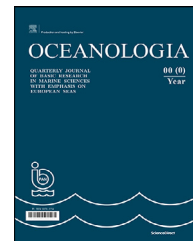


Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.journals.elsevier.com/oceanologia](http://www.journals.elsevier.com/oceanologia)

## ORIGINAL RESEARCH ARTICLE

# Benthic diffusive fluxes of organic and inorganic carbon, ammonium and phosphates from deep water sediments of the Baltic Sea

Monika Lengier<sup>a</sup>, Beata Szymczycha<sup>a</sup>, Aleksandra Brodecka-Goluch<sup>b</sup>,  
Żaneta Kłostowska<sup>a</sup>, Karol Kuliński<sup>a,\*</sup>

<sup>a</sup>Institute of Oceanology, Polish Academy of Sciences, Sopot, Poland

<sup>b</sup>Institute of Oceanography, University of Gdańsk, Gdynia, Poland

Received 2 September 2020; accepted 12 April 2021

Available online 27 April 2021

## KEYWORDS

Biogeochemistry;  
Benthic diffusive  
fluxes;  
Organic matter  
remineralization;  
Nutrients;  
Oxygen availability

**Abstract** In this study, Baltic Sea sediments, as a source of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), ammonium ( $\text{NH}_4^+$ ), and phosphates ( $\text{PO}_4^{3-}$ ), were investigated based on samples obtained in 2017 and 2018, shortly after a sequence of inflows from the North Sea that occurred between 2014 and 2017. Two different data sets (I and II) were used to assess benthic diffusive fluxes and thus elucidate both the temporal conditions at the time of sampling (data set I) and the diffusion potential of the sediments (data set II). The estimated fluxes were characterized by a high spatial variability within the whole Baltic Sea and ranged between  $-0.01$  and  $3.33 \text{ mmol m}^{-2} \text{ d}^{-1}$  for DIC,  $-0.02$  and  $0.44 \text{ mmol m}^{-2} \text{ d}^{-1}$  for DOC,  $-40.5$  and  $1370.1 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  for  $\text{NH}_4^+$ , and  $-5.9$  and  $60.9 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$  for  $\text{PO}_4^{3-}$ . The estimated benthic diffusive fluxes indicated a high potential for DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  release from Baltic Sea sediments. The high  $\text{O}_2$  concentrations in the water column of the Gulf of Bothnia together with major Baltic inflows (MBIs) bringing oxygenated seawater to the Baltic Proper and to some extent the Eastern Gotland Basin regulate the amounts of chemicals released from the sediment. Our study showed that a sequence of inflows has greater impact on the diminution of diffusive fluxes than does a single MBI and that the sediments of the Baltic Proper, even under the influence of inflows, are an important source of C, N, and P ( $159 \text{ kt yr}^{-1}$  for DIC+DOC,  $6.3$

\* Corresponding author at: Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81–712 Sopot, Poland.

E-mail address: [kroll@iopan.pl](mailto:kroll@iopan.pl) (K. Kuliński).

Peer review under the responsibility of the Institute of Oceanology of the Polish Academy of Sciences.



<https://doi.org/10.1016/j.oceano.2021.04.002>

0078-3234/© 2021 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

kt yr<sup>-1</sup> for N-NH<sub>4</sub><sup>+</sup> and 3.7 kt yr<sup>-1</sup> for P-PO<sub>4</sub><sup>3-</sup>) that should be considered in regional budget estimations.

© 2021 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

## 1. Introduction

The Baltic Sea is a semi-enclosed shelf sea with a catchment area (1 642 000 km<sup>2</sup>) roughly four times larger than the area of the sea itself (377 000 km<sup>2</sup>) (Figure 1). Significant nutrient inputs from land cause eutrophication of the basin, while stratification of the water column in the vast part of the central Baltic Sea precludes ventilation of its deep waters. Together, these features often lead to an oxygen deficiency in the bottom waters. Despite the considerable decrease in nitrogen and phosphorous loads from anthropogenic sources in the last 20 years, eutrophication of the Baltic Sea remains a major concern (HELCOM PLC-6, 2018), in part because of the slow response of the Baltic Sea ecosystem to reductions in nutrient loads. The exchange of waters between the Baltic Sea and the North Sea is a very slow process, requiring 20–25 year (Lass and Matthäus, 2008), and for phosphorus the residence time is even longer (Ahtiainen et al., 2014). According to recent studies, the residence time of nitrogen and phosphorus in the Baltic Sea is 9 and 49 years, respectively (Gustafsson et al., 2017; Savchuk et al., 2018).

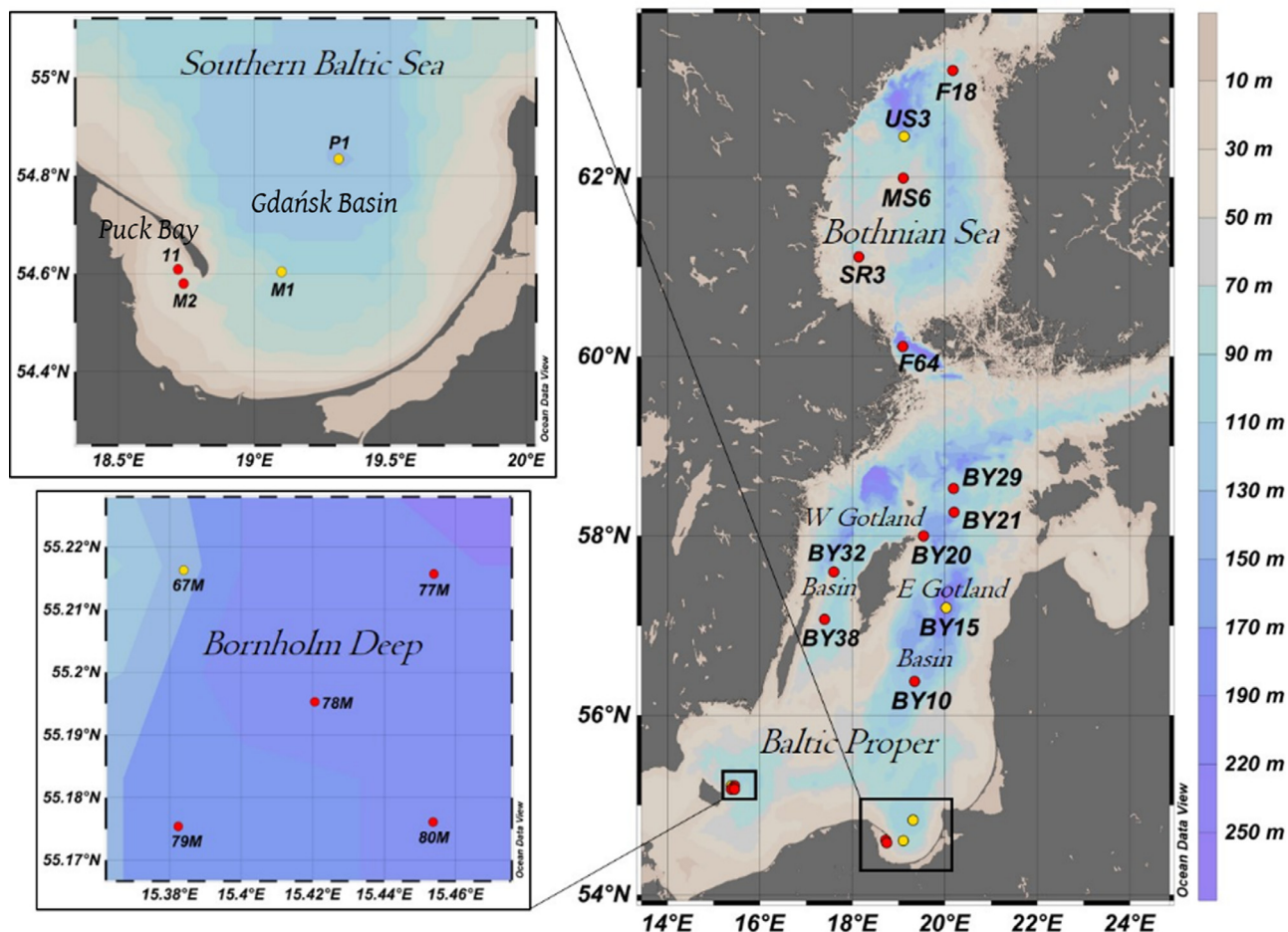
Nutrient enrichment in the Baltic Sea causes eutrophication, which in turn accelerates organic matter (OM) sedimentation, mainly in deep accumulation areas. Some of this OM is exported to the North Sea, whereas a large amount is buried in Baltic Sea sediments (Kuliński and Pempkowiak, 2011), which thus constitute an important OM sink. The amount of OM buried in deep depositional areas is estimated to be 2.64 Tg C yr<sup>-1</sup> (Thomas et al., 2010).

In general, the OM content in marine surface sediments, including those of the Baltic Sea, can vary significantly depending on OM sedimentation rates, preservation conditions, dilution by mineral matter, and sediment type (Hedges et al., 1997; Emerson and Hedges, 1988; Premuzic et al., 1982; Seiter et al., 2004). The OM content in the surface Baltic Sea sediments is significantly higher than that in the subsurface layers and was shown to be a direct consequence of eutrophication (Graca and Burska, 2011). During early diagenesis, some portion of OM deposited in the sediments undergoes hydrolysis and/or is remineralized in the course of both oxic and anoxic microbial processes (Arndt et al., 2013; LaRowe et al., 2020). Both mechanisms lead to the release of dissolved substances that supply the overlying water with carbon (C), nitrogen (N), and phosphorus (P) (Denis and Grenz, 2003). Therefore, sediments are a major sink for carbon and nutrients (Walsh, 1991) but also play a significant role in their recycling (Denis and Grenz, 2003; Hille et al., 2005). Kuliński and Pempkowiak (2011) determined that up to 30% of the OM deposited in Baltic Sea sediments returns to the water column as dissolved constituents. This has a substantial impact

on the Baltic Sea's eutrophication status over longer time scales, as it extends the residence times of major chemical elements (Carpenter, 2005) and strongly influences water properties and the biota (Gilbert et al., 2005). Over the long term, nutrients released from the sediments enter the N and P pools available for primary producers. Since both of these elements are growth-limiting, their release from sediments can shape ecosystem productivity. However, the response time may differ substantially between regions, occurring rapidly in shallow, well-mixed waters whereas in regions characterized by a stratification of the water column the time-scale is longer due to the slow circulation of the water (Puttonen et al., 2014).

The amount and form of the C, N, and P released from the sediments depend on the oxygen availability at the sediment surface (Conley et al., 2002). For the vast part of the stratified central Baltic Sea, near-bottom oxygen levels are primarily determined by the occurrence and strength of major Baltic inflows (MBIs), which bring saline and usually oxygen-rich surface water from the North Sea into the Baltic (Mohrholz, 2018; Naumann et al., 2018). Oxygen is especially important for controlling phosphate (PO<sub>4</sub><sup>3-</sup>) fluxes at the sediment-water interface (Savchuk et al., 2012). Anoxic conditions enhance phosphate efflux from the sediments to bottom waters (Conley et al., 2009) via the breakdown of iron oxyhydroxides and iron-humic-phosphorus complexes (Gustafsson et al., 2017) during iron reduction reactions. Anoxic conditions also favor ammonification and the release of ammonium (NH<sub>4</sub><sup>+</sup>) from sediments, while the remineralization of OM results in the production of dissolved inorganic carbon (DIC), a major component of the marine acid-base system. Quantifying the release of DIC from sediments is thus necessary to understand the pH dynamics occurring in deep water layers (Berelson et al., 2019). In parallel with remineralization, a portion of the OM deposited in sediments undergoes hydrolysis, releasing dissolved organic matter (DOM), which is approximated in analyses by dissolved organic carbon (DOC) (Benner, 2002). As DOM fuels the microbial loop, it is an important driver of C, N, and P biogeochemical cycles (Nebbioso and Piccolo, 2013; Kuliński et al., 2014).

