

ORIGINAL RESEARCH ARTICLE

Diurnal and seasonal DOC and POC variability in the land-locked sea

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Organic matter

Summary Organic matter is a minor yet important component of the marine environment. The aim of this study was to investigate the diurnal and seasonal changes in dissolved and particulate organic carbon (DOC and POC, respectively). Thus, DOC and POC as well as chlorophyll *a* (Chl *a*), $\delta^{13}\text{C}$, NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , salinity, pH, and temperature were regularly measured in samples collected for 24 h (2-h resolution) in the Gdańsk Deep (54°44.730'N, 19°08.531'E) at three water depths (1, 10, and 40 m) during sampling campaigns in 2011 (May), 2014 (May), and 2015 (January, March, May, July, September, November). Seasonal variations in DOC and POC followed the seasonality of Chl *a* (proportional trend) and nutrients (reverse trend) concentrations. Diurnal oscillations were detected in six out of the eight measurement series. The strongest diurnal variability in both POC and DOC occurred in May 2011 and March 2015, when phytoplankton activity was highest (high Chl *a*). The surprisingly low $\delta^{13}\text{C}$ values (range: -28% to -24%) measured over the course of the study revealed the gaps in our knowledge of the isotopic characteristics of terrestrial- vs. marine-derived particulate organic matter.

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1. Introduction

Organic substances, while present in the marine environment in low concentrations, play an important environmental role as they influence both the properties and processes of seawater. Moreover, they are an important factor in marine carbon cycling and energy fluxes (Hedges, 2002; Hoikkala et al., 2015; Kuliński et al., 2014). For practical reasons and due to differences in their functions, organic substances are divided into dissolved and particulate classes. The former

pass through filters with a pore size of 0.45 μm and the latter are retained on these filters. The occurrence of bulk organic substances in seawater is evaluated by measuring the concentration of organic carbon, which is the most abundant element in organic molecules. Organic carbon is divided, accordingly, into dissolved (DOC) and particulate (POC) pools.

Both DOC and POC are closely related to the activity of living organisms, beginning with phytoplankton (Dzierzbicka-Głowacka et al., 2010; Falkowska et al., 1998). Living cells and cell remnants contribute to POC in seawater, whereas DOC is directly linked to phytoplankton, as both exudates and the products of POM hydrolysis are sources of DOC. Thus, factors that are known to influence plankton activity are likely to influence POC and DOC concentrations. However, organic matter (OM, both dissolved and particulate) is readily decomposed or mineralized, either as a result of microbial activity (Hoikkala et al., 2015; Kuliński et al., 2016; Pempkowiak, 1983; Thomas et al., 2003) or exposure to UV irradiance. OM is also removed from the system via its deposition in the sediments, either directly or after sorption on suspended material. Thus the concentration of organic carbon reflects the steady state resulting from the production and removal of OM (Dzierzbicka-Głowacka et al., 2010; Hoikkala et al., 2012; Omstedt et al., 2014).

The distribution of organic substances in the surface water of the Baltic Sea has been well documented (Hoikkala et al., 2015; Kuliński et al., 2011; Maciejewska and Pempkowiak, 2014). Recent studies identified yearly fluctuations in the concentrations of POC and DOC, corresponding to annual changes in the phytoplankton abundance caused by light intensity (Hoikkala et al., 2015). DOC concentrations vary in the range of 3–6 mg L^{-1} , are larger in summer (5–6 mg L^{-1}) than in winter (3–4 mg L^{-1}), and are higher in the surface (4–6 mg L^{-1}) than in the subsurface (3–4 mg L^{-1}) layers (Kuliński et al., 2011; Maciejewska and Pempkowiak, 2014). Quantitative studies of the factors modulating the dynamics of DOC and POC indicated river run-off, primary production, groundwater seepage, inflows of North Sea water, and OM mineralization, sedimentation, and photo-oxidation as the most important contributors (Kuliński and Pempkowiak, 2008, 2011; Maciejewska and Pempkowiak, 2014, 2015; Szymczycha et al., 2014). A relationship between DOC and POC and nutrients seasonal levels was also documented (Maciejewska and Pempkowiak, 2014).

The diurnal variability in DOC is such that concentrations increase during daytime and are lower at night, thus demonstrating the importance of plankton exudates as the DOC source and microbial mineralization as its sink (Shinomura et al., 2005). Burska et al. (2005) described the diurnal variability in POC in early June in the Gdańsk Deep. By contrast, based on measurements carried out in Kiel Bay, there were no diurnal and only minor seasonal oscillations in the DOC and POC levels in its waters despite substantial variations of carbohydrates and fatty acids (Gocke et al., 1987; Osterroth et al., 1985). The concentrations of dissolved amino acids in the central Baltic underwent large changes over the course of a day (Mopper and Lindroth, 1982). Although the spatial distribution and seasonality of both DOC and POC have been described in several reports (e.g. Gustafsson et al., 2014; Hoikkala et al., 2015; Kuliński et al., 2011; Maciejewska and Pempkowiak, 2014), only a few

studies have examined their short-term (diurnal) fluctuations and related dynamics, both of which remain incompletely understood (Burska et al., 2005; Gocke et al., 1987; Mopper and Lindroth, 1982; Osterroth et al., 1985; Shinomura et al., 2005) while some features of the seasonal phenomenon, e.g. POC $\delta^{13}\text{C}$ -variability, are still lacking.

The goal of this study was to assess the diurnal and seasonal dynamics of DOC and POC in Baltic seawater. We hypothesized that diurnal and seasonal variations in both would be detected in the Baltic Sea and that they are especially pronounced during the productive season. The study was performed in the Gdańsk Deep (southern Baltic), which is relatively secluded from the direct influence of river run-off and water currents (Lass and Matthäus, 2008; Rak, 2016; Voipio, 1981). Analyses of POC and DOC were accompanied by measurements of seawater constituents indicative of the processes influencing the OM pool in seawater, including: Chl *a* and nutrient concentrations (phytoplankton activity), salinity (North Sea water inflow, river run-off), temperature (season, surface mixing) (Kuliński and Pempkowiak, 2008, 2011; Maciejewska and Pempkowiak, 2014), and the pH resulting from biological activity (CO_2 dynamics) (Maciejewska and Pempkowiak, 2015).

