

#### **ORIGINAL RESEARCH ARTICLE**

## Deposition, return flux, and burial rates of nitrogen and phosphorus in the sediments of two high-Arctic fjords

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Received 4 April 2018; accepted 4 May 2018 Available online 18 May 2018

#### **KEYWORDS**

Hornsund; Kongsfjorden; Sedimentary nitrogen and phosphorus; Pore water; Concentrations; Nutrients **Summary** The aim of this study was to determine the burial rates of nitrogen (N) and phosphorus (P) in the sediments of two high-latitude fjords: Hornsund and Kongsfjorden (Spitsbergen). Both deposition to sediments and the return flux from sediments to the water column of the various species of these elements were, therefore, quantified. The burial rate was then calculated as the difference between deposition and return flux. The required concentrations of N and P species were measured in surface sediments, in pore water extracted from the sediments, and in the above-bottom water at sampling stations situated along the axes of the fjords.

Annual deposition to sediments ranged between 2.3–8.3 g m<sup>-2</sup> for N and 0.9–2.8 g m<sup>-2</sup> for P. The nitrogen return fluxes ranged from 0.12 to 1.46 g m<sup>-2</sup> y<sup>-1</sup>. At most stations, the N flux was predominantly of dissolved organic (about 60–70%) rather than inorganic N. The P return flux varied between 0.01 and 0.11 g m<sup>-2</sup> y<sup>-1</sup>, with organic species constituting 60–97%. The N and P burial rates differed between fjords: 2.3–7.9 g N m<sup>-2</sup> y<sup>-1</sup> and 0.9–2.8 g P m<sup>-2</sup> y<sup>-1</sup> in Hornsund vs. 0.9–1.3 N g m<sup>-2</sup> y<sup>-1</sup> and 1.0–1.2 g P m<sup>-2</sup> y<sup>-1</sup> in Kongsfjorden. This was accompanied by a different efficiency of N and P burial – higher in Hornsund than in Kongsfjorden, in both cases. This suggests differences in the quality and quantity of N and P organic species deposited to sediments and therefore differences in the intensity of their mineralization and/or decomposition. © 2018 Institute of Oceanology of the Polish Academy of Sciences. Production and hosting by Elsevier Sp. z o.o. This is an open access article under the CC BY-NC-ND license (http:// creativecommons.org/licenses/by-nc-nd/4.0/).

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



#### https://doi.org/10.1016/j.oceano.2018.05.001

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#### 1. Introduction

Nitrogen (N) and phosphorus (P) limit or co-limit primary production in the global ocean (Moore et al., 2013; Tremblay et al., 2015). Some of the substances containing these elements are deposited to surface sediments, whether as organic or inorganic compounds. The differences in the chemical and physical forms (species) of these substances reflect their different sources. Inorganic species are mostly transported by river runoff, as a result of weathering and anthropogenic activity and/or from the exoskeletons or skeletons of dead marine organisms. In sediments, N is bound in organic substances or occurs as lattice-bound ammonium in clay minerals (Knies et al., 2007), while P is usually present as loosely sorbed phosphate ( $PO_4^{3-}$ ), iron-bound  $PO_4^{3-}$ , authigenic fluorapatite, detrital P, and organic P (Ruttenberg and Goni, 1997). Organic matter (OM) formed during autochthonous production and/or supplied from land is important form of N and P in sediments. Terrestrial OM may be fresh, produced recently on land, or ancient, mobilized by the melting and thawing of the permafrost. Hence, the processes related to OM production, mineralization, and transformation shape the pools of inorganic N and P species in the water column and thus primary production as well. The short loops between the organic and inorganic forms of N and P are strongly evidenced in productive coastal zones, where the inventories of both are supplemented by return fluxes from the sediments (Benitez-Nelson, 2000; Cloern, 2001; Nixon, 1995).

Global warming and its consequences are becoming increasingly evident, especially in the Arctic, where the respective changes have come early and are of particular intensity. Shifts such as a significant reduction in the amount of sea ice extent or, in some parts of the high Arctic, even the complete disappearance of sea ice, have increased the amount of irradiance reaching the water column and therefore the level of primary production (Fernandez-Mendez et al., 2015; Polyakov et al., 2017). Since it is known that, in the Arctic, N is the main element limiting production (Reigstad et al., 2002; Tremblay et al., 2015), studies on the cycling and origin of N have become particularly important.

Despite the many studies on OM cycling in the Arctic Ocean and especially in its fjords, very little is known about N and P deposition and burial in bottom sediments. Sedimentary N is usually analyzed as total nitrogen, without distinguishing between inorganic and organic forms, while phosphorus in sediments has been generally neglected (Carroll et al., 2008; Kim et al., 2011; Koziorowska et al., 2016; Kuliński et al., 2014; Zaborska et al., 2006, 2016). Moreover, investigations into N accumulation and burial rates in fjord sediments usually do not take into account the fraction of organic N that undergoes mineralization and/or hydrolysis in surface sediments and returns to the water column in the form of dissolved compounds. The only available results for the Svalbard region are those of Blackburn et al. (1996) and according to that study, only  $\sim$ 23% of the organic N deposited in surface sediments remains there, which suggests that sediments are a significant source of N in the water column. However, there are no published data on the burial of P in the sediments of the Svalbard region, nor on the return fluxes of phosphates from bottom sediments to the water column. In other regions, sediments were shown to be an important sink for P (burial), although some fraction of sedimentary P diffuses back into the water column in the form of bioavailable  $PO_4^{3-}$  (Filippelli, 2001; Rydin et al., 2011; van der Zee et al., 2002).

The goal of this study was to quantify the burial rates of N and P in the surface sediments of two high-latitude fjords located on the west coast of Spitsbergen: Hornsund and Kongsfjorden. This was achieved by measuring the concentrations of total N and total P (TN, TP), organic N and P (ON, OP) and inorganic N and P (IN, IP) in the surface sediments, pore water, and in the seawater overlying the sediments in samples acquired at four sampling stations in Hornsund and three in Kongsfjorden. The stations were situated along the axes of the respective fjords. The return fluxes of both dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) as well as inorganic forms of N and P, including nitrate  $(NO_3^{-})$ , nitrite  $(NO_2^{-})$ , and phosphate ( $PO_4^{3-}$ ) were calculated based on diffusion from the pore water to the bottom water using the Fick's first law of diffusion. N and P burial rates were calculated as the difference between the accumulation in the sediments and the return flux. The results presented in this report supplement those of studies on the deposition and burial of carbon in the same region (Koziorowska et al., 2018).