The efflux of carbon and nutrient from marine sediments in the Baltic Sea region has been studied during stagnation periods and under pre-inflow conditions (e.g. Denis and Grenz, 2003; Łukawska-Matuszewska and Burska, 2011; Noffke et al., 2016; Viktorsson et al., 2013; Winogradow and Pempkowiak, 2014; Wulff et al., 2001) as well as after MBIs (Hall et al., 2017; Sommer et al., 2017). Nevertheless, the transport of C, N, and P through the sediment-water interface still remains an important source of uncertainty in efforts to understand the biogeochemical functioning of the Baltic Sea ecosystem (Meier et al., 2019).



**Figure 1** Sampling stations in the Baltic Sea. At the stations marked in red, pore water was collected from the surface sediments (depth of 2.5 cm), while at stations marked in yellow pore water was collected from the sediments cores up to 30 cm.

The aim of this study was to quantify DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  diffusive return fluxes from the sediments of different Baltic Sea basins. Specifically, our analyses were conducted using samples collected after a sequence of MBIs and smaller intrusions of North Sea water that occurred between 2014 and 2017, which differentiated oxygen availability in Baltic Sea depositional areas. Using two different data sets, we estimated the concentration gradients of the investigated constituents at the sediment-water interface, in order to quantify the return fluxes at the time of sampling as well as the diffusive potential of the sediments. In addition, we calculated the molar ratios of the diffusive fluxes of DIC and  $\text{PO}_4^{3-}$  (C:P). The results were compared with those obtained in similar studies of the Gotland Basin at different stages of deep-water renewal/stagnation. The importance of benthic diffusive fluxes compared to other sources of C, N, and P in the Baltic Sea was also considered.

## 2. Material and methods

### 2.1. Study area

Due to the Baltic Sea's bottom topography and hydrographic features, sedimentary OM accumulates mostly in

deep depositional areas (Figure 1). As the oxygen consumption rates in those regions are therefore increased (Nausch et al., 2008), the oxygen distribution in the bottom waters of the different basins differs significantly. For instance, the whole water column in the Gulf of Bothnia is relatively well-oxygenated whereas large areas of the Baltic Proper suffer from at least temporary hypoxia or even anoxia (Matthäus et al., 2008). This is due to the permanent stratification of the water column (halocline at 60–80 m), which precludes ventilation of the bottom waters (Matthäus et al., 2008). Hence, in the Baltic Proper MBIs are the only source of oxygen (Naumann et al., 2018). The slow propagation of the dense bottom waters together with the oxygen consumption taking place along the way cause a gradual reduction in the effects of MBIs and significantly delay their impact in the distant basins of the Baltic Proper (Naumann et al. 2018). Although the series of MBIs between 2014 and 2017 and the smaller intrusions of North Sea water that sometimes followed them increased oxygen levels in Baltic Sea deeps, the effects were of relatively brief duration, as the oxygen was quickly consumed during OM remineralization (Hansson et al., 2017; Naumann et al., 2018). The MBIs that occurred between 2014 and 2016 came after several years of stagnation and brought 1080 km<sup>3</sup> of well-oxygenated water from the North Sea to the Baltic. Addi-

**Table 1** Sedimentary and bottom water characteristics.

Area	Station	Depth	Porosity	T (°C)	S	O <sub>2</sub> (μmol l <sup>-1</sup> )	Lat (N)	Long (E)	Year of sampling
<b>Bornholm Deep</b>	67M	90	0.88	7.3	17.1	100.6	55°21.628	15°38.389	2018
	77M	95	0.88	6.7	17.0	98.1	55°21.57	15°45.386	2018
	78M	98	0.88	5.8	16.5	51.6	55°19.532	15°42.059	2018
	79M	96	0.88	6.2	16.7	188.8	55°17.537	15°38.244	2018
	80M	96	0.88	6.2	13.9	57.8	55°17.606	15°45.373	2018
<b>Bothnian Sea</b>	US3	175	0.78	4.6	6.3	237.1	62°45.539	19°11.807	2017
	F64	285	0.67	2.8	7.0	303.1	60°10.987	19°09.073	2017
	MS6	69	0.56	3.6	5.9	285.0	61°99.02	19°09.997	2017
	F18	99	0.78	3.9	6.0	241.4	63°19.014	20°16.996	2017
	SR3	71	0.64	3.2	5.7	220.2	61°10.995	18°13.693	2017
<b>Gotland Basins</b>	BY10	140	0.82	7.2	10.2	50.8	56°37.992	19°34.829	2017
	BY15	231	0.97	7.2	13.4	5.3	57°20.011	20°03.026	2017
	BY20	189	0.81	6.8	12.7	4.4	58°00.023	19°54.024	2017
	BY21	119	0.90	6.4	11.5	19.6	58°26.47	20°20.043	2017
	BY29	157	0.73	6.4	11.7	11.2	58°53.053	20°18.952	2017
	BY32	164	0.76	5.6	10.4	4.0	57°59.986	17°59.893	2017
	BY38	107	0.84	5.5	10.2	16.4	57°07.057	17°39.939	2017
<b>Southern Baltic Sea</b>	11	36	0.82	5.6	7.5	329.2	54°38.865	18°41.937	2017
	M1	50	0.95	6.7	12.7	171.8	54°33.372	19°09.994	2017
	M2	50	0.85	5.4	7.6	321.6	54°35.989	18°43.973	2017
	P1	105	0.88	6.0	14.0	162.7	54°49.995	19°19.18	2017

tionally, in 2017, the Baltic Sea experienced smaller intrusions and two inflows, one in February and the other in October, with total volumes estimated at 210 km<sup>3</sup> and 188 km<sup>3</sup>, respectively (Naumann et al., 2018).

Due to the impediments in the flow of deep water over the bottom thresholds separating the individual basins in the Baltic Sea, North Sea inflows rarely reach greater depths in the far eastern and northern parts of the Baltic Proper. Moreover, the Bothnian Sea forms a basin and is thus not directly affected by MBIs (Matthäus et al., 2008). Compared to the bottom salinity of the Baltic Proper (7.5–17.1, Table 1), the salinity in the Bothnian Sea is significantly lower (5.7–7.0, Table 1); however, with vertical mixing down to the bottom, the entire water column, including the deep water layers, becomes well-oxygenated. In addition, the sediments of the Bothnian Sea have a relatively low organic carbon content, which in the surface layers varies from 1 to 3% dry weight (d.w.) (Leipe et al., 2011).

The Eastern and Western Gotland Basins are the deepest basins of the Baltic Proper and also serve as important depositional areas. Their sediments are characterized by a high organic carbon content, which varies from 8 to 16% d.w. (Leipe et al., 2011). In the deepest area of the Gotland's basins (i.e., the Gotland Deep), the organic carbon concentration oscillates between 14.8% in surface layers and 3.4% in subsurface layers (Winogradow and Pempkowiak, 2014). In the bottom waters, the hypoxic and at times even anoxic conditions prevent the oxic remineralization of OM and increase the proportion of autochthonous OM relative to that of the lithogenic material being transported by near-bed

currents (Eckhell et al., 2000; Hille et al., 2006; Leipe et al., 2011).

In the Southern Baltic Sea, defined in this study as encompassing the Gulf of Gdańsk, including the Gdańsk Deep, and outer Puck Bay, the deepest depositional area is the Gdańsk Deep, whose muddy sediments have a high organic carbon content (~10% d.w.). A large part of the Gdańsk Basin is stratified and thus impacted by MBIs and by a change in oxygen availability in the bottom waters (Naumann et al., 2018).

The Bornholm Deep, due to its proximity to the Danish Straits, receives significant water inflows from the North Sea that bring well-oxygenated water but, simultaneously, intrusions of dense seawater that frequently lead to the formation of a stronger halocline. Since the ventilation of deep waters is therefore prohibited, oxygen depletion is enhanced, especially in late summer and during longer stagnation periods (Leipe et al., 2011; Naumann et al., 2018). Sediments in the Bornholm Deep are predominantly muddy, with a moderate to high organic carbon content (4–8%; Leipe et al., 2011).

## 2.2. Sampling

Undisturbed sediment cores (100 cm in length and 10 cm in diameter) were collected using a gravity corer during two research cruises of the *r/v Oceania*: in May 2017, when samples were collected from 15 sites located along the north-south axis of the Baltic Sea, and in March 2018, with samples obtained at five sites in the Bornholm Deep (Figure 1).



Both bottom water and pore water were sampled from the intact cores (clear boundary between water and sediment, no particles resuspended) using a Rhizon® samplers (Rhizosphere, diameter of 2.5 mm, mean pore size of 0.15  $\mu\text{m}$ ) for analyses of DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ . Bottom water was carefully collected from 1 cm above the sediment surface, and surface pore water from 2.5 cm below the sediment-water interface. Additionally, at five stations, the pore waters were sampled to a depth of approximately 30 cm (depth resolution in the sediment cores of 2–4 cm; Figure 3). The locations represented depositional areas in the Gdańsk Deep (P1), Bornholm Deep (67M), Gotland Deep (BY15), Bothnian Sea (US3), and the methane release zone in the central Gulf of Gdańsk (M1) (Figure 1). To estimate the small-scale spatial variability in the concentrations and diffusive fluxes of the investigated constituents, additional stations (77M, 78M, 79M, 80M) in the Bornholm Deep that were separated from each other by  $\sim 2$  nautical miles were sampled (Figure 1). Depending on the porosity of the sediments,  $\sim 4$  ml was collected from each layer. The required volume ( $\sim 12$  ml) was obtained by merging the pore water samples from three sediment cores. Immediately after sampling, pore and bottom waters for DIC analyses were transferred to pre-cleaned glass vials and preserved with 50  $\mu\text{l}$  of saturated  $\text{HgCl}_2$ . Samples for DOC analysis were transferred to pre-combusted (300°C) glass bottles and acidified with 50  $\mu\text{l}$  of conc. HCl (30%). All DIC and DOC samples were stored in the dark at 5°C until analyzed.  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  analyses were conducted shortly after sampling. Samples collected in 2017 were measured immediately, while those collected in 2018 were stored at  $-20^\circ\text{C}$  and analyzed within three days after their collection. Additionally, samples of surface sediments (0–5 cm) were taken and stored frozen at  $-20^\circ\text{C}$  to determine water content.

### 2.3. Analyses of DIC, DOC, $\text{NH}_4^+$ , and $\text{PO}_4^{3-}$

DIC and DOC were analyzed using an automated total organic carbon analyzer (TOC-L, Shimadzu). The DIC samples were acidified with 25%  $\text{H}_3\text{PO}_4$  and purged with a carrier gas (synthetic air: 80%  $\text{N}_2$ , 20%  $\text{O}_2$ ); the DOC samples were oxidized at high-temperature (680°C) in the presence of a Pt catalyst. In both cases, the resulting  $\text{CO}_2$  was quantified using a NDIR  $\text{CO}_2$  detector. Quality control consisted of regular accuracy and precision checks based on comparisons with reference materials. The DIC results were corrected for the recovery determined in analyses of certified reference material (CRM, Batch #159) provided by A. Dickson (University of California, San Diego), with the precision of the method evidenced by a relative standard deviation (RSD) of  $< 1\%$ . For DOC, the quality of the results was confirmed by regular analyses of CRM (North Atlantic water) obtained from the Dennis Hansell Laboratory, University of Miami (recovery: 98.9%, RSD: 0.9%).