2. Material and methods

2.1. Study site

The study site was the Gdańsk Deep (54°44.730'N, 19°08.531'E, Fig. 1), a basin with a maximum depth of 117 m that is situated seaward of the Gulf of Gdańsk. A permanent halocline occurs at a depth of 60–80 m and separates the deep, dense, saline water masses originating from the North Sea from the brackish Baltic Sea water in the surface layer. The salinity of the surface water layer is ~ 7.1 , while that of the bottom water is usually in the range of 10.0–11.5. Permanent stratification often leads to oxygen deficits close to the sea bottom. In summer, a thermocline develops at a depth of 15–30 m (Voipio, 1981). Spring phytoplankton (diatoms) bloom usually start in mid-March whereas from late April until mid-summer phytoplankton activity is lower due to the low nutrient concentrations. At high temperatures, cyanobacterial blooms develop, as they are not limited by concentrations of nitrogen species. In autumn, phytoplankton again exhibit higher activity due to a deepening of the mixed layer and to the nutrients supplied from deeper water layers. Production terminates usually in October–November, when respiration predominates in the water column (Nausch et al., 2008; Wasmund and Uhlig, 2003).

2.2. Sampling and analyses

2.2.1. Sampling

Seawater samples were collected using Niskin bottles during *r/v Oceania* cruises in 2011 (May), 2014 (May), and 2015 (January, March, May, July, September, November). To identify diurnal changes in the investigated water properties, including DOC, POC, Chl *a*, $\delta^{13}\text{C}$, NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} , pH, salinity, and temperature, samples were collected for 24 h with a 2-h resolution at three depths: 1 m and 10 m

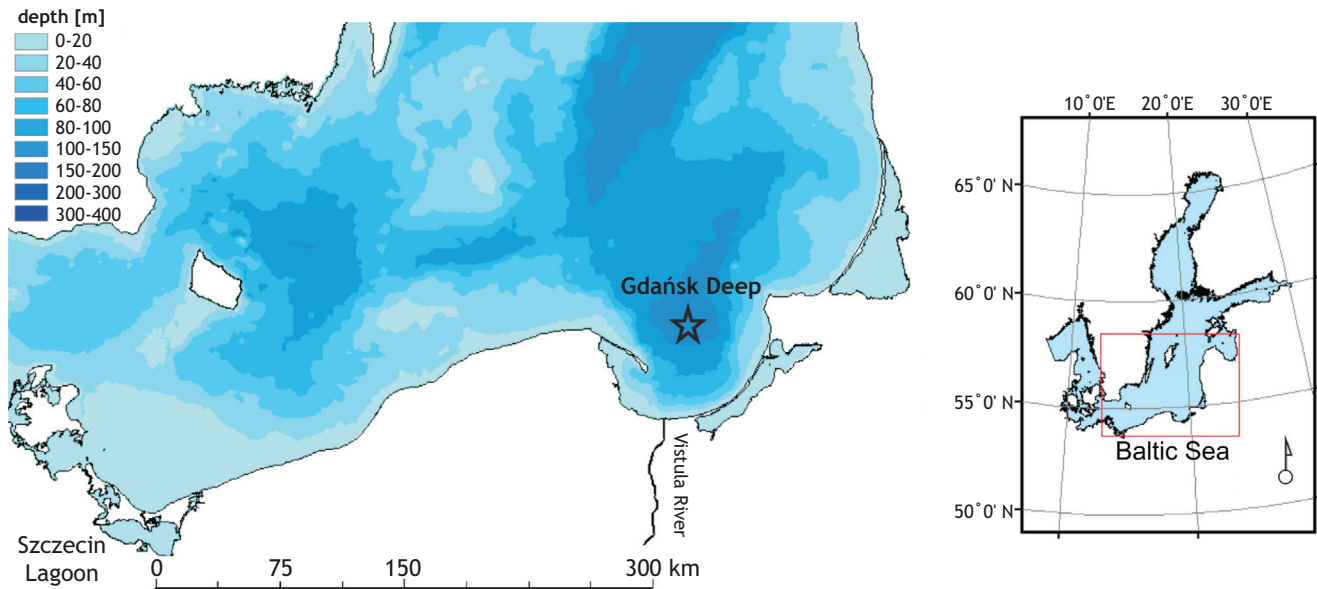


Figure 1 The location of the study area in the Gdańsk Deep (54°44.730'N, 19°08.531'E).

represent the euphotic zone and 40 m is below the euphotic zone but above the halocline. The time interval was set at 2 h, in order not to miss DOC/POC concentrations dynamics.

2.2.2. Temperature, salinity, and pH measurements

Temperature and salinity were measured in situ using a CTD SeaBird profiler, 911-Plus. The pH was measured using a WTW Multi 3400i pH meter (0.01 unit accuracy).

