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ORIGINAL RESEARCH ARTICLE

Seasonal changes in particulate organic matter (POM) concentrations and properties measured from deep areas of the Baltic Sea

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Summary In seawater particulate organic matter (POM) serves as a food source for heterotrophic bacteria and zooplankton and is a source of dissolved organic compounds and nutrients. POM plays a critical role in transporting carbon to marine sediments where a fraction of it is buried in subsurface sediments and thus avoids conversion to carbon dioxide on shorter time scales.

Distribution and properties of POM were investigated in the Baltic Proper from 2013 to 2015. Particulate organic carbon (POC) was used to investigate POM sources and dynamics. Stable carbon isotopes ($\delta^{13}C$), elemental composition (C, N), chlorophyll *a* and POM contribution to suspended particulate matter (SPM) were also measured and interpreted. The water column exhibited concentrations ranging from 0.2 mg POC/l (deep water layer — DWL, cold season — CS) to 1.7 mg POC/l (surface water layer — SWL, warm season — WS). POM represented 0.15 to 0.45 of SPM during respective cold and warm seasons. Stable carbon isotopes ($\delta^{13}C_{POC}$) ranged from −22.5‰ (WS) to −28.0‰ (CS), while the POC/Chl *a* ratio ranged from 180 g/g (SWL-WS) to 300 g/g (DWL-CS). Seasonal changes were attributed to high primary production in the SWL during the WS, which represented a major POM source. Continuous mineralization/sedimentation throughout the water column constituted a major POM sink.

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1. Introduction

Particulate organic matter (POM) nominally consists of detritus, fecal pellets, phyto- and zooplankton cells and bacteria (Chen and Wagnersky, 1993; Dzierzbicka-Głowacka et al., 2010; Hygum et al., 1997). POM is a minor but important constituent of seawater, because it causes most of the light scattering and some of the light absorption observed in natural waters (Ferrari et al., 2003; Meler et al., 2017b; Woźniak et al., 2016). It thereby significantly influences euphotic zone thickness. POM also serves as a food source for heterotrophic bacteria and zooplankton (Andersson et al., 2017; Dzierzbicka-Głowacka et al., 2010; Hygum et al., 1997; Lowe et al., 2014) and is a source of dissolved organic compounds and nutrients (Dzierzbicka-Głowacka et al., 2011; Hygum et al., 1997). POM plays a critical role in transporting carbon to marine sediments where a fraction of it is buried in subsurface sediments and thus avoids conversion to carbon dioxide on shorter time scales (Koziorowska et al., 2018; Omstedt et al., 2014). Since POM transports carbon to sediment, it represents a critical mechanism in the biological pump (De La Rocha, 2006). High phytoplankton productivity and associated carbon burial thus modulate atmospheric CO_2 concentration (Hagström et al., 2001; Thomas et al., 2003).

Properties of land and marine-derived POM (e.g. C/N ratio, particles size spectrum, light scattering and absorption, susceptibility to biochemical oxidation) can vary significantly to form a relatively heterogeneous trophic reservoir (Lowe et al., 2014, 2016) and may cause variable oxygen consumption (Omstedt et al., 2014; Pempkowiak, 1983). Studies have thus sought to differentiate POM according to its origin. C/N molar ratios, chlorophyll *a* (Chl *a*) concentration and both carbon and nitrogen stable isotopic compositions have been analyzed and interpreted to this end (Liu et al., 2018). Previous studies have differentiated a low nitrogen (C/N molar ratio > 20) terrestrial vegetation contribution to organic matter based on carbon and nitrogen isotopic signatures (δ^{15}N: -2.0‰ to 0‰ and δ^{13}C: -30.0‰ to -23.0‰) from marine plankton exhibiting both nitrogen (C/N < 10) and heavy carbon and nitrogen isotopes enrichments (δ^{15}N in the range of 4—6‰ and δ^{13}C equal to -22.0‰) (Thornton and McManus, 1994; Voss et al., 2005). An end-member approach has been used to evaluate proportions of marine-derived versus terrestrial POM fractions (Thornton and McManus, 1994). Quantifying contributions of marine and terrestrial POM using this model requires detailed knowledge on the natural elementals and isotopic ranges of end-members for a given study region (e.g. Goñi et al., 2003; Liu et al., 2018; Thornton and McManus, 1994). However, most reports simply cite "typical" end-member values such as -22.0‰ and -27.0‰ for $\delta^{13}C_{POC}$ values representing respective marine phytoplankton and terrestrial POC sources (Coban-Yıldız et al., 2006; Koziorowska et al., 2016; Kravchishina et al., 2018; Liu et al., 2018; Maksymowska et al., 2000; Szczepańska et al., 2012; Voss et al., 2005; Winogradow and Pempkowiak, 2014).

As the major component of POM, particulate organic carbon (POC) is interpreted as a proxy for POM (Chester, 2003). Recent optical methods, including remote sensing, have been used to directly assess both POM concentrations in seawater as well as inorganic and organic proportions in suspended particulate matter (SPM) (Meler et al., 2017b; Woźniak et al., 2016). Results obtained by these new approaches are a subject to substantial uncertainties. Reducing this uncertainty requires local empirical data. Remote sensing methods provide efficient, high coverage data on water bodies but can only survey surface layers for the parameters interpreted here.

Several sources contribute POM to seawater. The contribution of POM derived from a particular source to total POM depends on factors such as phytoplankton and zooplankton productivity, abrasion in coastal environments and proximity to estuaries. Atmospheric transport is considered to be of only minor importance (Dzierzbicka-Głowacka et al., 2010; Kuliński and Pempkowiak, 2011). Concentrations of POM in coastal areas are typically much higher than in open ocean environments as most POM sources derive, directly or indirectly, from river run-off. The sources include also seepage (Szymczycha et al., 2014) and direct discharges (Pempkowiak and Obarska-Pempkowiak, 2002). This is the case with coastal environments and land-locked seas like the Baltic Sea. The Baltic experiences enhanced primary production that reaches 250 g/m^2 per annum (Andersson et al., 2017; Kuliński and Pempkowiak, 2011; Leppakowski and Mihnea, 1996). POC concentrations in the Baltic Sea depend on Chl *a*, river run-off and on both water salinity and depth variation resulting from stratification of the Baltic water column (Kuliński and Pempkowiak, 2008; Maciejewska and Pempkowiak, 2014). Statistical studies have found that phytoplankton activity followed by water depth are the most important factors influencing POC concentrations in the water column of the southern Baltic (Maciejewska and Pempkowiak, 2015; Szymczycha et al., 2017). High phytoplankton productivity thus enhances POM abundance in the Baltic (Maciejewska and Pempkowiak, 2015). Concentrations of POC in the Baltic range from 0.05—1.80 mg/dm^3, while POC mass contribution to total SPM ranges from 0.13—0.42 (Andersson and Rudehall, 1993; Burska et al., 2005; Maciejewska and Pempkowiak, 2014; Meler et al., 2017b; Woźniak et al., 2018). POC concentrations exhibit seasonal and vertical gradients (Burska et al., 2005; Dzierzbicka-Głowacka et al., 2010; Maciejewska and Pempkowiak, 2014) and significant spatial variation in open water areas. These might arise due to shifts in the start of the growing season and its duration at different locations (Maciejewska and Pempkowiak, 2014). POM is exchanged horizontally through the Danish Straits with the North Sea (Hakanson and Eckhell, 2005; Kuliński et al., 2011; Thomas et al., 2003). The POM concentration depends on the distance from land with coastal and estuarine areas hosting more organic matter than open waters (Maciejewska and Pempkowiak, 2014). Planktonic activity may contribute to large seasonal fluctuations in POM (Dzierzbicka-Głowacka et al., 2011).

Many studies have examined POM properties and distribution in the Baltic Sea. The sampling campaigns from which these studies drew, however, often lasted only a matter of days and occurred mostly during the summer (Bianchi et al., 1997; Burska et al., 2005; Engel et al., 2002; Lundsgaard et al., 1999; Schumann et al., 2001; Tamelander and Heiskanen, 2004; Voss et al., 2005). Few studies have addressed seasonal variation in POM dynamics for open water environments (Schneider et al., 2015; Struck et al., 2004; Szymczycha et al., 2017) but considerable uncertainties about this topic remain. Studies on Baltic Sea POM revealed that in summer C/N ratios range from 7—10, δ^{13}C values — from -22.5‰ to -28.0‰ and δ^{15}N values — from 1.0‰ to 6.0‰

(Maksymowska et al., 2000; Szymczycha et al., 2017; Voss and Struck, 1997; Voss et al., 2005). A recent three-year study quantified organic carbon concentrations in Baltic waters to elucidate factors influencing this reservoir. Temperature, pH (photosynthesis intensity), Chl *a* (abundance of phytoplankton), Pheo *a* (sloppy feeding by zooplankton) and salinity (provenance of water masses) were used as proxies for environmental factors conditioning POC distribution (Maciejewska and Pempkowiak, 2014, 2015; Szymczycha et al., 2017). Using temperature to track seasonality, Chl *a* was interpreted as an index of live phytoplankton biomass (Wasmund and Uhlig, 2003) and Pheo *a* concentrations served as an index of phytoplankton mortality, including sloppy zooplankton grazing (Collos et al., 2005; Meyer-Harms et al., 1999). The influence of fluvial and oceanic water masses was interpreted from salinity measurements (Abril et al., 2002; Kuliński and Pempkowiak, 2011). The intensity of photosynthesis was interpreted from pH values.