Ammonium and phosphates were analyzed using colorimetric methods (indophenol blue and molybdenum blue, respectively), as described by Strickland and Parsons (1967) and Grasshoff et al. (1999). Quality control consisted of repeated measurements of CRM (RM-BU; National Meteorology Institute of Japan). The accuracies for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  were 98.3% and 99.1%, and the RSDs 0.3% and 1.4%, respectively.

### 2.4. Measurements of physico-chemical properties

At each station, CTD (conductivity, temperature, density) and oxygen profiles of the water column were recorded using a rosette equipped with the Seabird 9/11+ CTD sensor and the oxygen module SBE 43. Due to limitations in rosette deployment, CTD and  $\text{O}_2$  were measured  $\sim 5$  m above the seafloor. The accuracies of the CTD measurements were  $C=0.0003 \text{ S cm}^{-1}$ ,  $T=0.001^\circ\text{C}$ ,  $P=0.015\%$ ; for oxygen, the accuracy was 1%.

### 2.5. Calculations of the diffusive fluxes

The diffusive fluxes of the investigated seawater constituents were determined according to Fick's first law of diffusion (Eq. (1)):

$$J = -\Phi \cdot D_{sed} \cdot \frac{\Delta C}{\Delta x} \quad (1)$$

where  $J$  is the diffusion flux of DIC, DOC ( $\text{mmol m}^{-2} \text{ d}^{-1}$ ),  $\text{NH}_4^+$  or  $\text{PO}_4^{3-}$  ( $\mu\text{mol m}^{-2} \text{ d}^{-1}$ ),  $\Phi$  is the surface sediment porosity (dimensionless),  $D_{sed}$  is the substance-specific effective diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ), and  $\frac{\Delta C}{\Delta x}$  is the concentration gradient of the investigated substance at the sediment/water interface ( $\mu\text{g} \times \text{cm}^{-3} \times \text{cm}^{-1}$ ). Sediment porosity was calculated as shown in Eq. (2):

$$\Phi = W[(100 - W)d^{-1} + W]^{-1} \quad (2)$$

where  $W$  is the sediment water content (%) and  $d$  is the calculated sediment bulk density.

The  $D_{sed}$  values ( $\text{cm}^2 \text{ s}^{-1}$ ) for all of the investigated substances were calculated on the basis of dimensionless tortuosity ( $\theta$ ) and the diffusion coefficient in free solutions of seawater ( $D_{sw}$ ,  $\text{cm}^2 \text{ s}^{-1}$ ) (Eq. (3)). The results are presented in Table S1 of the Supplementary Material.

$$D_{sed} = D_{sw}/\theta^2 \quad (3)$$

Tortuosity was expressed as a function of the sediment's porosity (Table 1) and calculated using Eq. (4) (Boudreau 1997):

$$\theta^2 = 1 - \ln(\Phi^2) \quad (4)$$

The diffusion coefficients for free solutions of seawater ( $D_{sw}$ ,  $\text{cm}^2 \text{ s}^{-1}$ ) were determined separately for each station, taking into account local temperature according to Eq. (5):

$$D_{sw} = (m_0 + m_1 \cdot T) \cdot 10^{-6} \quad (5)$$

where:  $m_0$ ,  $m_1$  are linear coefficients (Boudreau, 1997) and  $T$  is the *in situ* temperature in the bottom water. All molecular diffusion coefficients in water were adjusted for temperature and salinity in accordance with the Stokes-Einstein equations (Li and Gregory, 1974). The temperature values are presented in Table 1. All data used for those calculations are presented in Table S3. Diffusion coefficient for DOC was adopted from Burdige et al. (2016).

The concentration gradients ( $\frac{\Delta C}{\Delta x}$ ) necessary to calculate diffusive fluxes (Eq. (1)) were determined based on two different approaches using two different data sets. In the first (data set I), the  $\frac{\Delta C}{\Delta x}$  between the bottom water (1 cm above the sediment) and the pore water (from 2.5 cm below the

sediment surface, i.e. the top-most sediment layer sampled), was calculated. This approach required only a small number of samples and thus allowed coverage of a vast sampling area. It also reflected the temporal conditions that prevailed at the sediment-water interface during sampling.

The second approach (data set II) was based on the pore water concentration profiles of the uppermost 30 cm of each sediment cores (Figure 3), with  $\frac{\Delta C}{\Delta X}$  determined from the mathematical functions best-fitted to the vertical profile of the considered solute. This was done by applying either a linear regression or the non-linear model described by Denis and Grenz (2003). The fitted functions and related determination coefficients ( $R^2$ ) are presented in Table S3. All five stations sampled for this approach were located in deep regions, at the accumulation-type bottom where the halocline occurs and benthic organisms are usually absent (no bioturbation), such that the method developed by Denis and Grenz (2003) was appropriate. The values of  $\frac{\Delta C}{\Delta X}$  were calculated as the first derivative for a sediment depth of 2.5 cm, as described for the approach based on data set I. The functions represented the diffusion potential of the sediments.

### 3. Results

#### 3.1. Physico-chemical conditions in the bottom water

The oxygen level at each of the investigated stations was determined at a depth of 5 m above the seafloor. The lowest  $O_2$  concentrations measured at this depth (4.0–50.8  $\mu\text{mol l}^{-1}$ ) occurred in the Gotland Basin and indicated hypoxic conditions. The other regions were identified as oxic, with the highest  $O_2$  concentration (329.2  $\mu\text{mol l}^{-1}$ ) measured in the Bornholm Deep (67M) (Table 1). For the Baltic Sea, this availability of oxygen in the deep basins was unusual. The temperature of the bottom water (5 m above the seafloor) ranged from 2.8°C at the deepest station, located in the Bothnian Sea (F64), to 7.2°C at station BY10, in the Eastern Gotland Basin. The salinity of the bottom water ranged from 5.7 in the Bothnian Sea (SR3) to 14.0 in the Gdańsk Deep (P1) (Table 1).

#### 3.2. DOC, DIC, $\text{NH}_4^+$ , and $\text{PO}_4^{3-}$ concentrations

##### 3.2.1. Bottom and pore waters from the upper sediment layer

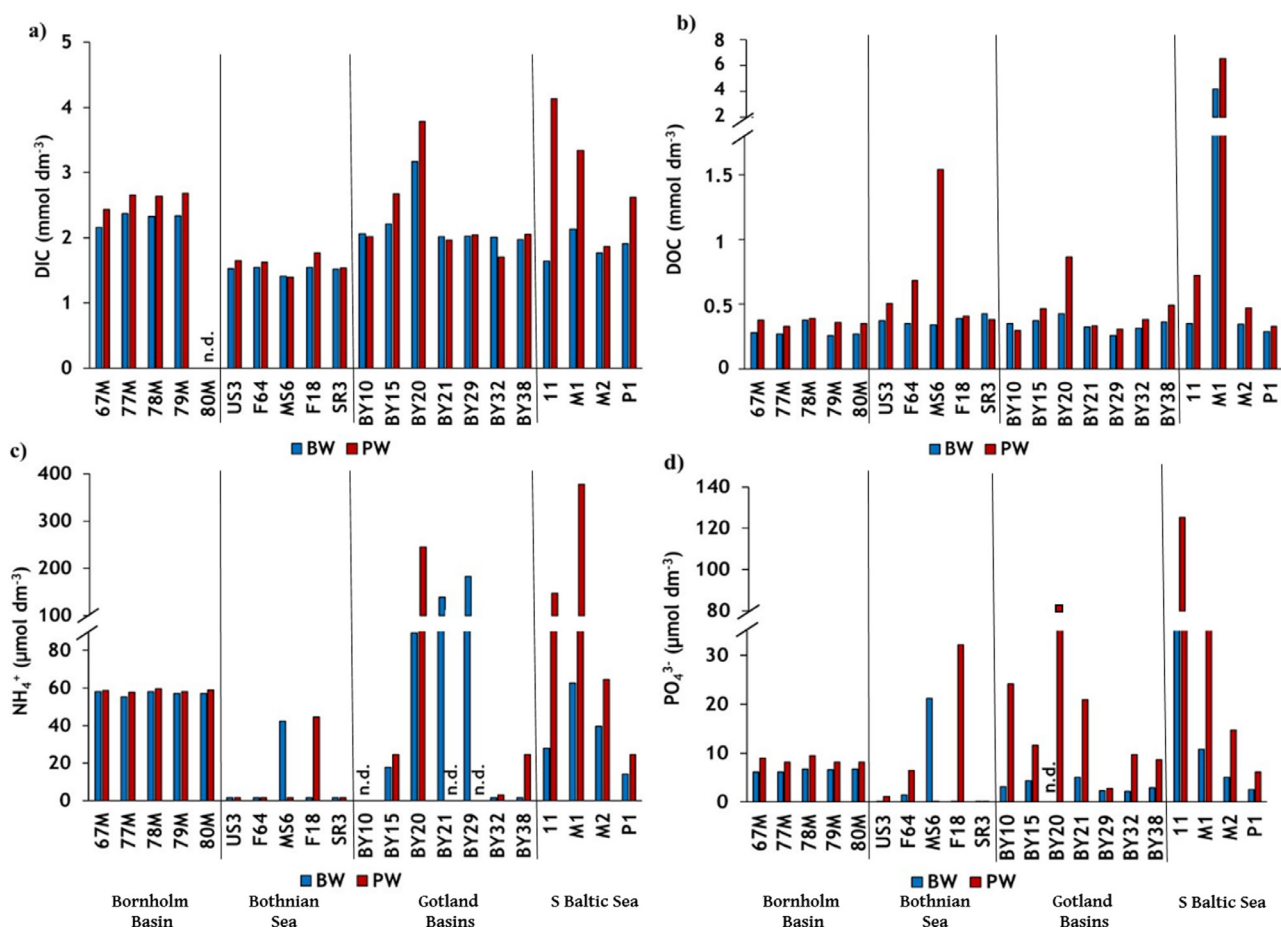
Concentrations of the investigated seawater constituents, both in the bottom water and the pore water from the upper sediment layer (0–5 cm) – data set I, are reported in Figure 2 and in the Supplementary Materials (Tables S1 and S2). Despite the high spatial variability, at most sampling sites the concentrations were higher in the pore water than in the bottom waters, indicating that the sediments were the predominant source of DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  in the investigated regions at the time of sampling. DIC concentrations ranged from 1.41 to 3.17  $\text{mmol dm}^{-3}$  in bottom waters and from 1.71 to 4.14  $\text{mmol dm}^{-3}$  in pore waters. The highest DIC values in both bottom and pore waters were measured in the Gdańsk Basin (11 and M1), in the deepest parts of the East Gotland Basin (BY15 and BY20), and

in the Gdańsk Deep (P1). DOC concentrations ranged from 0.26 to 0.43  $\text{mmol dm}^{-3}$  and from 0.31 to 6.53  $\text{mmol dm}^{-3}$  in the bottom water and pore water, respectively. The highest DOC concentration in both bottom water and pore water was measured at station M1, located in the Gdańsk Basin: 4.17 and 6.53  $\text{mmol dm}^{-3}$ , respectively. At most of the other stations, however, DOC concentrations did not exceed of 1  $\text{mmol dm}^{-3}$ .

$\text{NH}_4^+$  concentrations in the bottom water varied from 1.4 to 182.5  $\mu\text{mol dm}^{-3}$  and in the pore water from 1.4 to 377.9  $\mu\text{mol dm}^{-3}$ .  $\text{PO}_4^{3-}$  concentrations ranged from 0.2 to 37.6  $\mu\text{mol dm}^{-3}$  and from 0.2 to 125.2  $\mu\text{mol dm}^{-3}$ , respectively. The highest  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations were determined in the Gdańsk Basin: at station M1 and station 11, respectively (Figure 2).