2.2.3. POC and stable carbon isotope ($\delta^{13}\text{C}$) measurements

Seawater samples of known volume were passed through pre-combusted, pre-weighed MN GF 5 (0.4 μm pore size) glass-fiber filters and stored at -20°C . Before the analysis, the filters were dried at 60°C for 24 h. The samples were then homogenized and weighed (0.001 mg accuracy). To remove carbonates, the samples were acidified with 2 mol L^{-1} HCl. POC and carbon stable-isotope composition was measured in an Elemental Analyzer Flash EA 1112 Series combined with an isotopic ratio mass spectrometer (IRMS Delta V Advantage; Thermo Electron Corp., Germany) using high-temperature (1020°C) oxidation. Quality control to assess the precision and accuracy included regular measurements of procedural blanks, certified reference materials (Flußsediment, Heka-Tech GmbH), and standard materials (provided by Thermo Electron Corp). This methodology provided satisfactory accuracy and precision (average recovery $97.1 \pm 1.0\%$). Isotopic ratios $\delta^{13}\text{C}$ were calculated using laboratory-grade pure reference gases: CO_2 was calibrated against the IAEA standards CO-8 and USGS40. The $\delta^{13}\text{C}$ results are expressed in the conventional delta notation, i.e. versus PDB for $\delta^{13}\text{C}$ as parts per thousand according to the following equation:

$$\delta^{13}\text{C} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] \times 1000,$$

where R is the $^{13}\text{C}/^{12}\text{C}$ ratio. The precision was better than 0.20‰ for replicate samples ($n = 7$).

2.2.4. DOC measurements

Immediately after collecting 40 mL of filtered seawater were poured into a pre-combusted glass bottle and acidified with 50 μL of conc. HCl to both remove carbonates and stop mineralization. The bottles were stored in a refrigerator at 5°C . The DOC concentration was measured in a TOC-L analyzer (Shimadzu Corp.) using a high-temperature (680°C) oxidation method and a Pt catalyst. Quality control consisted of the regular analysis of blanks as well as accuracy and precision checks based on comparisons with the reference material: North Atlantic water obtained from the Hansell Laboratory (recovery = 95%, precision characterized by standard deviation: 0.1 mg L^{-1} , $n = 5$, the internal variability of DOC concentration measured in samples collected three times at 40 m depth in May 2014 was smaller than 0.06 mg L^{-1}). The obtained DOC concentrations in the procedural blank samples never exceeded 3% of concentrations measured in the actual samples.

2.2.5. Chlorophyll *a* (Chl *a*) measurements

Seawater was passed through MN GF 5 (0.4 μm pore size) glass-fiber filters. The filters were preserved at -80°C until the analysis. In the laboratory, the samples were extracted using 90% acetone according to the procedure developed by Parsons (1966) and then measured spectrophotometrically. Chl *a* concentrations were calculated using the Lorentz (1967) formulas.

2.2.6. Nutrient measurements

Seawater was collected into polyethylene bottles and analyzed for nutrient concentrations within 48 h of sampling. Nutrients were analyzed using the colorimetric methods described by Strickland and Parsons (1967) and Salley et al. (1986). Repeat measurements of the certified reference material – RM-BU (National Metrology Institute of Japan) were performed to assess the accuracy and precision of the nutrients analyses. The average relative standard

deviations were 0.4% for NO_3^- , 1.4% for NO_2^- , 0.3% for NH_4^+ , and 1.4% for PO_4^{3-} . Analyses indicated recoveries of 96.2% for NO_3^- , 101.4% for NO_2^- , 98.3% for NH_4^+ , and 99.1% for PO_4^{3-} . Dissolved inorganic nitrogen (DIN) was defined as the sum of NO_3^- , NO_2^- , and NH_4^+ .

3. Results and discussion

3.1. General physical variables

Salinity and temperature profiles for each sampling campaign are presented in Fig. 2. The water depth at the study site was 117 m, with the halocline located between 55 m and 75 m and the thermocline between 20 m and 40 m, both depending on the season (development of mixed layer depth) and sampling year (2011, 2014 and 2015).

Because long-lasting intensive winds can change the depth of the mixed layer, even in usually calm seasons the thermocline can be broken up and/or become indistinct. This was well demonstrated by the results from July 2015 (Fig. 2), when the mixed layer was at a much deeper depth (50 m) than usual (up to 15–20 m) (Lass and Matthäus, 2008; Voipio, 1981). Sea surface temperature (SST) followed its usual seasonal variability, with minimal values from January to March and maximum values from July to September. The SST ranged from 4.5°C in January 2015 to 16.8°C in July 2015. An inter-annual difference in SST was detected in samples collected in May: 2011 (5.8°C), 2014 (7.4°C), and 2015 (8.2°C). This was most likely due to shifts in the temporal development of temperature in the different years. In fact, 2014 was the warmest year recorded between 1990 and 2015 (Siegel and Gerth, 2015). As several major Baltic inflows (MBIs) occurred during the study (Rak, 2016), their temporal development was followed based on the vertical movements of the halocline and the changes in the salinity of the bottom water, which ranged from 12.1 to 14.5.

3.2. Seasonal variations

The seasonal variability of POC, DOC, DIN ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$), PO_4^{3-} , Chl *a*, and pH in the surface

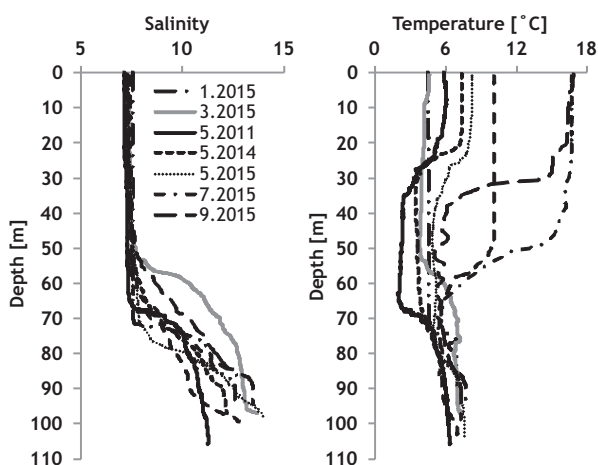


Figure 2 Salinity and temperature distributions in the water column of the study area.

water (1 m depth) during the study is discussed herein on the basis of the mean values from each sampling campaign (Fig. 3). Pronounced seasonal variability was observed for all investigated variables. The average POC and DOC concentrations were, respectively, 80% and 5% higher during the growing season (March–October 2015) than during the non-growing season (November–February 2015), in line with results obtained previously (Hoikkala et al., 2015; Kuliński et al., 2011; Maciejewska and Pempkowiak, 2014). However, a comparison of the maximum DOC concentration measured in the productive vs. the non-productive season showed a 10% increase in DOC variability.

