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Sediment DSi and DIP fluxes under changing oxygen availability in bottom waters

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In the present study, we investigated how sediment fluxes of dissolved silica (DSi) and dissolved inorganic phosphorus (DIP) were affected by dissolved oxygen (DO) availability in bottom waters. Sediments from two sites in the Baltic proper were incubated under changing oxygen conditions. Our results show that when DO availability decreased from oxic to hypoxic level, the average DSi fluxes decreased significantly at the two sites from 2.12 ± 0.04 to 0.87 ± 0.18 and from 2.37 ± 0.09 to 1.91 ± 0.55 mmol Si m^{-2} d^{-1}, respectively. Average DIP fluxes increased significantly at one site from 0.06 ± 0.01 to 0.14 ± 0.02 mmol P m^{-2} d^{-1}, but not at the other (from 0.06 ± 0.01 to 0.07 ± 0.01 mmol P m^{-2} d^{-1}). These results indicate that a change from highly oxic to hypoxic conditions in bottom waters may decrease DSi fluxes and increase DIP fluxes. However, sediment characteristics can lead to spatial differences in the response of DSi and DIP fluxes to oxygen availability.

Introduction

Silica (Si) and phosphorus (P) are key elements supporting phytoplankton growth in aquatic ecosystems (Canfield *et al.* 2005). Both originate from the weathering of rocks and are supplied to marine systems via riverine discharge and, but to a lesser extent, via atmospheric depositions and submarine groundwater discharge (Slomp 2011, Tréguer and De La Rocha 2013). In many aquatic ecosystems, their loads and concentrations have been affected by anthropogenic actions. One of the most affected areas in the world is the Baltic Sea. This water body has experienced increased P load and concentrations with simultaneously decreasing Si load and concentrations since the 1950s (Papush and Danielsson 2006, Conley *et al*. 2008). These higher loads of P originate mainly from agriculture, sewage-treatment plants and industry (Conley 2012). The decreasing Si load and concentrations are considered to be the result of two major causes: (1) the construction of dams on major rivers in the drainage area causing an increased retention of dissolved silica (DSi) behind dams and a 30%–40% decrease of riverine DSi loads (Humborg *et al.* 2008), and (2) eutrophication within the Baltic Sea with an increased DSi uptake in primary production followed by an enhanced accumulation of biogenic silica (BSi) in sediment (Conley *et al.* 2008). It has been shown that Si concentrations at the turn of the 20th century were almost three times higher than current concentrations (Conley *et al.* 2008), and as a result, signs of Si limitations have been found for different basins (Danielsson *et al.* 2008, Olli *et al.* 2008).

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Large efforts have been made to decrease the land-based P loads. Today, the importance of sediment release is largely recognised. Noffke *et al.* (2016) estimate that the sediment in the Baltic proper release almost 110 kt yr^{-1} of P. Thus, the sediment load exceeds the external loading by a factor of eight. In the Baltic Sea, about 70% of the primary production sinks to the sediment (Papush *et al.* 2009). Conley *et al.* (2008) estimate that more than 1000 kt of BSi accumulate annually in the Baltic Sea sediments. Tallberg *et al.* (2017) show that more than half of the biogenic silica (BSi) that reaches the sediment in the Baltic Sea is released back into the water column as DSi.

A major factor controlling sediment fluxes is oxygen availability in the bottom water (*see* e.g., Hietanen and Lukkari 2007). It is generally accepted that oxygen conditions affect the release of P included in organic matter and the P bound to redox-sensitive Fe oxyhydroxides (Lukkari *et al.* 2009, Thouvenot-Korpoo *et al.* 2012). Other pools, such as P bound to Al-oxides, to crystalline Fe-oxides or incorporated in mineral structure are, however, not affected by oxygen conditions in bottom waters (*ibid*). The release of P from Fe oxyhydroxides under hypoxic conditions, i.e. oxygen concentrations below 2 mg l^{-1} (Carstensen *et al.* 2014a), is often considered as the major internal source of P in the Baltic Sea (Puttonen *et al.* 2014). Studies about the effect of oxygen conditions on Si fluxes are still sparse and give contradicting results. Ekeroth *et al.* (2016) suggest a similar redox-dependency for both P and Si fluxes from sediment. However, Balzer *et al.* (1983) argue that Si fluxes are independent of oxygen conditions, whereas Rutgers van der Loeff *et al.* (1984) found that Si fluxes under oxic conditions were 2–10 times higher than those under anoxic conditions mainly due to bioturbation by benthic fauna. Hall *et al.* (2017) found that Si fluxes were not significantly affected after the anoxic bottom waters of the Eastern Gotland Basin were oxygenated by the 2014 Major Baltic Inflow. P fluxes, on the contrary, were significantly reduced. Siipola *et al*. (2016) argue that Si and P behave differently under anoxic conditions. They found that while anoxia increased P fluxes, due to the release of P bound to redox-sensitive Fe oxides, it decreased at the same time the release of Si loosely bound to particles and Si bound to redox-sensitive Fe oxides.

The present study focuses on how sediment fluxes of dissolved inorganic Si (DSi) and dissolved inorganic P (DIP) are affected by changing availability of dissolved oxygen (DO) from highly oxic to hypoxic conditions in bottom waters. Sediment cores were collected from two sites in the Baltic proper and incubated at near *in-situ* temperature and under decreasing oxygen concentrations. DSi and DIP concentrations were measured in the overlying water before and after incubation to estimate the nutrient fluxes.

Material and method

Collection of sediment cores and bottom water

Sediment samples were collected from two locations, Tvären (58°46.62´N, 17°25.91´E) and Käftudden (58°50.10´N, 17°33.73´E), both located in Stockholm archipelago in the north-west Baltic proper. These two stations represent different environmental conditions with regard to oxygen availability in bottom waters of the Baltic Sea. The first site, Tvären, is located in a near circular bay, of around 16 km^2 in area, surrounded by small islands (Jonsson *et al.* 2003). Water depths reach 76 m in the centre of the bay (Henkel *et al.* 2010), where also the present sediment and bottom water samples were collected. Most of the bottom area (~60% of the water surface) is an accumulation zone (Jonsson *et al.* 2003), and the bottom waters are frequently anoxic. The second site, Käftudden, is situated in an open zone more exposed to resuspension caused by waves and currents. This area is shallower with maximum water depth of 26 m, where also the sampling was performed. Bottom waters at Käftudden are oxic most of the time (B. Deutsch pers. comm.).