##### 3.2.2. Pore water in the sediment cores

The profiles of DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  in sediment cores i.e. data set II are shown in Figure 3 and in Table S2 of the Supplementary Material. For all investigated species, distinct decreasing trends in their concentrations towards the sediment-water interface were determined. For all constituents, the highest concentration gradients were within the sediment cores from station M1 (Figure 3), located in a region previously identified as a methane release zone (Brodecka-Goluch and Łukawska-Matuszewska, 2018). In general, the concentrations of DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  in the pore water were up to 10 times higher at station M1 than at the other four stations. The DIC concentration at M1 ranged between 2.13  $\text{mmol dm}^{-3}$  and 20.09  $\text{mmol dm}^{-3}$ , and the DOC concentration between 4.17 and 9.97  $\text{mmol dm}^{-3}$ . For  $\text{NH}_4^+$  the concentration gradient at M1 was highly pronounced, as even at the surface-most sediment layer (2.5 cm) the concentration was six times higher (377.9  $\mu\text{mol dm}^{-3}$ ) than in the bottom water (62.7  $\mu\text{mol dm}^{-3}$ ) and it increased downcore, reaching a maximum of 3551.1  $\mu\text{mol dm}^{-3}$  at a depth of 25 cm. Similarly, a large  $\text{PO}_4^{3-}$  gradient was determined within the sediment-water interface (from 10.9  $\mu\text{mol dm}^{-3}$  in the bottom water to 62.8  $\mu\text{mol dm}^{-3}$  in the first sediment layer), with further increases up to 369.5  $\mu\text{mol dm}^{-3}$  deeper into the sediment. At the other investigated stations, the slopes of the DIC, DOC,  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  profiles were less steep and the concentration ranges were comparable to one another. At station US3 in the Bothnian Sea,  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations were very low (< 1.5  $\mu\text{mol dm}^{-3}$ ) both in the bottom water and in the uppermost sediment layer, but in the deeper sediment layers the concentrations of these two constituents were much higher. In the Gotland Deep (BY15), the concentrations of all measured parameters were characterized by a small increase towards deeper layers (Figure 3). By contrast, a distinct concentration increase characterized the profiles of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  at the Gdańsk Deep (P1). The  $\text{NH}_4^+$  concentration ranged from 24.5 up to 888.8  $\mu\text{mol dm}^{-3}$ , and the  $\text{PO}_4^{3-}$  concentration from 6.2 to 157.7  $\mu\text{mol dm}^{-3}$ . At station P1, the DIC concentration followed a steep gradient in the pore waters, with a maximum comparable to that of the DIC level at M1. For DOC, however, a similar abrupt change was not observed. In the Bornholm Deep, the profiles of the DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  concentrations (67M) showed an increase with increasing sediment depth, but the changes were less steep than those determined at the other stations and the



**Figure 2** The concentrations of a) DIC, b) DOC, c),  $\text{NH}_4^+$ , and d)  $\text{PO}_4^{3-}$  in the bottom water (BW) and pore water (PW) sampled from the upper sediment layer (2.5 cm below the sediment surface). n.d.: no data.

concentration changes at the sediment surface were small for all measured constituents (Figure 3).

## 4. Discussion

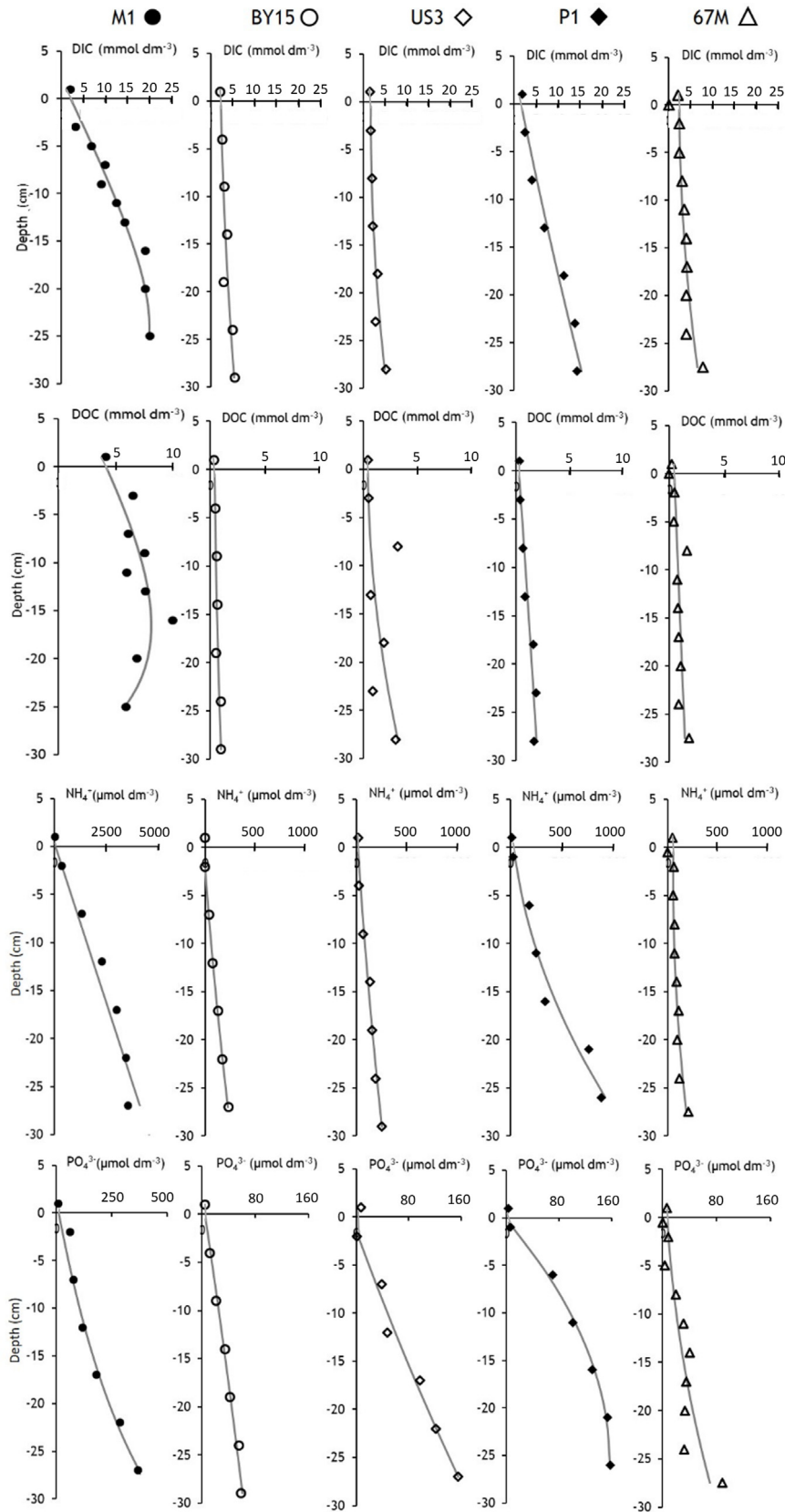
### 4.1. Bothnian Sea

Analyses of the samples from the Bothnian Sea indicated that the sediments are not a significant source of the dissolved products of OM remineralization and hydrolysis. Winogradow and Pempkowiak (2014) reported mean DIC and DOC return fluxes of  $0.82 \pm 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $0.20 \pm 0.02 \text{ mmol m}^{-2} \text{ d}^{-1}$ , respectively, whereas our maximum results are consistent with reported variability of DIC ( $0.25 \text{ mmol m}^{-2} \text{ d}^{-1}$ ), DOC ( $0.17 \text{ mmol m}^{-2} \text{ d}^{-1}$ ),  $\text{NH}_4^+$  ( $86.2 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ), and  $\text{PO}_4^{3-}$  ( $18.3 \text{ } \mu\text{mol m}^{-2} \text{ d}^{-1}$ ) (Figure 4). The return fluxes are characterized by high spatial variability within this basin (Figure 4 and Table S4). Interestingly, the results obtained from data set II identified the sediments at station US3 as an important source of dissolved products of OM remineralization. This was also supported by the C:P molar ratios (Figure 5), as their higher values indicated a large DIC outflow from the sediments. During the sampling period, the bottom waters of the Gulf of Bothnia were well-oxygenated ( $237.1 \text{ } \mu\text{mol l}^{-1}$ , Table 1), which ac-

counted for the diminished return fluxes, especially of ammonium and phosphates, because the oxic conditions would have prevented their accumulation in the pore waters due to oxidation of ammonium and formation of iron oxyhydroxides and iron-humic-phosphorus complexes (Freitas et al., 2020; Glud, 2008).

### 4.2. Gotland Basin

The high content of OM in the sediments of the Gotland Basin suggested that they are also a significant source of C, N, and P (Leipe et al., 2011). In the Gotland Deep, DIC and DOC return fluxes under anoxic conditions were previously shown to be  $2.05 \pm 0.14 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $0.23 \pm 0.04 \text{ mmol m}^{-2} \text{ d}^{-1}$ , respectively (Winogradow and Pempkowiak, 2014). According to that study, as much as 55% ( $0.282 \text{ Tg yr}^{-1}$ ) of the total organic carbon deposited in the sediments of the Gotland Deep ( $0.508 \text{ Tg yr}^{-1}$ ) returns to the water column, such that in the Baltic Sea this region has the highest proportion of carbon released from sediments relative to carbon subject to sedimentation (Winogradow and Pempkowiak, 2014). The diffusive fluxes obtained in the present study (Figure 4) indicated that sediments of the Gotland Basins are also a major source of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . Interestingly, with the exception of  $\text{NH}_4^+$ , the diffusive fluxes derived from data sets I and II were comparable (Figure 4).



**Figure 3** DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  concentration profiles in sediment cores as assessed with fitted functions (gray lines). The samples were collected in Puck Bay (M1; black points), the Gotland Deep (BY15; white circles), the Bothnian Sea (US3; white diamonds), the Gdańsk Deep (P1; black diamonds), and the Bornholm Deep (67M; white triangles). The fitted functions and related determination coefficients ( $R^2$ ) are presented in Table S3.