Results of numerical modeling indicate that POC concentrations depend on the light intensity, water temperature and nutrient availability (Almroth-Rosell et al., 2011; Dzierzbicka-Głowacka et al., 2010; Gustafsson et al., 2015; Segar, 2012).

The parameters listed above (C/N, δ^{13}C, δ^{15}N, Chl *a*, Pheo *a*, POC) depend on primary productivity. As such, they should vary systematically with season and water depth due to the interplay between marine and fluvial contributions in establishing the halocline and contributing POM from their respective marine and terrestrial sources. The nature of this systematic variation has never been documented for the Baltic Sea.

While studies have documented the concentration dynamics of organic matter in the Baltic, properties of POM have not been monitored in tandem with factors affecting its spatial and temporal variation. For example, little is known about POM and Chl *a* seasonal variations. Several studies have predicted shifts in both particulate and dissolved organic matter in the near future (Dzierzbicka-Głowacka et al., 2011; Gustafsson et al., 2015; Straat et al., 2018). Acquiring a robust baseline or present-day understanding of these parameters and of basin dynamics can help contextualize future changes. This study monitored POM characteristics and relationships between POM and environmental parameters in open water areas of the Baltic Sea from 2013—2015. The aim was to document and interpret seasonal changes in both POM concentrations and POM properties.

2. Study area

The Baltic Sea extends from 10—30°E and 54—64°N (Fig. 1) and represents the second largest brackish water body in the world. The connection with the North Sea via Danish straits and the Kattegat results in saline water inflows and stable stratification of the basinal water columns. Within the halocline, fully saline waters occur at 60—80 m depth. The sea water volume reaches some 22,000 km^3 with annual runoff equal to 440 km^3. Average annual precipitation is 270 km^3 and net inflow from the North Sea is 470 km^3 (Björck, 1995; HELCOM, 2007; Łomniewski et al., 1975). The Baltic Sea receives considerable volumes of freshwater (440 km^3; Voipio, 1981) and organic carbon (2.93 Tg C yr^1, Tg = 10^{12} g; Kuliński and Pempkowiak, 2011; Szymczycha et al., 2014).

The Baltic is a bathymetrically complex, brackish and enclosed shelfal sea (Leppakowski and Mihnea, 1996). The basin has an average depth of about 53 m but also consists of deeper bathymetric features called 'deeps'. These exhibit well-developed water column stratification. The main deeps of the Southern Baltic are the Gdańsk Deep, the Gotland Deep and the Bornholm Deep.

The Gdańsk Deep (maximum depth: 118 m) hosts a permanent halocline located at 60—80 m depth. Surface water layers have relatively low salinity ranges of between 7.1 and 7.8.

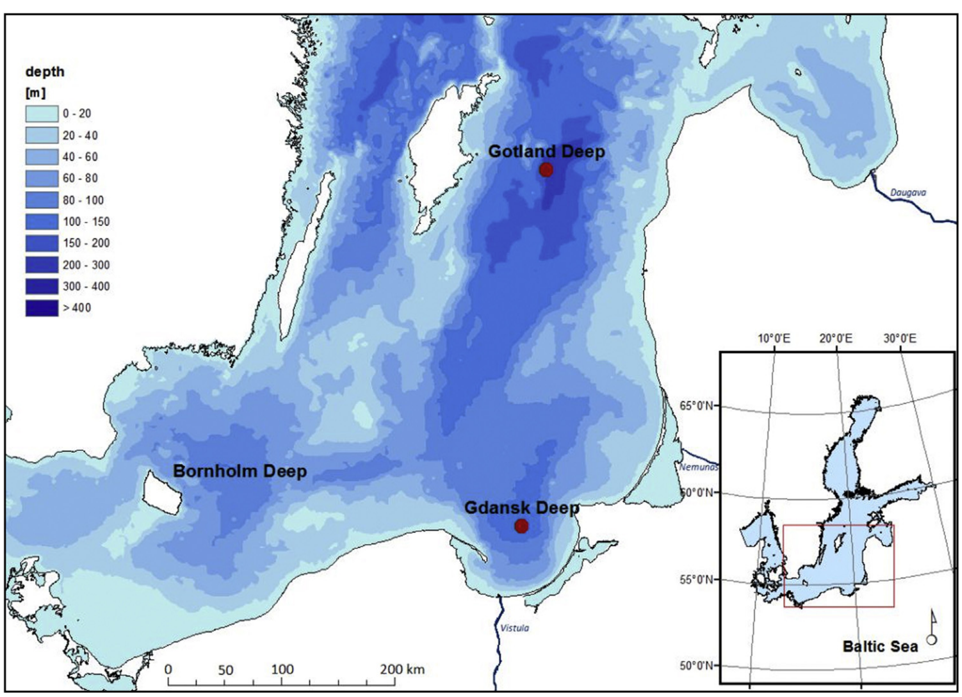

Figure 1 Location of the study sites, the Gdańsk Deep and Gotland Deep.

Seasonal temperature variation ranges from 1°C (January) and 20°C (July). Subsurface layers have higher salinity ranging from 10—13 and temperature of around 4°C (Szczepańska and Uścinowicz, 1994; Voipio, 1981). The Gotland Deep reaches a maximum depth about 250 m and is a stratified basin with a halocline developed at 60—70 m depth. The stratification of the water column limits oxygen concentration at depth and promotes bottom water oxygen depletion (Leipe et al., 2011; Szczepańska and Uścinowicz, 1994; Voipio, 1981).

Plankton in the Baltic Sea mostly appear during two seasonal blooms. The spring bloom (March—May) is typically dominated by dinophytes and/or diatoms (80—95% of total biomass) with a minority of chlorophytes, cryptophytes and cyanobacteria. This bloom contributes about half of the annual primary production. The autumn bloom (August—September) is dominated by cyanobacteria along with dinophytes and chlorophytes as the other main contributors (Andersson et al., 2017; Stoń et al., 2002; Wasmund and Uhlig, 2003). Previous field studies have suggested that Baltic primary production is mostly nitrogen limited, but the activity of nitrogen-fixing cyanobacteria during some periods of the year may result in phosphorus limitation (Kivi et al., 1993).

Primary productivity in the Baltic proper is nitrogen limited in the summer, and constrained by light and temperature in the winter (Dzierzbicka-Głowacka et al., 2010). Annual primary productivity showed distinct spatial and temporal variations of 100—200 g C m^{-2} yr^{-1} with the highest rates during late spring. Primary productivity increased between 1950 and 1990 by some 50% but has more or less stabilized since then (HELCOM, 2007; Szymczycha et al., 2019).

3. Material and methods

3.1. Sampling sites, temperature and salinity measurements

Sampling and analysis focused on two sites, the Gdańsk Deep (ϕ = 54°50′N, λ = 18°17′E) and Gotland Deep (ϕ = 57°18′N, λ = 19°53′E). Both sites are at a spatial remove from the influence of river run-off (Voss et al., 2005). The sites were sampled and monitored over 23 visits from March 2013 to July 2016. Site visits included in situ temperature and salinity measurements using a Sea-Bird Scientific SBE 911 Plus CTD profiler. The samples are attributed to two seasons: warm (WS) and cold (CS). The former includes samples collected in the period from April to September, while the latter samples collected from November to March.

3.2. Water sampling, pH measurements and SPM: separation and storage

Seawater samples were collected from several depths at study sites using Niskin bottles deployed during r/v *Oceania*, r/v *Alkor* and r/v *Aranda* research cruises. Immediately after sampling, pH was measured using a WTW Multi 3400i pH meter (0.01 unit accuracy), while 1—2 liters of seawater were passed through pre-combusted and pre-weighted MN GF 5 (0.4 μm nominal pore size) glass-fiber filters to collect SPM. Filters with SPM were stored at −80°C until further laboratory analysis. To characterize SPM, we measured POC (particulate organic carbon), PN (particulate nitrogen), Chl *a* (chlorophyll *a)*, Pheo *a* (pheopigment *a*), δ^{13}C of POM ($\delta^{13}C_{POC}$) and δ^{15}N of PN.

3.3. Chlorophyll *a* (Chl *a*) and pheopigment *a* (Pheo *a*) analyses

Chl *a* was measured spectrophotometrically (Hitachi U-2800 spectrophotometer) from solvent extracted SPM. Filters bearing SPM samples were rinsed in 90% acetone following procedures described in Parsons (1966). Chl *a* concentrations were calculated using the Lorenzen (1967) formulas. Spectrophotometry was also used to measure Pheo *a* from acetone extracts after acidification (60 μl of 1 M HCl were added to 5 ml of the extract). Quality control included measurements of blanks. Limit of detection, defined as average blank plus five times standard deviations of blank measurements, was far below the results of actual samples measurements (it was smaller than 3% of the smallest measured Chl *a* concentration).

