DOC and POC in the water column of the southern Baltic. Part I. Evaluation of factors influencing sources, distribution and concentration dynamics of organic matter*

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Abstract

Organic substances are important components of the marine environment as they determine the properties of seawater and the key biogeochemical processes taking place in it. Organic carbon (OC) is a measure of organic matter. For practical purposes, OC is divided into dissolved organic carbon (DOC) and particulate organic carbon (POC). Both DOC and POC play a major role in the carbon cycle, especially in shelf seas like the Baltic, where their concentrations are substantial. In a three-year study (2009–2011) seawater samples for DOC and POC measurements were collected from stations located in the Gdańsk Deep, the Gotland Deep and the Bornholm Deep. The accuracy and precision of analysis were satisfactory; the

recovery was better than 95%, and the relative standard deviation was 4% ($n = 5$). Concentrations of chlorophyll a, phaeopigment a, salinity, pH and temperature were also measured in the same samples. These parameters were selected as proxies of processes contributing to DOC and POC abundance.

The aim of the study was to address questions regarding the vertical, horizontal and seasonal dynamics of both DOC and POC in the Baltic Sea and the factors influencing carbon concentrations. In general, the highest concentrations of both DOC and POC were recorded in the surface water layer (DOC ~ 4.7 mg dm^{-3}, POC ~ 0.6 mg dm^{-3}) as a consequence of intensive phytoplankton activity, and in the halocline layer (DOC ~ 5.1 mg dm^{-3}, POC ~ 0.4 mg dm^{-3}). The lowest DOC and POC concentrations were measured in the sub-halocline water layer, where the values did not exceed 3.5 mg dm^{-3} (DOC) and 0.1 mg dm^{-3} (POC). Seasonally, the highest DOC and POC concentrations were measured during the growing season: surface DOC ~ 5.0 mg dm^{-3}; sub-halocline DOC ~ 4.1 mg dm^{-3} and surface POC ~ 0.9 mg dm^{-3}, sub-halocline POC ~ 0.2 mg dm^{-3}. The ANOVA Kruskal-Wallis test results indicate statistically significant differences among the three study sites regarding average concentrations, and concentrations in particular water layers and seasons. It shows that concentrations of DOC and POC differ in sub-basins of the Baltic Sea. The differences were attributed to the varying distances from river mouths to study sites or the different starting times and/or durations of the spring algal blooms. Statistically significant dependences were found between both DOC and POC concentrations and Chl a (phytoplankton biomass), pH (phytoplankton photosynthetic rate), pheo (zooplankton sloppy feeding), salinity (river run-off and North Sea water inflows) and water temperature (season). This was taken as proof that these factors influence DOC and POC in the study areas.

1. Introduction

The presence in seawater of dissolved and suspended organic substances, treated collectively as organic matter, means that this medium is not just a solution of inorganic salts. Organic matter plays a key role in a variety of natural (physical and biological) processes occurring in the marine environment, especially in shelf seas like the Baltic, where its concentration is substantial (Seager & Slabaugh 2004, Kuliński & Pempkowiak 2008). These processes include oxygen depletion, as well as complex formation with both organic and inorganic compounds, which facilitates the downward transport of chemical substances (C, N, P, heavy metals, organic pollutants) in the water column. Organic matter influences the chemical and physical properties of seawater, including the light field and alkalinity (Dera 1992, Hedges 2002, Kuliński et al. 2014).

Aquatic organic matter is commonly divided into particulate organic matter – POM and dissolved organic matter – DOM. Both fractions are important components of the carbon cycle. POM in the marine environment is composed of phytoplankton, zooplankton, bacteria and dead organic material (detritus), while dissolved organic matter comprises molecules of

both high and low molecular weight. Both POM and DOM originate from internal and external sources (river run-off, atmosphere, sediments) (Emerson & Hedges 2008). Organic matter is most often measured as organic carbon (OC), which makes up some 45% of organic matter (Chester 2003). In the oceans, the OC concentration is < 1.5 mg dm^{-3}, but in coastal areas it amounts to as much as 8 mg dm^{-3} (Hansell 2002, Gardner et al. 2006). Like organic matter, organic carbon is for practical purposes divided into two principal fractions: particulate organic carbon (POC) and dissolved organic carbon (DOC). Both fractions can be separated by passing seawater through, for example, 0.4 μm glass-fibre filters.

The POC and DOC concentrations in the Baltic Sea have been a subject of interest for many years (Jurkovskis et al. 1976, Pempkowiak 1983, Pempkowiak et al. 1984, Emelyanov 1995, Ferrari et al. 1996, Grzybowski 2003, Grzybowski & Pempkowiak 2003, Burska 2005, Pempkowiak et al. 2006, Kuliński & Pempkowiak 2008, Dzierzbicka-Głowacka et al. 2010, 2011, Szymczycha et al. 2014).

Concentrations of DOC and POC in Baltic seawater have been reported to range from 3.2 to 7.7 mgC dm^{-3} (Jurkovskis et al. 1976, Grzybowski & Pempkowiak 2003, Kuliński & Pempkowiak 2011) and from 0.1 to 1.4 mgC dm^{-3} (Burska 2005, Kuliński & Pempkowiak 2011). POC and/or DOC concentrations fluctuate seasonally (Burska 2005) and change vertically (Kuliński & Pempkowiak 2008). Mathematical modelling indicates that POC and DOC concentrations depend on light, water temperature and nutrient availability (Dzierzbicka-Głowacka et al. 2010, Almroth-Rosell et al. 2011, Segar 2012). Organic substances are exchanged horizontally through the Danish Straits with the North Sea (Thomas et al. 2005, Kuliński & Pempkowiak 2011). The OC concentration depends on distance from the land – coastal and estuarine areas are more abundant in organic matter than the open sea (Witek 1997, HELCOM 2005, 2006). Plankton activity may contribute to large seasonal fluctuations in both POC and DOC (Dzierzbicka-Głowacka et al. 2011). Although numerous studies have been carried out regarding the organic carbon concentration and its dynamics in Baltic seawater, most factors affecting its spatial and temporal distribution still require quantification. For example, nothing is known about the differences in carbon concentrations in the different sub-basins of the Baltic Sea. As changes in both particulate and dissolved organic matter concentration are to be expected in the near future (Dzierzbicka-Głowacka et al. 2011), the acquisition of basic knowledge regarding this important component of seawater is a matter of primary importance.

POC and DOC concentrations in Baltic seawater and the factors impacting on both in seawater were the subject of this study, carried out in

the southern Baltic in the period 2009–2011. The following questions were addressed: 1) What is the dynamics of the DOC and POC components in the Baltic Sea? 2) Do the dynamics and concentrations of both components differ in the sub-basins of the Baltic Sea? 3) What factors influence POC and DOC concentrations? The answers obtained are given in this paper.

2. Material and methods

2.1. Study area

One of the largest brackish seas in the world, the Baltic Sea lies between latitude 54°N and 66°N and between longitude 10°E and 30°E. This inland shelf sea is flanked by the Scandinavian Peninsula in the north and the east, continental Europe in the south and the Danish islands in the west. It is connected with the North Sea by the shallow Danish Straits, and the Kattegat and Skagerrak. The salinity of the surface sea water layer in the Baltic Proper is ca 7.1. This is a consequence of the large freshwater runoff from the catchment area and the limited exchange of water with the North Sea. Other factors contributing to the low salinity are the abundant precipitation and the shallowness of the sea (average depth = 53.2 m). The considerable inflow of nutrients from rivers and the atmosphere makes the Baltic one of the most productive marine ecosystems in the world. Occasional inflows of highly saline water masses from the North Sea lead to water stratification – the halocline lies at a depth of 70 m. The inflows also contribute to a north-eastward decrease in salinity (Hakanson 1991, Hagström 2001, Thomas et al. 2003, HELCOM 2005, 2006, 2007, Kuliński & Pempkowiak 2008, Uścinowicz 2011).

Baltic Sea water is vertically stratified. The upper layer has a constant salinity of ca 7.1 and the sub-halocline layer a salinity of 15 in the western Bornholm Deep and 10 in the central Gotland Deep. The salinity of the sub-halocline water in the Gdańsk Deep is ca 12. Both water layers are separated at 60–80 m depth by a halocline, which is defined as a water layer in which there is a distinct salinity (and density) gradient. Anoxic conditions, often reported under the halocline, are periodically improved by inflows of the well-oxygenated North Sea water masses (Voipio 1981, Kouts et al. 1993, Björck 1995, HELCOM 2007, The BACC Author Team 2008).