#### 2. Study area

The study area was already described in sufficient detail by Koziorowska et al. (2018). The important features as regards the study subject are as follows. Both fjords are situated on the west coast of Spitsbergen. Hornsund is the southernmost, medium-size fiord with a complex coastline (Beszczyńska-Moller et al., 1997; Blaszczyk et al., 2013). The largest bay – Brepollen is situated in the innermost part of the fjord and isolated from the central basin by an underwater riffle and the Treskelen Peninsula. Hornsund is influenced by two main current systems: the coastal Sørkapp Current and the West Spitsbergen Current (WSC; Piechura et al., 2001; Promińska et al., 2017). The sediments are composed of sandy mud and mud (Drewnik et al., 2016), with a maximum OC concentration  ${\sim}20~\text{mg}~\text{g}^{-1}$  at the inner part of the fjord (Koziorowska et al., 2016; Zaborska et al., 2016). Primary production ranges from 120 to 220 g C m<sup>-2</sup> y<sup>-1</sup> (Piwosz et al., 2009; Smoła et al., 2017).

Kongsfjorden, located on the northwestern Spitsbergen coast, is a relatively small fjord, divided into two parts by a chain of islands (Lovénøyane). The outer part is strongly affected by the WSC whereas the inner part is under the influence of tidewater glaciers (Promińska et al., 2017; Svendsen et al., 2002). The large supply of mineral material, arriving with the freshwater from melting glaciers, snow and ice in summer, accounts for the relatively high sediment accumulation rates (SAR). The surface sediments are composed of fairly uniform mud (Włodarska-Kowalczuk and Pearson, 2004), with a sedimentary OC concentrations from 1 to 20 mg g<sup>-1</sup> (Koziorowska et al., 2017). Annually, primary production is in the range of 20 and 50 g C m<sup>-2</sup> (Piwosz et al., 2009; Smoła et al., 2017).



Figure 1 Locations of the sampling stations in Hornsund and Kongsfjorden.

#### 3. Experimental

#### 3.1. Sampling

Surface sediments were collected using a Nemisto gravity corer from onboard the r/v "Oceania" in the summers of 2015 and 2016. Samples were obtained from seven stations: H1, H2, H3, and H4, representing the outer, central, inner, and glacial (Brepollen) parts of Hornsund, and Kb1, Kb2, and Kb3 – the outer, central, and inner parts of Kongsfjorden (Fig. 1). At each sampling station, two undisturbed sediment cores were collected and then combined to increase the amount of material for further analyses. The bottom water overlying the sediment (5 cm above the sediment surface - to avoid collecting pore water caused by possible sediment resuspension) was sampled using a pre-cleaned syringe for nutrients  $(N-NO_2^{-}, N-NO_3^{-}, P-PO_4^{3-})$  and DOC analyses. The topmost parts of the sediment cores (0-3 cm)were then sliced into 10-mm-thick layers and frozen (-20°C). In the laboratory, sediment samples were centrifuged (15 min, 5000 g) and the resulting pore water was analyzed for N-NO<sub>2</sub><sup>-</sup>, N-NO<sub>3</sub><sup>-</sup>, P-PO<sub>4</sub><sup>3-</sup> and DOC. Residual sediments were freeze-dried, homogenized, and analyzed for total, organic, and inorganic concentrations of N and P species. All analyses were carried out at the Marine Biogeochemistry Laboratory of the Institute of Oceanology of the Polish Academy of Sciences (Sopot, Poland), using the methods described below.

### 3.2. Analyses of total, organic, and inorganic nitrogen and phosphorus in sediment samples

Total N and inorganic N (bound as ammonium to fine-grained sediments) were analyzed in an elemental analyzer (Flash EA 1112 series) combined with a Delta VAdvantage isotopic ratio mass spectrometer (IRMS; Thermo Electron Corp., Germany). For both TN and IN,  $\sim$ 50 mg (10-µg accuracy) of freeze-dried and homogenized sediment was weighed into silver capsules. The IN sediment samples were first treated with a KOBr-KOH solution to remove ON, according to the method described by Silva and Bremner (1966). Quantitative measurements of TN were calibrated against certified reference materials (marine sediments) provided by HEKAtech GmbH (Germany). The precisions of the TN and IN measurements, reported as the relative standard deviations (RSDs), were better than  $\pm 1.7\%$ and  $\pm 2.4\%$  (*n* = 5), respectively. The ON concentration was calculated as the difference between the TN and IN concentrations.

Total P and IP concentrations were measured using a spectrophotometer (TECAN, Switzerland) and the ammonium molybdate method after digestion of the sediment samples according to the procedure described by Aspila et al. (1976). Briefly, the samples for TP analysis were combusted in a muffle furnace at  $550^{\circ}$ C for 5 h and then extracted with 1 M HCl for 16–18 h. Samples for IP were analyzed as described for TP except the combustion step was omitted. The measurements were calibrated against certified refer-

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ence materials (river sediment) provided by BCR<sup>®</sup> (Community Bureau of Reference, Belgium). The precisions of the TP and IP measurements, reported as the RSDs, were  $\pm$ 4.2% and  $\pm$ 3.8% (*n* = 5), respectively. The OP concentration was calculated as the difference between the TP and IP concentrations.

### 3.3. Analyses of dissolved nitrogen and phosphorus species in water samples

### 3.3.1. Nitrites (N-NO<sub>2</sub><sup>-</sup>), nitrates (N-NO<sub>3</sub><sup>-</sup>), and phosphates (P-PO<sub>4</sub><sup>3-</sup>)

Nutrient (nitrite, nitrate, and phosphate) concentrations were analyzed colorimetrically on a Dr 2800 spectrophotometer (Hach-Lange, Germany) using the methods described in detail by Strickland and Parsons (1967) and by Salley et al. (1986). The accuracy of the nutrients analyses was confirmed by measurements of certified reference material (RM-BU; National Metrology Institute of Japan). The precisions (RSDs) were  $\pm 1.5\%$  for N-NO<sub>2</sub><sup>-</sup>,  $\pm 1.2\%$  for N-NO<sub>3</sub><sup>-</sup>, and  $\pm 1.6\%$  for P-PO<sub>4</sub><sup>3-</sup>.

## 3.3.2. Dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP)

DOC analyses were carried out using a TOC-L analyzer (Shimadzu Corp., Japan) and a high-temperature (680°C) oxidation method performed in the presence of Pt catalyst. Quality control was based on measurements of reference material (North Atlantic water, obtained from the Hansell Laboratory). The precision (RSD) was  $\pm 0.8\%$ ; n = 5.

DON and DOP concentrations were calculated from the measured DOC concentrations and the DOC/DON or DOC/DOP ratios characteristics of pore water in marine sediments. The average values of these ratios, as reported in the available literature, were 14.1  $\pm$  3.7 for DOC/DON (Alkhatib et al., 2012, 2013; Burdige, 2001; Burdige and Komada, 2015; Burdige and Zheng, 1998; Lomstein et al., 1998) and 407.0  $\pm$  183.8 for DOC/DOP (Loh and Bauer, 2000; Tremblay et al., 2014; Yasui et al., 2016). As there are no literature data for the DOC/DOP ratio in pore water, we used the results reported for the water column. For each pore water sample, both the range and the average results were calculated (Fig. 3). However, for further calculations of the return fluxes and burial rates only the average values were used.

#### 3.4. Calculations

### 3.4.1. Nitrogen and phosphorus deposition to sediments

The deposition of N and P, both inorganic and organic, in sediments was calculated as the product of the sediment mass accumulation rate (MAR) and the ON, IN, OP, and IP concentrations in the sediment layers. The MAR values for each sampling station were those reported in the literature (Koziorowska et al., 2017, 2018; Zaborska, 2017) (Table 1).