3.4. Particulate organic carbon (POC), particulate nitrogen (PN) and stable isotopic analyses ($\delta^{13}C_{POC}$ and δ^{15}N)

For carbon and nitrogen analyses, the MN GF 5 (0.4 μm pore size) glass fiber filters with SPM samples were dried at 60°C for 24 h and then weighed (0.01 mg accuracy) and homogenized. POC, PN, $\delta^{13}C_{POC}$ and δ^{15}N analyses were carried out using an Elemental Analyzer Flash EA 1112 Series combined with the Isotopic Ratio Mass Spectrometer IRMS Delta V Advantage (Thermo Electron Corp., Germany). Analytical procedures followed those described in Winogradow and Pempkowiak (2018). Dry, homogenized filter with POM (30—40 mg) was weighed, transferred into a silver crucible and acidified with 2 M HCl to remove carbonates. After additional drying, samples were transferred to the instrument for high-temperature combustion (oxidation at 1020°C, followed by reduction over copper at 680°C). Analytical blanks were used to verify measurement stability. The LKSD-1 reference material was analyzed after every 10 unknowns to confirm accuracy. The average recovery (n = 5) was 97.1 ± 1.0%. Isotopic ratios $\delta^{13}C_{POC}$ and δ^{15}N were calculated using pure, laboratory grade CO_2 and N_2 reference gases calibrated against IAEA standards CO-8 and USGS40 for δ^{13}C and N-1 and USGS40 for δ^{15}N. Sample $\delta^{13}C_{POC}$ and δ^{15}N values are given in the conventional delta notation relative to PDB for $\delta^{13}C_{POC}$ and relative to atmospheric nitrogen for δ^{15}N.

Quality control included measurements of blanks and reference materials. Limit of POC and PON detections was respectively 0.001 mg/l and 0.002 mg/l, and was smaller than 3% of the smallest measured POC, and 8% of the smallest measured PN concentrations.

4. Results and interpretation

4.1. Temperature and salinity

Fig. 2 shows profiles of water column salinity for the Gdańsk Deep and the Gotland Deep. Surface water layers (SWL) for both deeps are characterized by a salinity range of 7.2 to 7.6 psu. Salinity increases up to 12.5 psu within the halocline

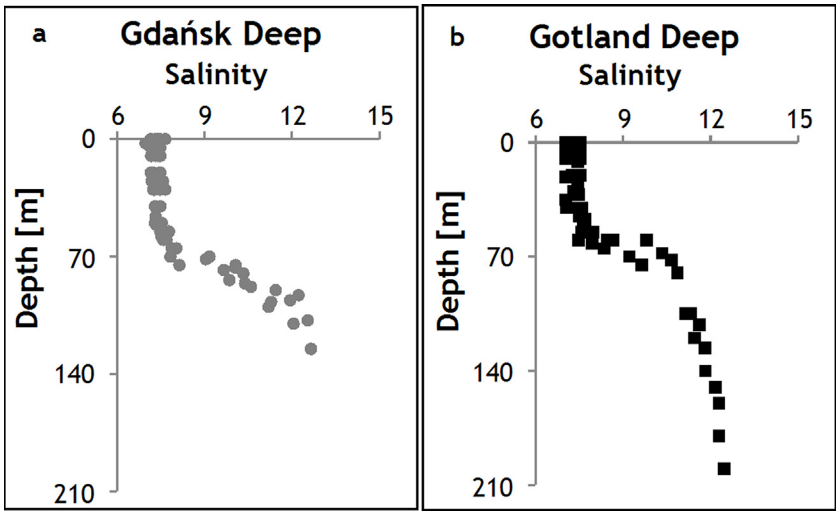

Figure 2 Vertical salinity profiles for the (a) Gdańsk Deep and (b) Gotland Deep as measured during the 2013—2015 study period.

and remains within a 12.5—12.8 psu range below the halocline, hereafter referred to as the deep water layer, or DWL (in the figures the 'deep water layer' is addressed as the 'subsurface water layer'). In both deeps, the halocline resides between 60 and 85 m depth requiring careful sampling of the Gdańsk Deep DWL so as not to re-suspend sediment. Both deeps exhibited halocline salinity gradients of 0.2 psu/m. Salinity showed no signs of systematic shifts over the course of a year. The salinity distribution in the study area indicates stratification caused by the salinity/density gradient and clearly distinguishes both the DWL and SWL. These two water layers persist throughout the year above and below the halocline. Stratification of the Baltic Proper water column arises due to the relatively high density of saline seawater entering the Baltic from the North Sea and fresher surface water contributed by river runoff (Burska et al., 2005; Rak, 2016; Voipio, 1981).

Fig. 3a shows typical water column temperature profiles for the two deeps. Temperatures for the SWL were lower during the cold season (4°C) than during the warm season (17°C) and displayed a range typical of the Baltic Proper (Szymczycha et al., 2019; Voipio, 1981). Temperature profiles for the WS did not appear to show well-developed thermoclines, possibly due to surface water mixing at the time of measurement (Szymczycha et al., 2017). The DWL exhibited a relatively consistent 4—6°C temperature range. Fig. 3b shows average monthly temperatures for the Gdańsk Deep (Figure S1 — Gotland Deep). The SWL exhibited temperature increases in April—July and decreases in September—January. The surface water layer thus appears to experience a cold season (CS: November to March) and a warm season (WS: April to October). This type of seasonal temperature oscillations is typical of seas in temperate climate regions (Sheppard (2019)) and is consistent with numerous previous observations of the Baltic (Rak, 2016; Szymczycha et al., 2019; Voipio, 1981).

4.2. Chlorophyll *a* (Chl *a*) and pheopigment *a* (Pheo *a*)

Fig. 4a shows typical profiles of Chl *a* concentrations in the water column for both deeps. Concentrations reached up to

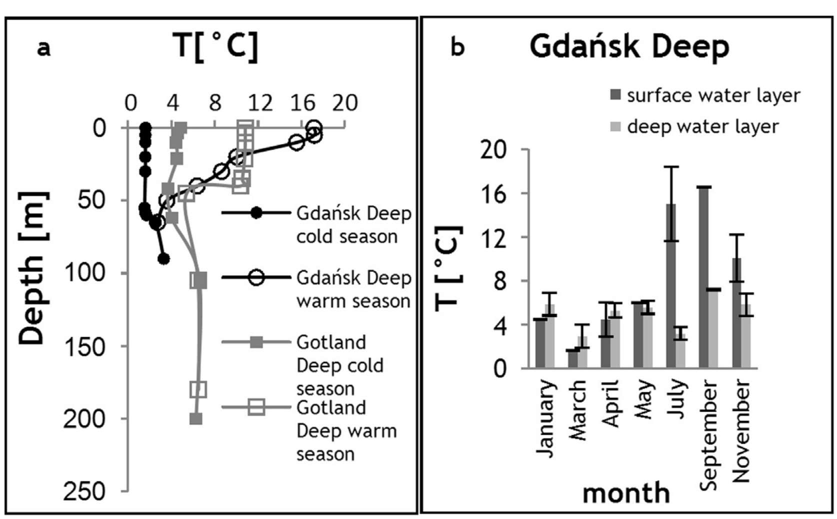

Figure 3 (a) Typical vertical profiles of water temperature in Gdańsk Deep and Gotland Deep during the cold season and warm season; (b) average monthly temperatures measured from surface and deep water layers of the Gdańsk Deep.

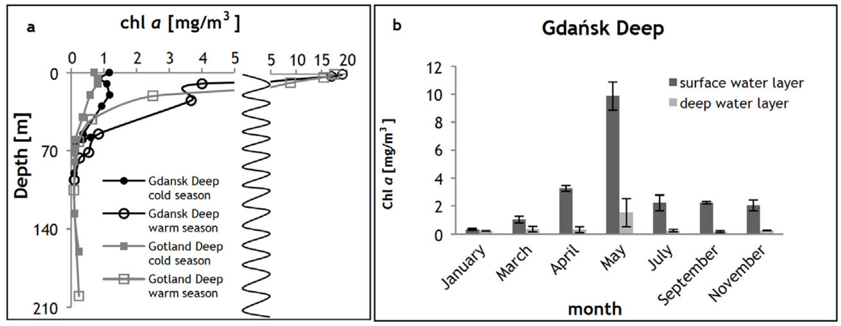

Figure 4 (a) Typical vertical profiles of chlorophyll *a* concentrations in water of Gdańsk Deep and Gotland Deep in cold season and warm season; (b) average monthly chlorophyll *a* concentrations in the surface and deep water layers of the Gdańsk Deep.

20 mg/m^3 in the SWL during the WS due to the spring bloom (Maciejewska and Pempkowiak, 2014). Concentrations in the DWL did not exceed 0.3 mg/m^3 indicating that sinking POM originating from the spring bloom had not reached the DWL at the time of measurement. Previous studies have reported similar Chl *a* values and water column distribution (Heiskanen et al., 1998; Maciejewska and Pempkowiak, 2014). Vertical Chl *a* profiles sometimes showed a shoulder or even a clear maximum at around 20 m depth (Fig. 4a shows Gdańsk Deep). This 'deep Chl *a* maximum' has been interpreted as evidence of increased phytoplankton abundance (Liu et al., 2018).

Fig. 4b shows the average monthly Chl *a* concentrations in the Gdańsk Deep (Figure S2 — Gotland Deep). The SWL exhibited greater Chl *a* concentrations (>1 mg/m^3, except January) than the DWL (<0.3 mg/m^3, except May). The SWL also showed an increase of Chl *a* beginning in March with a peak in May, followed by a decrease between November and January. During the CS, SWL Chl *a* concentrations did not exceed 1.3 mg/m^3 but were never lower than 2 mg/m^3 during the WS. Concentrations of Chl *a* in the DWL were constant at 0.3 mg/m^3 (except May) throughout the year.