Sampling was done at a time when bottom waters were oxic at both sites (Table 1) to ensure maximum sequestration of P in sediment (Gibbs and Özkundakci 2011). The sediment cores were collected on 31 August and 2 September 2015 using a multicorer (K.U.M Umwelt und Meerestechnik, Kiel, Germany). This multicorer samples four sediment cores (inner diameter 9 cm and 60 cm length) per sampling event (Bonaglia *et al.* 2014); thus, eight sediment cores were collected from each site. The cores were subsampled on-board in smaller Plexiglas liners (7 cm inner diameter and 40 cm length) using a plastic piston (*ibid*). The cores were fitted with water-tight plastic bottom and top stoppers after recovery. They contained approximately 20 cm of sediment and 20 cm of overlying water. Dissolved oxygen (DO) was measured directly in the overlying water of the Plexiglas tubes with a WTW sensor.

Bottom water for incubation was collected at 1–1.5 m above sediment surface, using a 20 l Niskin bottle, and immediately transferred to plastic bottles. In total, 80 l of bottom water was collected from respective site. A subsample was taken from the Niskin bottle for measuring dissolved oxygen (DO) via Winkler titration. On-board, DO was fixed in the water subsample by adding 2 ml of a 2 M manganous sulphate solution and 2 ml alkaline potassium iodide to 300 ml water sample, according to the procedures in Strickland and Parsons (1972).

Titration was done upon arrival at the Askö Laboratory. Thereafter, a stirring magnetic bar was inserted in each Plexiglas tube about 10 cm above the sediment surface and turned at 50 rpm. This allowed a mixing of the overlying water without causing resuspension of sediment (Gunnars and Blomqvist 1997). Stirring of the overlying water may affect the concentration gradients of oxygen and nutrients at the sediment-water interface, and thereby also the nutrient fluxes (Boynton *et al.* 1981). However, several studies show that a low to moderate stirring below sediment resuspension causes no major changes of oxygen and nutrients fluxes (Laima *et al.* 1998, House 2003, Dadi *et al.* 2015).

The collected bottom water and the sediment cores were stored, with the mixing system on, in a dark and cold room at 3.5 °C for 24–72 hours before they were transported to the laboratory at Linköping University. There, the water and sediment cores were stored in a climate room in dark and at near *in situ* temperature (7.5 °C). To avoid the accumulation of nutrients in the overlaying water that might develop during transport (Gunnars and Blomqvist 1997), 80% of the overlying water was replaced by bottom water before the incubation procedure. The amount of sediment and overlying water was adjusted so that the depth of sediment in each core was between 20–25 cm and the overlying water column was 13–18 cm. This was done by removing excessive sediment and adding bottom water collected at the corresponding site. Care was taken not to re-suspend sediment when adding bottom water.

Experimental design

Core incubation under varying DO conditions

Six sediment cores from each site were used for incubation together with a control containing only bottom water (i.e. no sediment). The remaining two sediment cores were used for sediment characterisation. The sediment cores were incubated in dark for 46 days in a climate room where temperature was maintained at near *in-situ* temperatures. The overall duration of the incubation

Table 1. Hydrographical and sediment characteristics (topmost 2 cm) at the two sampling sites Tvären and Käftudden.

	Tvären	Käftudden
Latitude	58°46.62´N	58°50.10´N
Longitude	17°25.91´E	17°33.73´E
Depth (m)	75	26
Bottom water characteristics		
Temperature (°C)	7.2	9.8
Salinity (PSU)	6.8	6.8
Oxygen (µM)	275	293
DSi (μmol l^{-1})	33.74	19.71
DIP (μmol l^{-1})	1.35	0.76
Sediment characteristics		
Sediment type	Silty	Muddy clay
Water content (%)	88	84
Density (g cm^{-3})	1.03	1.11
Porosity	0.91	0.92
C_{tot} (%)	6.08	5.51
N_{tot} (%)	0.82	0.81
C:N	8.87	7.99
Al (μmol g^{-1} dw)	154	146
Fe (μmol g^{-1} dw)	167	137
Mn (μmol g^{-1} dw)	4	4
Si (μmol g^{-1} dw)	127	137
P (μmol g^{-1} dw)	44	23
Al:P (mol:mol)	3.49	6.36
Fe:P (mol:mol)	3.78	5.96
Al:Si (mol:mol)	1.21	1.10
Fe:Si (mol:mol)	1.31	1.03

experiment was in the range of incubation period in previous similar studies (e.g. Hietanen and Lukkari 2007, Bonaglia *et al.* 2013). To exclude the effect of bioturbation on nutrient fluxes, burrow animals eventually present in sediment were removed before the flux incubation started. For this purpose, the overlying water was purged with N_2 gas for 20 minutes before the Plexiglas tubes were sealed with rubber stoppers and kept in dark for 24 hours (following the procedures in Andersen and Kristensen 1988). The few worms that came to the sediment surface were removed from the tubes. The relatively short-term anoxic defaunation should not have any measurable effect on the nutrient biogeochemistry (Kristiansen *et al.* 2002). The open Plexiglas tubes were thereafter placed in a bath of bottom water from the respective sampling location. The water bath was bubbled with air to replace the anoxic overlying water with oxic water. The mixing system in each core was kept running all time. Mixing the overlying water was important to prevent chemical stratification (Frindte *et al.* 2013) and formation of local anoxia at the sediment-water interface that can occur even though the overlying water remains fully oxygenated (Sundby *et al.* 1986). After three days of equilibration, the DO in the overlying water was measured to ascertain that the oxygen saturation was close to 100%. During all the incubation sessions, DO was measured using a multi-meter HACH HQ40d (Loveland, CO, USA). The instrument was calibrated against air-saturated water (100 cal.) and a sodium sulphite solution (0 cal.).

The incubation was conducted in two phases during which DO concentrations in the overlying water were progressively decreased from highly oxic down to hypoxic levels. The incubation set up was adapted from the one used by Gunnars and Blomqvist (1997).