2.2. The geographical location of the sampling sites

The research work described in this report is focused on three study sites located in the southern Baltic Sea (Figure 1)
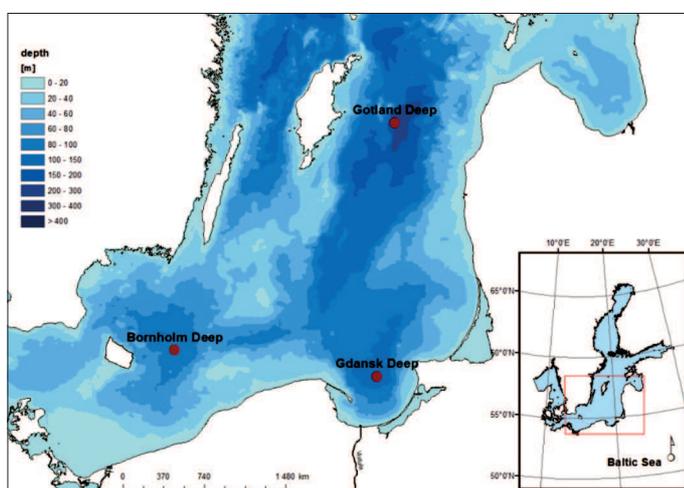
- Gdańsk Deep (54°50′N; 19°17′E),
- Gotland Deep (57°18′N; 19°53′E),

• Bornholm Deep (55°10′N; 15°53′E).

These regions were selected mainly because the water column in each is stratified: a stable halocline separates the water column into an upper, well-oxygenated layer and a sub-halocline, oxygen-deficient water layer.

Moreover, the different hydrological settings of these areas – different distances from estuaries and the North Sea, differences in depths, and varying ranges of water temperature – could influence the POC and DOC concentrations there.

The water column at each site was sampled several times in the period 2009–2011. Weather permitting, water samples were collected from several depths selected according to the salinity profile at the time of sampling.

Figure 1. Location of the sampling stations

Table 1. Sampling coverage of the study areas

Month	Sampling frequency in the study areas (2009–2011)		
	Gdańsk Deep	Gotland Deep	Bornholm Deep
March	2	2	–
April	3	2	1
May	2	1	1
June	2	–	1
July	1	1	1
August	1	1	–
September	1	–	–
October	1	1	1

The spatial and temporal coverage of the samplings is presented in Table 1. There were no cruises in January, February, November and December, so the average DOC and POC concentrations in the non-growing season given in this study may overestimate the actual ones.

2.3. Analytical methods

The seawater samples were collected in Niskin bottles during cruises of r/v 'Oceania', r/v 'Aranda' and r/v 'Alkor' between March 2009 and September 2011. The sampling schedule is presented in Table 1.

The measurements began with temperature and salinity using CTD Sea-Bird, 911-Plus. Throughout the manuscript salinity is given in Practical Salinity Units [PSU]. The depths of sampled layers were selected on the basis of temperature and salinity profiles. The pH of all the water samples was first measured using a WTW Multi 3400i pH meter. Concentrations of the following water constituents were also analysed: POC and DOC, chlorophyll a and phaeopigment a.

2.3.1. POC and DOC measurements

Seawater (1500 ml) was collected and passed through pre-combusted and pre-weighed MN GF 5 (0.4 μm pore size) glass fibre filters. The filters with the suspended matter were preserved at $-20°$C until POC analysis on shore. In the laboratory the filters for POC analysis were dried at $60°$C for 24 h and weighed (0.001 mg accuracy). The filters were then homogenised in a ball mill. Part of each sample was weighed into a tin vessel, acidified with 0.1 ml 2M HCl to remove carbonates, and dried at $90°$C for 24 h. The samples prepared in this way were analysed in a CHN elemental analyser (Flash EA 1112 Series) coupled with an IRMS Delta V Advantage/Conflo IV mass spectrometer using oxidation at $1020°$C, followed by reduction over copper in a furnace at $680°$C. Quality control consisted of regular assessments of accuracy, precision and the analysis of blanks. Accuracy checks were carried out with the following reference materials: acetanilide and Lake Sediment Reference Material LKSD-1 and LKSD-4 (recovery $= 97\%$, $n = 5$). The precision of POC measurements, given as the relative standard deviation (RSD), was based on the analysis of selected samples and the reference materials; RSD never exceeded 2% ($n = 5$).

A fraction of the filtered seawater (30 ml) for DOC measurements was immediately placed in a 40 ml glass bottle and acidified with 150 μl conc. HCl to remove carbonates. The samples prepared in this way were stored in a refrigerator at $5°$C until DOC analysis in a HyPerTOC analyser (Thermo Electron Corp.) using UV/persulphate oxidation and non-dispersive infrared detection of the evolving CO_2. Each sample was analysed

in triplicate. DOC concentrations were calculated from a calibration curve obtained by analysing potassium hydrogen phthalate dissolved in North Atlantic water (Sargasso Sea, 3000 m depth, Hansell Laboratory, University of Miami) diluted five times with Milli Q water as matrix. All DOC results were corrected for blanks (details of the analytical procedure are given in Kuliński & Pempkowiak (2008)). Quality control consisted of regular analysis of blanks, as well as accuracy and precision checks, assured by reference material: North Atlantic water obtained from the Hansell Laboratory (recovery $= 95\%$, precision characterised by RSD – 4%, $n = 5$).

2.3.2. Chlorophyll *a* and phaeopigment *a* measurements

Some 500 ml of seawater for chlorophyll *a* and phaeopigment *a* measurements were passed through MN GF 5 (0.4 μm pore size) glass fibre filters (immediately after collection) and the filters deep frozen at $-80°C$ until analysis. In the laboratory, before the spectrophotometric analysis, samples were extracted using 90% acetone according to the procedure developed by Parsons (1966). Chlorophyll *a* and phaeopigment *a* concentrations were calculated using the Lorentz (1967) formulas.

3. Results

3.1. DOC and POC concentrations in the study areas (geographical and vertical variabilities)
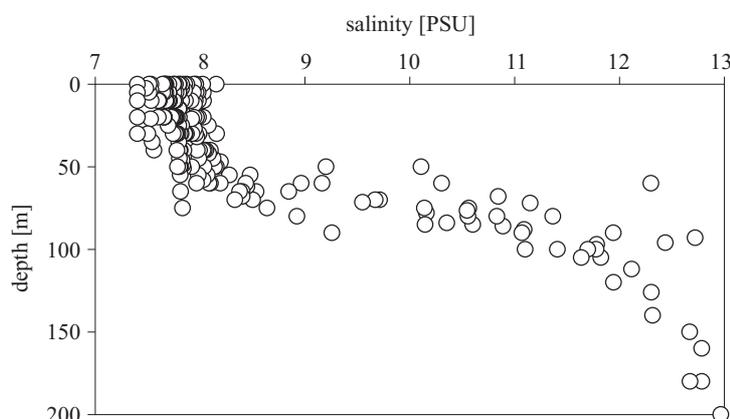
The DOC [mg dm^{-3}] and POC [mg dm^{-3}] concentrations in four vertical layers are summarised in Table 2.

Four vertical layers were selected based on the downward salinity changes in the seawater column (Figure 2): surface layer (low salinity), sub-surface layer (low salinity), halocline water layer (salinity gradient) and sub-halocline water layer (the highest salinity).

The highest concentrations of both POC and DOC were measured in the surface layer and the halocline layer (Table 2). The former layer contains well-mixed and well-oxygenated water, in which the intensity of phytoplankton activity is at its highest (Stedmon et al. 2007). The halocline layer is characterised by a salinity and density gradient, where the increasing density slows down the sedimentation rate of organic-rich suspended matter. The lowest concentrations of organic carbon were measured in the sub-halocline layer, below 80 m, where the former North Sea water persists. The North Sea water has much lower DOC and POC concentrations than Baltic Sea water (Kuliński & Pempkowiak 2011).