Kuliński et al. (2011) calculated a refractory DOC concentration in the Baltic Proper of $3.1 \pm 0.2 \text{ mg L}^{-1}$, while Maciejewska and Pempkowiak (2015) established it at 4.3 mg L^{-1} , both assuming that the winter DOC concentrations represent the refractory DOC pool, which is not bioavailable. In incubation experiments, based on samples collected from Vistula and Oder estuaries, the refractory DOC concentration was calculated again and equal to 2.7 mg L^{-1} (Kuliński et al., 2016). The DOC concentration measured in the surface layer in January in the present study was significantly higher than either of these values but comparable to refractory DOC concentrations reported by Maciejewska and Pempkowiak (2015), indicating, perhaps, the continued presence of labile compounds in the seawater at the time of sampling or specific characteristic sea water masses with respect to refractory DOC concentrations.

A statistically significant relationships between Chl *a* and both DOC and POC was previously demonstrated in the Gdańsk Deep (Maciejewska and Pempkowiak, 2014, 2015). This was confirmed by our dataset (Fig. 3) and is in line with the general understanding of a correlation between phytoplankton abundance and increased Chl *a* concentrations (Wasmund and Uhlig, 2003). In the Baltic Sea, three phytoplankton biomass peaks typically occur over the course of a year, in spring, summer, and autumn (Wasmund et al., 1998). According to our data (Fig. 3), Chl *a* concentrations were highest in March 2015 (3.5 mg m^{-3}), May 2011 (8.8 mg m^{-3}), May 2014 (3.2 mg m^{-3}), May 2015 (2.8 mg m^{-3}), and September 2015 (3.2 mg m^{-3}). Average POC concentrations were highest in March 2015 (0.9 mg L^{-1}) and May 2011 (1.1 mg L^{-1}), while DOC concentrations peaked in May 2011 (6.0 mg L^{-1}) and June 2015 (4.1 mg L^{-1}). The temporal shift among the highest POC (March and May 2015) and DOC (July 2015) concentrations is a common phenomenon attributable to the delayed occurrence of DOC (Dzierzbicka-Głowacka et al., 2010; Hoikkala et al., 2015; Shinomura et al., 2005). The hydrolysis of POC causes its removal and at the same time provides a source of DOC. POC is also removed from the water column by sedimentation, while DOC persists in the water column for a long period of time and contains substances with half-lives of months or even years. Together, these features account for the much greater seasonal oscillations of POC than DOC and the accumulation of DOC in water during the year (with a peak in summer), a feature not observed for POC.

Similar to DOC, a seasonal pH variability was observed, attributed mostly to shifts in the CO_2 system caused by the changing proportions of respiration (CO_2 source) and photosynthesis (CO_2 sink). As CO_2 exchange with the atmosphere is relatively slow, the temporal increase in pH is mostly related

