediments, proposed in this paper, could be a marker of seawater influences.

Principal Component Analysis (PCA) was applied to validate these results. The proxies for the 0–1 cm sediment layer, both that proposed in this work (ΣChlns-b/ΣChlns-a; Chls-c/ΣChlns-a) and the traditional one (C N^{-1}; $\delta^{13}C$; $\delta^{15}N$, as additional variables), were considered (Fig. 6a and b). The PCA data matrix model explains over 90% of the total variations with the first two principal components. The first principal component explains ~66% of the variations and is strongly correlated with four of the variables. It increases with increasing of ΣChlns-b/ΣChlns-a ratio and the percentage of lutein in the sum of carotenoids, and with decreasing of Chls-c/ΣChlns-a ratio and the percentage of fucoxanthin. The second principal component (~27% of the total variance) increases with increasing of percentage of diatoxanthin in the sum of carotenoids. The greatest input to organic matter in the sediments at the stations in Drammensfjord (stations A, B) is from freshwater organisms, containing chlorophyll-*b* (green algae and higher plants). The greatest input to organic matter in the sediments at the Oslofjord stations is from

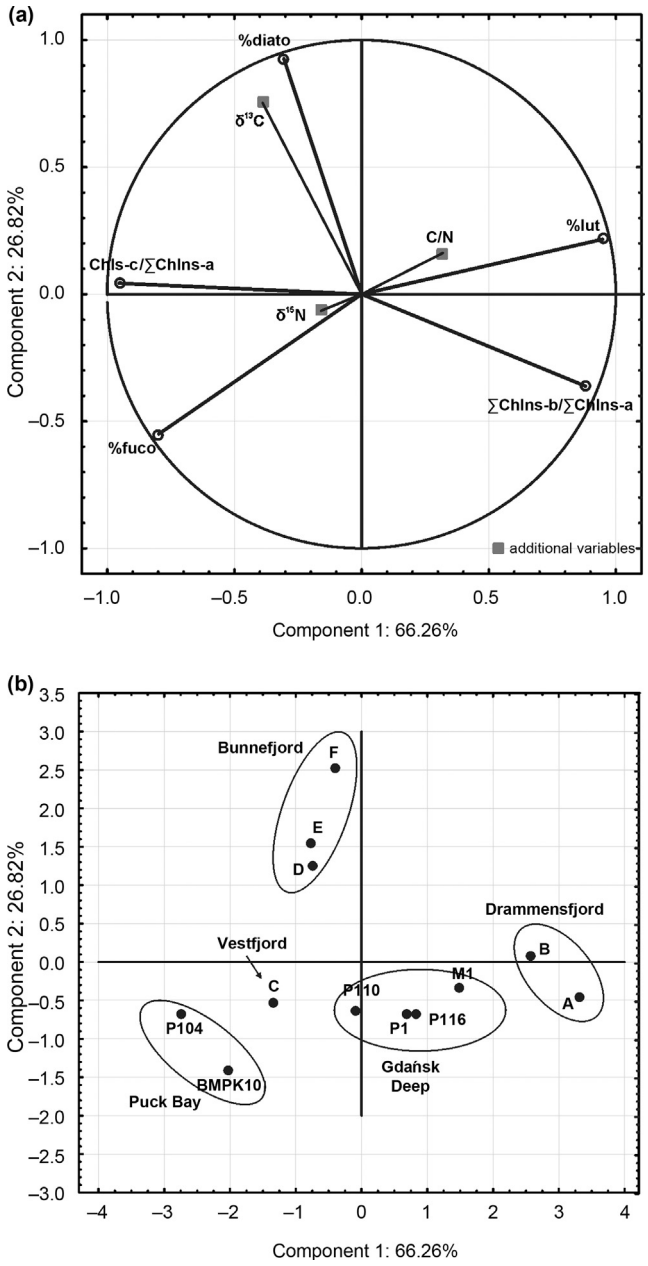

Figure 6 Results of the statistical analysis: scatter plot of (a) principal component loading by individual variables; (b) principal component object scores by sampling sites based on proposed indicators of the source of organic matter (ΣChlns-b/ΣChlns-a; Chls-c/ΣChlns-a), percentages of particular carotenoids in the sum of carotenoids (%fuco, %lut, %diato) and traditional proxies as additional variables (C N^{-1}; $\delta^{13}C$; $\delta^{15}N$) for the 0–1 cm sediment layer.