#### 3.4.2. Nitrogen and phosphorus return fluxes

The diffusion of dissolved N and P species from the sediments into the overlying bottom seawater was estimated based on Fick's first law of diffusion (Ullman and Aller, 1982).

$$J_{\mathbf{x}} = - \varphi imes \mathcal{D}_{\mathsf{sed}} imes rac{\Delta c}{\Delta \mathbf{x}},$$

where  $J_x$  is the diffusion flux of  $x [N-NO_2^{-}, N-NO_3^{-}, P-PO_4^{3-}, DON, or DOP; <math>\mu g \text{ cm}^{-2} \text{ s}^{-1}]; \varphi$  is the porosity of the sediment,  $D_{\text{sed}}$  is the specific sediment diffusion coefficient for  $NO_2^{-}, NO_3^{-}, PO_4^{3-}, DON, \text{ or DOP [cm}^2 \text{ s}^{-1}], \text{ and } \Delta c/\Delta x$  is the N-NO<sub>2</sub><sup>-</sup>, N-NO<sub>3</sub><sup>-</sup>, P-PO<sub>4</sub>^{3-}, DON, or DOP concentration gradient between the pore water of the surface-most sediment layer and the seawater overlying the sediments [ $\mu g \text{ cm}^{-3}/\text{cm}$ ].

The  $D_{sed}$  values used in the calculations were derived from the literature and corrected for temperature and sediment porosity according to Boudreau (1997) and Holcombe et al. (2001):  $5.54 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for NO<sub>2</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>,  $1.53 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for PO<sub>4</sub><sup>3-</sup>, and  $1.22 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> for DON and DOP. Since, under oxic conditions, ammonium is oxidized to nitrate, its presence and release from the oxic surface-most sediment layer is unlikely (see Chapter 5.1 for the subject discussion; Glud et al., 1998; Kotwicki et al., 2018) and, therefore, ammonium was disregarded in the analyses described herein.

### 3.4.3. Burial rates of total nitrogen (TN $_{BR}$ ) and total phosphorus (TP $_{BR}$ )

 $TN_{BR}$  (or  $TP_{BR}$ ) were calculated as the difference between TN (or TP) deposition in the surface-most sediments and the sum of the return fluxes of  $N-NO_2^-$ ,  $N-NO_3^-$ , and DON for  $TN_{BR}$  or  $P-PO_4^{3-}$  and DOP for  $TP_{BR}$ .

Station	MAR $[g m^{-2} y^{-1}]$	Reference
H1	1310	Koziorowska et al. (2018)
H2	2330	Koziorowska et al. (2018)
H3	3070	Zaborska (2017)
H4	6250	Zaborska (2017)
Kb1	1160	Koziorowska et al. (2018)
Kb2	1950	Koziorowska et al. (2018)
Kb3	_a	Koziorowska et al. (2017)

 Table 1
 Sediment mass accumulation rates (MAR) at the investigated sampling stations.

See Chapter 4.2 for details.

**Table 2** Concentrations  $[mg g^{-1}]$  of sedimentary nitrogen: total (TN), organic (ON), and inorganic (IN) and sedimentary phosphorus (TP, OP and IP) in the top-most (0–3 cm) sediment layer.

Station	Concentrations in sediments $[mg g^{-1}]$						
	TN	ON	IN	TP	OP	IP	
H1	2.22	1.49	0.72	0.69	0.30	0.39	
H2	1.94	1.26	0.68	0.63	0.23	0.40	
H3	1.38	0.67	0.72	0.48	0.15	0.33	
H4	1.33	0.47	0.86	0.45	0.14	0.30	
Kb1	2.37	2.15	0.23	0.97	0.25	0.72	
Kb2	1.19	1.07	0.12	0.68	0.18	0.51	
Kb3	0.35	~0.35 <sup>b</sup>	<lod<sup>a</lod<sup>	0.21	0.03	0.18	

 $^{\rm a}$  LOD: limit of detection (LOD: 0.01 mg g  $^{-1}).$ 

<sup>b</sup> Difference between TN and IN (<LOD).

#### 4. Results

#### 4.1. Nitrogen and phosphorus concentrations

#### 4.1.1. Sedimentary N and P concentrations

The TN concentrations in the surface sediments of Hornsund and Kongsfjorden were  $1.33-2.22 \text{ mg g}^{-1}$  and 0.35-2.37 mg  $g^{-1}$ , respectively (Table 2), and they increased towards the mouths of the fjords. The spatial distribution of the ON concentration was similar to that of TN, with higher concentrations measured at outer regions (1.49 mg  $g^{-1}$  and 2.15 mg  $g^{-1}$ , respectively) and lower concentrations at inner regions (0.47 mg  $g^{-1}$  and 1.07 mg  $g^{-1}$ , respectively). By contrast, there was no distinct spatial difference in the IN concentrations measured at stations within the fjords, although the values were significantly higher in Hornsund  $(0.68-0.86 \text{ mg g}^{-1})$  than in Kongsfjorden (ranging from below the limit of detection [LOD] to 0.23 mg g<sup>-1</sup>). The TN, ON, and IN concentrations determined in this study were close to those previously reported for the sediments of Arctic fjords. Specifically, TN, ON, and IN concentrations of 0.5- $3.7 \text{ mg g}^{-1}$ ,  $0.2-2.9 \text{ mg g}^{-1}$ , and  $0.2-1.0 \text{ mg g}^{-1}$ , respectively, were measured by Knies et al. (2007),  $0.5-1.5 \text{ mg g}^{-1}$ , 0.3–0.9 mg g<sup>-1</sup>, and 0.2–0.6 mg g<sup>-1</sup> by Schubert and Calvert (2001), and  $0.7-4.7 \text{ mg g}^{-1}$ ,  $0.4-3.4 \text{ mg g}^{-1}$ , and 0.2-1.3 mg  $g^{-1}$  by Winkelmann and Knies (2005).

As was the case for the TN and ON concentrations, the concentrations of all P fractions increased towards the mouths of the fjords (Table 2). TP, OP, and IP concentrations were  $0.45-0.69 \text{ mg g}^{-1}$ ,  $0.14-0.30 \text{ mg g}^{-1}$ , and  $0.30-0.40 \text{ mg g}^{-1}$ , respectively, in Hornsund and  $0.21-0.97 \text{ mg g}^{-1}$ ,  $0.03-0.25 \text{ mg g}^{-1}$ , and  $0.18-0.72 \text{ mg g}^{-1}$  in Kongsfjorden. Slightly higher TP and IP concentrations were measured in Kongsfjorden than in Hornsund. Unlike N, the inorganic P fraction predominated over the organic P fraction. In the only report on sedimentary P in Kongsfjorden (Zhu et al., 2014) available to us, IP concentrations were similar (0.01-0.6 mg g^{-1}) while those of TP and OP were higher (0.2-5.9 mg g^{-1} and 0.01-5.9 mg g^{-1}, respectively).