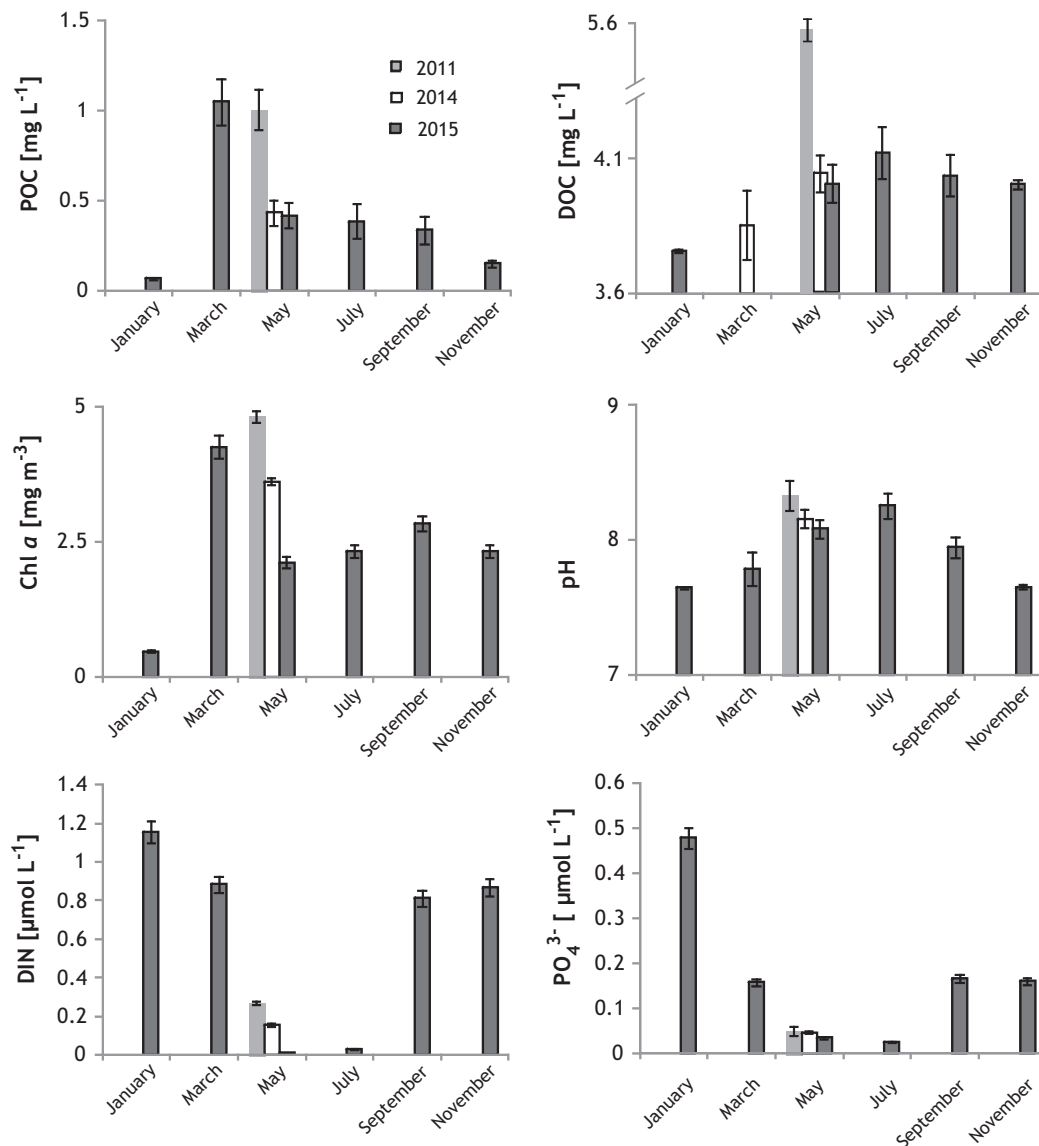


Figure 3 Seasonal variability of POC, DOC, Chl α , pH, DIN ($\text{NO}_3^- + \text{NO}_2^- + \text{NH}_4^+$) and, PO_4^{3-} measured in surface-water samples collected at a water depth of 1 m. The concentrations are the averages determined during each sampling campaign.

to the occurrence of phytoplankton blooms, while the CO_2 decrease – to non-productive periods (Maciejewska and Pempkowiak, 2015; Omstedt et al., 2014).

Fig. 3 shows the clear dependence between POC and DOC and the development of both as a function of the DIN and PO_4^{3-} concentrations. Average concentrations of nutrients were highest in January (DIN: $1.15 \pm 0.01 \mu\text{mol L}^{-1}$, PO_4^{3-} : $0.48 \pm 0.01 \mu\text{mol L}^{-1}$) then started to decrease as a consequence of spring bloom, however, were still high in March 2015 (DIN: $0.88 \pm 0.07 \mu\text{mol L}^{-1}$, PO_4^{3-} : $0.16 \pm 0.04 \mu\text{mol L}^{-1}$). A further decrease in nutrient concentrations occurred in May 2015. This was caused by the uptake of nutrients during ongoing production in the water column, evidenced by the shallowing of the mixed layer as well as increases in both temperature and PAR (Gao et al., 2012; Ilis and Keskitalo, 2008). In July 2015, nutrient levels were slightly higher than in May 2015, likely due to an equilibrium

between production and mineralization processes, and they increase again beginning in September 2015, in response to ongoing recycling processes and a deepening of the mixed layer (Thomas et al., 2003).

3.3. Diurnal variations

The diurnal variabilities in the DOC and POC concentrations at water depths of 1 m, 10 m, and 40 m are presented in Fig. 4.

In January 2015, there was no diurnal variability in either POC or DOC, most likely due to a low level of overall phytoplankton activity (Fig. 3). The slight fluctuations in the DOC concentrations could be attributed to local water movements and/or analytical uncertainty.

Although the water temperature was still low in March 2015 (Fig. 2), a diurnal variability of POC and DOC was