Phase 1: high DO availability phase (day 1–7)

DO concentrations in the overlying water were maintained above 10 mg l^{-1} (corresponding to 7 ml l^{-1}). Three flux incubations were done during this phase, at day 1, 4 and 7. At each incubation, a sample of 60 ml from the overlying water was collected from respective core. After an equal volume of unfiltered bottom water was added to replace the sampled water the cores were stoppered. After 10 hours of incubation a second sample was taken. At the end of each measurement the stoppers were removed and the overlying water in the cores equilibrated with the water bath for two days. During these two days air was bubbled into the bath using an air pump and an air stone.

From day 8, the cores were kept closed in order to decrease the DO in the overlying water. The DO was regularly monitored to ensure a stable decrease. At day 40, DO concentration was below 1 mg l^{-1} in most of the cores, and phase 2 began.

Phase 2: low DO availability phase (day 41–46)

On day 41, N_2 gas was bubbled in all cores for one hour to make sure that DO concentrations in the overlying water in all cores were kept below 1 mg l^{-1}. Bubbling with N_2 gas is routinely used to create hypoxic conditions in core incubations experiments (e.g., Hietanen and Lukkari 2007, Bartoli *et al.* 2009, Ogdahl *et al*. 2014). The cores were hermetically stoppered and allowed to equilibrate for one day. Three incubation sessions were performed, at day 42, 44 and 46, respectively. For each session, the incubation duration was between 8.3 and 9.4 hours (Table 2). Between measurement events, the cores were left for a one-day stabilisation period. The sampled volume of overlying water was replaced with an equal volume of unfiltered bottom water turned anoxic.

Water sampling

At the start and end of each incubation, water samples were taken from each core with a 60-ml, acid-rinsed plastic syringe and syringe-filtered through a 0.45 µm cellulose acetate membrane filter (Whatman Puradisc 30 syringe filter, GE Healthcare Bio-Sciences, Piscataway, NJ, USA). The sampled water was used for the analysis of DSi and DIP. Syringes and sample containers were initially rinsed with about five ml of water sample. Samples for DSi analyses were stored in a fridge at 4 °C, whereas samples for DIP were stored frozen at –20 °C following the recommendations by HELCOM (2014).

Sediment characteristics and porewater extraction

Sediment cores were cut into 0.5 cm slices in the uppermost 1 cm layer, 1 cm slices in the 1–8 cm layer and 2 cm slices in the 8–10 cm layer. For this purpose, a plastic cutter was used in order to avoid metal contamination (Blomqvist and Abrahamsson 1987). Sub-samples of sediment slices from each depth interval were used to determine sediment characteristics. These characteristics include water content (WC), wet density and loss on ignition (LoI). Water content was determined as the weight loss of wet sediment after oven-drying overnight (14 hours) at 105 °C. LoI was determined as the weight loss of dry sediment after combustion for five hours at 520 °C (Valdemarsen *et al.* 2010). The organic content was calculated by multiplying LoI by 0.5 (Jonsson *et al.* 1990). Wet density was estimated by determining the weight and the volume of a wet sediment sample (Dalsgaard *et al.* 2000). Finally, porosity was calculated as the product of water content and wet density.

Another sediment sub-sample of each sediment layer was used to extract porewater for DSi and DIP analyses. The sediment slices were centrifuged at 2500 rpm for 30 minutes (Andersen and Kristensen 1988), and the extracted porewater was syringed-filtered and preserved as previously described. Dried sediment sub-samples from the topmost 2 cm layer were analysed for total carbon (C_{tot}) and total nitrogen (N_{tot}). The capacity of sediment to retain P is related to its Fe:P ratio (Gunnars and Blomqvist 1997) as well as its Al:P ratio (Kopáček *et al.* 2005). Therefore, Si, P, Fe and Al were analysed in the solid phase of the sediment. Total amounts of adsorbed Si and P as well as total amounts of Al, Fe and Mn (sesqui)oxides in sediment solid phase were estimated after extraction with acidified ammonium oxalate, following the procedure of McKeague and Day (1966). The ammonium-oxalate method does not dissolve completely the sediment sample but rather the amorphous Fe and Al oxides as well as part of the organically-bound Fe (e.g. del Campillo and Torrent 1992, Lee *et al.* 2007). Since the amorphous Fe and Al oxides are considered the main P-sorbing compounds in soil, the ammonium oxalate method has proven to give satisfactory results in extracting the potentially mobile P and Si (e.g. Fransson (2001) and references therein, Siipola *et al.* 2016).

Chemical analyses

Overlying water and porewater samples were analysed for DSi and DIP. DSi concentrations were determined after reduction of molybdosilicate to molybdenum blue by ascorbic acid (following the procedures by Koroleff 1976). Interferences

Table 2. Dissolved oxygen (DO) concentrations in the core overlying water at the start (DO Init.) and end (DO End) of each incubation session. Mean ± standard deviation (SD), *n* = 6. Note that SD is zero for DO Init. under the High DO experimental phase as the six cores from respective site had the same DO after being immersed in the same water bath for two days before incubation.

Experimental phase	Incubation session	Site	DO Init. (μM)	DO End (μM)	Incubation duration (h)
High DO	Day 1	Tvären	435 ± 0	379 ± 12	10.0
High DO	Day 4	Tvären	428 ± 0	368 ± 9	10.0
High DO	Day 7	Tvären	420 ± 0	357 ± 9	10.0
High DO	Day 1	Käftudden	434 ± 0	404 ± 5	10.0
High DO	Day 4	Käftudden	430 ± 0	403 ± 4	10.0
High DO	Day 7	Käftudden	425 ± 0	399 ± 4	10.0
Low DO	Day 42	Tvären	25 ± 3	20 ± 2	9.4
Low DO	Day 44	Tvären	18 ± 2	17 ± 2	8.5
Low DO	Day 46	Tvären	14 ± 2	11 ± 2	8.6
Low DO	Day 42	Käftudden	23 ± 1	21 ± 1	9.0
Low DO	Day 44	Käftudden	19 ± 1	17 ± 2	8.3
Low DO	Day 46	Käftudden	13 ± 1	12 ± 1	9.0

by DIP were reduced by addition of oxalic acid. The formed blue colour was measured with a Ultrospec 2100 Pro spectrophotometer at 810 nm (Piscataway, NJ, USA). Detection limit for DSi was 0.1 µmol l^{-1} using a 10-cm cell. Determination of DIP was also based on the molybdenum blue method (Koroleff 1976). The analysis was performed by Segmented Flow Analysis using a Bran+Luebbe AutoAnalyzer 3 (Norderstedt, Germany). Detection limit for DIP was 0.02 µmol l^{-1} for low concentrations (0–6.5 µmol l^{-1}). The certified reference seawater material for nutrients MOOS-1 was used for quality control. C_{tot} and N_{tot} in the solid phase were determined by combustion of samples using a Perkin Elmer Elemental analyser EA 2400 (Waltham, MA, USA). An internal standard sediment, prepared by Stockholm University, was used for quality control.