#### 4.1.2. N and P concentrations in pore and sea water

The concentrations of the measured nutrients in pore water are presented in Fig. 2, and those of the dissolved species of organic C, N, and P - in Fig. 3. The measured N-NO<sub>2</sub> concentrations were generally low and did not exceed  $0.1 \text{ mg L}^{-1}$ . Concentrations were highest at stations located in the outer parts of the fjords, and were especially high in the pore water extracted from the surface-most layers (Fig. 2a, b, e, and f), while concentrations were much lower in the inner regions (Fig. 2c, d and g). Significantly higher concentrations, reaching  $2.0-3.0 \text{ mg L}^{-1}$ , were measured for  $N-NO_3^{-}$ . This was observed at all stations except H4 and Kb3, located close to the glacier fronts, where N-NO<sub>3</sub><sup>-</sup> concentrations did not exceed  $0.20 \text{ mg L}^{-1}$ . At all stations, the highest N-NO3<sup>-</sup> concentrations occurred in the surface-most sediment layers and the lowest concentrations in the deeper layers (except stations H1 and Kb1; Fig. 2a and e). These are typical nitrate concentration profiles for surface sediments, where oxic conditions prevail (Schulz and Zabel, 2006). The measured concentrations were higher than the  $0.5 \text{ mg NO}_3^ L^{-1}$  previously reported for the Arctic region by several teams (Blackburn et al., 1996; Gihring et al., 2010; Hulth et al., 1996; Rysgaard et al., 1998; Thibodeau et al., 2010).

Similarly to nitrates and nitrites, higher concentrations of phosphates  $(P-PO_4^{3-})$  were measured in the outer and central parts of both fjords (up to 0.9 mg  $L^{-1}$ ; Fig. 2). The vertical distribution of P was more diverse than that of N, as P concentrations decreased towards the sediment surface at stations H1, H3, H4, Kb1, and Kb3. These profiles were in agreement with the  $PO_4{}^{3-}$  concentrations in pore waters reported in the literature (Schulz and Zabel, 2006). However, at stations H2 and Kb2, located in the central part of the fjords, the profiles of  $P-PO_4^{3-}$  were reversed and phosphate concentrations decreased with increasing depth (Fig. 2b and f). This reversed gradient of concentrations may suggest more intense organic matter mineralization in surface sediments caused by a larger contribution of fresh OM at these stations, caused by a local increase of primary production or organic matter preferential deposition. The hypothesis is supported by a higher return flux of dissolved inorganic carbon there (Koziorowska et al., 2018). However, further research is required to explain the phenomenon exclusively.

Wide ranging DON and DOP concentrations were found in the pore water of the two fjords (Fig. 3). Like the inorganic fractions, DON and DOP concentrations were higher at stations in the outer and central parts  $(4.5-23.4 \text{ mg L}^{-1} \text{ and}$  $0.4-1.8 \text{ mg L}^{-1}$ , respectively). The low DON and DOP concentrations in the inner parts of the fjords  $(0.4-5.4 \text{ mg L}^{-1})$ and  $0.0-0.4 \text{ mg L}^{-1}$ , respectively) may have been caused by the proximity of glaciers. Regions characterized by a high freshwater supply usually have lower rates of primary production and thus a smaller supply of fresh OM for deposition to the sediment surface. This is due to the high turbidity of the land-derived, mineral-rich, material discharged in large amounts by glaciers and river runoff, especially during the ablation season in the summer and early autumn (Moskalik et al., 2018). Typically, the concentration of dissolved constituents originating from mineralization and hydrolysis should decrease towards the sediment surface (Alkhatib et al., 2013; Blackburn et al., 1996; Winogradow and Pempkowiak, 2014; Yasui et al., 2016). However, at the investigated stations, the DON and DOP concentrations varied



**Figure 2** Concentrations of nitrites  $(N-NO_2^{-})$ , nitrates  $(N-NO_3^{-})$ , and phosphates  $(P-PO_4^{3-})$  in the pore water of the surface sediment layers (0-3 cm) at stations (a) H1, (b) H2, (c) H3, (d) H4, (e) Kb1, (f) Kb2, and (g) Kb3.

widely. At stations H1, Kb1 and Kb2 the values decreased towards the surface while at the other stations they increased, which suggested a difference in the quality of the OM supplied to the sediments. Nutrients (nitrites, nitrates, and phosphates) concentrations were significantly lower in the seawater overlying the sediments than in the pore waters (Table 3).  $N-NO_2^-$  concentrations were below the LOD for all sampling stations, N-



**Figure 3** Concentrations of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) in the pore water of the surface sediment layers (0-3 cm) at stations (a) H1, (b) H2, (c) H3, (d) H4, (e) Kb1, (f) Kb2, and (g) Kb3. The error bars represent the uncertainty resulting from the use of DOC/DON and DOC/DOP molar ratios to calculate DON and DOP concentrations (see Section 3.3.2 for details).

**Table 3** Concentrations  $[mg L^{-1}]$  of nitrites  $(N-NO_2^{-})$ , nitrates  $(N-NO_3^{-})$ , phosphates  $(P-PO_4^{3-})$ , dissolved organic carbon (DOC), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) in the seawater overlying the sediments.

Station	n Concentrations in water [mg L <sup>-1</sup> ]					
	$N-NO_2^-$	$N-NO_3^-$	P-P04 <sup>3-</sup>	DOC	DON	DOP
H1	<lod<sup>a</lod<sup>	0.05	0.02	1.90	0.16	0.01
H2	<LOD <sup>a</sup>	0.02	0.02	0.84	0.07	0.01
H3	<LOD <sup>a</sup>	0.05	0.04	1.16	0.10	0.01
H4	<lod<sup>a</lod<sup>	0.03	0.01	1.34	0.11	0.01
Kb1	<lod<sup>a</lod<sup>	0.02	0.02	1.09	0.09	0.01
Kb2	<LOD <sup>a</sup>	0.02	0.03	2.28	0.19	0.01
Kb3	<lod<sup>a</lod<sup>	0.03	0.01	1.60	0.13	0.01

<sup>a</sup> LOD: limit of detection.

 $NO_3^-$  varied between 0.02 and 0.05 mg L<sup>-1</sup>; and P-PO<sub>4</sub><sup>3-</sup> ranged from 0.02 to 0.04 mg L<sup>-1</sup>. These concentrations in the overlying seawater were close to those previously measured in the bottom water of the Arctic Ocean (Blackburn et al., 1996; Gihring et al., 2010; Thibodeau et al., 2010). For the organic fractions, the average concentrations varied between 0.09 and 0.19 mg L<sup>-1</sup> for DON and ~0.01 mg L<sup>-1</sup> for DOP. For all dissolved species of C, N, and P (both organic and inorganic) investigated in this study, the differences between the two fjords and the different stations were not significant.