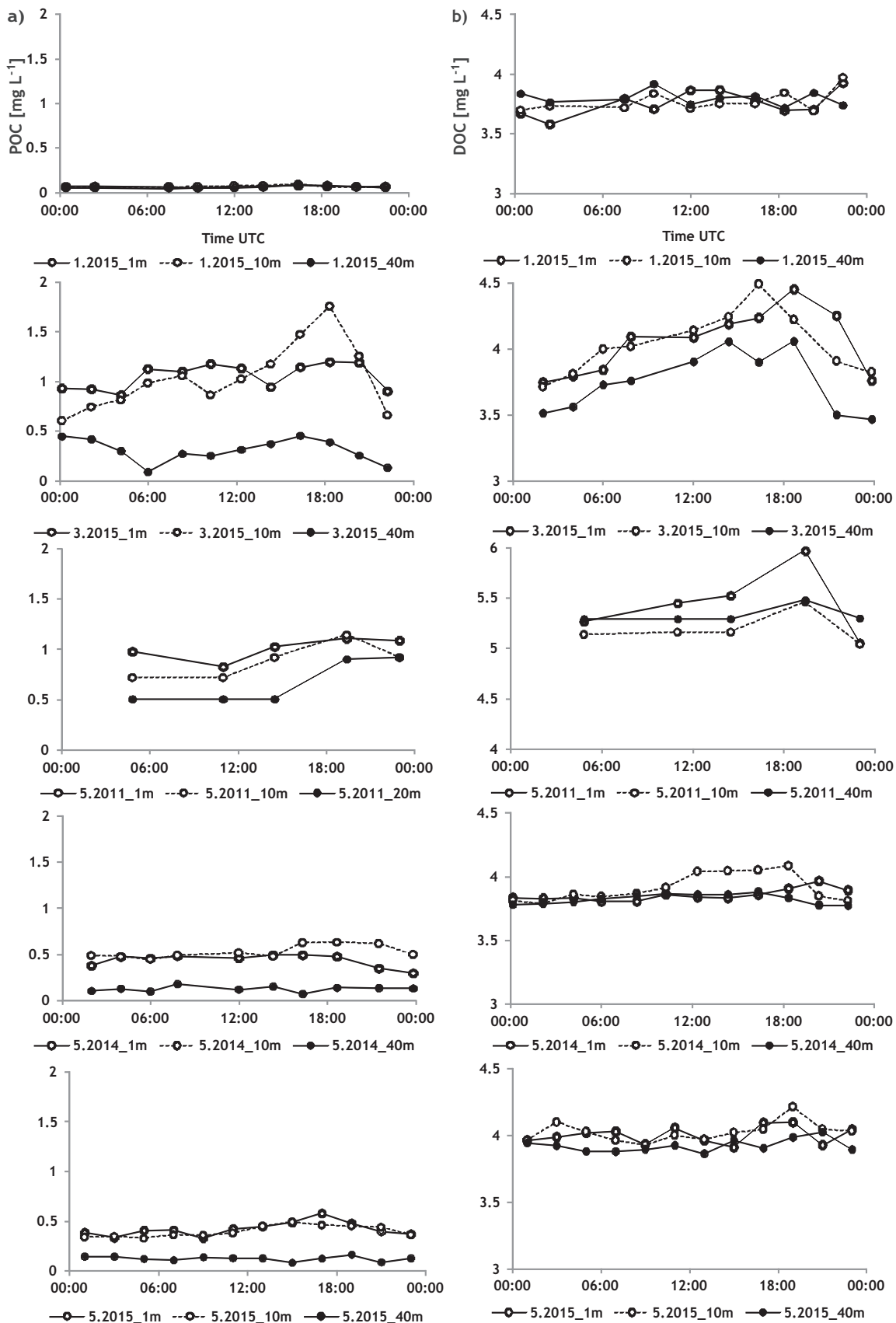


Figure 4 Diurnal variability in the (a) POC and (b) DOC concentrations measured in samples collected within a 24-h period (2-h resolution) in the Gdańsk Deep in May 2014, January, March, May, July, September, and November 2015 at water depths of 1 m, 10 m, and 40 m (in May 2011 samples were collected at water depths of 1 m, 10 m, and 20 m).

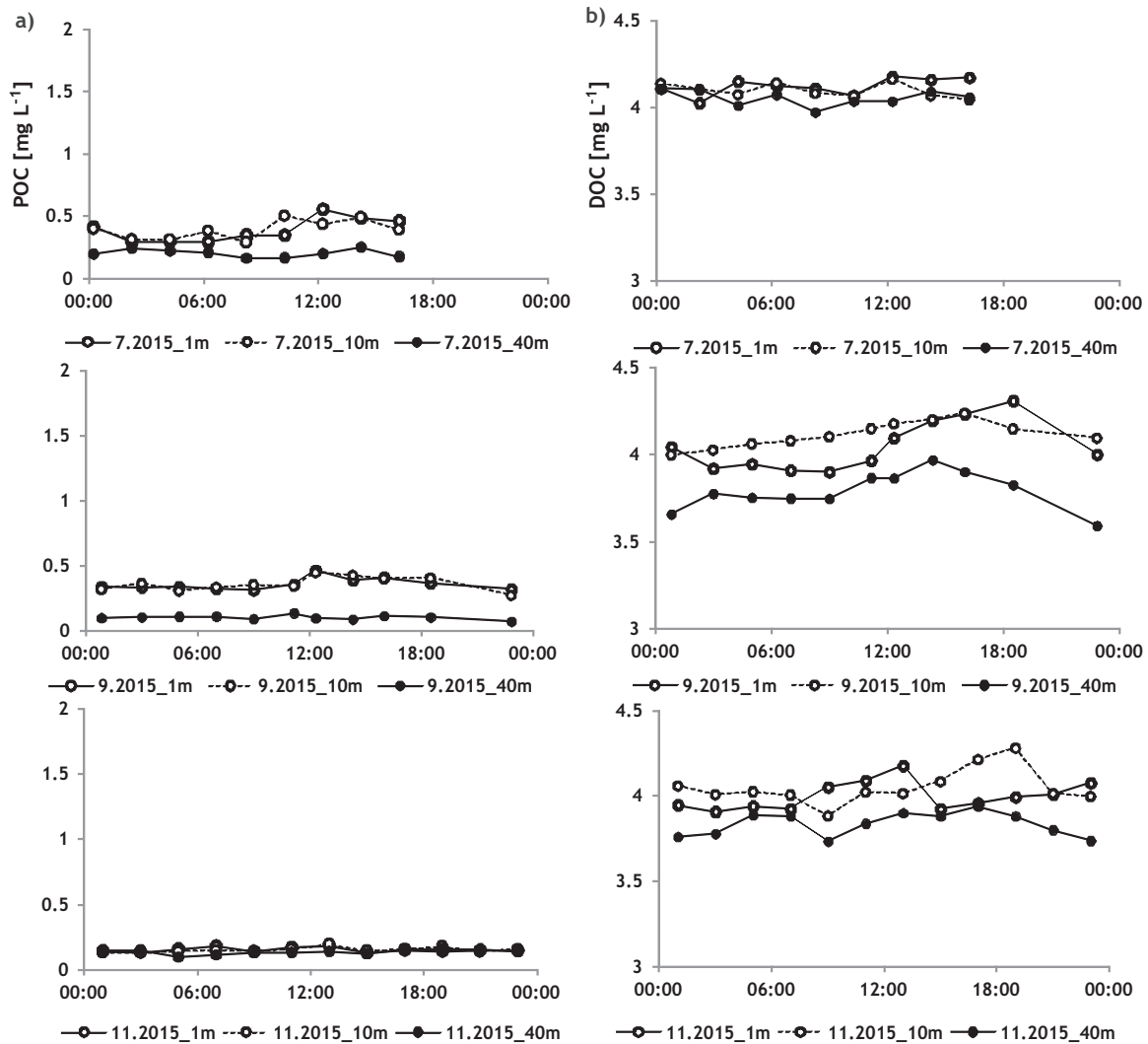


Figure 4. (Continued).

apparent at each of the investigated depths. The most pronounced diurnal changes were at a water depth of 10 m, where POC ranged from 0.6 mg L^{-1} to 1.8 mg L^{-1} and DOC from 3.8 mg L^{-1} to 4.1 mg L^{-1} . Chl *a* concentrations fluctuated as well. A statistically significant correlation ($R^2 = 0.7529$) between POC and Chl *a* in March 2015 together with a statistical discrepancy ($R^2 = 0.0999$) in January 2015 (Fig. 5) supported the conclusions that phytoplankton blooms are an important source of organic carbon in Baltic seawater (Dzierzbicka-Głowacka et al., 2010; Maciejewska and Pempkowiak, 2014, 2015) and that significant changes in the concentration of organic carbon can occur in a relatively short time.