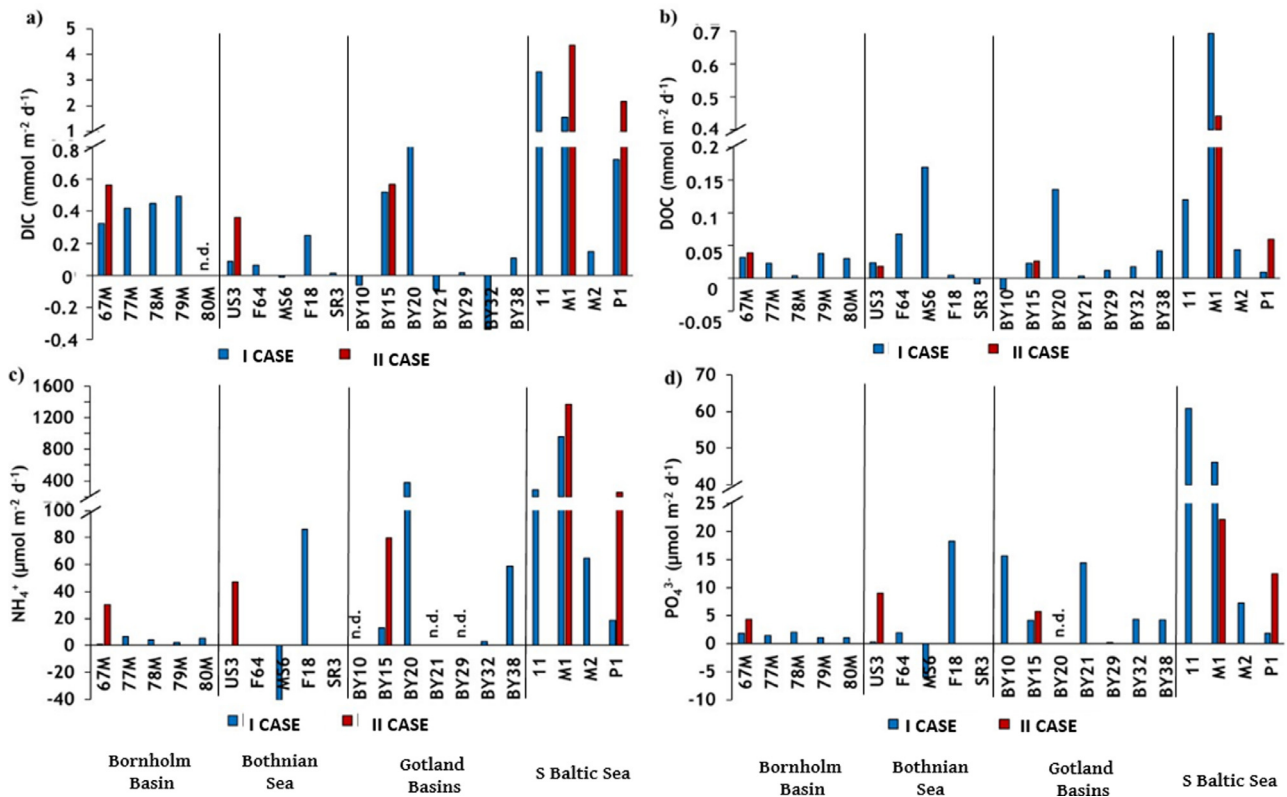


Figure 4 Diffusive fluxes of a) DIC, b) DOC, c)  $\text{NH}_4^+$ , and d)  $\text{PO}_4^{3-}$  obtained from data sets I and II.

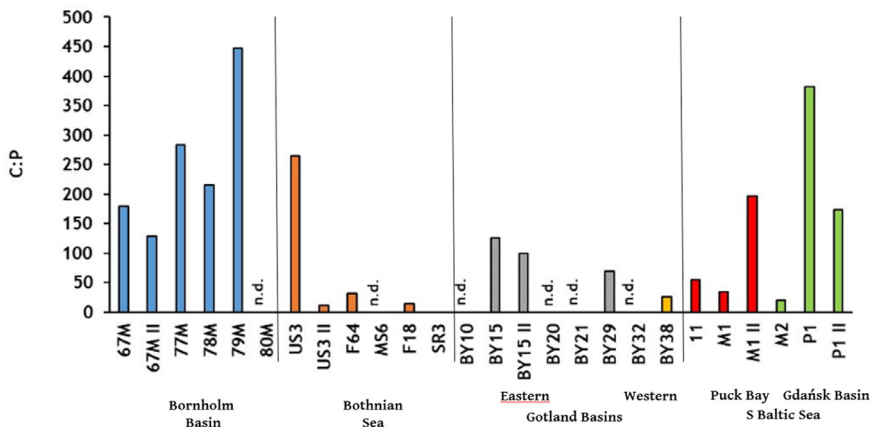
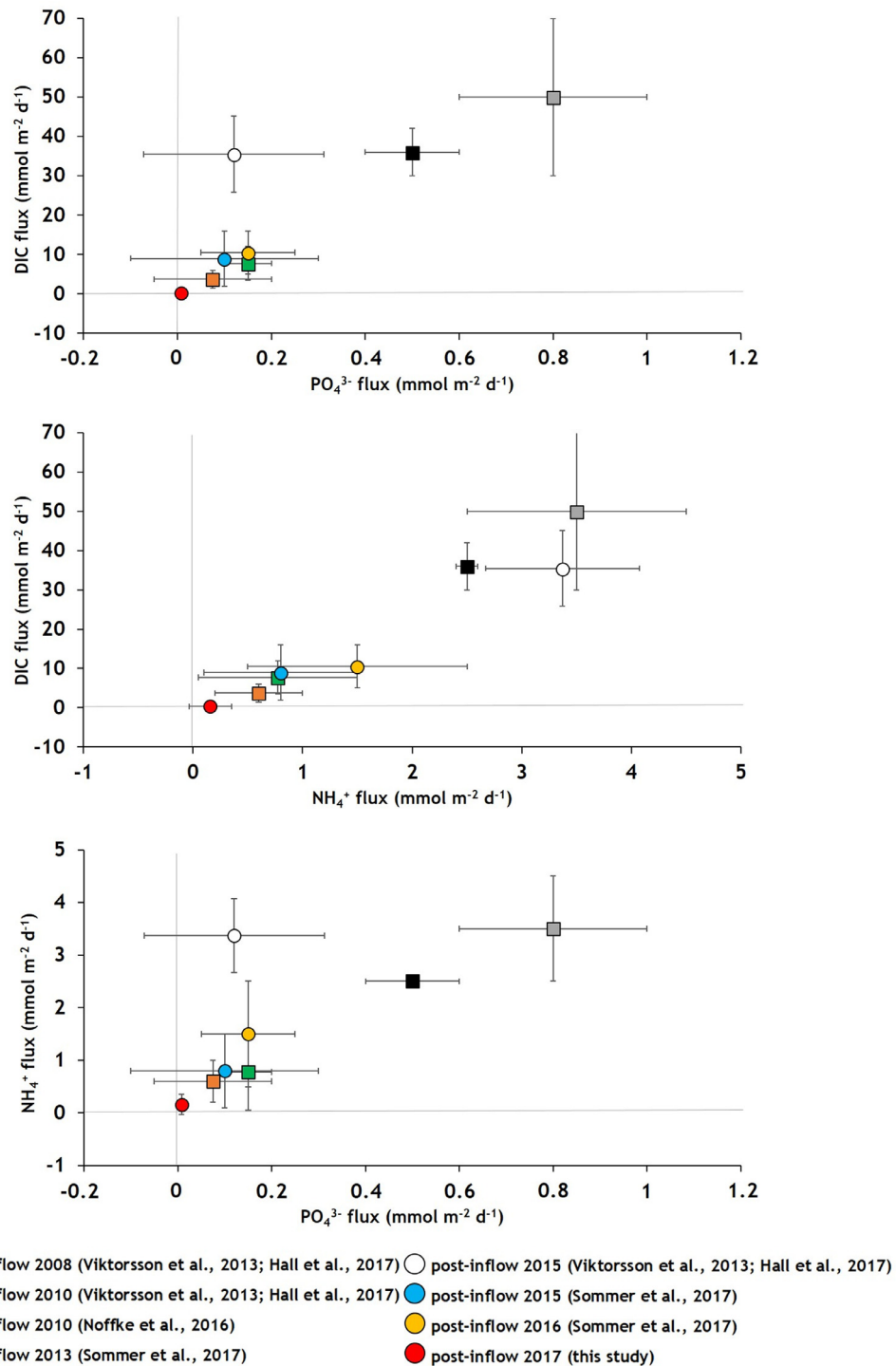


Figure 5 C:P molar ratios of the diffusive fluxes of DIC and  $\text{PO}_4^{3-}$  as estimated from data sets I and II in the Bornholm Deep (blue), Bothnian Sea (orange), Eastern (grey) and Western (yellow) Gotland Basins, methane sites (red), and the Southern Baltic Sea (green).

For  $\text{NH}_4^+$ , the strong decrease in its fluxes between data set I and data set II may reflect nitrification (oxic conditions) or anaerobic ammonium oxidation (anammox) (Kuypers et al., 2003). However, the relatively small difference in the  $\text{PO}_4^{3-}$  fluxes and the similar C:P ratios indicated by the two data sets pointed to anoxic conditions at the sediment surface and anammox as the  $\text{NH}_4^+$  sink. It could be the case, since it has been reported that anammox process is also responsible for the anaerobic oxidation of  $\text{NH}_4^+$  in the sediments of Skagerrak (Dalsgaard and Thamdrup, 2002). What is more, the signals of intensified anammox were spotted after temporal changes in the water column at redoxcline of Gotland

Basin resulting from the MBI (Hannig et al., 2007). Additionally, by adsorbing to clay minerals in sediment, ammonium may be removed from pore waters and its release across the sediment-water interface thus prevented (Freitas et al., 2020); it is, however, unknown if this process is relevant also for the Baltic Sea. In the Eastern Gotland Basin, including the Gotland Deep, a pronounced decreasing trend in the  $\text{O}_2$  concentration prevailed after the brief oxygenation events related to the MBIs that occurred in 2014–2017, but hydrogen sulfide was detected in the water overlying the sediment already in 2017 (Naumann et al., 2018). Thus, while our results indicated hypoxic conditions ( $4.0\text{--}50.8 \mu\text{mol l}^{-1}$ )



**Figure 6** Compilation of a) DIC vs.  $\text{PO}_4^{3-}$ , b) DIC vs.  $\text{NH}_4^+$ , and c)  $\text{NH}_4^+$  vs.  $\text{PO}_4^{3-}$  fluxes under pre- and post-inflow conditions in the Eastern Gotland Basin and Gotland Deep. The diffusive fluxes obtained in this study based on data sets I and II are presented.

5 m above the seafloor, the sediment surface was most probably anoxic.

Since the diffusive fluxes of DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  in the Eastern Gotland Basin had already been intensively studied, we compared those results with our own (Figure 6). The previous studies were performed during periods of stagnation (pre-inflow) (Noffke et al., 2016) or shortly after individual MBIs (Hall et al., 2017;

Sommer et al., 2017; Viktorsson et al., 2013). Among the former, Hall et al. (2017) reported DIC and  $\text{NH}_4^+$  return fluxes of  $36 \pm 6 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $2.5 \pm 0.1 \text{ mmol m}^{-2} \text{ d}^{-1}$ , respectively, in 2008, and  $50 \pm 20 \text{ mmol m}^{-2} \text{ d}^{-1}$  and  $3.5 \pm 1 \text{ mmol m}^{-2} \text{ d}^{-1}$ , respectively, in 2010. The change during post-inflow conditions was limited, with return fluxes of  $35.5 \pm 9.67 \text{ mmol m}^{-2} \text{ d}^{-1}$  for DIC and  $3.37 \pm 0.702 \text{ mmol m}^{-2} \text{ d}^{-1}$  for  $\text{NH}_4^+$  (Hall et al., 2017). In the case of phosphate,

Viktorsson et al. (2013) determined return fluxes of  $0.5 \pm 0.1$  mmol  $m^{-2} d^{-1}$  in 2008 and  $0.8 \pm 0.2$  mmol  $m^{-2} d^{-1}$  in 2010, but lower return fluxes of  $0.12 \pm 0.19$  mmol  $m^{-2} d^{-1}$  under the post-inflow conditions of 2015 (Hall et al., 2017). Sommer et al. (2017) measured  $NH_4^+$  release rates during the ventilation period ( $0.8 \pm 0.7$  mmol  $m^{-2} d^{-1}$  in 2015 and  $1.5 \pm 1.0$  mmol  $m^{-2} d^{-1}$  in 2016) and showed that they were comparable to those measured during euxinic conditions ( $0.78 \pm 0.72$  mmol  $m^{-2} d^{-1}$  in 2013) and thus not enhanced by dissimilatory nitrate reduction to ammonium, which retains  $NH_4^+$  in the ecosystem and is an important benthic mechanism under low-oxygen conditions (Noffke et al., 2016 and references therein). Sommer et al. (2017) detected only a minor decrease in  $PO_4^{3-}$  and  $NH_4^+$  (2% and 12%, respectively) release from sediments in response to deep-water renewal. However, Hall et al. (2017) found that MBIs may have a considerable influence on P and N budgets in the Baltic Proper. The authors reported that a natural oxygenation event led to a 23% decrease in  $PO_4^{3-}$  release from sediments while simultaneously enhancing total denitrification by 18% (Hall et al., 2017). The differences in the reported benthic fluxes of P in the eastern part of the Eastern Gotland Basin are often explained by the presence of massive benthic mats of vacuolated sulfur bacteria in the hypoxic transition zone, at 80–120 m depth (Hall et al., 2017; Noffke et al., 2016). These bacteria are able to modulate P fluxes in hypoxic transient zones by storing and releasing it under different redox conditions (Noffke et al., 2016 and references therein).