#### 4.2. Deposition rates of nitrogen and phosphorus

#### 4.2.1. Sediment dating

The data indicated a steep gradient along the fjord axis, with low MARs in the outer parts and high MARs in the inner parts of both fjords (Table 1). At station Kb3, the MAR could not be determined due to sedimentation rates that were too fast to be determined using the radiolead method. The differences in the MARs along the axes of the two fjords indicated suspended matter loads differing in their intensity due to differences in their proximity to the sources of the sedimentary material, i.e., glacier fronts and/or rivers.

### 4.2.2. Deposition of inorganic and organic N and P to sediments

Recent annual rates of total (TN<sub>AR</sub>), organic (ON<sub>AR</sub>) and inorganic (IN<sub>AR</sub>) nitrogen deposition as well as total (TP<sub>AR</sub>), organic (OP<sub>AR</sub>) and inorganic (IP<sub>AR</sub>) phosphorus deposition are presented in Fig. 4. Despite the lower TN concentrations in the surface sediments of the inner stations in Hornsund (Table 2), the high MARs resulted in an increasing TN<sub>AR</sub> towards the inner part of the fjord (from 2.9 g m<sup>-2</sup> y<sup>-1</sup> at H1 to 8.3 g m<sup>-2</sup> y<sup>-1</sup> at H4; Fig. 4a). In Kongsfjorden, despite the differences in the MAR and TN concentrations, the TN<sub>AR</sub> was relatively constant: 2.8 g m<sup>-2</sup> y<sup>-1</sup> at Kb1 and 2.3 g m<sup>-2</sup> y<sup>-1</sup> at Kb2 (Fig. 4c). In spite of the variance of MARs, ON<sub>AR</sub> values measured at the two fjords were quite similar, ranging between 2.0 and 2.9 g m<sup>-2</sup> y<sup>-1</sup> in Hornsund and between 2.1 and 2.5 g  $m^{-2} y^{-1}$  in Kongsfjorden. Moreover, the organic fraction accounted for up to 90% of the total amount of N deposited in the surface sediments of Kongsfiorden, whereas in Hornsund the contribution varied between 35% and 67%. The gradual decrease in the share with increasing proximity to the inner part of the fjord indicated an important role for autochthonous production in the supply of ON. The pattern of  $IN_{AR}$  was similar to that of TN<sub>AR</sub>. Thus, in Hornsund the annual rates increased with increasing distance from the fjord entrance (from 0.9 g m<sup>-2</sup> y<sup>-1</sup> at H1 to 2.8 g m<sup>-2</sup> y<sup>-1</sup> at H4), while in Kongsfjorden there was a slight decrease in the annual rate (from  $0.3 \text{ g m}^{-2} \text{ y}^{-1}$  at Kb1 to  $0.2 \text{ g m}^{-2} \text{ y}^{-1}$  at Kb2). These results are consistent with those reported previously by Rysgaard et al. (1998), who estimated TN<sub>AR</sub> in the Svalbard fjords sediments at 5.6 g m<sup>-2</sup> y<sup>-1</sup>, a rate significantly higher than the TN<sub>AR</sub> reported by Muzuka and Hillaire-Marcel (1999) for the Eastern Canadian Margin  $(0.06-0.2 \text{ g m}^{-2} \text{ y}^{-1})$ .

Similarly, TPAR values increased along the axes of Hornsund and Kongsfjorden, from 0.9 g m<sup>-2</sup>  $y^{-1}$  at station H1 to 2.8 g m<sup>-2</sup> y<sup>-1</sup> at station H4 and from 1.1 g m<sup>-2</sup> y<sup>-1</sup> at station Kb1 to 1.3 g m<sup>-2</sup> y<sup>-1</sup> at station Kb2, respectively (Fig. 4b, d). The contribution of  $OP_{AR}$  to  $TP_{AR}$  was much lower than was the case for N, accounting for only  $\sim 26\%$  ( $\sim 0.3 \text{ g m}^{-2} \text{ y}^{-1}$ ) in Kongsfjorden and 32-43% (0.4-0.9 g m<sup>-2</sup> y<sup>-1</sup>) in Hornsund. However, as for N, the contribution decreased towards the fjord interior. The IP<sub>AR</sub> values also differed along the fjord axis, with higher IP loads deposited in the inner and central parts (1.9 g  $m^{-2}$  y<sup>-1</sup> and 1.0 g  $m^{-2}$  y<sup>-1</sup> at H4 and Kb2, respectively) and lower loads in the outer region (0.5 g  $m^{-2}$   $y^{-1}$  and  $0.8 \text{ g m}^{-2} \text{ y}^{-1}$  at H1 and Kb1, respectively). This suggested a larger supply of IP from land and/or melting glaciers. Data on P accumulation rates in marine surface sediments are scarce. According to van der Zee et al. (2002), TP<sub>AR</sub> in the NE Atlantic varies between 0.4 and 6.7 g m<sup>-2</sup> y<sup>-1</sup>, while Rydin et al. (2011) estimated TP<sub>AR</sub> of 1.7–2.8 g m<sup>-2</sup> y<sup>-1</sup> in the Baltic Sea, and Yang et al. (2017)  $TP_{AR}$  of 1.9–6.4 g m<sup>-2</sup> y<sup>-1</sup> and  $OP_{AR}$  of 0.4–1.0 g m<sup>-2</sup> y<sup>-1</sup> in the East China Sea.

### 4.3. Return fluxes of nitrogen and phosphorus ( $N_{RF}$ and $P_{RF}$ )

Fick's first law of diffusion was applied to estimate the N and P return fluxes from the bottom sediments to the water column. The N return flux (N<sub>RF</sub>) ranged from 0.43 to 1.38 g m<sup>-2</sup> y<sup>-1</sup> in Hornsund and from 0.12 to 1.46 g m<sup>-2</sup> y<sup>-1</sup> in Kongsfjorden (Table 4). In Hornsund, higher values were measured at the central stations (H2 and H3), and in Kongsfjorden at the outer and central stations (Kb1 and Kb2). For both fjords (except stations H1 and H3), the contribution of DON to the TN return flux was significant, amounting to 60-70% (0.07–0.97 g m<sup>-2</sup> y<sup>-1</sup>). This DON return flux ( $J_{DON}$ ) was much lower than that reported by Blackburn et al. (1996) for Svalbard sediments ( $\sim 4.8 \text{ g m}^{-2} \text{ y}^{-1}$ ) and generally at the lower limits of the DON fluxes previously reported for other world regions, including Laholmm Bay, Sweden: 0.5- $2.0 \text{ g m}^{-2} \text{ y}^{-1}$  (Enoksson, 1993), Chesapeake Bay: 0.2– 2.8 g m<sup>-2</sup> y<sup>-1</sup> (Burdige and Zheng, 1998), and the Laurentian and Anticosti Channel, Canada:  $0.6-2.2 \text{ g m}^{-2} \text{ y}^{-1}$  (Alkhatib et al., 2013). The diffusion flux of DIN ( $J_{\text{DIN}}$ ) was 0.05- $0.63 \text{ g m}^{-2} \text{ y}^{-1}$ , which is slightly lower than the fluxes deter-



**Figure 4** Recent deposition rates of nitrogen: total  $(TN_{AR})$ , organic  $(ON_{AR})$  and inorganic  $(IN_{AR})$ , and of phosphorus: total  $(TP_{AR})$ , organic  $(OP_{AR})$  and inorganic  $(IP_{AR})$  at Hornsund (a) and Kongsfjorden (b). Deposition rates were not calculated at station Kb3.