The molar C:N ratio in the topmost two cm sediment layer gives information on the quality of organic matter reaching the sediment (Tengberg *et al.* 2003). This C:N ratio in the topmost sediment layer was calculated from the C and N concentrations determined in dried sediment samples. Determination of Si, P as well as Al, Fe and Mn oxides in the solid phase extract were performed using a Perkin Elmer NexION 300D Inductively Coupled Plasma-Mass Spectrometry (Waltham, MA, USA).

Flux measurements

DSi and DIP fluxes from sediment were calculated from the concentration changes in the overlying water before and after each incubation session (Dalsgaard *et al.* 2000). The flux was calculated according to:

$$\text{Flux} = \frac{\left(C_\text{f} - C_\text{i}\right) \times V}{A \times t} \qquad (1)$$

where C_i and C_f were the concentrations at the beginning and at the end of the incubation, respectively. V is the volume of the overlying water in the core tube, A is the planar surface area of the sediment core tube and t is the duration of incubation. A correction was made for C_i to take into account the volume of bottom water that was used to replace the sampled volume of water before the incubation started.

The flux combined the amount of nutrient (DSi and DIP) that resulted from the remineralisation of organic matter in the overlying water as well as the amount that was released from the sediment. The remineralisation component was assumed to be equal to the concentration change observed in the control core weighed to the volume of overlying water in each sediment core. The nutrient flux from sediment was corrected by removing this remineralisation component from the concentration change observed in each sediment core:

$$F_\text{Sed} = \frac{\Delta C_\text{Sed} - \left(\Delta C_\text{Ctrl} \times \frac{V_\text{Sed}}{V_\text{Ctrl}}\right)}{A \times t} \qquad (2)$$

where F_Sed was the nutrient flux from the sediment, ΔC_Sed was the concentration change in the overlying water of the sediment core tube, ΔC_Ctrl was the concentration change in the control core tube, V_Sed was the volume of the overlying water in the sediment core tube and V_Ctrl was the volume of water in the control core.

Statistical analysis

To test if there were significant differences between treatments and sites, respectively, two-way repeated measures ANOVA was used. The analysis was performed with two fixed factors, namely experimental phase and site, respectively, and the interaction factor of the two. Days of incubation was used as repeated measures per sampling core. As the samples represented pseudo-replicates, a two-way repeated measures ANOVA was an appropriate statistical test for the present experimental design (Hurlbert 1984). All tests were performed at a significance level of 0.05.

Results

Bottom water and sediment characteristics

At the time of sampling, the bottom waters at Tvären had higher DSi and DIP concentrations compared to Käftudden bottom waters (Table 1).

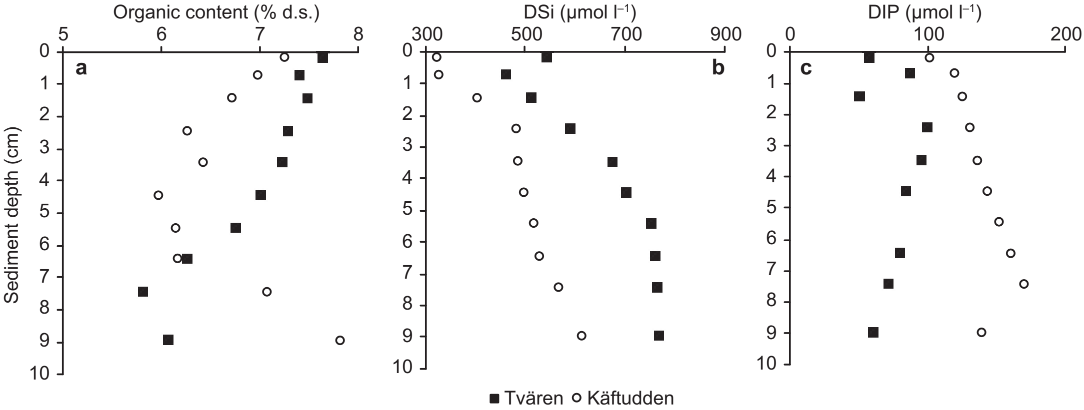

Fig. 1. Porewater profiles of (**a**) organic content, (**b**) DSi and (**c**) DIP at sites Tvären and Käftudden, respectively.

Temperature of Tvären was slightly lower than that at Käftudden while salinity was similar at the two sites. DO concentrations were 275 µM and 293 µM at Tvären and Käftudden, respectively.

The sediment cores collected at Tvären were silty, black in colour and had a strong smell of hydrogen sulphide (H_2S). At Käftudden, the sediment cores were muddy clay, grey in colour with a brownish aspect in the surface layer. The porosity in the topmost 5 cm sediment layer was similar at the two sites (0.90–0.92). The organic content in the sediment samples ranged between 6% and 8% at both sites. In the uppermost 5 cm, the organic content in Tvären was slightly higher than in Käftudden, while the opposite was true further down (Fig. 1a). The molar C:N ratio was ~9 in Tvären and ~8 in Käftudden (Table 1). Käftudden's sediment had slightly lower Si, P, Fe and Al concentrations than Tvären's sediment. As a consequence the Fe:P and Al:P molar ratios in the sediment at Käftudden were slightly higher than those in sediment at Tvären (Table 1).

Porewater profiles of DSi concentrations showed an increase with depth at both sites, although Tvären had slightly higher concentrations (Fig. 1b). The concentrations ranged between 465 and 773 µmol Si l^{-1} in Tvären and 324–617 µmol Si l^{-1} in Käftudden. For DIP, the porewater DIP concentrations were lower in Tvären than in Käftudden at all depths (Fig. 1c). The concentrations ranged between 52–101 µmol P l^{-1} in Tvären and 102–162 µmol P l^{-1} in Käftudden.