The benthic fluxes determined in our study fall within the lower ranges of previous estimates (Figure 6) and may reflect deep-water renewal. Our study was performed in 2017–2018, after the sequence of MBIs that occurred between 2014 and 2017, whereas the above-cited studies referring to post-inflow conditions were performed in 2015–2016 (Hall et al., 2017; Sommer et al., 2017). The discrepancies may also be the result of the different methods employed to measure benthic fluxes. In the studies referenced in Figure 6 (Hall et al., 2017; Noffke et al., 2016; Sommer et al., 2017; Viktorsson et al., 2013), in situ incubations with benthic chambers were used. Additionally, Noffke et al. (2016) and Viktorsson et al. (2013) determined the profiles of the investigated species in pore water. For the calculations in our study, we used Fick's first law of diffusion and pore water was extracted using Rhizons. Although this sampling technique minimizes the risk of sediment oxygenation, which is essential when working with anoxic/hypoxic sediments, caution must be exerted to avoid contaminating the samples with pore water from adjacent sediment layers (Seeberg-Elverfeldt et al., 2005). For this reason, we lowered the vertical resolution of the pore water sampling, but this could have reduced the accuracy of the benthic fluxes estimated with Fick's first law. Viktorsson et al. (2013) showed that too-coarse pore water sampling may strongly affect the quantification of  $PO_4^{3-}$  effluxes from sediments, but the effect may differ depending on the oxygen availability in the water overlying the sediments. At oxic sites, the  $PO_4^{3-}$  fluxes determined from the pore water profiles may have been too high because the sampling may have been too coarse to allow for the detection of  $PO_4^{3-}$  captured in the surface oxic sediment layer. At anoxic sites, the low sampling resolution may have re-

sulted in an underestimation of the steepness of the gradient near the water/sediment interface. For DIC and DOC, however, this effect would have been smaller, as both fluxes are hardly sensitive to changes in redox conditions.

### 4.3. Gdańsk Basin

The Gdańsk Deep is an important source of both DIC ( $2.39 \pm 0.01$  mmol  $m^{-2} d^{-1}$ ) and DOC ( $0.27 \pm 0.04$  mmol  $m^{-2} d^{-1}$ ) (Winogradow and Pempkowiak 2014). According to Łukawska-Matuszewska and Kietczewska (2016), the Gulf of Gdańsk serves as a region of intensive carbon regeneration, with DIC fluxes of up to  $2.78$  mmol  $m^{-2} d^{-1}$  under oxic conditions, whereas under hypoxic and anoxic conditions the DIC return fluxes are lower ( $1.02$ – $1.21$  mmol  $m^{-2} d^{-1}$ ). These data show the high potential for benthic efflux in the Gdańsk Deep, which, according to the DIC values, is comparable to the return flux obtained in this study using data set II ( $2.16$  mmol  $m^{-2} d^{-1}$ ). Previous data also pointed to this region as a source of  $NH_4^+$ , based on a flux ranging from  $106$   $\mu\text{mol} m^{-2} d^{-1}$  in a euxinic area of the Gdańsk Deep to  $924$   $\mu\text{mol} m^{-2} d^{-1}$  under hypoxic conditions (Łukawska-Matuszewska and Kietczewska, 2016). In another study, the  $NH_4^+$  flux in the Gdańsk Deep, under conditions of oxygen deficiency was  $602.4$   $\mu\text{mol} m^{-2} d^{-1}$  (Graca et al., 2006). Recently reported  $PO_4^{3-}$  return fluxes in the Gdańsk Deep ranged from  $19.1$  to  $36.6$   $\mu\text{mol} m^{-2} d^{-1}$  in summer 2015 and from  $18.9$  to  $32.1$   $\mu\text{mol} m^{-2} d^{-1}$  in winter 2016; i.e., shortly after the MBIs that improved the  $O_2$  conditions in the bottom waters (Łukawska-Matuszewska and Graca, 2018). In our study, the  $NH_4^+$  and  $PO_4^{3-}$  fluxes in the Gdańsk Deep, obtained from data set II, amounted to  $254.6$   $\mu\text{mol} m^{-2} d^{-1}$  and  $12.5$   $\mu\text{mol} m^{-2} d^{-1}$ , respectively, which is in the lower range of previously reported results (Łukawska-Matuszewska and Graca, 2018; Łukawska-Matuszewska and Kietczewska, 2016). Since the sampling and preservation methods as well as the calculations of benthic fluxes in those studies were the same as in ours, the discrepancies can be attributed to the shift in environmental conditions. At the time of sampling, the oxygen concentration in the Gdańsk Deep (station P1:  $162.7$   $\mu\text{mol} l^{-1}$ ) was higher than occurs under hypoxic or euxinic conditions (e.g., Łukawska-Matuszewska and Kietczewska, 2016). The elevated  $O_2$  concentration and the low diffusive fluxes of  $NH_4^+$  and  $PO_4^{3-}$ , obtained from data set I, suggest the influence of inflow waters from the North Sea, which could have led to the oxidation of  $NH_4^+$  and prevented  $PO_4^{3-}$  release from the sediments (Figure 4). The high C:P ratio, especially for the results obtained from data set I, suggested that diffusive fluxes in the Gdańsk Deep are shaped by oxic conditions in the bottom waters that lead to the retention of P in the sediments (Figure 5). This contrasts with the results from stations located in the Gdańsk Basin (M1, M2, 11), where C:P ratios were generally low (34–55), except for the value derived from data set II for station M1 (196). Brodecka-Goluch and Łukawska-Matuszewska (2018) identified stations M1 and M2 within methane release zones, where intensive methanogenesis occurs in the upper layers of the sediments. The authors reported that these regions (methane sites) can be an important source of DIC ( $3.43$  mmol  $m^{-2} d^{-1}$ ) and DOC ( $0.004$ – $0.68$  mmol  $m^{-2} d^{-1}$ ). Our results indicate that high carbon release can also be accom-

panied by elevated diffusive fluxes of  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  that may be several-fold to as much as one order of magnitude higher than in regions not affected by methane production in shallow sediment layers (Figure 4, Table S4).

Although a low C:P ration was determined at both M1 and M2, the individual fluxes were significantly lower at M2 than at M1. This may be related to the shallower depth at M2 (50 m) and the lack of a halocline in this region, such that deep waters are better ventilated and oxic conditions extend down to the sea bottom. Site 11, although not previously investigated with respect to methane occurrence and release from the sediments, is located in proximity to M2 and characterized by high diffusive fluxes similar to those at M1. Additionally, the low C:P ratio of M2 suggests low redox conditions, probably related to the intensive remineralization of OM and, consequently, to methane production and its efflux from the sediments. Therefore, this site was grouped with the other methane sites, which, due to their exceptional characteristics, were excluded from further analyses related to budget calculations.

#### 4.4. Bornholm Deep

In the Bornholm Basin, small diffusive fluxes of all the investigated substances at the time of sampling (Figure 4) were determined along with moderate to relatively high  $\text{O}_2$  concentrations (51.6 and 188.8  $\mu\text{mol l}^{-1}$ ). The DIC (0.33–0.49  $\text{mmol m}^{-2} \text{d}^{-1}$ ) and DOC (0.02–0.04  $\text{mmol m}^{-2} \text{d}^{-1}$ ) diffusive fluxes were lower than those reported previously for this region during the stagnation period (DIC 2.12±0.07  $\text{mmol m}^{-2} \text{d}^{-1}$  and DOC 0.20±0.02  $\text{mmol m}^{-2} \text{d}^{-1}$ , and DOC 0.21–0.37  $\text{mmol m}^{-2} \text{d}^{-1}$ ; Winogradow and Pempkowiak, 2014), which may be a consequence of recent MBIs. Furthermore, in the study of Winogradow and Pempkowiak (2014) the sediment samples were frozen after their collection, which could have increased the DIC and, especially, the DOC concentrations. Freezing has the potential to change not only the concentration, but the chemical character of the DOM pool as the most aromatic fractions of DOM are likely to precipitate out of solution during freezing (Fellman et al., 2008). Naumann et al. (2019) measured elevated concentrations of  $\text{PO}_4^{3-}$  (4.73±1.56  $\mu\text{mol l}^{-1}$ ) in the bottom waters of the Bornholm Deep in 2018, which is consistent with the concentration in the bottom waters measured in our samples (6.00  $\mu\text{mol l}^{-1}$ , Table S2). According to Naumann et al. (2019), these high concentrations are the effect of a rapid decrease in oxygen availability after the MBIs. Overall, the Bornholm Deep had the lowest diffusive fluxes of all the basins investigated (Figure 4). The low DOC (0.03–0.04  $\text{mmol m}^{-2} \text{d}^{-1}$ ),  $\text{NH}_4^+$  (1.1–30.4  $\mu\text{mol m}^{-2} \text{d}^{-1}$ ), and  $\text{PO}_4^{3-}$  (1.8–4.4  $\mu\text{mol m}^{-2} \text{d}^{-1}$ ) diffusive fluxes obtained using data set I suggest that the influence of inflow events was still present at the time of our study, while data set II indicates the large diffusive potential of sediments during a stagnation period (Figure 4). Discrepancies between our findings and those reported in the literature may thus reflect the rapidly changing conditions in the bottom waters due to the counteracting influence of MBIs and the strengthening of the halocline, with the latter hampering vertical mixing and ventilation of the water column. In addition, strong bottom water currents driven by North Sea water inflows cause

high spatial differences in the mud deposits and the distribution of OM (Christoffersen et al., 2007). This “patchiness” in the bottom waters and sediment conditions may lead to large differences within the same region. We chose the Bornholm Deep as an extreme example of the extent of variation of benthic diffusive fluxes and based our study on samples collected from bottom and pore waters at several stations located in close proximity to each other (67M, 77M, 78M, 79M, 80M; Figure 1). The bottom water concentrations reached 2.3±0.1  $\text{mmol l}^{-1}$ , 0.3±0.1  $\text{mmol l}^{-1}$ , 57.1±1.2  $\mu\text{mol l}^{-1}$ , and 6.5±0.3  $\mu\text{mol l}^{-1}$  for DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ , respectively, whereas concentrations in the surface-most pore waters were 2.6±0.1  $\text{mmol l}^{-1}$ , 0.4±0.02  $\text{mmol l}^{-1}$ , 58.6±0.8  $\mu\text{mol l}^{-1}$ , and 8.6±0.6  $\mu\text{mol l}^{-1}$  for DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ , respectively. The variability within the bottom and pore water concentrations had a moderate to high impact on the return fluxes: 0.4±0.1  $\text{mmol m}^{-2} \text{d}^{-1}$ , 0.03±0.01  $\text{mmol m}^{-2} \text{d}^{-1}$ , 3.9±2.2  $\mu\text{mol m}^{-2} \text{d}^{-1}$ , and 1.5±0.4  $\mu\text{mol m}^{-2} \text{d}^{-1}$  for DIC, DOC,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ , respectively. This assessment allowed us to define a spatial representativeness able to account for the uncertainties in the return fluxes of DIC (17%), DOC (33%),  $\text{NH}_4^+$  (57%), and  $\text{PO}_4^{3-}$  (29%) as calculated using data set I. These relatively high uncertainties, especially for  $\text{NH}_4^+$ , suggest the need for more detailed studies on representativeness of experimentally derived benthic diffusive fluxes, which should be broadened also to other basins characterized with different oxygen availability (and variability) and sediment type.