**Table 4** Porosity and the return fluxes (*J*) of dissolved nitrogen: inorganic ( $J_{DIN}$ ), organic ( $J_{DON}$ ) and total ( $N_{RF}$ ); return fluxes of dissolved phosphorus: inorganic ( $J_{DIP}$ ), organic ( $J_{DOP}$ ) and total ( $P_{RF}$ ).

Stations	Porosity	Return flux $[g m^{-2} y^{-1}]$					
		$J_{\rm DIN}$	$J_{\rm DON}$	N <sub>RF</sub>	$J_{\rm DIP}$	$J_{\rm DOP}$	P <sub>RF</sub>
H1	0.78	0.39	0.26	0.64	0.002	0.020	0.022
H2	0.76	0.41	0.97	1.38	0.029	0.074	0.103
H3	0.73	0.63	0.24	0.87	0.001	0.019	0.019
H4	0.76	0.15	0.28	0.43	0.001	0.021	0.022
Kb1	0.78	0.52	0.94	1.46	0.024	0.072	0.095
Kb2	0.81	0.55	0.86	1.41	0.043	0.066	0.109
Kb3	0.73	0.05	0.07	0.12	0.001	0.005	0.006

mined for the Svalbard sediments in the Arctic:  ${\sim}0.7~g~m^{-2}~y^{-1}$  (Blackburn et al., 1996) and 0.9–  $2.0~g~m^{-2}~y^{-1}$  (Gihring et al., 2010).

The P return flux (P<sub>RF</sub>) was much lower than N<sub>RF</sub> and varied from 0.02 to 0.10 g m<sup>-2</sup> y<sup>-1</sup> in Hornsund and from 0.01 to 0.11 g m<sup>-2</sup> y<sup>-1</sup> in Kongsfjorden (Table 4). As for N, the highest P values were measured at stations H2, Kb1, and Kb2. In both fjords, the return flux of the organic P fraction accounted for 60–97% (0.02–0.07 g m<sup>-2</sup> y<sup>-1</sup>) of the annual TP return flux, while in many places the diffusion flux of DIP ( $J_{\text{DIP}}$ ) was very low. While published data on the P return flux in the Arctic region are lacking, Yasui et al. (2016) estimated the  $J_{\text{DOP}}$  at Tokyo Bay, reporting a rate of 0.06 ± 0.06 g m<sup>-2</sup> y<sup>-1</sup>, close to the value obtained in this study. For P<sub>RF</sub> our results are similar to those previously reported for the NE Atlantic (van der Zee et al., 2002) and East China Sea (Yang et al., 2017): 0.01– 0.20 g m<sup>-2</sup> y<sup>-1</sup> and 0.04–0.40 g m<sup>-2</sup> y<sup>-1</sup>, respectively.

#### 5. Discussion

The recent reduction in both the spatial extent and the duration of the ice cover in the Arctic Ocean has increased the annual availability of light. Together, these conditions may substantially increase primary production (Fernandez-Mendez et al., 2015). However, the presence of nutrients is also critical, as nitrogen, silica, and phosphorus may limit or co-limit primary production in seawater (Moore et al., 2013; Tremblay et al., 2015). For example, in the Arctic, IN species are the primary yield-limiting nutrient (Reigstad et al., 2002; Tremblay et al., 2002, 2008). Given the importance of nutrient availability for ecosystem functioning, the identification and quantification of nutrient sources have been the focus of considerable research. Benthic fluxes of N and P species from the sediment are an important but still awaiting quantification component of the respective marine cycles, and thus their determination seems of importance.

### 5.1. Sources of dissolved inorganic N and P species in pore water

In sediments where oxic conditions prevail, ammonia is quantitatively oxidized to nitrate. Below the oxygen penetration depth, where oxygen is depleted, denitrification reduces nitrates to dinitrogen (Schulz and Zabel, 2006). Basing on measurements in single cores Kotwicki et al. (2018) reported that in the Hornsund sediments oxygen penetrates to a depth of 1-2 cm, while in Kongsfjorden – to a depth of 2–3 cm. Within these sediment layers, ammonium is oxidized to nitrate and thus cannot be released from the sediment to the overlying water. Findings of Kotwicki et al. (2018) confirm results of earlier studies (Glud et al., 1998) on diffusive fluxes of  $NH_4^+$  both from sedimentary anoxic zone into the oxic zone and from the sediments to bottom water to be  ${\sim}0.1{-}0.5\,\text{mmol}\,\text{m}^{-2}\,\text{d}^{-1}$  and 0 $\pm$  0 mmol m<sup>-2</sup> d<sup>-1</sup>, respectively. This confirms that ammonia diffusing up from the deeper sediments is guickly nitrified in the oxic zone before it is released from sediments. Surface sediments were not considered a source of ammonia, even when traces of this nitrogen species (mostly in the range  $\sim$ 10–20  $\mu$ mol L<sup>-1</sup>) were found in pore water of the surface sediments (Gihring et al., 2010). Kotwicki et al. (2018) also determined rather steep oxygen concentration gradients in the sediment of both fiords, with oxygen saturation falling to below 25% already at a depth of 1.0-1.5 cm. These results correlate well with the distribution of  $NO_3^-$  determined in our studies. As oxygen was not measured in our study, we can only presume that the higher  $NO_3^-$  concentrations in the deeper sediment layers at stations in the outer parts of the fjords reflected the deeper penetration of oxygen into sediments there. It is worth noting that  $NO_3^-$  concentrations in pore waters were much higher than in the seawater overlying the sediments. It is, most likely, caused by organic matter mineralization as concentration of organic matter in sediments is orders of magnitude larger than concentration in bottom water. OM mineralization delivers huge loads of ammonia that is guickly oxidized to nitrate. Subsequently, some part of newly produced nitrate diffuses upward into the water overlaying sediments, and is immediately diluted in a large volume of seawater. Some part of the newly formed  $NO_3^-$  diffuses downward to be denitrified. Low  $NO_2^-$  concentrations, both in pore waters and bottom water, confirm the above described sequence of processes as NO2<sup>-</sup> is immediately oxidized to  $NO_3^{-}$ . In the case of phosphate, changes in its concentrations were likely caused by its release after previous adsorption to iron and manganese oxyhydroxides and carbonates. This could have occurred both by the anaerobic degradation of the OP adsorbed to the solid phase of sediments and/or reduction of insoluble Fe (III) and Mn (IV) oxy-hydroxides to soluble Fe (II) and Mn (II) species and releasing adsorbed, N and P containing organic compounds. Moreover, a different speciation of the IP that accumulated in the sediments cannot be overruled (Baldwin et al., 2001; Lehtoranta et al., 2015; Schulz and Zabel, 2006; Yasui et al., 2016).