marine organisms containing chlorophylls-c, such as diatoms and dinoflagellates (Fig. 6a and b). The $\delta^{13}C$ values measured for sediment cores collected from the Oslofjord are in agreement with these pigment markers. The results of this work have confirmed the previous observations for the Gulf of Gdańsk (Kowalewska et al., 1996). Chls-c/ΣChlns-a may thus be a simple marker of seawater organic matter input and ΣChlns-b/ΣChlns-a a marker of freshwater organic matter

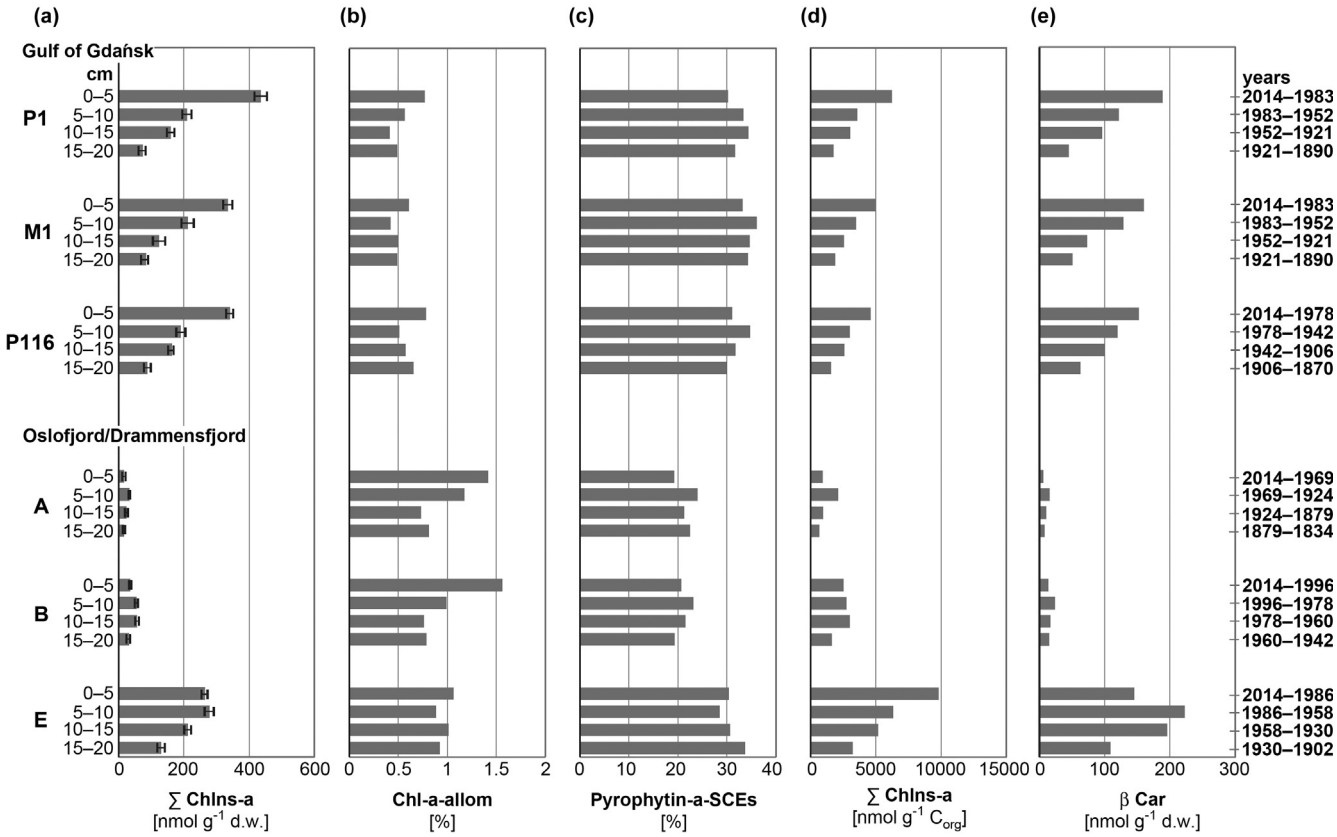

Figure 7 Pigment content profiles for selected non-mixed sediments: (a) ΣChlns-a [nmol g^{-1} d.w.]; (b) the percentage of chlorophyll-a-allomers in the sum of chloropigments-a ('oxic' indicator); (c) percentage of the sum of pyropheophytin-a and steryl chlorin esters in the sum of chloropigments-a ('anoxic' indicator); (d) ΣChlns-a [nmol g^{-1} C_{org}]; (e) β-carotene [nmol g^{-1} d.w.].