Shifts in both temperature and Chl *a* concentrations (Fig. 3a and Fig. 4a) indicate that the SWL can assume two states. In one, the WS experiences increased Chl *a* concentrations indicative of phytoplankton abundance and high growth rates. In the other, the CS exhibits low Chl *a* concentrations indicating limited phytoplankton activity and lack of growth. The temperature and Chl *a* concentrations in the DWL remain constant throughout the year, except for Chl *a* in May. Elevated Chl *a* concentrations in the Gdańsk Deep in May most likely arise from the sinking of biomass products of a spring bloom that must have begun early enough for products to reach the DWL within several weeks. Previous studies have described similar concentration ranges and timing of Chl *a* changes in the Gdańsk Deep (Burska et al., 2005; Szymczycha et al., 2017) and the Gotland Deep (Maciejewska and Pempkowiak, 2014).

Fig. 5a shows concentrations of Pheo *a* measured from the Gdańsk Deep and Gotland Deep. Fig. 5b shows monthly averages of Pheo *a* in Gdańsk Deep (Figure S3 — Gotland Deep). Concentrations from the SWL (0.1—0.5 mg/m^3 during the CS and 0.7—1.5 mg/m^3 during the WS) exceeded those measured from the DWL (0.1—0.3 during the CS and 0.1—0.5 mg/m^3 during the WS). The observed concentrations fell within the range of previously reported values for the Gdańsk Deep by Burska et al. (2005). Pheo *a* concentrations and dynamics were interpreted as reflecting cycling of phytoplankton biomass (Burska et al., 2005; Struck et al., 2004) and sloppy zooplankton feeding (Collos et al., 2005; Meyer-Harms et al., 1999; Spence and Steven, 1974).

4.3. Suspended particulate matter (SPM)

Fig. 6a shows typical SPM profiles from water columns of the study area. Concentrations in the SWL (0.6—1.1 mg/l during the CS and 2—4 mg/l during the WS) exceeded those observed

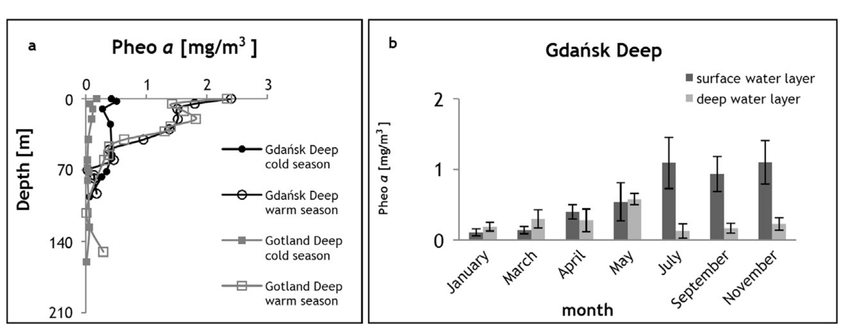

Figure 5 (a) Typical vertical profiles of pheopigment *a* concentrations measured from the Gdańsk Deep and Gotland Deep during the cold and warm seasons; (b) average monthly pheopigment *a* concentrations measured from surface and deep water layers of the Gdańsk Deep.

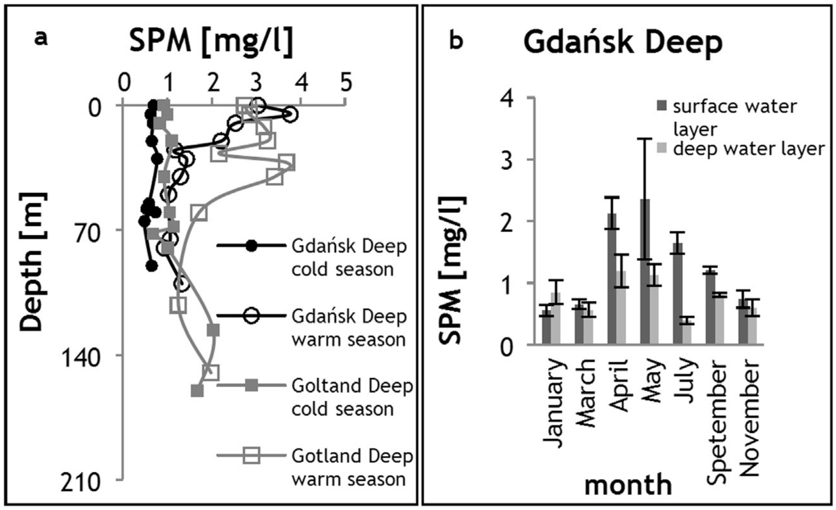

Figure 6 (a) Typical vertical profiles of suspended particulate matter (SPM) concentrations measured from the Gdańsk Deep and Gotland Deep during the cold and warm seasons; (b) average monthly SPM concentrations measured from surface and deep water layers of the Gdańsk Deep.

from the DWL (0.6 mg/l during the CS and 1.6 mg/l during the WS). The concentrations fell within ranges reported in previously published studies of the Gdańsk Deep (Burska et al., 2005; Maciejewska and Pempkowiak, 2014) and the Gotland Deep (Maciejewska and Pempkowiak, 2014; Meler et al., 2017b; Struck et al., 2004; Woźniak et al., 2018). Concentration profiles shown in Fig. 6a indicate similar SPM values for the SWL and DWL during the CS (concentrations were constant at some 0.4 mg/l) but higher SPM concentrations in the SWL (1.5 mg/l) relative to the DWL (0.4 mg/l) during the WS.

Fig. 6b shows monthly average SPM concentrations in the Gdańsk Deep (Figure S4 shows monthly average SPM for the Gotland Deep). From November to March, the DWL and SWL exhibited similar SPM concentrations of about 0.6—0.8 mg/l. Average SPM concentrations exceeding 2 mg/l (SWL) and 1 mg/l (DWL) were measured in April and May. Previously published studies have described seasonal variation in vertical SPM gradients (Burska et al., 2005; Struck et al., 2004; Szymczycha et al., 2017; Tamelander and Heiskanen, 2004). Burska et al. (2005) and Woźniak et al. (2018) reported that the POM contribution to SPM varies over the course of a year from 30% (CS) to 80% (WS). This highlights the significance of the planktonic biomass contribution to SPM.

4.4. Particulate organic carbon (POC) and particulate nitrogen (PN)

Fig. 7a and b show vertical POC and PN profiles. The SWL POC concentrations during the WS (up to 1.4 mg/l) exceeded those observed during the CS (0.1 mg/l). Respective CS and WS PN concentrations were 0.03 mg/l and up to 0.15 mg/l. The respective CS and WS DWL POC concentrations were 0.02 mg/l and 0.4 mg/l while PN concentrations were 0.04 mg/l and 0.015 mg/l (respectively for CS and WS). Fig. 7c and d show average monthly POC and PN concentrations for the Gdańsk Deep (Figure S5 — Gotland Deep). These show an increase in SWL POC between March (0.1 mg/l) and April (0.3 mg/l) with maximum concentrations observed in May (0.8 mg/l). These were followed by a steady decline to 0.3 mg/l in September, 0.15 mg/l in November and 0.08 mg/l in January. The DWL POC concentrations ranged from 0.07 mg/l (March) to 0.23 mg/l (May). These variations reflect phytoplankton and cyanobacterial abundance (source) vs grazing activity of zooplankton, POM mineralization and POM particle sedimentation (sinks) (Grossart and Ploug, 2001; Maciejewska and Pempkowiak, 2015; Struck et al., 2004).

The period from November to March experienced low PN concentrations (below 0.05 mg/l in the SWL and 0.02 mg/l in the DWL). The period from April to September experienced elevated PN concentrations (0.08 mg/l in the SWL and 0.02 mg/l in the DWL). May observations include exceedingly high PON concentrations (on average 0.08 mg/l in the SWL and 0.02 mg/l in the DWL). The concentrations observed fell within ranges reported for the Baltic Proper water column and typical seasonal SWL and DWL values therein (Andersson and Rudehall, 1993; Burska et al., 2005; Engel et al., 2002; Maciejewska and Pempkowiak, 2014; Struck et al., 2004; Szymczycha et al., 2017).