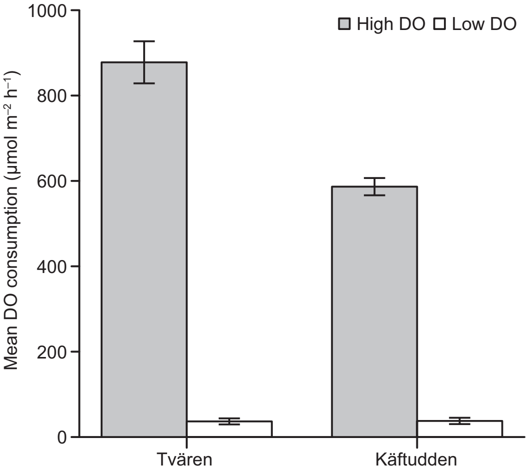

Fig. 2. Mean oxygen consumption during the incubation sessions at sites Tvären and Käftudden, respectively. Error bars represent ±1 SE (*n* = 18). Two experimental phases were used: high dissolved oxygen availability (high DO) respective low dissolved oxygen availability (low DO).

Concentration changes during incubation

Oxygen was consumed during all incubation sessions. The average oxygen consumption under high DO availability was 878 ± 209 µmol DO m^{-2} h^{-1} and 587 ± 86 µmol DO m^{-2} h^{-1} in the cores from Tvären and Käftudden, respectively (Fig. 2). Under low DO availability, the average DO consumption decreased to 37 ± 30 µmol DO m^{-2} h^{-1} and 38 ± 31 µmol DO m^{-2} h^{-1} at Tvären and Käftudden, respectively.

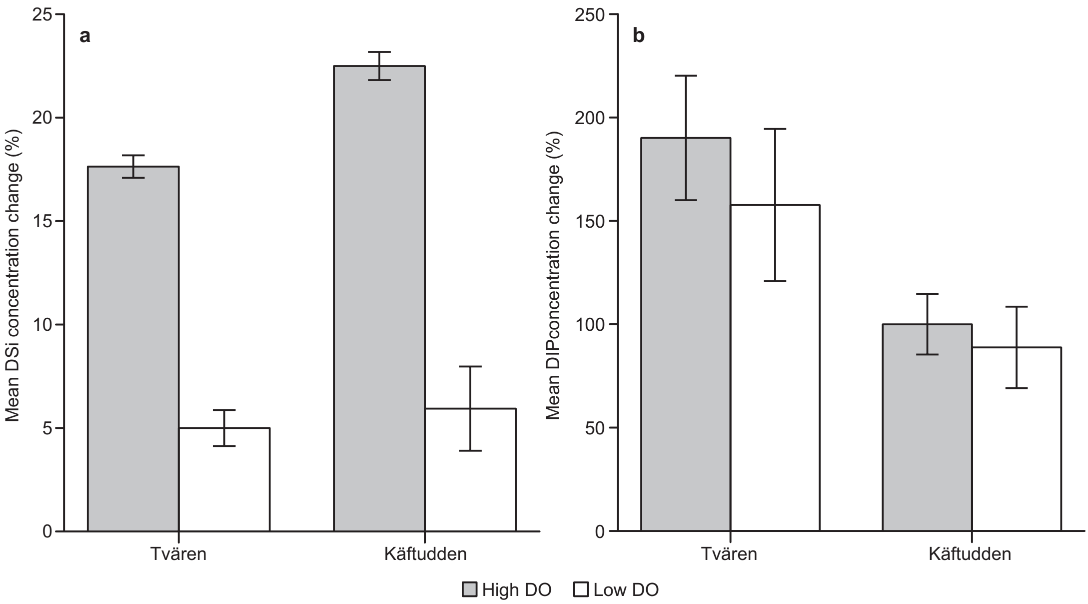

Fig. 3. (**a**) DSi and (**b**) DIP concentrations changes during the incubation sessions at sites Tvären and Käftudden, respectively. Error bars represent one standard error ($n = 18$). Two experimental phases were used: high dissolved oxygen availability (high DO) respective low dissolved oxygen availability (low DO).

DSi and DIP concentrations in the overlying water increased during incubation for both experimental phases. The increase in DSi concentrations was, however, moderate compared to the increase on DIP concentrations (Fig. 3a). There was a significant difference in DSi concentration between high and low DO availability (ANOVA: $F_{1,14.6} = 203.67$, $p < 0.001$). Tvären had significantly lower DSi concentrations than Käftudden (ANOVA: $F_{1,10.9} = 345.6$, $p < 0.001$). Also, the interaction affect was significant (ANOVA: $F_{1,24} = 17.37$, $p < 0.001$). On average, the DSi concentrations increased by 17% and 22% during high DO availability at Tvären and Käftudden, respectively. This corresponded to a DSi concentration increase between 3%–23% of the initial concentration. In the second phase, with low DO availability, the DSi concentration increase was smaller (5% and 6% in Tvären and Käftudden, respectively).

For DIP, the average concentrations change ranged between 50%–180% of the concentration at the beginning of the incubation. The concentrations at the end of incubation exhibited large variability within and between experimental phases. There was no significant difference in DIP concentration changes between the high and the low DO experimental phases (ANOVA: $F_{1,44} = 1.49$, $p = 0.228$). However, a significant difference in the DIP concentration changes between sites was found (ANOVA: $F_{1,42} = 9.42$, $p = 0.004$), where Tvären had, on average, 72% higher DIP concentrations than Käftudden (Fig. 3b). The interaction effect was not significant (ANOVA: $F_{1,36} = 1.46$, $p = 0.235$), and the DIP concentration change due to experiment phase did no differ significantly between the sites.