# 5.2. Burial rates of total nitrogen $(TN_{BR})$ and total phosphorus $(TP_{BR})$ and their burial efficiencies

The return fluxes, burial rates, and efficiencies of the burial rates for N and P are presented in Fig. 5. For both  $TN_{BR}$  and  $TP_{BR}$ , the results differed between the fjords, with higher rates calculated for the Hornsund stations (2.3–7.9 g m<sup>-2</sup> y<sup>-1</sup> and 0.9–2.8 g m<sup>-2</sup> y<sup>-1</sup>, respectively) than for



**Figure 5** Return fluxes (RFs) and burial rates (BRs) of nitrogen (a) and phosphorus (b) in Hornsund and Kongsfjorden. Values above the bars are the burial efficiencies (%).

the Kongsfjorden stations  $(0.9-1.3 \text{ g m}^{-2} \text{ y}^{-1} \text{ and } 1.0-$ 1.2 g m<sup> $-\bar{2}$ </sup> y<sup>-1</sup>, respectively). The higher values in Hornsund suggest a larger OM supply from land and/or higher in situ production. The two explanations are equally likely, given the higher rate of primary production (Piwosz et al., 2009; Smola et al., 2017) and greater contribution of terrestrial OM (Koziorowska et al., 2016; Zaborska et al., 2016) in Hornsund than in Kongsfjorden. Another possibility was a larger supply of inorganic species to the Hornsund sediments (higher MAR). Numerous studies (Comans et al., 1989; Muller, 1977; Schubert and Calvert, 2001) have shown that ammonium ions are preferentially fixed in illites, but Knies et al. (2007) reported that this is probably not the case for Spitsbergen sediments, where IN concentrations correlated negatively with the occurrence of illites. Alternative sources of IN are so far unknown, but may be of terrestrial origin. This would agree with the higher IN concentration and accumulation rate measured in Hornsund (especially at H4 station), where the contribution of terrigenous material was higher than in other areas (Koziorowska et al., 2016; Zaborska et al., 2016).

Generally, the burial efficiency determined in our study was much higher for P (92–99%) than for N (39–95%). During OM decomposition, P is released to the pore water in the form of phosphate and diffuses as a return flux to the overlying water. However, phosphates can also be retained in sediments, whether adsorbed to clay minerals, transformed to authigenic carbonate fluorapatite, or bound to iron oxyhydroxides (Cha et al., 2005; Ruttenberg and Goni, 1997; van der Zee et al., 2002). Retention can significantly reduce the return flux of P from sediments and increase the efficiency of P burial. In addition to the different efficiencies of N and P burial, the difference between the two fjords was significant, with the generally lower values in Kongsfjorden (39.2-47.0% for TN and 91.6-91.8% for TP) than in Hornsund (69.5-94.9% and 93.0–99.2%, respectively), indicating a more effective mineralization and/or decomposition during the early stage of diagenesis and therefore a higher return flux from the sediments to the water column. This may have been due to differences in the quality of the OM deposited to the sediments. Literature data (Koziorowska et al., 2016; Zaborska et al., 2016) indicated that Kongsfjorden sediments contain much more marine OM than do Hornsund sediments. Marine OM is considered to be more available for benthic organisms and more efficiently degraded in sediments. In addition, diagenetic processes may be influenced by the oxygen con-

tent in the sediments. According to Kotwicki et al. (2018), the slightly deeper oxygen penetration of Kongsfjorden sediments may enhance aerobic mineralization, which is probably more efficient than anoxic mineralization (Schulz and Zabel, 2006). At station H4, the  $TN_{BR}$  and  $TP_{BR}$  were higher than at any other station (7.9 g m<sup>-2</sup> y<sup>-1</sup> and 2.8 g m<sup>-2</sup> y<sup>-1</sup> respectively) as were the efficiencies of N and P burial (94.9% and 99.2%, respectively). Several factors may have contributed to these results. First, a role for the MAR can be assumed because a high MAR causes a high  $TN_{BR}$  and  $TP_{BR}$  even in the presence of moderate concentrations of N and P in the sediments, as was the case in this study  $(1.33 \text{ mg N g}^{-1})$ and 0.45 mg P  $g^{-1}$ ). A high MAR also causes a low return flux because freshly deposited material is guickly covered with new material and thus transported below the biologically active surface layer, where OM degradation proceeds at a slower pace (Arndt et al., 2013). Second, Brepollen Bay (where station H4 is located) is separated from the rest of the fjord by an underwater riffle and by the Treskelen Peninsula in addition to being surrounded by glaciers. Its conditions therefore differ from those of the other regions of Hornsund and include an intense freshwater discharge, strong stratification of the water column, and large quantities of suspended material delivered with meltwaters. Consequently, the supply of terrestrial, refractory OM strongly predominates over marine OM production, which is additionally limited by the high turbidity of the water.

#### 5.3. Global perspective

There are few published estimates of N and P burial rates in sediments (Table 5). In the case of N, most studies have focused on the processes occurring in the sediments, including denitrification, nitrification, and the return flux of the inorganic fraction (Alkhatib et al., 2012, 2013; Yasui et al., 2016). Our results (except at station H4, with its significantly different environment and therefore unique results) are consistent with those previously reported for sediments of the Arctic. Blackburn et al. (1996) reported  $TN_{BR}$  efficiencies of 51% and Rysgaard et al. (1998)  $ON_{BR}$  efficiencies of ~21%. These values are close to those obtained in Kongsfjorden in this study and suggest that the studied areas are rich in autochthonous OM. For other regions investigated throughout the world, very different  $TN_{BR}$  rates have been obtained, with higher values measured in

Table 5	Total nitrogen and total	. phosphorus burial	rates (TN <sub>BR</sub> and T	TP <sub>BR</sub> ) and burial	efficiencies at	different locations.
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Region	Nitrogen burial charact	Reference		
	$TN_{BR} [g m^{-2} y^{-1}]$	TN <sub>BR</sub> efficiency [%]		
Hornsund, Spitsbergen	2.3–7.9	69–95	This study	
Kongsfjorden, Spitsbergen	0.9–1.3	39–42	This study	
Svalbard, Norway	1.6 <sup>ª</sup>	23 <sup>a</sup>	Blackburn et al. (1996)	
Young Sound, Greenland	2.9	51	Rysgaard et al. (1998)	
Chesapeake Bay	$9.2\pm2.0$	_	Kemp et al. (1990)	
Laurentian Channel, Canada	0.5–1.0	5–1.0 – T		
Yellow Sea	0.01-1.2	16—30	Lu et al. (2005)	
Region	Phosphorus burial chara	Reference		
	$TP_{BR} [g m^{-2} y^{-1}]$	TP <sub>BR</sub> efficiency [%]		
Hornsund, Spitsbergen	0.9–2.8	93–99	This study	
Kongsfjorden, Spitsbergen	1.0–1.2	92	This study	
NE Atlantic	0.3–7.3	86—100	van der Zee et al. (2002)	
Saanich Inlet, Canada	3.1–18.6	35–37	Filippelli (2001)	
Baltic Sea	1.7–2.8	51—66	Rydin et al. (2011)	
East China Sea	1.9–6.0	93—99	Yang et al. (2017)	
Middle Shelf, East China Sea	0.3–7.2 90–95		Fang et al. (2007)	

<sup>a</sup> Organic nitrogen burial rate (ON<sub>BR</sub>).