Table 2. Average POC and DOC concentrations in the vertical water layers of the Gdańsk Deep, Gotland Deep and Bornholm Deep

Seawater layer	Study area								
	Gdańsk Deep			Gotland Deep			Bornholm Deep		
	No. of samples	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]	No. of samples	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]	No. of samples	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]
surface layer (0–5 m)	31	**4.92 ± 1.42**	**0.73 ± 0.4**	16	**4.33 ± 0.89**	**0.51 ± 0.38**	16	**4.84 ± 0.89**	**0.59 ± 0.34**
'middle' layer (6–59 m)	67	**4.85 ± 0.61**	**0.32 ± 0.15**	33	**4.28 ± 0.71**	**0.24 ± 0.10**	34	**4.73 ± 0.85**	**0.30 ± 0.17**
halocline (60–80 m)	21	**5.15 ± 1.00**	**0.51 ± 0.31**	13	**5.05 ± 1**	**0.27 ± 0.11**	–	no measurements	no measurements
subhalocline (> 80 m)	15	**3.91 ± 0.82**	**0.21 ± 0.09**	14	**3.92 ± 0.49**	**0.14 ± 0.07**	–	no measurements	no measurements
average concentrations of all samples	133	**4.64 ± 1.16**	**0.37 ± 0.33**	76	**4.2 ± 0.98**	**0.25 ± 0.23**	50	**4.63 ± 0.82**	**0.35 ± 0.24**
range of concentrations in all samples	133	**2.73–8.24**	**0.05–1.40**	76	**2.58–7.25**	**0.05–1.40**	50	**2.38–5.89**	**0.07–1.31**

Figure 2. Relationship between salinity and depth (for all samples)

The concentrations of both DOC and POC in the successive layers at the study sites varied in broad, overlapping ranges, whereas the average concentrations were most often different. To establish the statistical significance of the differences, ANOVA (the Kruskal-Wallis test) was performed. It was assumed that if $p < 0.05$ ($p < 0.05$) the differences were statistically significant. The results show that the average concentrations of both DOC ($p = 0.002$) and POC ($p = 0.007$) in the three study areas differ in a statistically significant manner (Table 3). Thus, it may be concluded that statistically significant geographical differences of both DOC and POC concentrations occur in the vertical profile.

Strangely enough, there are no statistically significant differences of either DOC or POC concentrations in the surface water layers of the investigated areas (Table 3; DOC: $p = 0.078$, POC: $p = 0.169$). This may be an artifact caused by the timing of sampling and/or of primary productivity, a recognised source of DOC and POC. The average concentration recorded in the Gotland Deep (Table 2) is clearly lower than in the Gdańsk and Bornholm Deeps. This can be attributed to the different geographical positions of the deeps: the Gotland Deep lies far away from the estuaries of big rivers. Thus, phytoplankton activity, supported by nutrients discharged from land, is less intensive there. Phytoplankton activity is thought to be an important source of organic carbon to seawater (Kuliński & Pempkowiak 2008). The results from the sub-surface layer show that there is a statistically significant difference ($p = 0.001$) only in DOC concentrations, in contrast to the results from the halocline ($p = 0.001$) and the deep water ($p = 0.001$) layers, where only the difference in POC concentrations is statistically significant, probably because of the differing density gradient (halocline) or the reduced sedimentation rate of organic

Table 3. The ANOVA (Kruskal-Wallis test) results (p-values) performed on data sets comprising POC and DOC concentrations from the Gdańsk Deep, Gotland Deep and Bornholm Deep

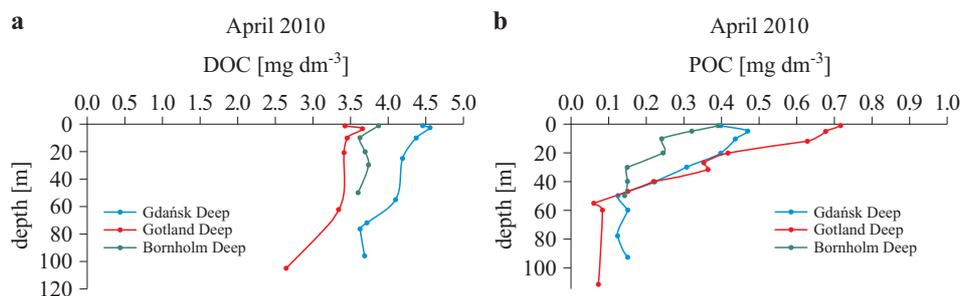| Seawater layer/season	p-value; statistically significant values are underlined (between the Gdańsk, Gotland and Bornholm Deeps)	
	DOC	POC
all samples	**0.002**	**0.007**
surface layer (0–5 m)	0.078	0.169
'middle' layer (6–59 m)	**0.001**	0.500
halocline (60–80 m)	0.680	**0.001**
subhalocline (> 80 m)	0.590	**0.001**
growing season[*]	**0.003**	**0.020**
non-growing season[*]	0.285	0.403

[*]See Table 4 for characteristics of DOC and POC concentrations in the growing and non-growing seasons.

particles (deep-water layer). There are also pronounced, statistically significant differences between the three study areas in the growing season (April–October) (Table 3; DOC: $p = 0.003$, POC: $p = 0.020$), unlike the results in the non-growing season (DOC: $p = 0.285$, POC: $p = 0.403$).

It follows from the statistical evaluation that there are both horizontal (geographical) and vertical (in the water column) differences in DOC and POC concentrations in the Baltic Proper. It must be borne in mind that the average carbon levels at a given location and in a given layer are based on a number of results collected in different years and seasons. Therefore, dependences of carbon concentrations on depth in the study areas better represent the actual distribution of organic matter. Relevant examples are presented in Figure 3.

3.2. Vertical variability of DOC and POC concentrations

The DOC and POC profiles show a steady decrease in concentrations from the surface to the sub-halocline water layer. The highest levels of both DOC and POC in the surface layer are caused by intensive primary production. The POC concentration peaks at 60 m depth (Gdańsk Deep

Figure 3. Vertical profiles of a) DOC [mg dm^{-3}] and b) POC [mg dm^{-3}] concentrations in the Gdańsk Deep, Gotland Deep and Bornholm Deep in April 2010

and Gotland Deep, Figure 3b) are caused by the density gradient in the halocline; organic-rich suspended matter falls at a slower rate in this layer, hence the higher POC concentrations there. Just above the bottom the DOC concentration increases slightly (Gdańsk Deep, Figure 3a). This may be caused by decomposition of POC residing on the sediment surface (Pempkowiak et al. 1984, Leipe et al. 2011), and/or by the diffusion of DOC from interstitial water (Kuliński & Pempkowiak 2011). The highest concentration of DOC recorded in the vertical profile of the Gdańsk Deep, may be due to the proximity of the Vistula river mouth. The highest POC concentration in the surface layer over the Gotland Deep can be attributed to the very recent phytoplankton bloom. The result is substantiated by the DOC concentrations that are still rather low there and the steep downward gradient of POC concentrations.

3.3. Seasonal variability of DOC and POC concentrations

The seasonal average (growing and non-growing seasons) DOC and POC concentrations are presented in Table 4.
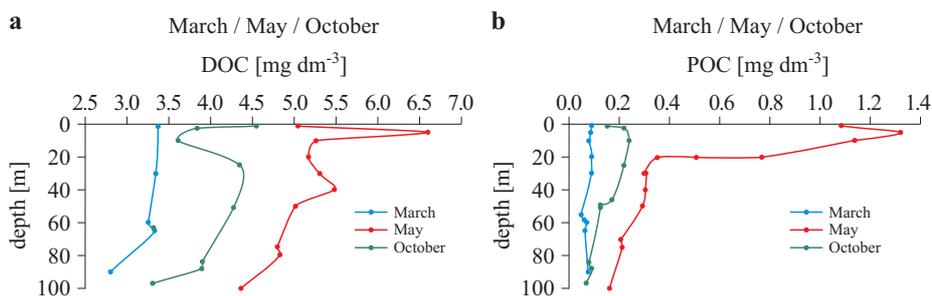
Concentrations of both DOC and POC in the growing season are much higher than in the non-growing season at each of the sampling stations. This can be attributed to intensive primary production caused by high phytoplankton activity related to high concentrations of nutrients from different sources (river run-off and atmospheric deposition), elevated temperature and abundant solar radiation (Stedmon et al. 2007, Segar 2012, Maric et al. 2013) This is in agreement with the results of earlier studies indicating phytoplankton as the most important source of organic carbon in seawater (Hagström et al. 2001, Dzierzbicka-Głowacka et al. 2010). Other factors may also influence DOC and POC concentrations. These include the sloppy feeding of zooplankton or river runoff (Kuliński & Pempkowiak 2008).