#### 4.5. Benthic loads of carbon (DIC+DOC), N- $\text{NH}_4^+$ and of P- $\text{PO}_4^{3-}$

This study showed that the diffusive fluxes from marine bottom sediments can be spatially variable and that their quantification can be burdened by relatively high uncertainties. Nevertheless, to emphasize the importance of bottom sediments in the functioning of the marine ecosystem, especially with respect to the eutrophication of the Baltic Sea basin, we extrapolated our data to quantify the bulk diffusive loads of the investigated constituents. This was done only for the Baltic Proper (excluding the methane stations), which has a total surface area of 78,280  $\text{km}^2$ . The extrapolation of the limited number of available values from the Bothnian Sea would have resulted in a large distortion of the calculated diffusive loads. All of the calculations are summarized in Table S6. Although the estimated values varied over a wide range, in general, the sediments of the Baltic Sea can still be considered as a source of total carbon (DIC+DOC) 159  $\text{kt yr}^{-1}$ , N- $\text{NH}_4^+$  6.3  $\text{kt yr}^{-1}$ , and P- $\text{PO}_4^{3-}$  3.7  $\text{kt yr}^{-1}$  (Table S6). These median values were compared to previously reported loads of C, N, and P in the Baltic Sea. Recently, the annual efflux for the complete coastal zone of the Gdańsk Bay was estimated for 6.9  $\text{ktN}$  and 0.9  $\text{ktP}$  (Thoms et al., 2018). Kulinski and Pempkowiak (2011) reported total carbon loads from different sources: riverine inflow (10,900  $\text{kt yr}^{-1}$ ), input from the North Sea (3,910  $\text{kt yr}^{-1}$ ), atmospheric deposition (precipitation; 570  $\text{kt yr}^{-1}$ ), and point sources (40  $\text{kt yr}^{-1}$ ). They found that total benthic carbon release constitutes 1.5% of riverine run-off, ~4% of the North Sea input, and ~28% of atmospheric deposition. The carbon loads from sediment obtained in the present



study can also be compared with the annual carbon loads resulting from submarine groundwater discharge (SGD), which is the source of 310 kt yr<sup>-1</sup> of carbon in the Baltic Sea (Szymczycha et al., 2014). The total carbon loads from sediments therefore constitute up to 51% of the total SGD-related loads. The HELCOM PLC-6 report (2018) provides data on the annual loads of total N and P for the whole Baltic Sea. For nitrogen the major pathways are: air deposition (149.9 kt yr<sup>-1</sup>), riverine loads (294.8 kt yr<sup>-1</sup>), and direct point sources (10.3 kt yr<sup>-1</sup>). According to the report, benthic loads of N-NH<sub>4</sub><sup>+</sup> contribute ~4% to air deposition, ~2% to riverine inflow, about the same as point sources. For phosphorus the main source was riverine load (18.5 kt yr<sup>-1</sup>), with the remainder coming from direct point sources (0.7 kt yr<sup>-1</sup>). Annual sediment loads of P-PO<sub>4</sub><sup>3-</sup> made up ~20% of the riverine inflow, a contribution almost six times larger than that of direct point sources. While the assessment of chemical substance loads from sediments requires caution, a comparison of the major pathways of C, N, and P must be taken into account in estimates of their budgets in the Baltic Sea.

## 5. Conclusions

In general, higher benthic diffusive fluxes of DIC, DOC, NH<sub>4</sub><sup>+</sup>, and PO<sub>4</sub><sup>3-</sup> were calculated from data set II than from data set I, indicating the high potential of Baltic Sea sediments to release those substances and that conditions at the sediment-water interface can effectively limit the respective fluxes. Return fluxes in the Bornholm Basin, in the Gdańsk Basin, including the Gdańsk Deep, and probably also to some extent in the Eastern Gotland Basin could be largely attributed to inflows of saline and oxygen-rich waters from the North Sea. A comparison of our data with previously reported findings clearly showed that a sequence of inflows has a greater ability to diminish diffusive fluxes than does a single MBI. Nevertheless, Baltic Sea sediments, and in particular sediments in the Baltic Proper, remain a source of DIC, DOC, NH<sub>4</sub><sup>+</sup> and PO<sub>4</sub><sup>3-</sup> inputs into the water column, even during the prolonged influence of MBIs. This study demonstrates the importance of the approach used to assess diffusive fluxes. This was well exemplified by the results from the Bothnian Sea, where the values obtained from the pore waters profiles (data set II) showed the high diffusive potential of sediments in that basin. However, due to the predominantly oxic conditions in the bottom waters, the concentration gradients would be low, thus causing no (or very low) return fluxes, a situation very well illustrated by the values obtained from data set I.

## Acknowledgements

This study was conducted within the framework of the following projects: 2015/19/B/ST10/02120, 2016/21/B/ST10/01213, and 2019/33/N/ST10/00161, sponsored by National Science Centre and WaterPUCK BIOS-TRATEG3/343927/3/NCBR/2017, financed by the National Centre of Research and Development (NCBiR) within the BIOS-TRATEG III program.

## Supplementary materials

Supplementary material associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.oceano.2021.04.002>.

## References

- Ahtiainen, H., Artell, J., Elmgren, R., Hasselström, L., Håkanson, C., 2014. Baltic Sea nutrient reductions – What should we aim for? *J. Environ. Manage.* 145, 9–23. <https://doi.org/10.1016/j.jenvman.2014.05.016>
- Arndt, S., Jørgensen, B.B., LaRowe, D.E., Middelburg, J.J., Pancost, R.D., Regnier, P., 2013. Quantifying the degradation of organic matter in marine sediments: A review and synthesis. *Earth-Sci. Rev.* 123, 53–86. <https://doi.org/10.1016/j.earscirev.2013.02.008>
- Benner, R., 2002. Chapter 3 – Chemical composition and reactivity. In: Dennis, A.H., Craig, A.C. (Eds.), *Biogeochemistry of Marine Dissolved Organic Matter*. Academic Press, San Diego, 59–90.
- Berelson, W.M., McManus, J., Severmann, S., Rollins, N., 2019. Benthic fluxes from hypoxia-influenced Gulf of Mexico sediments: Impact on bottom water acidification. *Mar. Chem.* 209, 94–106. <https://doi.org/10.1016/j.marchem.2019.01.004>
- Boudreau, B.P., 1997. *Diagenetic models and their implementation: Modelling transport and reactions in aquatic sediments*. Springer-Verlag, Berlin-Heidelberg-New York.
- Brodecka-Goluch, A., Łukawska-Matuszewska, K., 2018. Pore water dissolved organic and inorganic carbon in relation to methane occurrence in sediments of the Gdańsk basin (southern Baltic Sea). *Cont. Shelf Res.* <https://doi.org/10.1016/j.csr.2018.08.008>
- Burdige, D.J., Komada, T., Magen, C., Chanton, J.P., 2016. Modeling studies of dissolved organic matter cycling in Santa Barbara Basin (CA, USSA) sediments. *Geochim. Cosmochim. Acta* 195, 100–119 <http://dx.doi.org/10.1016/j.gca.2016.09.007>
- Carpenter, S.R., 2005. Eutrophication of aquatic ecosystems: biostability and soil phosphorus. *Proc. Natl. Acad. Sci. U.S.A* 102 (29), 10002–10005. <https://doi.org/10.1073/pnas.0503959102>
- Christoffersen, P.L., Christiansen, C., Jensen, J.B., Leipe, T., Hille, S., 2007. Depositional conditions and organic matter distribution in the Bornholm Basin, Baltic Sea. *Geo-Mar. Lett.* 27, 325–338.
- Conley, D.J., Humborg, C., Rahm, L., Savchuk, O.P., Wulff, F., 2002. Hypoxia in the Baltic Sea and Basin-Scale Changes in Phosphorus Biogeochemistry. *Environ. Sci. Tech.* 36, 5315–5320. <https://doi.org/10.1021/es025763w>
- Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling Eutrophication: Nitrogen and Phosphorus. *Science* 323, 1014–1015. <https://doi.org/10.1126/science.1167755>
- Dalsgaard, T., Thamdrup, B., 2002. Factors controlling anaerobic ammonium oxidation with nitrite in marine sediments. *Appl. Environ. Microbiol.* 68 (8), 3802–3808. <https://doi.org/10.1128/AEM.68.8.3802-3808.2002>
- Denis, L., Grenz, C., 2003. Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean Sea). *Oceanol. Acta* 26, 373–389. [https://doi.org/10.1016/S0399-1784\(03\)00017-3](https://doi.org/10.1016/S0399-1784(03)00017-3)
- Eckhell, J., Jonsson, P., Meilli, M., Carman, R., 2000. Storm influence on the accumulation and lamination of sediments in the deep areas of the north-western Baltic Proper. *Ambio* 29, 238–245.
- Emerson, S., Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* 3, 621–634. <https://doi.org/10.1029/PA003i005p00621>