4.5. POM stable isotopic data: $\delta^{13}C_{POC}$ and $\delta^{15}N$

Fig. 8a shows water column $\delta^{13}C_{POC}$ profiles for selected areas. These exhibit a steep vertical $\delta^{13}C_{POC}$ gradient during both the CS and WS. In Gotland Deep the WS SWL values exceeded those measured from the DWL (−24.0‰ vs. −27.5‰) but CS data showed the opposite trend (−27.5‰ vs. −25.5‰). Average monthly $\delta^{13}C_{POC}$ values in the Gdańsk Deep (Fig. 8b) increased from January to May and decreased from July to January in the SWL. The DWL data exhibits a similar but more subtle trend. SWL $\delta^{13}C_{POC}$ ranged from −27.0‰ to −28.0‰ during the CS, while WS $\delta^{13}C_{POC}$ ranged from −23.0‰ to −26.0‰ (except July: −25.0‰). DWL $\delta^{13}C_{POC}$ values ranged from −26.0‰ to −28.0‰ throughout the year. Both deeps exhibit similar $\delta^{13}C_{POC}$ values and patterns (Fig. 8a, Figure S6) indicating comparable $\delta^{13}C$ distribution and dynamics (Table 1). The $\delta^{13}C_{POC}$ also resembled that reported from earlier studies of the Gdańsk

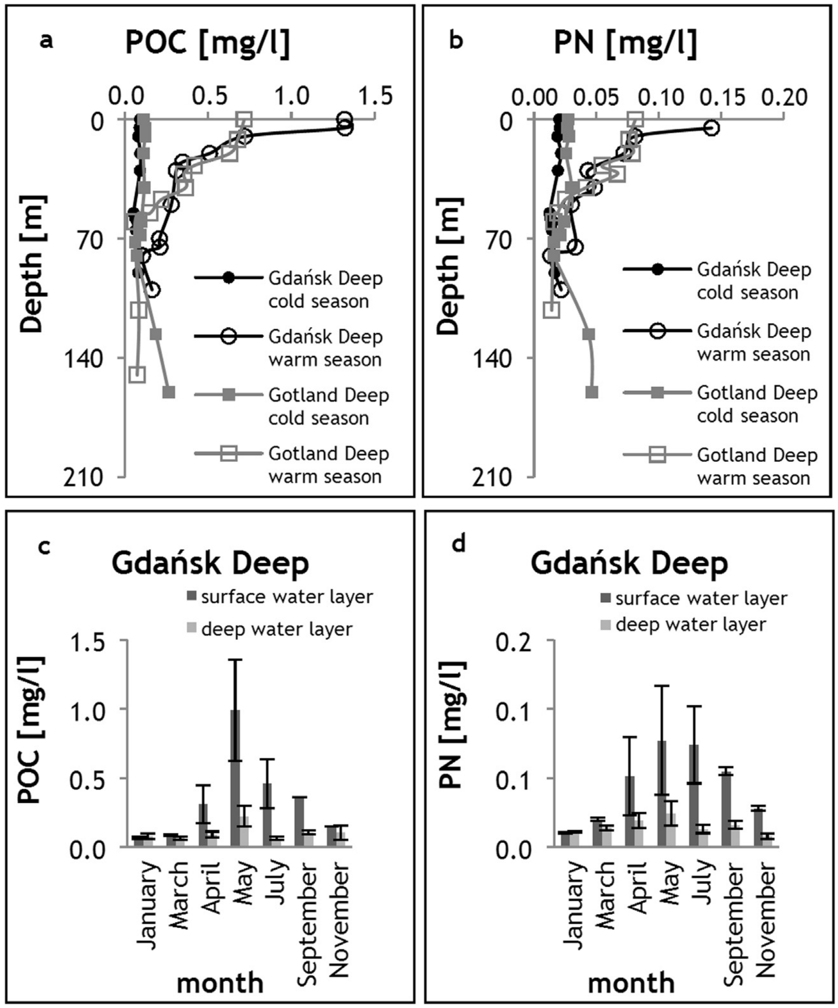

Figure 7 (a) Typical vertical profiles of POC concentrations in Gdańsk Deep and Gotland Deep; (b) typical vertical profiles of PN concentrations measured from the Gdańsk Deep and Gotland Deep; (c) average monthly POC concentrations measured from the Gdańsk Deep; (d) average monthly PN concentrations measured from the Gdańsk Deep.

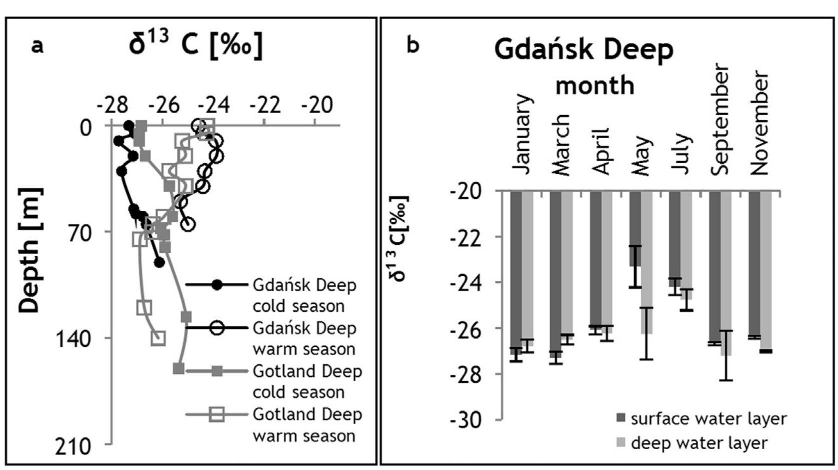

Figure 8 (a) Typical vertical profiles of $\delta^{13}C_{POC}$ values measured from the Gdańsk Deep and Gotland Deep during the cold and warm seasons; (b) average monthly $\delta^{13}C_{POC}$ values measured from surface and deep water layers of the Gdańsk Deep.

Table 1 Average concentrations and properties of particulate organic matter analyzed from the Gdańsk Deep and the Gotland Deep in surface water layer (SWL) and deep water layer (DWL) during warm season (WS) and cold season (CS).

Property	Unit	Average $\pm\ \sigma$(*)							
		Gdańsk Deep				Gotland Deep			
		SWL		DWL		SWL		DWL	
		WS	CS	WS	CS	WS	CS	WS	CS
Salinity	–	7.19 ± 0.16	7.27 ± 0.13	11.78 ± 0.63	11.18 ± 0.64	7.34 ± 0.12	7.29 ± 0.17	11.50 ± 0.87	11.53 ± 0.42
Temperature	°C	10.75 ± 4.51	4.94 ± 1.94	4.29 ± 1.08	4.27 ± 1.37	11.09 ± 4.52	308 ± 1.22	4.15 ± 1.57	4.68 ± 0.47
pH	–	8.62 ± 0.61	8.00 ± 0.32	7.79 ± 0.30	7.58 ± 0.58	8.34 ± 0.11	7.97 ± 0.16	7.73 ± 0.40	7.34 ± 0.14
Chl *a*	mg/m^3	6.11 ± 4.09	1.18 ± 0.99	1.66 ± 0.78	0.33 ± 0.20	6.77 ± 3.59	0.70 ± 0.10	0.50 ± 0.31	0.18 ± 0.11
Pheo *a*	mg/m^3	0.82 ± 0.61	0.71 ± 0.31	0.31 ± 0.11	0.21 ± 0.13	0.88 ± 0.64	0.11 ± 0.06	0.24 ± 0.19	0.08 ± 0.04
SPM	mg/l	1.92 ± 0.38	0.83 ± 0.21	0.62 ± 0.19	0.64 ± 0.16	1.68 ± 0.87	0.69 ± 0.30	0.84 ± 0.41	1.21 ± 0.42
POC	mg/l	0.96 ± 0.41	0.19 ± 0.13	0.22 ± 0.11	0.10 ± 0.03	0.58 ± 0.32	0.13 ± 0.02	0.19 ± 0.05	0.10 ± 0.04
POC	mg/g	332.5 ± 41.1	194.7 ± 77.9	181.3 ± 71.7	160.7 ± 57.0	263.6 ± 62.00	176.1 ± 23.29	145.1 ± 64.73	130.1 ± 16.7
PN	mg/l	0.16 ± 0.34	0.03 ± 0.02	0.02 ± 0.01	0.01 ± 0.001	0.10 ± 0.11	0.02 ± 0.01	0.03 ± 0.06	0.01 ± 0.005
PN	mg/g	37.82 ± 13.30	28.69 ± 11.43	16.88 ± 7.95	23.21 ± 5.46	37.90 ± 11.63	28.12 ± 4.51	22.03 ± 9.52	18.58 ± 2.78
$\delta^{13}C$	‰	−24.20 ± 0.63	−26.90 ± 0.51	−26.48 ± 0.72	−26.88 ± 0.70	−25.45 ± 0.39	−25.81 ± 0.49	−25.86 ± 0.74	−25.94 ± 0.34
$\delta^{15}N$	‰	4.2 ± 0.4	nd	4.9 ± 0.6	nd	4.3 ± 0.3	4.8 ± 0.5	nd	nd

σ, standard deviation; nd, no data available.

Deep during the WS (Maksymowska et al., 2000; Szymczycha et al., 2017; Voss et al., 2005), of the Gotland Deep's DWL (Struck et al., 2004) and northern areas of the Baltic Sea (Heiskanen et al., 1998). The surface most sediment layers in both the Gdańsk Deep and the Gotland Deep exhibited $\delta^{13}C_{POC}$ values ranging from −26.0‰ to −27.0‰ (Szczepańska et al., 2012; Winogradow and Pempkowiak, 2014, 2018). This indicates transport and burial of PSM from the water column to surface sediments without considerable fractionation. Geochemical modeling by Gustafsson et al. (2015), surprisingly, indicates that $\delta^{13}C_{POC}$ in the Gotland Deep will shift from −24.0‰ to −23.0‰ by 2050 with seasonal variation limited to 2 ppm.

The low amounts of PTN captured by water sample filtration methods used here limited $\delta^{15}N$ measurements. Table 1 lists the few results obtained.