Table 4. Average POC and DOC concentrations in the growing and non-growing seasons recorded in the Gdańsk Deep, the Gotland Deep and the Bornholm Deep in 2009–2011
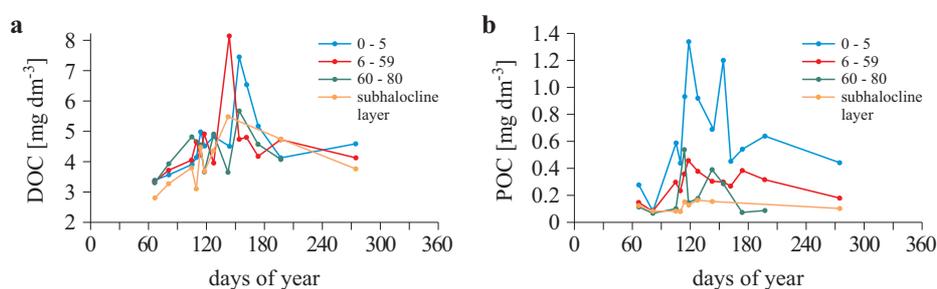
Season		Study area								
		Gdańsk Deep (133 samples)			Gotland Deep (76 samples)			Bornholm Deep (50 samples)		
		No. of samples	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]	No. of samples	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]	No. of samples	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]
growing season	surface layer	19	5.22 ± 0.81	1.15 ± 0.44	10	4.64 ± 0.79	0.77 ± 0.39	9	5.14 ± 0.93	0.91 ± 0.49
	sub-halocline	9	4.13 ± 0.95	0.26 ± 0.11	8	4.05 ± 0.99	0.18 ± 0.09	–	–	–
non-growing season	surface layer	12	4.62 ± 0.54	0.31 ± 0.17	6	4.02 ± 0.39	0.25 ± 0.14	7	4.54 ± 0.71	0.27 ± 0.19
	sub-halocline	6	3.69 ± 0.49	0.16 ± 0.07	6	3.79 ± 0.33	0.10 ± 0.06	–	–	–

The lowest average concentration of DOC and POC noted in the Gotland Deep in the growing season (compared to the Gdańsk Deep and the Bornholm Deep) may be due to the already mentioned different geographical position (northernmost) leading to a later start of the growing season. The differences between the study areas proved to be statistically significant in the growing period (Table 3; DOC: $p = 0.003$, POC: $p = 0.02$), in contrast to the non-growing period, when the differences were statistically insignificant (DOC: $p = 0.285 > 0.05$, POC: $p = 0.403 > 0.05$). This substantiates the overall conclusion that a pool of resistant organic substances occurs in the southern Baltic (average values for non- growing season are: surface DOC ~ 4.4 mg dm^{-3}, sub-halocline DOC ~ 3.7 mg dm^{-3}; surface POC ~ 0.3 mg dm^{-3}, sub-halocline POC ~ 0.1 mg dm^{-3}) throughout the year. In the growing season fresh, labile organic matter is supplied to the system. This increases concentrations of organic matter (average values for the growing season are: surface DOC ~ 5.0 mg dm^{-3}; sub-halocline DOC ~ 4.1 mg dm^{-3}; surface POC ~ 0.9 mg dm^{-3}, subsurface POC ~ 0.2 mg dm^{-3}) with labile substances (Table 4). As soon as the supply is terminated, the labile organic matter is mineralised. This leaves the pool of resistant organic matter in the period late November–mid-April. Then the cycle commences again.

The seasonal dynamics of both DOC and POC concentrations (based on Gdańsk Deep results) is quite well developed, as can be seen in Figure 4. DOC and POC profiles (Figure 4) indicate (in the surface layer): residual (DOC: 3.4 mg dm^{-3}; POC: 0.1 mg dm^{-3}) concentrations in March; the highest concentrations (close to 6.5 mg dm^{-3} – DOC; and 1 mg dm^{-3} – POC) in May and again smaller concentrations (DOC: 4.5 mg dm^{-3}; POC: 0.2 mg dm^{-3}) in October. The March vertical DOC and POC profiles show the smallest concentrations and almost no vertical gradient. This can be attributed to the lack of biological activity (the temperature at the time of sampling was in the range 3–5°C). Stable concentrations in the surface water layer can be explained as resulting from intensive vertical mixing, while low concentrations in the sub-halocline layer can be explained by small DOC and POC concentrations in the North Sea water that had entered the Baltic and had formed the dense, sub-halocline water layer (Thomas et al. 2005, Maar 2011). DOC and POC concentrations in May are much larger throughout the water profile, with high concentrations in the surface layer caused by phytoplankton activity and freshwater runoff rich in organic matter. The increase of both DOC and POC concentrations between March and May clearly shows that the fresh dissolved and suspended organic matter, originating from biological activity and river runoff, substantially increase DOC and POC concentrations. The decrease in DOC and POC

Figure 4. Vertical profiles of a) DOC [mg dm^{-3}] and b) POC [mg dm^{-3}] concentrations in the Gdańsk Deep in March, May and October

Figure 5. Variability of a) DOC and b) POC concentrations in the annual cycle in the Gdańsk Deep in 2009–11

concentrations from May to October and from the surface downwards to the bottom are the result of decreased phytoplankton activity – the dominant source of organic carbon in seawater (Hagström et al. 2001). Similar profiles and dependences that lead to the same conclusions were observed in the Gotland Deep and the Bornholm Deep.

Obviously, there are numerous factors that influence the intensity and timing of carbon sources and sinks in the course of a year. Thus, it is difficult to expect seasonal fluctuations of both DOC and POC that begin and terminate precisely at the same time. This variability is illustrated by the data presented in Figure 5. Nevertheless, the strong seasonal dependence of carbon concentrations is evident. Seasonal changes are best developed in the case of POC concentrations in the surface water layer (Figure 5). Few changes are observed in the sub-halocline layer. This can be attributed to the bloom of phytoplankton. Seasonal changes are also clearly evident in the dependence of DOC concentration on time in the course of a year (Figure 5). In the non-growing season, DOC concentrations do not exceed 3.5 mg dm^{-3} while in the growing season they reach as much as 8.2 mg dm^{-3}. This supports the conclusion that here are two pools of dissolved
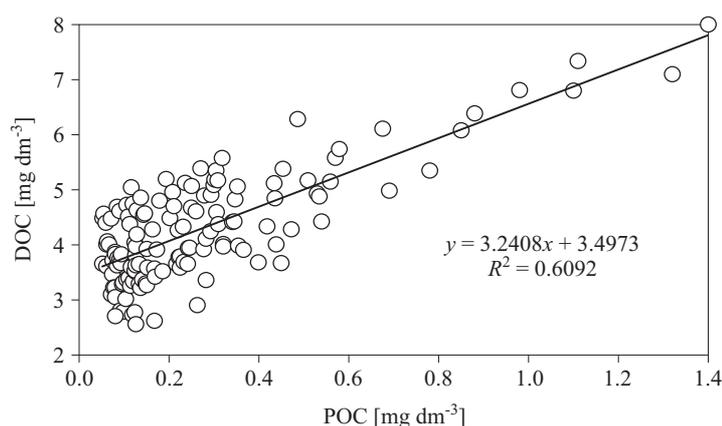
organic substances, labile and resistant to biochemical oxidation. The labile fraction of DOC is supplied to seawater in the period of intensive primary production, whereas the stable form persists in seawater throughout the year.

Fluctuations of DOC and POC in Baltic seawater were reported by Jurkovskis et al. (1976), Pempkowiak et al. (1984), Grzybowski & Pempkowiak (2003), Burska (2005) and Woźniak (2014), while Kuliński & Pempkowiak (2008) suggested the existence of two DOC fractions of varying biochemical stability.