- Fellman, J.B., D'Amore, D.V., Hood, E., 2008. An evaluation of freezing as a preservation technique for analysing dissolved organic C, N and P in surface water samples. *Sci. Total Environ.* 392, 305–312. <https://doi.org/10.1016/j.scitotenv.2007.11.027>
- Freitas, F.S., Hendry, K.R., Henley, S.F., Faust, J.C., Tessin, A.C., Stevenson, M.A., Abbott, G.D., März, C., Arndt, S., 2020. Benthic-pelagic coupling in the Barents Sea: an integrated data-model framework. *Phil. Trans. R. Soc. A.* 378, 20190359. <https://doi.org/10.1098/rsta.2019.0359>
- Gilbert, D., Sundby, B., Gobeil, C., Mucci, A., Tremblay, G.H.A., 2005. A seventy – two – year record of diminishing deep-water oxygen in the St. Lawrence estuary: The northwest Atlantic connection. *Limnol. Oceanogr.* 50, 1657–1666.
- Glud, R.N., 2008. Oxygen dynamics of marine sediments. *Mar. Biol. Res.* 4, 243–289. <https://doi.org/10.1080/17451000801888726>
- Graca, B., Burska, D., 2011. Organic Carbon and Nutrients in the Baltic Sea Sediments. In: Uścinowicz, S. (Ed.), *Geochemistry of Baltic Sea surface sediments*. Polish Geological Institute-National Research Institute, Warsaw, 172–209.
- Graca, B., Witek, Z., Burska, D., Białkowska, I., Łukawska-Matuszewska, K., Bolalek, J., 2006. Pore water phosphate and ammonia below the permanent halocline in the south-eastern Baltic Sea and their benthic fluxes under anoxic conditions. *J. Mar. Syst.* 63, 141–154. <https://doi.org/10.1016/j.jmarsys.2006.06.003>
- Grasshoff, K., Kremling, K., Ehrhardt, M., 1999. *Methods of Seawater Analysis*. Wiley-VCH Verlag. <https://doi.org/10.1002/9783527613984>
- Gustafsson, E., Savchuk, O.P., Gustafsson, B.G., Müller-Karulis, B., 2017. Key processes in the coupled carbon, nitrogen, and phosphorus cycling of the Baltic Sea. *Biogeochemistry* 134, 301–317. <https://doi.org/10.1007/s10533-017-0361-6>
- Hall, P.O., Almroth Rosell, E., Bonaglia, S., Dale, A.W., Hylén, A., Kononets, M., Nilsson, M., Sommer, S., van de Velde, S., Viktorsson, L., 2017. Influence of natural oxygenation of Baltic proper deep water on benthic recycling and removal of phosphorus, nitrogen, silicon and carbon. *Front. Mar. Sci.* 4, 27. <https://doi.org/10.3389/fmars.2017.00027>
- Hannig, M., Lavik, G., Kuypers, M.M.M., Woebken, D., Martens-Habben, W., Jürgens, K., 2007. Shift from denitrification to anammox after inflow events in the central Baltic Sea. *Limnol. Oceanogr.* 52 (4), 1336–1345. <https://doi.org/10.2307/4502294>
- Hansson, M., Viktorsson, L., Andersson, L., 2017. *Oxygen Survey in the Baltic Sea 2017 – Extent of Anoxia and Hypoxia, 1960–2017*. Rep. *Oceanogr.* 63 ISSN: 0283-1112 © SMHI.
- Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? *Org. Geochem* 27 (5–6), 195–212. [https://doi.org/10.1016/S0146-6380\(97\)00066-1](https://doi.org/10.1016/S0146-6380(97)00066-1)
- HELCOM, 2018. Sources and pathways of nutrients to the Baltic Sea. In: *Baltic Sea Environment Proceedings No. 153*.
- Hille, S., Nausch, G., Lepie, T., 2005. Sedimentary deposition and reflux of phosphorus (P) in the Eastern Gotland Basin and their coupling with P concentrations in the water column. *Oceanologia* 47 (4), 663–679.
- Hille, S., Leipe, T., Seifert, T., 2006. Spatial variability of recent sedimentation rates in the Eastern Gotland Basin (Baltic Sea). *Oceanologia* 48, 297–317.
- Kuliński, K., Pempkowiak, J., 2011. The carbon budget of the Baltic Sea. *Biogeosciences* 8, 3219–3230. <https://doi.org/10.5194/bg-8-3219-2011>
- Kuliński, K., Schneider, B., Hammer, K., Machulik, U., Schulz-Bull, U., 2014. The influence of dissolved organic matter on the acid-base system of the Baltic Sea. *J. Mar. Syst.* 132, 106–115. <https://doi.org/10.1016/j.jmarsys.2014.01.011>
- Kuypers, M.M.M., Sliemers, A.O., Lavik, G., Schmid, M., Jørgensen, B.B., Kuenen, J.G., Sinninghe, J.S., Strous, M., Jetten, M.S.M., 2003. Anaerobic ammonium oxidation by anammox bacteria in the Black Sea. *Nature* 422 (6932), 608–611. <https://doi.org/10.1038/nature01472>
- LaRowe, D.E., Arndt, S., Bradley, J.A., Burwicz, E., Dale, A.W., Amend, J.P., 2020. Organic carbon and microbial activity in marine sediments on a global scale throughout the Quaternary. *Geochim. Cosmochim. Acta* 286, 227–247. <https://doi.org/10.1016/j.gca.2020.07.017>
- Lass, H.-U., Matthäus, W., Feistel, R., Nausch, G., 2008. General Oceanography of the Baltic Sea. In: Wasmund, N. (Ed.), *State and Evolution of the Baltic Sea, 1952–2005: A Detailed 50-Year Survey of Meteorology and Climate, Physics, Chemistry, Biology, and Marine Environment*. John Wiley & Sons, 5–43. <https://doi.org/10.1002/9780470283134.ch2>
- Leipe, T., Tauber, F., Vallius, H., Virtasalo, J., Uścinowicz, S., Kowalski, N., Hille, S., Lindgren, S., Myllyvirta, T., 2011. Particulate organic carbon (POC) in surface sediments of the Baltic Sea. *Geo-Mar. Lett.* 31, 175–188. <https://doi.org/10.1007/s00367-010-0223-x>
- Li, Y.-H., Gregory, S., 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* 38, 703–714.
- Łukawska-Matuszewska, K., Burska, D., 2011. Phosphate exchange across the sediment-water interface under oxic and hypoxic/anoxic conditions in the southern Baltic Sea. *Oceanol. Hydrobiol. Stud.* 40 (2), 57–71. <https://doi.org/10.2478/s13545-011-0017-4>
- Łukawska-Matuszewska, K., Kielczewska, J., 2016. Effects of near-bottom water oxygen concentration on biogeochemical cycling of C, N and S in sediments of the Gulf of Gdańsk (southern Baltic). *Cont. Shelf Res.* 177, 30–42. <https://doi.org/10.1016/j.csr.2016.02.001>
- Łukawska-Matuszewska, K., Graca, B., 2018. Pore water alkalinity below the permanent halocline in the Gdańsk Deep (Baltic Sea) – Concentration variability and benthic fluxes. *Mar. Chem.* 204, 49–61. <https://doi.org/10.1016/j.marchem.2018.05.011>
- Matthäus, W., Nehring, D., Feistel, R., Nausch, G., Mohrholz, V., Lass, H., 2008. The Inflow of Highly Saline Water into the Baltic Sea. In: Feistel, R., Nausch, G., Wasmund, N. (Eds.), *State and Evolution of the Baltic Sea, 1952–2005*. John Wiley & Sons, Inc., 265–309. <https://doi.org/10.1002/9780470283134.ch10>
- Meier, H.E.M., Edman, K., Eilola, K., Placke, M., Neumann, T., Andersson, H., Brunnabend, S.-E., Dieterich, C., Frauen, C., Friedland, R., Gröger, M., Gustafsson, B.G., Gustafsson, E., Isaev, A., Kniebusch, M., Kuznetsov, I., Müller-Karulis, B., Naumann, M., Omstedt, A., Ryabchenko, V., Saraia, S., Savchuk, O.P., 2019. Assessment of uncertainties in scenario simulations of biogeochemical cycles in the Baltic Sea. *Front. Mar. Sci.* 6, art. 46. <https://doi.org/10.3389/fmars.2019.00046>
- Mohrholz, V., 2018. Major Baltic Inflow Statistics – Revised. *Front. Mar. Sci.* 22. <https://doi.org/10.3389/fmars.2018.00384>
- Naumann, M., Umlauf, L., Mohrholz, V., Kuss, J., Siegel, H., Waniek, J.J., Schulz-Bull, D.E., 2018. Hydrographic-hydrochemical assessment of the Baltic Sea 2017. *Marine Science Reports* 107.
- Naumann, M., Gräwe, U., Mohrholz, V., Kuss, J., Siegel, H., Waniek, J.J., Schulz-Bull, D.E., 2019. Hydrographic-hydrochemical assessment of the Baltic Sea 2018. *Mar. Sci. Rep.* 110.
- Nausch, M., Nausch, G., Wasmund, N., Nagel, K., 2008. Phosphorus pool variations and their relation to cyanobacteria development in the Baltic Sea: A three-year study. *J. Mar. Syst.* 71 (1–2), 99–111. <https://doi.org/10.1016/j.jmarsys.2007.06.004>
- Nebbioso, A., Piccolo, A., 2013. Molecular characterization of dissolved organic matter (DOC): a critical review. *Anal. Bioanal. Chem.* 405, 109–124. <https://doi.org/10.1007/s00216-012-6363-2>
- Noffke, A., Sommer, S., Dale, A.W., Hall, P.O.J., Pfannkuche, O., 2016. Benthic nutrient fluxes in the Eastern Gotland Basin (Baltic Sea) with particular focus on microbial mat ecosystems. *J.*

- Mar. Syst. 158, 1–12. <https://doi.org/10.1016/j.jmarsys.2016.01.007>
- Premuzic, E.T., Benkovitz, C.M., Gaffney, J.S., Walsh, J.J., 1982. The nature and distribution of organic matter in the surface sediments of world oceans and seas. *Organic Geochem* 4 (2), 63–77. [https://doi.org/10.1016/0146-6380\(82\)90009-2](https://doi.org/10.1016/0146-6380(82)90009-2)
- Puttonen, I., Mattila, J., Jonsson, P., Karlsson, O.M., Kohonen, T., Kotilainen, A., Lukkari, K., Malmaeus, J.M., Rydin, E., 2014. Distribution and estimated release of sediment phosphorus in the northern Baltic Sea archipelagos. *Estuar. Coast. Shelf Sci.* 145, 9–21. <https://doi.org/10.1016/j.ecss.2014.04.010>
- Savchuk, O.P., Gustafson, B.G., Müller – Karulis, B., 2012. **BALTSEM – a marine model for the decision support within the Baltic Sea Region**. Technical Report No 7, Baltic Nest Institute, Stockholm University Baltic Sea Centre, 60 pp.
- Savchuk, O.P., 2018. Large-scale nutrient dynamics in the Baltic Sea, 1970–2016. *Front. Mar. Sci.* 5, 95. <https://doi.org/10.3389/fmars.2018.00095>
- Seeberg-Elverfeldt, J., Schlüter, M., Feseker, T., Kölling, M., 2005. Rhizon sampling of porewaters near the sediment-water interface of aquatic systems. *Limnol. Oceanogr. Methods* (8) 3. <https://doi.org/10.4319/lom.2005.3.361>
- Seiter, K., Hensen, C., Schröter, J., Zabel, M., 2004. Organic carbon content in surface sediments – defining regional provinces. *Deep Sea Res. Pt. I: Oceanogr. Res. Papers* 51 (12), 2001–2026. <https://doi.org/10.1016/j.dsr.2004.06.014>
- Sommer, S., Clemens, D., Yücel, M., Pfannkuche, O., Hall, P.O.J., Almroth-Rosell, E., Schulz-Vogt, N.H., Dale, A.W., 2017. Major bottom water ventilation events do not significantly reduce basin-wide benthic n and p release in the Eastern Gotland Basin (Baltic Sea). *Front. Mar. Sci.* 4, art. 18. <https://doi.org/10.3389/fmars.2017.00018>
- Strickland, J.D.H., Parsons, T.R., 1967. *A Practical Handbook of Seawater Analysis*. Fish. Res. Board Canada Bull., Ottawa 310 pp.
- 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. <https://doi.org/10.5697/oc.56-2.327>
- Thomas, H., Pempkowiak, J., Wulff, F., Nagel, K., 2010. The Baltic Sea. In: Liu, K-K., Atkinson, L., Quinones, R.A., Talaue-McManus, L. (Eds.), *Carbon and Nutrient Fluxes in Continental Margins*. Springer-Verlag, Berlin, 334–346.
- Thoms, F., Burmeister, C., Dippner, J.W., Gogina, M., Janas, U., Kendzierska, H., Liskow, I., Voss, M., 2018. Impact of Macrofaunal Communities on the Coastal Filter Function in the Bay of Gdansk. *Baltic Sea. Front. Mar. Sci.* 5, 201. <https://doi.org/10.3389/fmars.2018.00201>
- Viktorsson, L., Ekeröth, N., Nilsson, M., Kononets, M., Hall, P.O.J., 2013. Phosphorus recycling in sediments of the central Baltic Sea. *Biogeosciences* 10, 3901–3916. <https://doi.org/10.5194/bg-10-3901-2013>
- Walsh, J.J., 1991. Importance of continental margins in the marine biogeochemical cycling of carbon and nitrogen. *Nature* 350, 53–55.
- Winogradow, A., Pempkowiak, J., 2014. Organic carbon burial rates in the Baltic Sea sediments. *Esuar. Coast. Shelf Sci.* 138, 27–36. <https://doi.org/10.1016/j.ecss.2013.12.001>
- Wulff, F., Rahm, L., Hallin, A.-K., Sandberg, J., 2001. *Nutrient Budget Model of the Baltic Sea*. In: Wulff, F.V., Rahm, L.A., Larsson, P. (Eds.), *A System analysis of the Baltic Sea*. Springer-Verlag, Berlin, 354–372.