5. Discussion

5.1. Hydrological and seasonal constraints

Data presented in Figs. 2—5 and Figures S1—S5 clearly indicate two water masses (SWL and DWL) of different salinity separated by a well-established halocline. The SWL experiences annual temperature variation associated with seasonal irradiance effects (Dera and Woźniak, 2010; Voipio, 1981). This variation was parsed as warm and cold seasons (WS and CS) in data interpretation. Favorable conditions during the WS lead to increased abundance and activity of phytoplankton (Schneider et al., 2006, 2015; Wasmund and Uhlig, 2003) evident as elevated Chl *a* concentrations during the WS relative to the CS (Fig. 4a and b). An increased supply of planktonic POM however also causes a rapid increase in SPM concentrations (Fig. 6a and b) as well as concentrations of both measured components of POM (POC and PN; Fig. 7a and b). The WS also experiences increased contribution of POC to

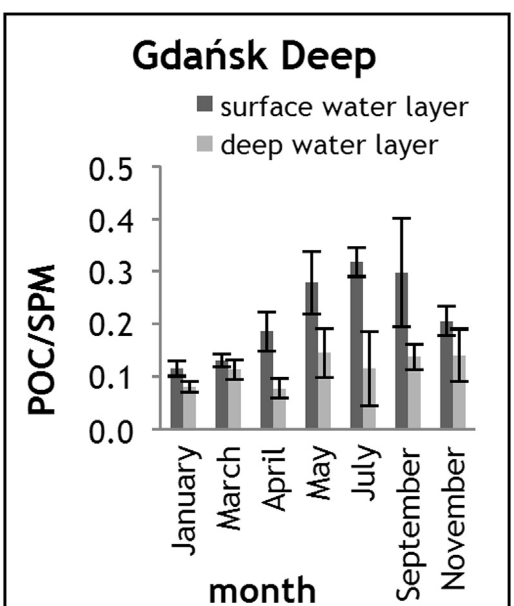

Figure 9 Average monthly POC/SPM ratios measured from surface and deep water layers of the Gdańsk Deep.

SPM (Fig. 9) and exhibits higher $\delta^{13}C_{POC}$ values (Fig. 10a and b). Interpretation of SWL dynamics must, therefore, assume seasonal variation in POM. A stable halocline separates the DWL from the SWL and the DWL exhibits constant salinity and temperature throughout the year. These stable stratification parameters suggest that surface and bottom water masses do not mix at any time. Many other studies have detected this feature of the Baltic Proper water column (Łomniewski et al., 1975; Rak, 2016; Voipio, 1981). Schneider et al. (2003) suggested that diffusion due to a concentration gradient causes widening of the halocline. This mechanism could influence salinity and possibly other dissolved species without affecting POM.

Mass transfer of SPM across the halocline occurs due to sedimentation (Burska et al., 2005; Lundsgaard et al., 1999; Struck et al., 2004). This causes deep water POM and Pheo *a* concentrations to increase in May during peak primary productivity in the SWL (see Fig. 5a and b, Figure S4). However, the DWL experiences only limited POM and Pheo *a* variation relative to the SWL. Data indicate a time lag between maximum Pheo *a* concentrations in the SWL and DWL (Fig. 5b and Figure S4). Conversion of Chl *a* to Pheo *a* evident from visible shifts and timing of peak concentrations takes several weeks as previously documented (Burska et al., 2005; Collos et al., 2005).

The consistency of salinity values in the SWL throughout the year signifies that river run-off does not significantly influence the water column of open sea regions. Similarly, Voss et al. (2005), found that run-off from the Vistula River does not influence the Baltic water column beyond a distance of 50 km from the river mouth (also see Maksymowska et al., 2000; Szymczycha et al., 2017).

As a proxy for phytoplankton abundance, SWL POM concentrations and other properties consistently varied according to seasonal forcing. POM concentrations and properties in the DWL remained more or less stable throughout a year (excluding the period of phytoplankton bloom in the SWL during May). Major saline water inflows from the North Sea to the Baltic Sea may influence POM in the DWL. The last major inflow occurred in 2015 however (Mohrholz et al., 2015; Rak, 2016), after DWL sampling for this study had already been completed. The general frequency of major saline inflows has decreased to one or two per decade within the last fifty years (Mohrholz et al., 2015; Szymczycha et al., 2019).

5.2. POM properties

5.2.1. POM contribution to SPM

Recent research on Baltic Proper seawater found that POC constitutes 49% of the POM mass. Regression analysis of POM and POC gave correlation coefficients $R^2 = 0.99$ (Woźniak et al., 2018). These relationships are typical of marine POM (Ríos et al., 1998), which represents a much larger (2×) contribution to SPM than POC.

The POC contribution to SPM (or POC/SPM ratio) for the study area varied by season as well as between surface and deep water layers (DWL: 0.12 for the CS and 0.14 for the WS; SWL: 0.15 for the CS and 0.32 for the WS) (Table 2; Fig. 9, Figure S7 — Gotland Deep). The POC/SPM ratio has been studied previously for both the Gdańsk Deep (Burska et al., 2005; Woźniak et al., 2018) and the Baltic Proper (Hakanson and Eckhell, 2005; Meler et al., 2017a, 2017b; Schumann et al., 2001; Woźniak et al., 2016, 2018). Contributions to the

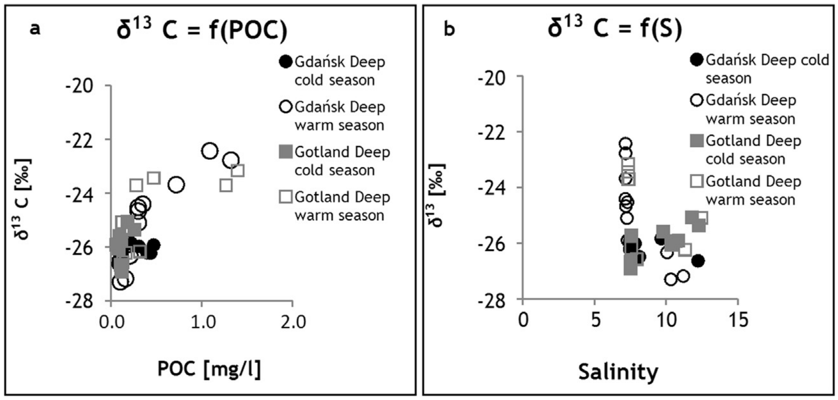

Figure 10 (a) Relationship between $\delta^{13}C_{POC}$ and POC; (b) the relationship between $\delta^{13}C_{POC}$ and salinity observed from the study area.

Table 2 Average ratios of selected POM constituents in surface water layer (SWL) and deep water layer (DWL) during warm season (WS) and cold season (CS).

Ratio	Unit	Average $\pm\sigma$							
		Gdańsk Deep				Gotland Deep			
		SWL		DWL		SWL		DWL	
		WS	CS	WS	CS	WS	CS	WS	CS
POC/PN	mg/mg	5.8 ± 0.5	6.3 ± 0.6	10.8 ± 0.7	10.1 ± 1.2	5.9 ± 0.7	6.5 ± 0.4	7.7 ± 1.0	9.6 ± 0.6
POC/chl *a*	g/mg	0.14 ± 0.05	0.17 ± 0.08	0.13 ± 0.07	0.31 ± 0.22	0.085 ± 0.06	0.18 ± 0.07	0.38 ± 0.08	0.55 ± 0.18
PN/chl *a*	g/mg	0.04 ± 0.02	0.03 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.04 ± 0.02	0.06 ± 0.04
POC/SPM	mg/mg	0.32 ± 0.07	0.15 ± 0.07	0.14 ± 0.07	0.12 ± 0.02	0.33 ± 0.06	0.18 ± 0.02	0.23 ± 0.06	0.08 ± 0.03
PN/SPM	mg/mg	0.08 ± 0.01	0.04 ± 0.01	0.03 ± 0.01	0.015 ± 0.01	0.06 ± 0.04	0.03 ± 0.02	0.03 ± 0.02	0.01 ± 0.00

σ, standard deviation.

SWL were 0.29 during the WS and 0.16 during the CS. Respective DWL contributions were about 2 times smaller. The POC/SPM ratio reported in the literature resembles that reported here. Seasonal dynamics reflect the increased inflow of planktonic organic matter to the POM reservoir during the WS (Andersson and Rudehall, 1993; Woźniak et al., 2018). Lower DWL ratios indicate POM mineralization during particle sinking (Andersson and Rudehall, 1993; Burska et al., 2005; Gustafsson et al., 2013). Increases of $\delta^{13}C_{POC}$ (Fig. 8) and POC concentration (Fig. 7a) during the WS support this interpretation as do the respective lower and higher C/N molar ratios in the DWL and SWL (Table 2; Fig. 11a).