3.4. Factors influencing DOC and POC concentrations

It has been speculated throughout this text that both DOC and POC concentrations are influenced by the activity of plankton. The idea is firmly established in the literature (Thomas & Schneider 1999, Hagström et al. 2001, Stoń et al. 2002, Doney et al. 2003, Thomas et al. 2005, Sarmiento & Gruber 2006, Segar 2012). Also zooplankton can influence organic carbon concentrations in seawater (Dzierzbicka-Głowacka et al. 2011). The abundance of plankton can be approximated by proxies: chlorophyll *a*, phaeopigment *a* (Bianchi et al. 1996, Meyer-Harms & von Bodungen 1997, Wasmund & Uhlig 2003, Collos et al. 2005), while the phytoplankton activity influences the pH of seawater (Edman & Omstedt 2013).

To find answers to questions regarding the factors influencing POC and DOC concentrations, chlorophyll *a* (Chl *a*) and phaeopigment *a* (Feo) concentrations, pH and temperature of seawater were measured simultaneously with DOC and POC. The measured water properties were used as proxies of phytoplankton abundance (Chl *a*), photosynthetic activity

Figure 6. Relationship between POC and DOC concentrations – combined results for the Gdańsk Deep, Gotland Deep and Bornholm Deep
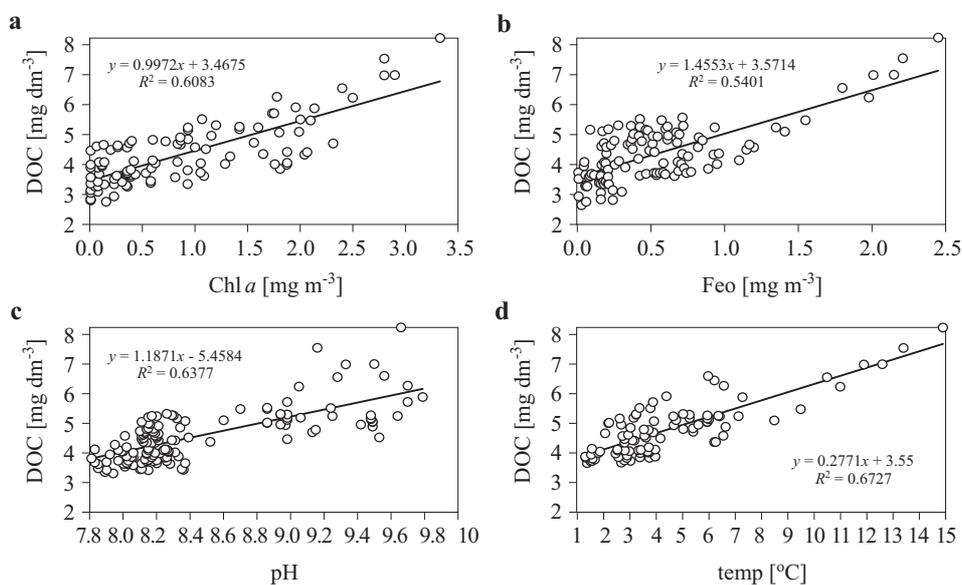
of phytoplankton (pH), activity of zooplankton (Feo), and season (Temp) (Voipio 1981, Omstedt & Axel 2003, Schneider et al. 2003, Kuliński & Pempkowiak 2008)

The relationships between the concentrations of DOC and POC are presented in Figure 6. They are characterised by a coefficient of determination $R^2 = 0.61$, which gives a coefficient of correlation $R = 0.78$. This strong correlation can be attributed to the composition of POM, comprising both phyto- and zooplankton – direct sources of DOC, and to the bacterial disintegration of detritus (Hoikkala et al. 2012), also a component of POM (Dzierzbicka-Głowacka et al. 2011).
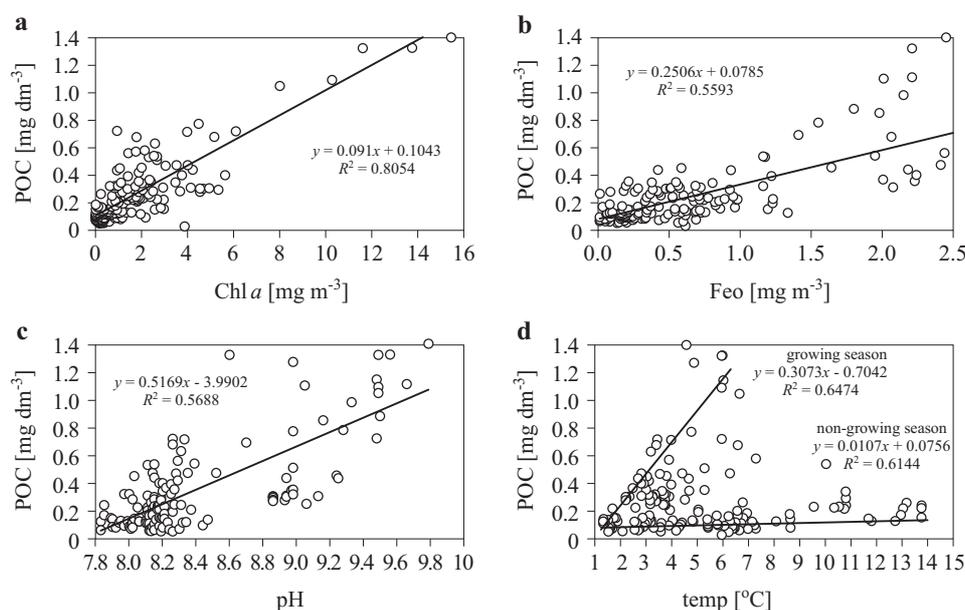
The relationships between DOC and POC and the other individual factors – chlorophyll *a*, phaeopigment *a*, pH and temperature (combined results for the Gdańsk, Gotland and Bornholm Deeps) – are presented in Figures 7 and 8 for DOC and POC respectively.

The dependences were approximated by linear equations. The slope coefficients and coefficients of determination (R^2) are listed in Table 5.

Statistically significant correlations between DOC and chlorophyll *a* (the measure of phytoplankton biomass) indicates that the concentration of DOC depends closely on phytoplankton abundance. The dependence between DOC and phaeopigment *a* (here used as a measure of phytoplankton

Figure 7. Relationship between DOC concentration and the other measured properties of seawater: a) chlorophyll *a*, b) phaeopigment *a*, c) pH, d) temperature – combined results from the Gdańsk Deep, Gotland Deep and Bornholm Deep

Figure 8. Relationship between POC concentration and the other measured properties of seawater : a) chlorophyll a, b) phaeopigment a, c) pH, d) temperature – combined results for the Gdańsk Deep, Gotland Deep and Bornholm Deep

Table 5. Slope coefficients and determination coefficients of linear dependences between DOC, POC and the other measured properties of sea water

OC fraction	Coefficient	POC	Chl a	Feo	pH	Temp
DOC	slope coefficient	3.24	1.00	1.46	1.19	0.28
	R^2	0.61	0.61	0.54	0.64	0.67
	[%] increase of DOC[1]	59%	18%	27%	22%	5%
POC	slope coefficient	–	0.09	0.25	0.52	0.31[*]; 0.01[**]
	R^2	–	0.81	0.56	0.57	0.65[*]; 0.61[**]
	[%] increase of POC[1]	–	6%	18%	37%	22%[*]; 1%[**]

[1] [%] increase in DOC/POC (in the range presented in Figure 6, where DOC changes from 2.73 to 8.24 mg dm^{-3} and POC changes from 0.05 to 1.40 mg dm^{-3}) on the assumption that the given properties change by one unit (1 mg dm^{-3} POC, 1 mg m^{-3} Chl a, 1 mg m^{-3} Feo, 1 pH and 1°C Temp).
[*]Growing season.
[**]Non-growing season.

mortality caused by zooplankton grazing, see Kuliński & Pempkowiak 2008) shows a positive correlation but one that is not as strong as in the case of chlorophyll a. It is interesting to see a strong correlation ($R = 0.80$) between DOC and pH. This could have been due to CO_2 absorption in the course

of photosynthesis, the subsequent decrease in the CO_2 concentration and the increase in pH (Wåhlström et al. 2012). Thus, a higher phytoplankton activity causes a lower CO_2 concentration in seawater and a higher pH (IPPC 2007).