Chesapeake Bay  $(9.2 \pm 2.0 \text{ gm}^{-2} \text{ y}^{-1}; \text{Kemp et al., 1990})$ and lower values in the sediments of the Yellow Sea  $(0.01 - 1.2 \text{ gm}^{-2} \text{ y}^{-1}; \text{Lu et al., 2005})$  and the Laurentian Channel, Canada  $(0.5-1.0 \text{ gm}^{-2} \text{ y}^{-1}; \text{Thibodeau et al., 2010}).$ 

By contrast, the P burial rates in the Arctic have yet to be reported. However, the comparable  $TP_{BR}$  values reported for other regions, e.g. the Baltic Sea, the East China Sea, and the NE Atlantic (Fang et al., 2007; van der Zee et al., 2002; Yang et al., 2017) suggest that a large share of the P deposited in the sediments is retained there.

# 5.4. Significance of surface sediments as a source of nitrogen and phosphorus to the water column

In this study, the yearly N and P return fluxes in Hornsund and Kongsfjorden were estimated. First, based on the depth, slope, and type of sediments, the sediment accumulation area in these fjords was estimated to be 100  $\pm$  15 km<sup>2</sup> and 95  $\pm$  15 km<sup>2</sup>, respectively, which amounts to 30–40% of their total surface areas. The accumulation areas were then multiplied by the N and P return fluxes of Hornsund and Kongsfjorden, which revealed the annual release into the water column of 0.8  $\pm$  0.4  $\times$  10<sup>5</sup> kg N and 0.04  $\pm$  0.04  $\times$  10<sup>5</sup> kg P in and of  $1.0 \pm 0.8 \times 10^5$  kg N and Hornsund 0.07  $\pm$  0.06 imes 10<sup>5</sup> kg P in Kongsfjorden. These fluxes largely constitute organic N and P compounds (DON and DOP), which, after their release from the sediments, may enter the microbial loop, undergo mineralization, and finally enrich the inorganic nutrient pool (Nausch et al., 2004). Because there is no information on the amount of dissolved N and P supplied to Svalbard fjords from the atmosphere and via either rivers and melting glaciers or the inflow of shelf water, we were unable to determine the contributions of the return fluxes to the nutrient budget. However, based on the literature data on annual primary production (120–220 g C  $m^{-2}$  in Hornsund and  $20-50 \text{ g C m}^{-2}$  in Kongsfjorden), we calculated the possible contribution of average return flux of N and P to the nutrients loads required to support primary production (assuming that the released dissolved organic species enter the microbial loop, as mentioned above, and turn into bioavailable forms). First, based on the Redfield ratio (106:16:1), the amount of N and P required to support the primary production was calculated to be  $20-40 \text{ g N m}^{-2}$  and 3-5 g P m<sup>-2</sup> in Hornsund, and 3–9 g N m<sup>-2</sup> and 0.5–1.2 g P m<sup>-2</sup> in Kongsfjorden. Then, the contributions of N and P originating from return fluxes were estimated - much lower in Hornsund (2-4% for N and 0.8-1.4% for P) than in Kongsfjorden (11-33% and 6-14% respectively), mainly because of huge difference in primary production in these fjords. Moreover, it is worth emphasizing that nutrients are used many times during a growing season, so the above calculated contributions are underestimated. While we are aware of the very high uncertainty underlying conclusions on the nutrients loads transfers, and thus the need for further research, our results nevertheless indicate that diffusion flux from sediments is substantial and thus is an important component of the N and P cycling in the fjords.

#### 6. Conclusions

This study provided qualitative and quantitative analyses of the N and P return fluxes from sediments to the bottom-water as well as estimations of the N and P burial rates in the surface sediments of two high-latitude Arctic fjords, Hornsund and Kongsfjorden. The N<sub>RF</sub> ranged from 0.43 to 1.38 g m<sup>-2</sup> y<sup>-1</sup> in Hornsund and from 0.12 to 1.46 g m<sup>-2</sup> y<sup>-1</sup> in Kongsfjorden. At most stations, DON was responsible for 60–70% of the N<sub>RF</sub> For P<sub>RF</sub> the corresponding values were 0.02–0.10 g m<sup>-2</sup> y<sup>-1</sup> and 0.01–0.11 g m<sup>-2</sup> y<sup>-1</sup>, respectively, with 60–97% of the flux assigned to DOP. Since N is the main limiting factor of primary production in this region, these results supplement already available knowledge on the origins of N and P in the sea water. Up till now most studies have focused on external sources of N (and P), such as delivery with freshwater inputs from rivers or melting glaciers, whereas sediments as a nutrient source have hardly been investigated. According to our results, a large fraction of the deposited N returns to the bottom water, enriching the pool available for phytoplankton. The consequences of this return may be significant, especially as climate warming increases annual light availability and nutrient limitations restrict phytoplankton primary production.

Both  $TN_{BR}$  and the  $TP_{BR}$  differed between the two fjords, with rates of 2.3–7.9 g N m<sup>-2</sup> y<sup>-1</sup> and 0.9–2.8 g P m<sup>-2</sup> y<sup>-1</sup> in Hornsund vs. 0.9–1.3 N g m<sup>-2</sup> y<sup>-1</sup> and 1.0–1.2 g P m<sup>-2</sup> y<sup>-1</sup> in Kongsfjorden. This difference was accompanied by different efficiencies of N and P burial rates, higher in Hornsund (69-95% for TN<sub>BR</sub> and 93–99% for TP<sub>BR</sub>) than in Kongsfjorden (39– 42% and 92%, respectively). The difference between the two fjords was likely due to the larger contribution of fresh, marine OM to the Kongsfjorden sediments. Additionally, the slightly deeper penetration of oxygen at the Kongsfjorden sediments may enhance aerobic mineralization, which is more efficient than anoxic mineralization. The generally much higher burial efficiency of P than N would suggest the greater retention of P in the sediments. Our  $TN_{BR}$  and TP<sub>BR</sub> results as well as the determined efficiencies indicate significant differences in the quality and quantity of material deposited to the sediments of these two fjords, especially in the case of N. Moreover, the differences followed a pattern similar to that previously determined for carbon burial rates.

Finally, the N and P burial rates determined in this study are characteristic of the present-day conditions. Climate warming may cause the deposition of OM to sediments increase and shifts in the redox conditions and nutrient burial rates.

#### Acknowledgements

Katarzyna Koziorowska's participation in the study was supported by the Centre for Polar Studies, KNOW—Leading National Research Centre, Sosnowiec, Poland. The financial support from the National Science Centre, Poland, grant no. 2015/19/N/ST10/01652, and the statutory activities of the Institute of Oceanology (Sopot, Poland) are acknowledged.

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