5.2.2. Dynamics of $\delta^{13}C_{POC}$

Fig. 10a shows the relationship between POM $\delta^{13}C_{POC}$ and salinity. Salinity ranges of 9—13 psu indicate that SPM was filtered out of water samples collected from the DWL. These POM samples also gave depleted $\delta^{13}C_{POC}$ values. The SWL POM (salinity ranging from 7.3—7.6 psu) exhibited $\delta^{13}C_{POC}$ values of −22.5‰ to −27.0‰ (WS) and −25.5‰ to −27.3‰ (CS). This means that larger $\delta^{13}C_{POC}$ values measured in marine POM (−22.5‰ to −26.0‰) occur during increased primary production. The surface water layer of the Baltic Proper during this period also displays $(CO_2)_{aq}$ partial pressures well below 300 μatm (Schneider et al., 2006, 2015). Relative enrichment in $^{13}C_{POC}$ may arise from limited isotopic fractionation under low CO_2 availability or other disequilibrium conditions (Kopczyńska et al., 1995; Laws et al., 1995; Liu et al., 2018). During the CS, the equilibrium between $(CO_2)_{aq}$ and seawater is restored (Omstedt et al., 2014; Schneider et al., 2015) leading to lower $\delta^{13}C_{POC}$ values in POM.

Fig. 10b shows dependent relations between POC concentration and $\delta^{13}C_{POC}$. Plots generally show increasing $\delta^{13}C_{POC}$ with increasing POC concentrations, which accord with increased primary production during the WS. Measured $\delta^{13}C_{POC}$ values could be incorrectly interpreted as indicating a terrestrial POM contribution to the open Baltic POM, since its range overlaps with that of mixed land/marine-derived POM (Goñi et al., 2003; Hayes, 1993; Sauer et al., 2016; Szczepańska et al., 2012; Thornton and McManus, 1994; Voss and Struck, 1997). Recent studies have reported $\delta^{13}C_{POC}$ values ranging from −23.0‰ to −26.0‰ for marine planktonic biomass (Liu et al., 2018; Lowe et al., 2016; Miller et al., 2013). Neither hydrologic (salinity) nor biochemical (C/N ratios, POM/Chl *a* ratios) data ranges would support the interpretation that terrestrial organic matter makes a direct contribution to open water Baltic POM. The POM measured here thus appears to derive from planktonic biomass. Earlier studies of marine POM reported $\delta^{13}C_{POC}$ values ranging from −24.0‰ to −26.0‰ for coastal areas (Liu et al., 2018; Lowe et al., 2016; Miller et al., 2013) including the Baltic Sea coastal areas (Maksymowska et al., 2000; Struck et al., 2004). As indicated above these values may reflect limited fractionation of carbon isotopes due to low $(CO_2)_{aq}$ partial pressure

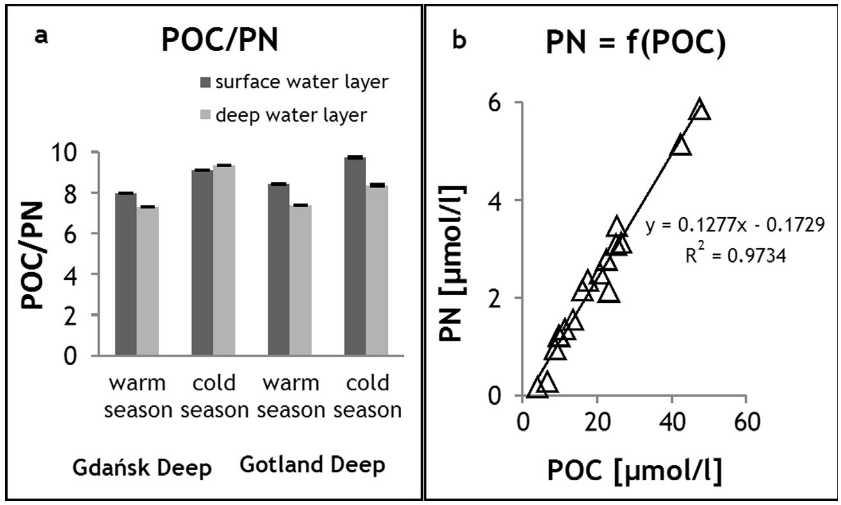

Figure 11 (a) Seasonal POC/PN ratios observed for the Gdańsk Deep and Gotland Deep; (b) relationship between PN and POC for the study area.

caused by intensive $(CO_2)_{aq}$ uptake during photosynthesis (Kopczyńska et al., 1995; Laws et al., 1995; Liu et al., 2018). Reports on Baltic Sea $\delta^{13}C_{POC}$ values indicate major seasonal variation in $\delta^{13}C_{POC}$ (Struck et al., 2004; Szymczycha et al., 2017). The relatively wide range of $\delta^{13}C_{POC}$ values observed throughout the year and throughout the water column reflects general $\delta^{13}C_{POC}$ increase with increasing phytoplankton abundance and variations due to temperature and compositional shifts in phytoplankton assemblages (Liu et al., 2018).

The observed $\delta^{13}C_{POC}$ values for water column POM shift from −22.5‰ to −27.0‰ but still, most likely, represent marine phytoplankton derived biomass generated during primary production or subjected to aging.

5.2.3. Molar ratios of organic carbon to nitrogen (C/N)

Molar ratios of carbon to nitrogen (C/N) are frequently used to assess POM provenance and/or age (Burska et al., 2005; Chester, 2003; Liu et al., 2018). Carbon to nitrogen (C/N) ratios of less than 9 (Koziorowska et al., 2016) or 12 (Liu et al., 2018) have been attributed to POM originating from marine primary production. Ratios measured by this study ranged from 5.8—10.8 (Table 2, Fig. 11). These values are typical of marine POM measured from the southern Baltic (Burska et al., 2005; Struck et al., 2004) but they differ from the Redfield ratio of 6.6. The departure from the Redfield ratio reported here (Fig. 11a) may arise from a contribution of zooplankton and relatively rapid PON ammonification in the SWL during the WS (Burska et al., 2005). Certain phytoplankton assemblages developed in the open Baltic during the WS could also give rise to the departure (Andersson et al., 2017; Wasmund et al., 1998). Hagström et al. (2001) attributed plankton biomass POC/PON ratios measured from the Baltic to this latter cause. During the CS, the DWL exhibited greater C/N ratios than during the WS (Fig. 11a) probably due to preferential mineralization of organic nitrogen relative to organic carbon during the sinking and/or aging of POM particles (Burska et al., 2005; Struck et al., 2004). The relatively narrow range of POC/PN ratios observed throughout most of the water column indicates, again, that terrestrial POM depleted of organic nitrogen contributes but little to SPM of the deeps studied (Liu et al., 2018). Lower POC/PN values from near-bottom water layer may reflect microbial communities in SPM floc settled out as surface sediment (Burska et al., 2005; Emeis et al., 2002; Rheinheimer et al., 1989).

A linear relationship observed between POC and PN (PN = 0.13, POC = 0.173, R^2 = 0.97) indicates that PN covaries with POM (Fig. 11b). A regression coefficient of 0.13 indicates the average total nitrogen to organic carbon ratio. This dependence can also be used to document inorganic nitrogen contribution to the PON pool (Liu et al., 2018). Studies interpreting C/N ratios have sometimes considered nitrogen speciation into organic and inorganic fractions (Grossart and Ploug, 2001; Koziorowska et al., 2016; Liu et al., 2018; Schubert and Calvert, 2001). The occurrence of ammonium ions in PSM could influence C/N ratios if SPM contains sufficient amounts of ammonium. Contrary to the expected effect of inorganic nitrogen, a plot of POC versus PN (Fig. 11b) predicts negative PN values for POC = 0. This indicates the presence of carbon that, under the analytical procedure used, is assumed to be sedimentary organic carbon. This fraction of carbon is deprived of organic nitrogen. The evidence thus indicates inorganic nitrogen (IN) is not incorporated into SPM in amounts influencing POC/TN ratio.

5.2.4. POC/Chl *a* ratio

The POC/Chl *a* ratio indicates the amount of biomass related to a Chl *a* unit and serves as a proxy for live phytoplanktonic contribution to the POM pool. Fig. 12a shows POC dependence on Chl *a*. Observed POC/Chl *a* values range from 85 (WS) to 180 (CS) in the SWL and from 170 (WS) to 550 (CS) in the DWL (Table 2, Fig. 12a). While seasonal oscillation in the SWL POC/Chl *a* ratio intuitively results from phytoplankton growth during the WS (Stoń et al., 2002; Tamm et al., 2019), variation in the DWL is more difficult to interpret. Live phytoplankton cells host abundant Chl *a*. Phytoplankton expiry and zooplankton grazing lyses cells to release labile components into the environment (Conover et al., 1988). This process and the exposure to environmental factors can transform Chl *a* into Pheo *a*. The POC/Chl *a* ratios for live marine phytoplankton varies from 50 mg/mg to 200 mg/mg. Values below 200 indicate POM derived from living