Figure 7 presents relationships between DOC and chlorophyll a (Chl a), phaeopigment a (Feo), pH (pH) and temperature (Temp). The following coefficients of determination for the linear dependence were established: $R^2 = 0.61$ (Chl a), $R^2 = 0.54$ (Feo), $R^2 = 0.64$ (pH), $R^2 = 0.67$ (Temp). The determination coefficients between DOC and the listed water properties indicate a strong relation between the variables. This shows the important role of phytoplankton biomass (Chl a as the index of phytoplankton biomass), phytoplankton activity (pH as the index of the photosynthetic phytoplankton activity), zooplankton (Feo as the index of zooplankton grazing) and season (Temp as the index of season) in the process of organic carbon pool formation in seawater. As temperature increases, the activities of phyto- and zooplankton increase as well.

The dependences of POC concentrations on the measured properties of seawater are presented in Figure 8. The relationship between POC and chlorophyll a is characterised by a high determination coefficient ($R^2 = 0.81$, Figure 8a). This highly statistically significant correlation is comprehensible and easily explained. POC is composed of phytoplankton, zooplankton and detritus – mainly of phytoplankton (Dzierzbicka-Głowacka et al. 2010). Chlorophyll a is a measure of phytoplankton biomass. A good correlation also occurs between POC and phaeopigment a. Phaeopigment a as a proxy of zooplankton activity is also indicative of POC. The satisfactory correlation between POC and pH can be explained in the same way as the proportion pH = f(DOC). Contributing to POC concentrations, phytoplankton influences the pH in the same way as DOC does. The relationship between temperature and POC (Figure 8d) is presented separately for samples from the growing and non-growing seasons. The 'growing season' dependence is much steeper than the results for the 'non-growing season'. This again supports the importance of plankton in organic matter pool formation. With the onset of the growing season, phyto- and zooplankton activities increase. This indicates that the excretion of organic substances from living cells exceeds the biogeochemical degradation of organic matter in seawater. The former takes place during blooms, while the latter in both the growing and non-growing periods.

Slope coefficients of linear dependences (Figures 6, 7, 8) were used (Table 5) to characterise further the relations between the individual environmental factors (Chl a, Feo, pH, Temp) and the DOC and POC concentrations. Each slope coefficient indicates a change in DOC/POC

concentration [mg dm^{-3}] when the given property changes by one unit (1°C, 1 mg m^{-3} Chl a, 1 mg m^{-3} Feo, 1 pH). The results, also given as the percentage increase of DOC and POC, show that each of the environmental factors influences DOC and POC concentrations to a different extent (Table 5). Thus, when Chl a, Feo, pH and Temp change by one unit, the DOC concentration increase is equal to 18% (Chl a), 27% (Feo), 22% and (pH), 5% (Temp). In the case of the POC concentration, the increase of Chl a, Feo, pH and Temp by one unit causes POC to increase by 6% (Chl a), 18% (Feo), 37% (pH), 22% (Temp, growing season) and 12.5% (Temp, non-growing season). The highest increase ion DOC concentration was due to a 1 mg dm^{-3} increase in POC concentration (59%). The largest increase in POC was related to pH increase (37% per unit).

4. Discussion

The Baltic is still a poorly investigated sea with respect to DOC and POC concentrations. A comparison of DOC and POC concentrations from this study (separately for the growing and non-growing seasons) with literature data is given in Table 6.

The low concentrations of DOC (2.4–3.8 mg dm^{-3}) reported in this study are characteristic of the sub-halocline water layer for the non-growing period. The high concentrations (6.0–8.2 mg dm^{-3}) are characteristic of the short periods associated with the late spring algal blooms. Apart from this, the DOC concentrations in the surface water layer range from 3.6 mg dm^{-3} (non-growing season) to 5.0 mg dm^{-3} (growing season). As far as POC is concerned, the extreme concentrations are 0.05 mg dm^{-3} (sub-halocline/non-growing season), and 1.4 mg dm^{-3} (surface/late spring), while typical concentrations range from 0.2 to 0.6 mg dm^{-3}. The concentrations reported in this study differ considerably from those reported in the literature. For one thing, concentrations < 3.2 mg dm^{-3} (DOC) and 0.1 mg dm^{-3} (POC) have not been reported so far, most likely because the sub-halocline water layer in the non-growing season has never yet been sampled. Moreover, the average concentrations are substantially lower than those reported in the literature, except for the concentrations measured by Kuliński & Pempkowiak (2008). This can be attributed to incidental sampling during the course of individual, one-two week long cruises that most often took place in spring or summer. Thus the DOC and POC concentrations typical of offshore Baltic water and the dynamics of the concentrations are better characterised thanks to the data presented here. This is an important outcome of the study, as both the water properties and the intensity of processes occurring there depend on the organic matter concentrations.

Table 6. DOC and POC concentrations in the surface layer in the southern Baltic Sea

Study area	DOC [mgC dm^{-3}]	POC [mgC dm^{-3}]	Study year	Source
Gdańsk Deep	2.80–8.24*	0.05–1.40*	2009–11	present study
	2.73–4.97**	0.01–0.70**	2009–11	present study
Gotland Deep	2.76–7.25*	0.06–1.40*	2009–11	present study
	2.58–4.51**	0.05–0.34**	2009–11	present study
Bornholm Deep	3.62–5.89*	0.08–1.31*	2009–11	present study
	2.38–4.77**	0.07–0.63**	2009–11	present study
southern Baltic Sea	3.86–4.09	–	2006	Kuliński & Pempkowiak 2008
Gdańsk Deep	–	0.29–1.43	2001	Burska et al. 2005
Gulf of Gdańsk	6.24–7.68	–	2000	Grzybowski & Pempkowiak 2003
Gulf of Gdańsk	5.76–6.24	–	2000	Grzybowski 2003
southern Baltic Sea	–	0.3–0.48	2001	Schneider et al. 2003
southern Baltic Sea	–	0.05–0.25	1996	Pempkowiak et al. 2000
southern Baltic Sea	5.58 (±0.46)	–	1994	Ferrari et al. 1996
southern Baltic Sea	4.6–7.1	0.12–0.52	1982	Pempkowiak et al. 1984
southern Baltic Sea	3.2–6.2	–	1974	Jurkovskis et al. 1976

*Growing season.
**Non-growing season.

In this study, several questions were answered: 1) What is the dynamics of both carbon components in the Baltic Sea? 2) Do the dynamics and concentrations of both carbon pools differ in different regions of the southern Baltic Sea? 3) What factors influence POC and DOC concentrations?

The highest fluctuations of DOC and POC occurred in the growing period (spring/summer) in the surface water layer. Concentrations changed rapidly during a year. This is attributed to DOC and POC concentrations strongly depending on recurrent intensive phytoplankton blooms (Dunalska et al. 2012, Gustafsson et al. 2013).

The most characteristic feature of both DOC and POC concentrations in the Baltic are distinct seasonal fluctuations. Best developed in the surface water layer, they are caused by phytoplankton activity in the growing period that exceeds microbiological degradation/mineralisation. Surprisingly enough, seasonal dynamics is evident in both the subsurface (above the halocline) and the sub-halocline water layers. This can be attributed

to particulate organic matter sinking (POC source) and biodegradation (DOC source) (Amann et al. 2012). As phytoplankton activity ceases in late autumn, the supply of fresh, labile DOC and POC stops as well, and constant DOC concentrations (biochemically stable DOC) and residual POC are observed from then on until the resumption of biological activity in April of the following year.

The importance of phytoplankton in developing pools of DOC and POC in Baltic seawater is best indicated by the high correlation coefficients ($R = 0.8$) of the linear dependences $DOC = f(pH)$ and $POC = f(Chl\ a)$ ($R = 0.9$) (Table 5). The abundance of dissolved organic substances in seawater depends on the POC concentration, water temperature and the intensity of photosynthesis. The last-mentioned process is responsible for CO_2 depletion in seawater, which governs the seawater pH (Omstedt et al. 2014). The chlorophyll a concentration, used in this study as a measure of living phytoplankton biomass (Wasmund & Uhlig 2003, Granskog et al. 2005), demonstrated that phytoplankton must be the main source of POC in Baltic seawater.

Hence, the natural variability of DOC and POC concentrations and its large fluctuations can be attributed to the main processes, namely, phytoplankton and zooplankton activities, bacterial decomposition and mineralisation of organic matter, and the contribution of fresh (river run-off) and highly saline (North Sea inflows) water masses. We can therefore conclude that organic matter in Baltic seawater, and most likely in seawater in general, consists of two fractions – labile and stable – with respect to biochemical degradation and mineralisation. Labile organic matter is for the most part supplied in the course of primary production, while the stable matter is carried to sea with the river-runoff and as the non-mineralisable residue of the labile fraction.