Nutrients fluxes

There was a significant difference in DSi fluxes depending on DO availability (ANOVA: $F_{1,21} = 16.4$, $p = 0.001$), and a significant difference between sites (ANOVA: $F_{1,10} = 71.0$, $p < 0.001$). The average DSi fluxes under high DO availability were 2.12 ± 0.04 mmol Si m^{-2} d^{-1} and 2.37 ± 0.09 mmol Si m^{-2} d^{-1} for Tvären and Käftudden, respectively (Fig. 4a). Under low DO availability the DSi fluxes decreased to 0.87 ± 0.18 mmol Si m^{-2} d^{-1} and 1.91 ± 0.55 mmol Si m^{-2} d^{-1}

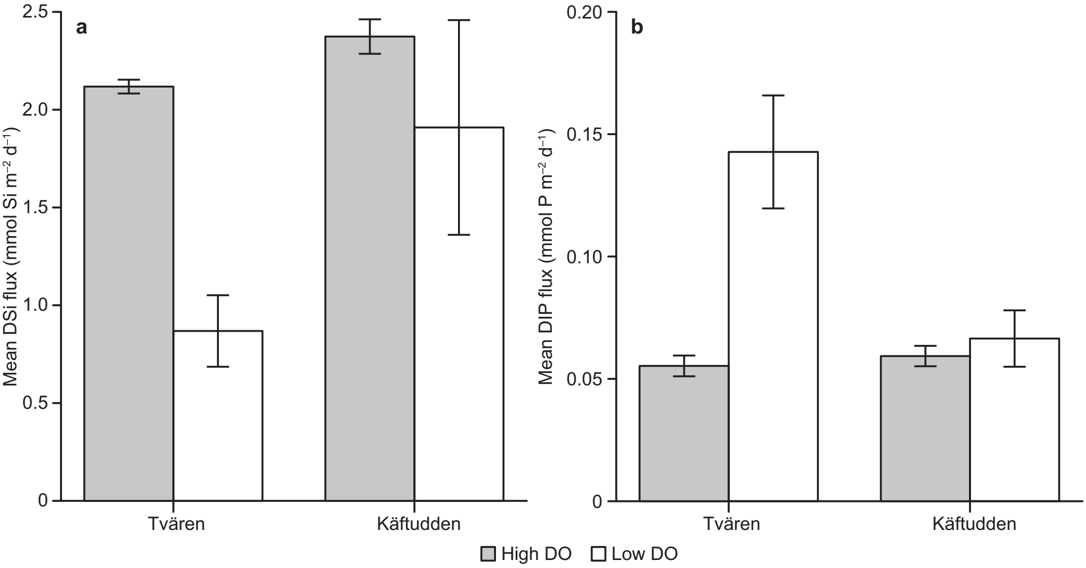

Fig. 4. Mean (**a**) DSi and (**b**) DIP fluxes calculated at sites Tvären and Käftudden, respectively. Error bars represent one standard error (n = 18). Two experimental phases were used: high dissolved oxygen availability (high DO) respective low dissolved oxygen availability (low DO).

at Tvären and Käftudden, respectively (Fig. 4a). However, the interaction effect was not significant (ANOVA: $F_{1,19}$ = 0.091, p = 0.766).

The DIP fluxes differed significantly between high and low DO availability (ANOVA: $F_{1,25}$ = 13.0, p = 0.001). The DIP fluxes were, on average, 0.05 mmol m^{-2} d^{-1} higher under low DO availability (Fig. 5). The DIP average fluxes under high DO availability were equal at both sites ~0.06 mmol P m^{-2} d^{-1} (Fig. 4b). There was also significant difference in DIP fluxes between the two sites (ANOVA: $F_{1,25}$ = 5.79, p = 0.024). Under high DO availability, DIP fluxes were equal at both sites ~0.06 mmol P m^{-2} d^{-1}, Under low DO availability, DIP fluxes increased to 0.14 ± 0.02 mmol P m^{-2} d^{-1} at Tvären and 0.07±0.01 mmol P m^{-2} d^{-1} at Käftudden. This difference between sites was significant as shown by the interaction effect (ANOVA: $F_{1,25}$ = 6.96, p = 0.014).

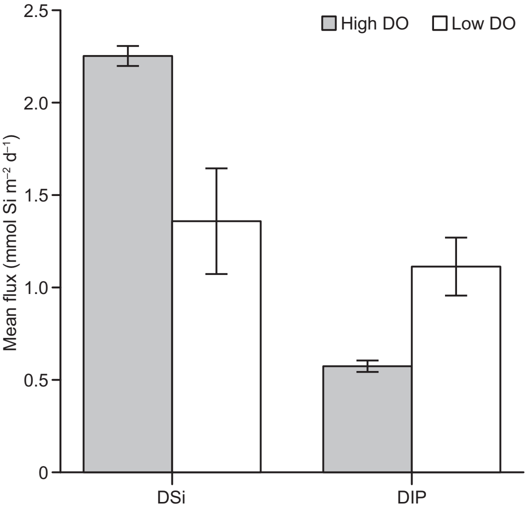

Fig. 5. Averages of compiled DSi and DIP fluxes under high and low DO availability experimental phases. DIP fluxes were multiplied by 10 for scaling purpose. Error bar represents one standard error (n = 36).

Discussion

Effect of oxygen availability on Si fluxes

The Si fluxes obtained in the present study are in the same range as those found previously in the Baltic Sea. Bonaglia *et al.* (2013) found fluxes of 0.96 mmol Si m^{-2} d^{-1} and 1.19 mmol Si m^{-2} d^{-1} from sediments under oxic and hypoxic conditions, respectively. Tallberg *et al.* (2017) presented fluxes between –0.4 mmol Si m^{-2} d^{-1} and 4.9 mmol Si m^{-2} d^{-1} under oxic conditions and 0.7–1.5 mmol Si m^{-2} d^{-1} under hypoxic conditions. Si fluxes up to 8 mmol Si m^{-2} d^{-1} and 10 mmol Si m^{-2} d^{-1} under oxic and hypoxic conditions, respectively, were reported by Norkko *et al.* (2015) for different sites in the open Baltic Sea.

In the present study, sediments released Si regardless of the oxygen availability in the overlying water. The porewater DSi concentrations were more than 15 folds the concentrations in bottom water. This large concentration gradient should be strong enough to cause the release of DSi from sediment by diffusion (Aston 1983). Also, the large stock of Si accumulated in the sediments of the Baltic Sea may cause Si to be released regardless of the DO availability (Conley *et al.* 1997).