Diurnal oscillations of POC and DOC were less obvious in May 2014, May 2015, July 2015, and September 2015 than in May 2011 (Fig. 4), perhaps due to the strong winds that prevailed before and at the time of sampling in 2014 and 2015. These would have caused water mixing down to a depth of $\sim 30 \text{ m}$ (Fig. 2) and thus dilution of the POC and DOC concentrations in the surface water layer by the deeper

water, which contains smaller organic substances concentrations (Fig. 4). Given that the diurnal variability was spread over depths of 1 m and 10 m, the arithmetic means of the DOC and POC concentrations at both were determined (Fig. 6). This allowed separation of the diurnal variations in the euphotic zone. The obtained results indicated that POC and DOC concentrations changed diurnally by 30% and 11% in May 2014, 35% and 6% in May 2015, 40% and 3% in July 2015, and 35% and 6% in September 2015, respectively. By contrast, the diurnal increase in the integrated concentrations of POC and DOC measured in the euphotic zone in January reached 15% and 1.5%, respectively.

POC and DOC diurnal oscillations were also observed at a water depth of 40 m in March 2015 and May 2011. This depth is located below the euphotic zone and above the halocline (transition zone, Fig. 2) therefore, identified organic carbon fluctuations, are most probably highly influenced by the downward flux of OM (Dzierzbicka-Głowacka et al., 2010; Maciejewska and Pempkowiak, 2014; Shinomura et al., 2005).

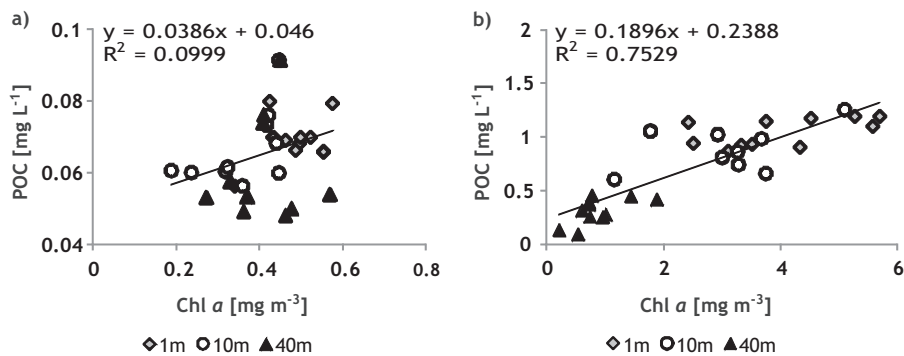


Figure 5 Plots of POC vs. Chl *a* based on measurements in samples collected within a 24-h period (2-h resolution) in the Gdańsk Deep at water depths of 1 m, 10 m and 40 m in (a) January 2015 and (b) March 2015.

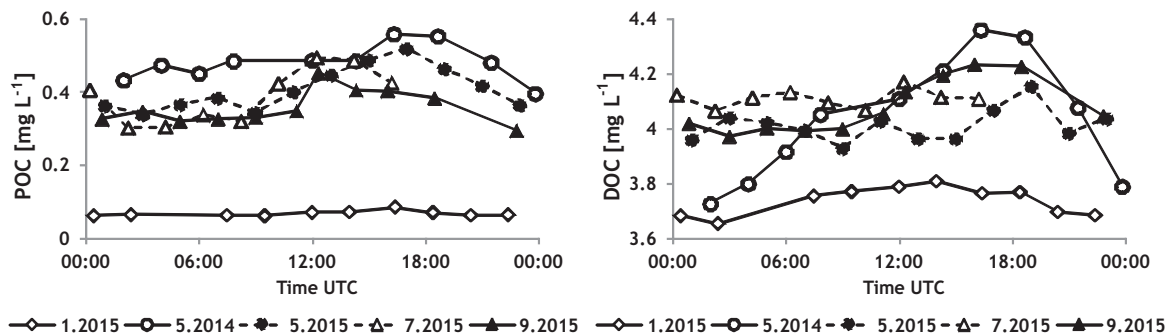


Figure 6 Diurnal variability in the integrated DOC and POC concentrations measured in samples collected within a 24-h period (2-h resolution) in the Gdańsk Deep at water depths of 1 m and 10 m.

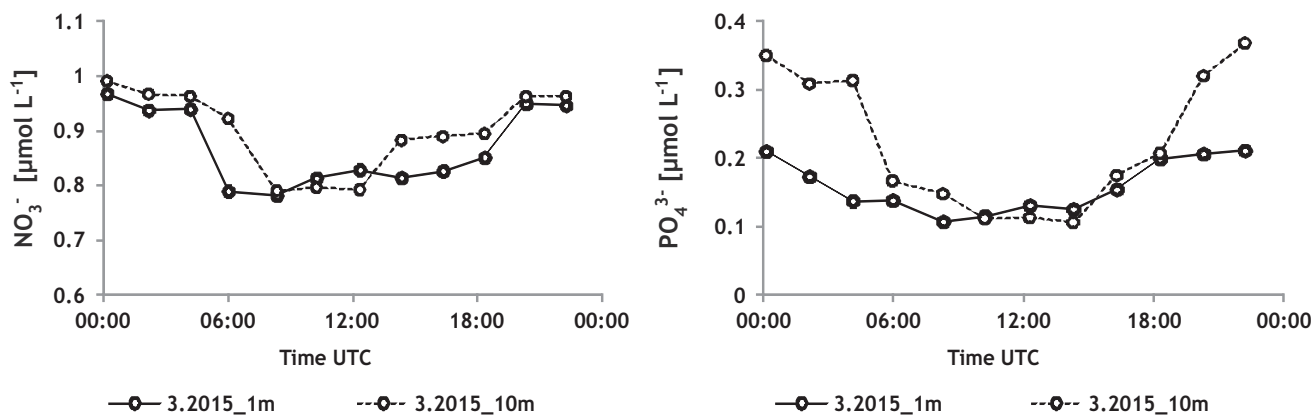


Figure 7 Diurnal variability of NO_3^- and PO_4^{3-} as measured in samples collected within a 24-h period (2-h resolution) in the Gdańsk Deep in March 2015 at water depths of 1 m and 10 m.