References

Almroth-Rosell E., Eilola K., Hordoir R., Meier M. H. E, Hall P. O. J., 2011, *Transport of fresh and resuspended particulate organic material in the Baltic Sea – a model study*, J. Mar. Sys., 87 (1), 1–12, http://dx.doi.org/10.1016/j.jmarsys.2011.02.005.

Amann T., Weiss A., Hartmann J., 2012, *Carbon dynamics in the freshwater part of the Elbe estuary, Germany: Implications of improving water quality*, Estuar. Coast. Shelf Sci., 107, 112–121, http://dx.doi.org/10.1016/j.ecss.2012.05.012.

Andrulewicz E., Szymelfenig M., Urbański J., Węsławski J. M., 1998, *Morze Bałtyckie – o tym warto wiedzieć*, Zesz. Zielonej Akad., 7, 1–115.

Bianchi T. S., Demetropoulos A., Hadjichristophorou M., Argyrou M., Baskaran M., Lambert C., 1996, *Plant pigments as biomarkers of organic matter sources*

in sediments and coastal waters of Cyprus (eastern Mediterranean), Estuar. Coast. Shelf Sci., 42, 103–115, http://dx.doi.org/10.1006/ecss.1996.0008.

Burska D., Pryputniewicz D., Falkowska L., 2005, *Stratification of particulate organic carbon and nitrogen in the Gdańsk Deep (southern Baltic Sea)*, Oceanologia, 47, 201–217.

Björck S., 1995, *A review of the history of the Baltic Sea, 13.0-8.0 ka BP*, Quater. Int., 27, 19–40, http://dx.doi.org/10.1016/1040-6182(94)00057-C.

Chester R., 2003, *Marine geochemistry*, 2nd edn., Blackwell Sci., London, 506 pp.

Collos Y., Husseini-Ratrema J., Bec B., Vaquer A., Hoai T. L., Rougier C., Pons V., Souchu P., 2005, *Phaeopigment dynamics, zooplankton grazing rates and the autumnal ammonium peak in a Mediterranean lagoon*, Hydrobiologia, 550 (1), 83–93, http://dx.doi.org/10.1007/s10750-005-4365-1.

Dera J., 1992, *Marine physics*, Elsevier, Amsterdam, 515 pp.

Doney S. C., Linsay K., Moore J. K., 2003, *Global ocean carbon cycle modeling*, [in:] *Ocean biogeochemistry*, M. J. R. Doney (ed.), Springer-Verlag, Berlin, 217–238.

Dunalska J. A., Górniak D., Jaworska B., Geiser E. E., 2012, *Effect of temperature on organic matter transformation in a different ambient nutrient availability*, Ecol. Eng., 49, 27–34, http://dx.doi.org/10.1016/j.ecoleng.2012.08.023.

Dzierzbicka-Głowacka L., Kuliński K., Maciejewska A., Jakacki J., Pempkowiak J., 2011, *Numerical modelling of POC dynamics in the Baltic under possible future conditions determined by nutrients, light and temperature*, Oceanologia, 53 (4), 971–992, http://dx.doi.org/10.5697/oc.53-4.971.

Dzierzbicka-Głowacka L., Kuliński K., Maciejewska A., Pempkowiak J., 2010, *Particulate Organic Carbon in the southern Baltic Sea: numerical simulations and experimental data*, Oceanologia, 52 (4), 621–648, http://dx.doi.org/10.5697/oc.52-4.621.

Edman M., Omstedt A., 2013, *Modeling the dissolved CO2 system in the redox environment of the Baltic Sea*, Limnol. Oceanogr., 58 (1), 74–92, http://dx.doi.org/10.4319/lo.2013.58.1.0074.

Emelyanov E., 1995, *Baltic Sea: geology, geochemistry, paleoceanography, pollution*, P.P. Shirshov Inst. Oceanol. Russian Acad. Sci., Kaliningrad, 119 pp.

Emerson S. R., Hedges J. I., 2008, *Chemical oceanography and the marine carbon cycle*, Cambridge Univ. Press, Cambridge, 453 pp., http://dx.doi.org/10.1017/CBO9780511793202.

Ferrari G. M., Dowell M. D., Grossi S., Targa C., 1996, *Relationship between the optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region*, Mar. Chem., 55, 299–316, http://dx.doi.org/10.1016/S0304-4203(96)00061-8.

Gardner W. D., Mishonova A. V., Richardson M. J., 2006, *Global POC concentrations from in situ and satellite data*, Deep-Sea Res. Pt. II, 53 (5–7), 718–740, http://dx.doi.org/10.1016/j.dsr2.2006.01.029.

Granskog M. A., Kaartokallio H., Thomas D. N, Kuosa H., 2005, *Influence of freshwater inflow on the inorganic nutrient and dissolved organic matter within*

coastal sea ice and underlying waters in the Gulf of Finland (Baltic Sea), Estuar. Coast. Shelf Sci., 65 (1–2), 109–122.

Grzybowski W., 2003, *Are data on light-induced ammonium release from dissolved organic matter consistent?*, Chemosphere, 52, 933–936, http://dx.doi.org/10.1016/S0045-6535(03)00290-X.

Grzybowski W., Pempkowiak J., 2003, *Preliminary results on low molecular weight organic substances dissolved in the waters of the Gulf of Gdańsk*, Oceanologia, 45 (4), 693–704.

Gustafsson E., Deutsch B., Gustafsson B. G., Humborg C., Mörth C.-M., 2013, *Carbon cycling in the Baltic Sea - the fate of allochthonous organic carbon and its impact on air-sea CO2 exchange*, J. Marine Syst., 129, 289–302, http://dx.doi.org/10.1016/j.jmarsys.2013.07.005.

Hagström Å., Azam F., Kuparinen J., Zweifel U. L., 2001, *Pelagic plankton growth and resource limitations in the Baltic Sea*, [in:] *A systems analysis of the Baltic Sea*, F. V. Wulff, L. A. Rahm & P. Larsson (eds.), Ecol. Stud., 148, 177–210.

Hakanson L., 1991, *Charakterystyka fizycznogeograficzna zlewiska Morza Bałtyckiego*, Środowisko Morza Bałtyckiego, 1, 1–37.

Hedges J. I., 2002, *Why dissolved organic matter*, [in:] *Biogeochemistry of marine dissolved organic matter*, D. A. Hansell & C. A. Carlson (ed.), Elsevier Sci., San Diego, 1–33.

Hansell D. A, 2002, *DOC in the Global Ocean carbon cycle*, [in:] *Biogeochemistry of marine dissolved organic matter*, D. A. Hansell & C. A. Carlson (eds), Elsevier Sci., San Diego, 685–715, http://dx.doi.org/10.1016/B978-012323841-2/50017-8.

The BACC Author Team, 2008, *The BALTEX Assessment of Climate Change for the Baltic Sea Basin*, Springer-Verlag, Berlin, 1–34.

HELCOM, 2005, *Nutrient pollution to the Baltic Sea in 2000*, Baltic Sea Environ. Proc., 100, 24 pp.

HELCOM, 2006, *Development of tools for assessment of eutrophication in the Baltic Sea*, Baltic Sea Environ. Proc., 104, 64 pp.

HELCOM, 2007, *Climate change in the Baltic Sea area*, Baltic Sea Environ. Proc., 111, 54 pp.

Hoikkala L., Lahtinen T., Perttila M., Lignell R., 2012, *Seasonal dynamics of dissolved organic matter on a costal salinity gradient in the northern Baltic Sea*, Cont. Shelf Res., 45, 1–45, http://dx.doi.org/10.1016/j.csr.2012.04.008.

IPCC, 2007, *Climate Change Synthesis Report. Contribution of working groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge Univ. Press, Cambridge, 73 pp.

Jurkovskis A. K., Formych T. A., Grotanie B. J., 1976, *Cikl izmienienij fosfora, azota i organiczeski sviazannogo uglieroda v Baltijskom Morie*, Okieanologia, 16, 79–86.