However, the size of the Si fluxes under the two oxygen conditions differed largely. This pattern was seen for both sites. The Si fluxes at high DO availability were significantly higher than those under low DO availability (Fig. 5). It is generally assumed that a decrease in DO availability (from oxic levels down to hypoxic levels) will cause a dissolution of the redox-sensitive Fe oxyhydroxides. This should cause the release of the Si that was adsorbed onto these oxides. Consequently, Si fluxes would increase when DO conditions change from highly oxic to hypoxic levels. To have such a flux increase, two assumptions need to be fulfilled. Firstly, this redox-sensitive Si must be a major pool to cause a significant increase of the Si flux. Secondly, this change of DO availability must not significantly reduce the release of Si from the redox-insensitive pools of Si (i.e. DSi in porewater, BSi and the Si bound to non-reducible Al and/or Fe-oxides). The results in the present study indicated that these conditions were not fulfilled. The higher fluxes at high DO availability, indicated that the redox-sensitive pool of Si only contributed marginally to the overall Si fluxes. Under low DO availability the release of Si from this pool could not compensate for the reduction of Si released from other pools. This is supported by results of sequential fractionation studies, which showed that the redox-sensitive Fe-oxide pool of Si represents only about 3% of the total potentially mobile pool of Si in sediments of the Baltic Sea (Tallberg *et al.* 2009). Comparatively, BSi and the non-reducible Al and Fe-oxides bound Si are dominating, constituting more than 80% of the potentially mobile Si pools (*ibid.*).

The lesser Si fluxes under low DO availability in the present study indicated that low DO availability hampered the release of Si from the redox-insensitive pools, as also shown by Siipola *et al.* (2016). The average DSi concentration change under high DO availability was at least twice that observed under low DO availability. This indicated that BSi dissolution is faster under high DO availability. Similar results were found by Lehtimäki *et al.* (2016). In addition, these authors showed that more BSi is dissolved under hypoxic condition when the dissolution is allowed to last longer (> 100 days). The present study lasted for 46 days which was probably not long enough to reach the point where the release rate under low DO availability would exceed that of high DO availability. It could also be argued that the decrease of Si fluxes under low oxygen availability might be caused by the depletion of labile forms of BSi during the initial days of the experiment which coincided with the high DO availability phase. Still, Lehtimäki *et al.* (2016) showed that Si regeneration from sediment was still intense after 50 days of incubation. Another mechanism that could cause the observed decrease of Si fluxes under low DO availability is the resorption of Si released from the redox-sensitive pool by the non-reducible Al oxide (Siipola *et al.* 2016). This resorption has a stabilising effect on the Al oxides and thus further limits the release of Si from this pool (*ibid.*). A similar resorption by the non-reducible Al oxides is well known for P in lakes (e.g. Rydin *et al.* 2000, Kopáček *et al.* 2005), but the conditions under which it occurs for Si are yet to be established.

It is generally agreed that bacterial activity enhances the dissolution of BSi (Bidle and Azam 2001). Lehtimäki *et al.* (2016) showed that the difference between the DSi release rate under oxic respective hypoxic conditions are primarily related to differences in the composition and activity of microbial communities. However, it is still not clear whether the composition and activity of these microbial communities change significantly with oxygen conditions or not.

Effect of oxygen availability on P fluxes

The P fluxes estimated in the present study were in the same range as those reported in previous studies. In roughly the same area as in the present study, Karlson *et al.* (2005) found P fluxes ranging between 0.02–0.39 mmol P m^{-2} d^{-1}. Bonaglia *et al.* (2014) estimated that P fluxes at a reference oxic station in the Stockholm archipelago ranged between 0.02–0.06 mmol P m^{-2} d^{-1}.

The sediment in the present study released P regardless of the oxygen availability, but the average DIP flux under high DO was lower than that observed under low DO. This agrees well with the generally accepted view that sediment sequestrates P under oxic condition as a result of the adsorption of P on Fe-oxyhydroxides (Mortimer 1942) and bacterial P uptake (Gächter *et al.* 1988, Steenbergh *et al.* 2013). P adsorbed to the redox-sensitive Fe oxyhydroxides is an important pool of potentially mobile P. In the Baltic Sea, this pool represents up to 60%–80% of the total potentially mobile pool of P (Tallberg *et al*. 2009, Rydin *et al.* 2011). When conditions turn hypoxic, the P desorption from Fe-oxyhydroxide and the bacterial P release explain the higher P fluxes. These mechanisms seemed to be clearly at work in Tvären, where the average P flux under low oxygen availability was twice the flux under high oxygen availability. In Käftudden, on the other hand, P fluxes did not seem to be mainly controlled by oxygen availability. Other redox-insensitive P-binding factors, such as Al-oxides and non-reducible Fe-oxides, may strengthen the sediment P sorption capacity and prevent higher P fluxes under low oxygen availability (Hupfer and Lewandowski 2008).

Difference between sites

The decreasing effect of low DO availability on Si fluxes can to some extent explain the difference in porewater Si concentrations at the two sites. Käftudden has oxic bottom water most of the year, whereas the deeper Tvären experiences hypoxic bottom waters most of the time. High DO availability at Käftudden may enhance a higher Si release from sediment resulting in lower porewater DSi. Comparatively, in Tvären low DO availability limits Si fluxes from sediment and thus results in higher DSi concentration in porewater.

Resuspension is known to increase DSi flux from sediment by enhancing the upward diffusion of DSi out from sediment (Tengberg *et al.* 2003). It also helps transferring BSi particles from deeper layers of the sediment to the surface where they dissolve (Katz *et al.* 2009). Due to its localisation in a more open area and its shallowness Käftudden is likely more affected by resuspension from waves and currents (Suomela *et al.* 2005, Danielsson *et al.* 2007). Thereby resuspension might contribute to the lower DSi concentrations in porewater at Käftudden compared to Tvären. Another reason for the slightly higher DSi flux at Käftudden was probably the presence of fresher and better quality organic matter in these sediments compared to Tvären. This was indicated by the slightly lower C:N ratio in Käftudden, but more studies are needed to confirm the difference in the quality of organic matter in the sediments. Yet, another factor for the higher Si release in Käftudden was the higher clay content there. Clay minerals are known to contribute significantly to short-term release of DSi (Maurice *et al.* 2001, Koning *et al.* 2002, Ragueneau *et al.* 2005).

P fluxes in Käftudden were less affected by changes in DO availability than in Tvären. One reason could be that the sediment contained a low amount of redox-Fe bound P. But since the redox-Fe bound is generally the dominant potentially mobile pool of P at oxic sites in the Stockholm archipelago (Rydin *et al*. 2011), a more plausible explanation could be that sediment at Käftudden have a stronger capacity to retain P than the sediment at Tvären. The P sorption capacity is closely related to e.g. sediment clay content (Gerard 2016), the molar Fe:P ratio (Blomqvist *et al.* 2004) and Al:P ratio (Kopáček *et al.* 2005). The two sites were slightly different based on these characteristics. Käftudden contained more clay and had higher Fe:P (5.96) and Al:P molar ratios (6.36) than Tvären (3.78 for Fe:P and 3.49 for Al:P). This meant that Käftudden had more Fe and Al adsorbing sites available to bind P which could, at least partly, explain why P concentrations changes were lower at Käftudden than at Tvären under all experimental phases.