Similarly to POC and DOC, the strongest diurnal changes of NO_3^- and PO_4^{3-} concentrations were observed in March 2015 (Fig. 7) and displayed opposite pattern to that of diurnal fluctuations in DOC and POC concentrations. Nutrients concentrations were generally low during the day, but increased at night which is in line with results obtained by Falkowska et al. (1998) and Sikorowicz et al. (2005). Diurnal changes of NO_3^- and PO_4^{3-} during others sampling campaigns were more random (May, July, September) or the concentrations were rather stable throughout the study period (January,

November). The measured diurnal oscillations in nutrient levels indicated that the recovery of the nutrient pool and the recycling of the organic matter is fast, taking place within hours.

Our results demonstrate the significant diurnal and seasonal variability of POC and DOC measured in samples collected in the Gdańsk Deep. Hoikkala et al. (2015) compiled DOC data from the Baltic Sea and found significant spatial variability in DOC levels in the surface open waters, ranging from 3.1 mg L^{-1} to 5.8 mg L^{-1} . Maciejewska and Pempkowiak

(2015) attributed the horizontal DOC and POC variability in the Baltic Proper to temporal shifts in the spring bloom, whereas vertical changes were limited to the euphotic water layer and were accompanied by the mineralization of DOC released from sinking POC. In the deeper water layer, POC and DOC concentrations reflect the history of the inflows from the North Sea into the Baltic Sea.

3.4. Seasonal variability in $\delta^{13}\text{C}$ and its relationship to the origin of organic matter in the Baltic Sea

Organic matter is an important component of seawater as it influences the properties and processes occurring therein. In the Baltic Sea, most DOM is of terrestrial origin (Szczepańska et al., 2012). Generally, the geochemistry and properties of OM are complex and they depend on the proportion of terrestrial- vs. marine-derived fractions. The origin of OM is typically identified using an “end members” approach, which takes advantage of the stable isotopic composition of the C3 plants common on land and the C4 plants that comprise marine phytoplankton (Emerson and Hedges, 1988; Fontugne and Jouannea, 1987). Previous studies (Szczepańska et al., 2012; Voss et al., 2005) reported $\delta^{13}\text{C}$ values of approximately -22‰ and -28‰ for marine- and terrestrial-derived OM, respectively. In our investigations, the $\delta^{13}\text{C}$ of POC was measured in samples collected both diurnally and seasonally (Fig. 8). A significant seasonal variability in the average $\delta^{13}\text{C}$ content was determined that correlated well with the average POC concentrations; however as expected, no diurnal changes were observed. Based on the seasonal $\delta^{13}\text{C}$ characteristics, the values attributed to January (non-productive season) and March–May (productive season) may be those of refractory-terrestrial- and marine-derived OM, respectively. Thus, the average $\delta^{13}\text{C}$ values of the POC samples were $-27.4 \pm 1.1\text{‰}$ in winter (January) and $-25.7 \pm 0.8\text{‰}$ in spring (March and May 2015). As the $\delta^{13}\text{C}$ signature commonly assigned to marine-derived OM is -22‰ , estimates of the origin of sedimentary OM determined according to the end members method might be grossly biased and should be re-evaluated.

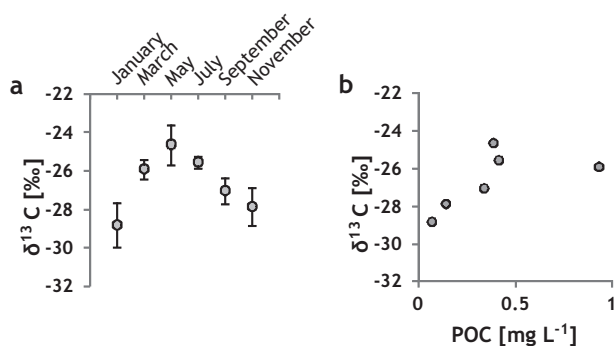


Figure 8 (a) Seasonal variability of the averaged $\delta^{13}\text{C}$ measured in surface samples collected in the Gdańsk Deep in 2015. (b) Plot of the averaged $\delta^{13}\text{C}$ vs. POC concentration measured in samples collected in the Gdańsk Deep in 2015.

4. Conclusions

Pronounced seasonal dynamics, characterized by much larger concentrations in the growing season than in winter, were determined. Out of eight series of measurements, two showed clear diurnal changes. The lack of distinct changes in the other six could be attributed to the absence of phytoplankton activity (January 2015 and November 2015) and/or the dilution of DOC and POC caused by intense water mixing (May 2014, May 2015, July 2015 and September 2015). By averaging the POC and DOC concentrations from the euphotic zone we were able to document their diurnal variability while ignoring the dilution of carbon species that occurred due to the mixing of water masses in May 2014, May 2015, July 2015, and September 2015.

Our results showed both seasonal and diurnal variabilities in the DOC and POC concentrations of the Baltic Sea. These should be taken into account in the planning of sampling campaigns and the interpretation of existing (e.g. monitoring) data, especially those obtained in productive seasons, when the diurnal variability (or lack thereof) in DOC, POC, and nutrient concentrations may (or may not) be significantly different depending on the time of day.

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