Kouts T., Omstedt A., 1993, *Deep water exchange in Baltic Proper*, Tellus A, 45 (4), 311–324. http://dx.doi.org/10.1034/j.1600-0870.1993.t01-1-00006.x.

Kuliński K., Pempkowiak J., 2008, *Dissolved organic carbon in the southern Baltic Sea: Quantification of factors affecting its distribution*, Estuar. Coast. Shelf Sci., 78 (1), 38-44, http://dx.doi.org/10.1016/j.ecss.2007.11.017.

Kuliński K., Pempkowiak J., 2011, *The carbon budget of the Baltic Sea*, Biogeosciences, 8, 3219–3230, http://dx.doi.org/10.5194/bg-8-3219-2011.

Kuliński K., Schneider B., Hammer K., Machulik U., Schulz-Bull D., 2014, *The influence of dissolved organic matter on the acid-base system of the Baltic Sea*, J. Marine Syst., 132, 106–115, http://dx.doi.org/10.1016/j.jmarsys.2014.01.011.

Leipe T., Tauber F., Vallius H., Virtasalo J., Uścinowicz Sz., Kowalski N., Hille S., Lindgren S., Myllyvirta T., 2011, *Particulate organic carbon (POC) in surface sediments of the Baltic Sea*, Geo-Mar. Lett., 31 (3), 175–188, http://dx.doi.org/10.1007/s00367-010-0223-x.

Lorentz C. J., 1967, *Determination of chlorophyll in pheo-pigments: spectrophotomatric equations*, Limnol. Oceanogr., 12 (2), 343–346, http://dx.doi.org/10.4319/lo.1967.12.2.0343.

Maar M., Møller E. F., Larsen J., Madsen K. S., Wan Z., She J., Jonasson L., Neumann T., 2011, *Ecosystem modelling across a salinity gradient from the North Sea to the Baltic Sea*, Ecol. Model., 222 (10), 1696–1711, http://dx.doi.org/10.1016/j.ecolmodel.2011.03.006.

Maric D., Frka S., Godrija J., Tomazic I., Penezic A., Djakovac T., Vojvodic V., Precali R., Gasparovic B., 2013, *Organic matter production during late summerwinter period in a temperate sea*, Cont. Shelf Res., 55 (1), 52–65, http://dx.doi.org/10.1016/j.csr.2013.01.008.

Meyer-Harms B., von Bodungen B., 1997, *Taxon-specific ingestion rates of natural phytoplankton by calanoid copepods in an estuarine environment (Pomeranian Bight, Baltic Sea) determined by cell counts and HPLC analyses of marker pigments*, Mar. Ecol.-Prog. Ser., 153, 181–190, http://dx.doi.org/10.3354/meps153181.

Omstedt A., Axell L. B., 2003, *Modeling the variations of salinity and temperature in the large Gulfs of the Baltic Sea*, Cont. Shelf Res., 23 (3–4), 265–294, http://dx.doi.org/10.1016/S0278-4343(02)00207-8.

Omstedt A., Humborg C., Pempkowiak J., Perttilä M., Rutgersson A., Schneider B., Smith B., 2012, *Biogeochemical control of the coupled CO2-O2 system of the Baltic Sea: A review of the results of Baltic-C*, AMBIO, 43, 49–53, http://dx.doi.org/10.1007/s13280-013-0485-4.

Parsons T. R., 1969, *Determination of photosynthetic pigments in sea-water. A survey of methods*, UNESCO, Paris, 69 pp.

Pempkowiak J., 1983, *C18 reversed-phase trace enrichment of short- and long-chain (C2-C8-C20) fatty acids from dilute aqueous solutions and sea water*, J. Chromatography A, 258, 93–102, http://dx.doi.org/10.1016/S0021-9673(00)96401-X.

Pempkowiak J., Chiffoleau J.-F., Staniszewski A., 2000, *Vertical and horizontal distribution of selected heavy metals in the southern Baltic off Poland*, Estuar. Coastal Shelf Sci., 51 (1), 115–125, http://dx.doi.org/10.1006/ecss.2000.0641.

Pempkowiak J., Walkusz-Miotk J., Bełdowski J., Walkusz W., 2006, *Heavy metals in zooplankton from the Southern Baltic*, Chemosphere, 62 (10), 1697–1708, http://dx.doi.org/10.1016/j.chemosphere.2005.06.056.

Pempkowiak J., Widrowski M., Kuliński W., 1984, *Dissolved organic carbon and particulate carbon in the Southern Baltic in September*, Proc. XIV Conf. Baltic Oceanogr., IMGW, Gdynia, 699–713.

Sarmiento J. L., Gruber N., 2006, *Ocean biogeochemical dynamics*, Princeton Univ. Press, New York, 526 pp.

Schneider B., Nausch G., Nagel K., Wasmund N., 2003, *The surface water CO2 budget for the Baltic Proper: a new way to determine nitrogen fixation*, J. Marine Syst., 42 (1–2), 53–64.

Seager S. L., Slabaugh M. R., 2004, *Chemistry for today: general, organic, and biochemistry*, Thomson Brooks/Cole, Bedmont, 342 pp.

Segar D. A., 2012, *Introduction to ocean science*, 3rd edn., 1st electr. edn., ver. 3.0. 525 pp.

Stedmon C. A., Markager S., Tranvik L., Kronberg L., Slätis T., Martinsen W., 2007, *Photochemical production of ammonium and transformation of dissolved organic matter in the Baltic Sea*, Mar. Chem., 104 (3–4), 227–240, http://dx.doi.org/10.1016/j.marchem.2006.11.005.

Stoń J., Kosakowska A., Łotocka M., Łysiak-Pastuszak E., 2002, *Pigment composition in relation to phytoplankton community structure and nutrient content in the Baltic Sea*, Oceanologia, 44 (4), 419–437.

Szymczycha B., Maciejewska A., Winogradow A., Pempkowiak J., 2014, *Could submarine groundwater discharge be a significant carbon source to the southern Baltic Sea?*, Oceanologia, 56 (2), 327–347, http://dx.doi.org/10.5697/oc.56-2. 327.

Thomas H., Schneider B., 1999, *The seasonal cycle of carbon dioxide in Baltic Sea surface waters*, J. Marine Syst., 22 (1), 53–67, http://dx.doi.org/10.1016/S0924-7963(99)00030-5.

Thomas H., Pempkowiak J., Wulff F., Nagel K., 2003, *Autotrophy, nitrogen accumulation and nitrogen limitation in the Baltic Sea: a paradox or a buffer for eutrophication?*, Geophys. Res. Lett., 30 (21), 2130 p.

Thomas H., Bozec Y., de Baar H. J. W., Elkalay K., Frankignoulle M., Schiettecatte L.-S., Kattner G., Borges A. V., 2005, *The carbon budget of the North Sea*, Biogeosciences, 2, 87–96, http://dx.doi.org/10.5194/bg-2-87-2005.

Uścinowicz Sz., 2011, *Geochemistry of Baltic Sea surface sediments*, Polish Geol. Inst. – Nat. Res. Inst., Warsaw, 356 pp.

Voipio A., 1981, *The Baltic Sea*, Elsevier, Amsterdam, 148 pp.

Wåhlström I., Omstedt A., Björk G., Anderson L.G., 2012, *Modelling the CO2 dynamics in the Laptev Sea, Arctic Ocean: Part I*, J. Mar. Syst., 102–104, 29–38, http://dx.doi.org/10.1016/j.jmarsys.2012.05.001.

Wasmund N., Uhlig S., 2003, *Phytoplankton trends in the Baltic Sea*, J. Mar. Sci.,
60, 177–186.

Witek Z., Ochocki S., Maciejowska M., Pastuszak M., Nakonieczny J.,
Podgórska B., Kownacka J. M., Mackiewicz T., Wrzesińska-Kwiecień M., 1997,
*Phytoplankton primary production and its utilization by the pelagic community
in the coastal zone of the Gulf of Gdańsk (southern Baltic)*, Mar. Ecol.-Prog.
Ser., 148, 169–186, http://dx.doi.org/10.3354/meps148169.

Woźniak S., 2014, *Simple statistical formulas for estimating biogeochemical
properties of suspended particulate matter in the southern Baltic Sea
potentially useful for optical remote sensing applications*, Oceanologia, 56 (1),
7–39, http://dx.doi.org/10.5697/oc.56-1.007.