input, complementing the traditional proxies, which are often ambiguous and contradictory, especially $\delta^{15}N$ (Kenney et al., 2010; Schulz and Zabel, 2006; Torres et al., 2012).

4.3. Eutrophication trends

Six stations were selected for tracking eutrophication trends in the two basins. These were stations with unmixed sediments according to the ^{210}Pb analysis (Table 1): three in the Gdańsk Deep (P1, M1, P116), two in the Drammensfjord (A and B) and one in the Oslofjord (E). Looking at the sum of chloropigments-a profiles for these stations (Fig. 7a), one can see that there is a temporal increase in the chloropigments-a content in the sediments at all the Gdańsk Deep stations; this is particularly obvious in the surface sediments, which were formed in the last 30—40 years. The pigment contents were averaged for 0—5 cm basing on weighted mean for 0—1 cm and 1—5 cm layers. This is in agreement with other observations that eutrophication of the southern Baltic increased in the 1970s (Fleming-Lehtinen et al., 2015). In the Oslofjord/Drammensfjord maximum of chloropigments-a content corresponds to deeper layers (A, 5—10 cm; B, 10—15 cm; E, 5—10 cm), formed when the nutrient load was at its highest in the 1970s (Hess et al., 2014). This indicates a decrease in eutrophication in the past 30—40 years. Moreover, one can see that allo-chlorophyll-*a* derivatives forming in oxic conditions (Fig. 7b) take minimum values in the sediments accumulated during the 1970s, and in general are lower in the Gulf of Gdańsk than in the Oslofjord/Drammensfjord. The derivatives preserved in old sediments — 'anoxic' indicators (pyropheophytin-a and steryl chlorins) — have opposite profiles to allo-chlorophylls and in general are more abundant in sediments of the Gulf of Gdańsk than in the Oslofjord/Drammensfjord, although the chloropigments-a at station E are the richest in these compounds (Fig. 7c), indicating a high level of anoxia. The sum of chloropigments-a normalized to the organic carbon content (Fig. 7d) demonstrates similar trends to those of chloropigments-a calculated to dried weight of sediments, with the exception of station E, where there is an increase in the surface 0—5 cm layer in comparison with the next 5—10 cm. This difference is obvious, as normalization of the chloropigments-a content mirrors a stage in the decomposition of pigments, not their content in the sediments. The β-carotene profiles are similar to those for chloropigments-a (Fig. 7e), which indicates that chloropigments-a, despite being less stable than β-carotene (Leavitt and Hodgson, 2001), are good markers for tracking eutrophication trends.

5. Conclusions

Comparison of pigments in the sediments in the two basins shows that eutrophication in the Gulf of Gdańsk has increased over the last 30—40 years but has decreased in the Oslofjord/Drammensfjord during the same period. The results presented in this paper prove that the sum of chloropigments-a in

sediments, calculated per dry weight of sediment, is a valuable measure of eutrophication in an area. The advantage of chloropigments-a over the other proxies (e.g. β-carotene) is that the percentage of particular chlorophyll-a derivatives (pyropheophorbides-a, chlorophyll-a-allomers, pyropheophytin-a and steryl chlorin esters) in the sum of chloropigments-a provide information on syn- and post-depositional environmental conditions. They are universal markers of grazing, oxic and anoxic conditions in a basin. The sum of chloropigments-b to chloropigments-a ratio (ΣChlns-b/ΣChlns-a) is a marker of freshwater organic matter input and the chlorophylls-c to chloropigments-a ratio (Chls-c/ΣChlns-a) is a marker of seawater organic matter input. When applying these markers for tracking eutrophication trends it is very important to select a suitable monitoring site, i.e. where the sediments are unmixed (laminated) and hypoxic/anoxic.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.oceano.2016.08.003.

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