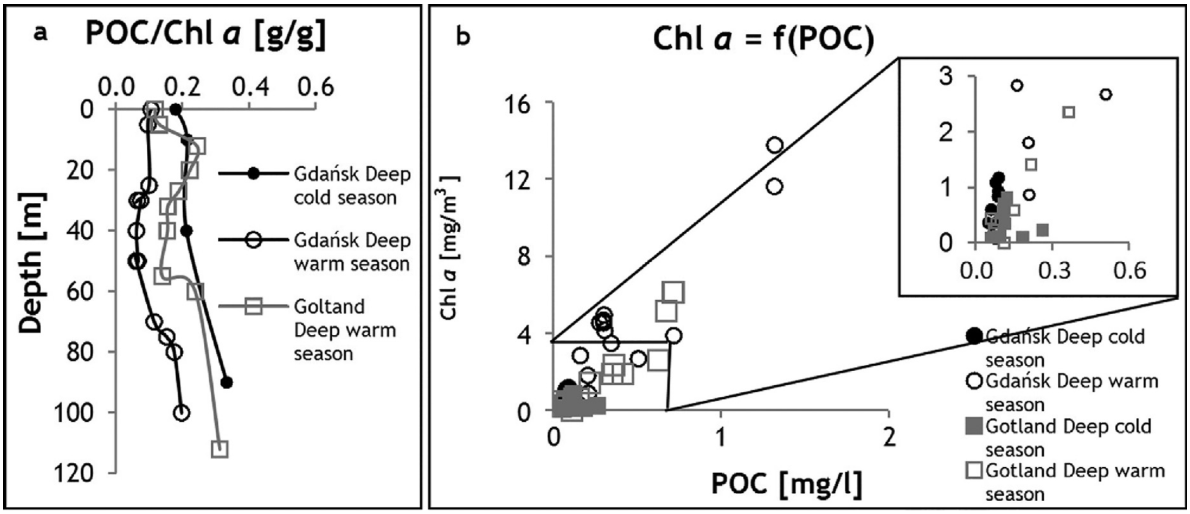

Figure 12 (a) Typical vertical profiles of the POC/Chl *a* ratio measured from the Gdańsk Deep and Gotland Deep; (b) relationship between Chl *a* and POC.

phytoplankton cells (Liu et al., 2018). The intercept of the Chl *a* versus POC curve at Chl *a* = 0 ranges from 40—50 μg POC/l, while the Chl *a* increase is equal to 0.008 mg Chl *a*/mg POC.

Woźniak et al. (2018) reported that the Baltic Sea samples exhibit an average POC/Chl *a* ratio of 125 for the SWL during the WS. The coefficient of variation assigned to the ratio was 68% indicating that the ratio varies over a relatively large range (Woźniak et al., 2018). The POC/Chl *a* ratios reported here range from 80—300. Differences in literature and measured ranges may result from different analytical methods used. For example, Liu et al. (2018) and Woźniak et al. (2018) used remote sensing while this study used extraction and spectroscopic absorption measurements, as did Andersson and Rudehall (1993), Burska et al. (2005) and Maciejewska and Pempkowiak (2014). The considerable POC/Chl *a* gradient at the halocline (Fig. 12b) indicates aged POM in the DWL consistent with other POM characteristics observed (smaller $\delta^{13}C_{POC}$, smaller contribution of POC to SPM, larger POC/PN ratio). Properties thus indicate POM produced by phytoplankton in the SWL during the WS and then aged in the DWL throughout the year.

An extended study devoted to optical properties of SPM in Baltic surface waters (Meler et al., 2017b; Woźniak et al., 2016; Woźniak et al., 2018) reported Chl *a*/POM ratios ranging from 2.5×10^{-3} g/g to 5.0×10^{-3} g/g. These data were derived from samples mostly collected from coastal localities, however, which showed considerable seasonal variation. The Chl *a*/POM values reported correspond to respective POC/Chl *a* ratios of 400 g/g and 200 g/g (using standard biogeochemical conventions; Liu et al., 2018). As such, they fell within the range of values reported in this study. The POC/Chl *a* ratios reported by Burska et al. (2005) study of the Gdańsk Deep ranged from 200—300 (g/g) in surface waters and from 2000—4000 in deeper layers. The latter range indicates that sediment was re-suspended and collected with analyzed samples.

The depth and seasonal dependence of Pheo *a* concentrations (Fig. 5a and b) relate to production rates of Pheo *a* and associated microzooplankton grazing rates. Pheopigment production in the absence of grazing may indicate irradiance and photo-degradation of these compounds. Year to year variation in the timing of the spring bloom between regions supports the interpretation that the Chl *a*/Pheo *a* ratio primarily reflects the rate of phytoplankton growth and is most strongly influenced by chlorophyll *a* levels. Zooplankton digestion of phytoplankton cells can account for observed correlations (Collos et al., 2005; Conover et al., 1988; Spence and Steven, 1974). The occurrence of Chl *a* in the DWL indicates that Chl *a* associated with POM persists long enough to be present after POM transport below the halocline. The Chl *a* concentration in the DWL is higher during the more productive WS than during the CS.

5.2.5. Implications of $\delta^{13}C_{POC}$ values and dynamics: POM origin

The $\delta^{13}C_{POC}$ data can help constrain the origin of POM and sedimentary organic matter in coastal waters (Goñi et al., 2003; Koziorowska et al., 2017; Sauer et al., 2016; Schubert and Calvert, 2001; Szczepańska et al., 2012; Thornton and McManus, 1994; Voss and Struck, 1997; Winogradow and Pempkowiak, 2018). Large differences between $\delta^{13}C_{POC}$ values for phytoplankton biomass and fluvial POM delivered to the marine environment form an end member model (Thornton and McManus, 1994). End members vary within a relatively narrow range of −21.0‰ to −22.5‰ for marine phytoplankton biomass (Sauer et al., 2016; Winogradow and Pempkowiak, 2018) and −27.0‰ to −28.5‰ for terrestrial POM (Sauer et al., 2016). Studies addressing the origin of POM in the Baltic Sea defined respective marine and terrestrial $\delta^{13}C_{POC}$ values of −22.0‰ (marine) and −27.0‰ (terrestrial) (Pempkowiak and Pocklington, 1983; Szczepańska et al., 2012; Winogradow and Pempkowiak, 2018), −21.5‰ and −27.0‰ (Voss et al., 2005) and −21.0‰ and −29.0‰ (Maksymowska et al., 2000) as end members.

As shown above (Fig. 10a, Table 1), $\delta^{13}C_{POC}$ values for POM from open Baltic Sea water ranged from −22.5‰ to −27.5‰. The POM $\delta^{13}C_{POC}$ contributed by river run-off also differs from that reported as characteristic of terrestrial POM. Two recent studies of POM contributions from river runoff into the Bay of Gdańsk (Gębka et al., 2018) and the Curonian Lagoon

(Lesutienė et al., 2018) reported average $\delta^{13}C_{POC}$ values of −30.1‰ and −31.8‰. The $\delta^{13}C_{POC}$ measurements reported in this study suggest that while WS $\delta^{13}C_{POC}$ POM values (−23.0‰) resemble those reported in the literature, $\delta^{13}C_{POC}$ values vary considerably throughout the year (Fig. 8a and b) but generally exhibit lower $\delta^{13}C$ values (−27.5‰) in the DWL during the CS. Struck et al. (2004) reported similar annual trends in both POM concentrations and $\delta^{13}C$ values for the Gotland Deep at 140 m water depth.

This study measured an annual average $\delta^{13}C_{POC}$ value for POM from the Gdańsk Deep and the Gotland Deep POM of −24.2‰. Concentrations of POM vary throughout the year from 3.1 mg/l during the WS to 0.4 mg/l during the CS. A weighted average of surface water POM $\delta^{13}C_{POC}$ is −23.2‰. This indicates that Baltic Sea average (end member) $\delta^{13}C_{POC}$ values are: −31.7‰ for fluvial POM and −23.2‰ for planktonic POM. Comparing marine and terrestrial $\delta^{13}C_{POC}$ values to those measured from sedimentary organic matter (e.g. −26.0‰; Szczepańska et al., 2012) indicates a terrestrial organic matter fraction of 0.70 or 0.67 assuming older estimates. Comparison with values from literature sources indicates that the proportion of terrestrial/planktonic organic matter in Baltic sedimentary organic matter does not significantly change (Maksymowska et al., 2000; Szczepańska et al., 2012; Voss et al., 2005; Winogradow and Pempkowiak, 2018).

While interpretations of sedimentary organic matter sources in the Baltic Sea remain somewhat tentative, the evidence suggests a major terrestrial contribution (43—67%; Winogradow and Pempkowiak, 2018). This is contradictory to the conclusion of preferentially autochthonous provenience of POC in the open Baltic. However, most sedimentary POC is transported and deposited, in the above bottom water layer, as floc (Emeis et al., 2002; Winogradow and Pempkowiak, 2018) and thus there is no contradiction between the reported here and the literature results.

6. Conclusions

This research investigated seasonal changes in the concentrations and character of POM from open water areas of the Baltic Sea, the landlocked sea characterized by a permanent stratification.

POM concentrations exhibited considerable seasonal variation indicating primary production as a major POM source. Mineralization and sedimentation serve as POM sinks for fresh and aged planktonic biomass. The POM properties measured included Chl *a*, contribution of POM to SPM, POM/Chl *a* ratio, C/N molar ratio and $\delta^{13}C_{POC}$ values. These revealed the interplay between live planktonic biomass and aged POM.

Measured POM $\delta^{13}C$ values were more depleted than those reported for other coastal areas. These lower values may arise from relatively short productive periods with low $(CO_2)_{aq}$ concentrations when assimilation of ^{13}C-enriched CO_2 takes place, at variance with longer periods of CO_2 assimilation in seawater at equilibrium with the atmosphere. Average $\delta^{13}C_{POC}$ of POM values adjusted for POM concentrations oscillations were −23.2‰. Literature-reported $\delta^{13}C_{POC}$ values for terrestrial POM range from −31.0‰ to −33.0‰. Given these values, terrestrial/marine end-member models indicate no significant shifts in sedimentary organic matter provenance.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.oceano.2019.05.004.

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