Implications for the Baltic Sea

Areas of hypoxic bottom in the Baltic Sea have spread during the last century mainly because of eutrophication and climate change (Conley *et al.* 2011, Carstensen *et al.* 2014b). The present results show that DSi and DIP fluxes may not be always affected in the same way by short periods of low DO availability in bottom water. With lower DO availability, DSi fluxes from the sediment decreased, while DIP fluxes increased (or remained unchanged). Since sediments contribute significantly to the Si pools in the water column (Tréguer and De La Rocha 2013), reduced DSi fluxes as a consequence of low DO availability may lead to decreased DSi concentrations available for primary production. This could cause deviations from the Redfield Si:P ratio favourable for diatoms (Olli *et al*. 2008). Consequently, diatoms could be outcompeted by potentially toxic dinoflagellates or cyanobacteria (Tallberg *et al.* 2009).

It has been observed that hypoxic/anoxic deep bottom waters in the Baltic Sea have high DSi concentrations (Danielsson 2014) and high DIP concentrations (e.g. Conley *et al.* 2002). These observations support the view that low DO availability in bottom water lead to higher DSi and DIP fluxes. In the Baltic Sea, hypoxic/anoxic areas are generally located in sheltered deep accumulation zones or enclosed bays. In these areas, nutrients released at the sediment surface accumulate in the bottom waters. Accumulation is favoured by limited nutrients uptake in primary production due to low light availability (Suomela *et al.* 2005). Moreover, the existence of a strong halocline limits the mixing of bottom waters with the overlaying water mass, thus keeping high concentrations of nutrients in the bottom waters. Contrary to hypoxic/anoxic areas, oxic areas are generally found in shallower open areas. In these areas, DSi and DIP fluxes may be high (e.g. Lehtoranta and Heiskanen 2003, Suomela *et al.* 2005, Tallberg *et al.* 2017). Moreover, the oxic areas are generally located in highly dynamic erosion-transport zones where part of the released DSi can be transported out of these zones to deeper zones.

The present study shows that Si and P fluxes cannot be predicted solely from changes of DO availability in bottom waters. Sediment characteristics are site-specific factors that can explain differences in DSi and DIP fluxes, causing sediment to release Si while increasing sediment capacity to retain DIP. Other site-specific conditions that may cause opposite trends in DSi and DIP fluxes include resuspension by waves and currents (Tengberg *et al.* 2003) as well as bioturbation (Bonaglia *et al*. 2013, Danielsson *et al*. 2018).

Future research

Sulphide in porewater can react with Fe(II) and lead to its precipitation as iron-sulphur minerals such as mackinawite and pyrite (Canfield 1989, Holmqvist *et al.* 2014). Because DIP has a low capacity to adsorb to these iron-sulphur minerals (Krom and Berner 1980), the precipitation of Fe by sulphides can be followed by a continuous release of DIP deeper in the sediment (e.g. Ingall *et al.* 1993, Slomp *et al.* 2002). The potential effect of sulphide on DSi fluxes is not well known (Tallberg *et al.* 2009). It would be interesting to clarify in further studies to what extent the accumulation of sulphides in sediment porewater affect DSi fluxes. In this study, we assumed that sulphides occurred in the water overlying the sediment only when DO was completely depleted (Gustafsson and Omstedt 2009). Therefore, we excluded the presence of sulphides during both experimental phases as small DO concentrations were detected even during incubation session under low DO availability (Table 2). However, Yücel *et al.* (2017) found recently that sulphides can be present in bottom waters at low DO < 15 µM. We also assumed that sulphide concentrations in the top most sediment layer were low as indicated by various studies. Poulton *et al.* (2004), for instance, explain that the 10 cm uppermost portion of sediment is commonly characterised by low levels of sulphides because Fe oxides minerals react with sulphides to form precipitates of FeS and FeS_2. Yücel *et al.* (2017) found no sulphides in sediment retrieved at 65 m in the eastern Gotland Basin (Baltic proper) but only in sediments collected from 82 m or deeper, in locations where bottom waters were completely depleted of DO.

Bacterial activity determines the amount of nutrients released from decomposition of organic material. Whether bacterial mineralisation of organic material was differently efficient under high and low DO availability was not assessed. In further studies assessing Si fluxes, it would be interesting to assess the effect of oxygen conditions on bacterial dissolution of biogenic silica and dissolution of mineral silica. Also, the effect of low oxygen conditions on the potential resorption of the Si released from redox-sensitive metal oxides onto redox-insensitive Al-oxides as hypothesised by e.g. Siipola *et al.* (2016) needs to be further studied.

Conclusions

Low DO availability in bottom waters is generally believed to enhance DIP fluxes from sediments. It has been discussed whether DSi fluxes are affected in the same way. Some studies have shown that low DO availability in bottom waters resulted in decreased DSi fluxes. This decrease of DSi fluxes was mainly explained by the inhibition of bioturbation and bioirrigation by benthic fauna. The present study shows that even in the absence of benthic fauna activity, DSi fluxes tend to decrease when DO availability falls to hypoxic level whereas DIP fluxes increase.

The difference in DSi and DIP response to DO conditions may be explained by the relative importance of the redox-sensitive pools of Si and P. While this pool is highly important for P it is only marginal for Si. The decrease of DSi fluxes when DO conditions falls to hypoxic level also suggested that the dissolution of redox-insensitive pools of Si may be faster under high DO availability than under low DO availability. Additional studies are needed to clarify how DO availability affects the release of Si from this pool in general and most particularly the bacterial enhanced dissolution of biogenic silica and clay minerals in sediments.

The result indicates that besides DO conditions in bottom waters, site specific factors such as sediment clay, Al contents and resuspension may contribute in regulating DSi and DIP fluxes. To evaluate which of the characteristics that are of major importance, further studies are needed including a larger set of stations before generalising to other areas of the Baltic Sea with similar oxygen conditions. Nevertheless, the results in this study give indications about the role of sediment characteristics on Si and P fluxes and help understanding when specific oxygen conditions may lead to an increase or decrease of Si and P fluxes.

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