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Effects of re-oxygenation and bioturbation by the polychaete *Marenzelleria arctia* on phosphorus, iron and manganese dynamics in Baltic Sea sediments

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Sediments underlying hypoxic or anoxic water bodies constitute a net source of phosphorus to the bottom water. This source has the potential to enhance eutrophication. Benthic fluxes of dissolved phosphorus, iron and manganese were measured from hypoxic, normoxic, and normoxic bioturbated by the invasive polychaete *Marenzelleria arctia* sediment in a mesocosm experiment. The highest benthic phosphorus efflux was detected in mesocosms with the hypoxic treatment. Normoxic, bioturbated sediments led to weaker retention of phosphorus compared to oxic, defaunated sediments. Both iron and manganese fluxes increased under bioturbated conditions compared to defaunated sediments. This study shows that re-oxygenation of previously anoxic coastal sediments enhance phosphorus retention in the sediments. Colonisation by *M. arctia* induce strong mobilisation of iron and manganese due to its intense bioirrigation, which facilitates organic matter degradation and decreases the phosphorus retention by metal oxides in sediment.

Introduction

Eutrophication in coastal waters has resulted in an exponential increase of hypoxic waters over the last century (Diaz and Rosenberg 2008). In the Baltic Sea with its limited water exchange with the North Sea the increased nutrient load has led to an increased primary production since the 1950s, leading to large deposition of organic matter in the sediments as a consequence (Boesch *et al.* 2006). Remineralisation has led to increased oxygen deficiency and hypoxia below the halocline (Vahtera *et al*. 2007). Despite numerous regional remedy actions to limit nitrogen (N) and phosphorus (P) loads the spread of hypoxic areas has continued (Hansson *et al*. 2011) and the Baltic Proper is now one of the largest oxygen deficient marine areas in the

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world. Conley *et al.* (2002) showed that dissolved inorganic phosphorus (DIP) is positively correlated to the hypoxic bottom area in the Baltic Proper. Further, Stigebrandt *et al.* (2014) showed that despite a 50% reduction of external P load during the last decades, both P concentration and spread of anoxic bottom areas have increased in the Baltic Proper.

Oxygen conditions are key processes in the retention/mobilisation of DIP and metals in sediments (Mortimer 1941). Under oxic conditions, iron (Fe) and manganese (Mn) oxy-hydroxides can sorb and precipitate DIP on or in sediments (Ruttenberg 2003). Under hypoxic conditions bacterial sulphate reduction as well as release of DIP from Fe and Mn oxides will occur (Hyacinthe and Van Cappellen 2004). Some of this DIP may recycle back into the water mass, while the rest is buried in various forms of P (Ruttenberg 2003, Reed *et al*. 2011). Today, the DIP leakage from hypoxic/anoxic sediments is ~2.3 g P m^{-2} yr^{-1}, which is three to five times greater than under oxic conditions (Stigebrandt *et al*. 2014).

When macrofauna recolonise previous anoxic sediments they will bioturbate and mobilise nutrients. The brackish Baltic Sea has a low biodiversity compared to more typical marine systems. In the Baltic, the benthic macrofauna community has mainly consisted of only a few invertebrate species dominated by the clam *Macoma balthica* as well as the amphipod species *Monoporeia affinis* and *Pontoporeia femorata*. Karlson *et al*. (2007) carried out a bioturbation/bioirrigation experiment with both anoxic and previously anoxic sediments loaded with nutrients. They found that DIP flux out from sediment increased fourfold by the pumping of reduced compounds by the clam *M. balthica*, while the amphipod *M. affinis* resulted in a 20% increase in efflux. This was partly attributed to more effective oxygenation of sediment by *M. affinis* which should increase the retention capacity of phosphate in sediment.

During the last three decades the spionid polychaete genus *Marenzelleria spp.* has invaded the entire Baltic proper (Renz and Forster 2013). It has significantly changed the composition of the benthic community and is now one of the dominant macrofaunal species with a seasonal population dynamics (Kauppi *et al*. 2017). Three siblings of *Marenzelleria* are co-occurring: *M. neglecta,* which is established all over the Baltic Sea in both muddy and sandy shallow sediments (Kauppi *et al*. 2017), *M. viridis,* which is dominating in the southern basins with shallow sandy sediments (*ibid*.), and *M. arctia,* which is found in the northern basins with deep muddy sediments (Blank *et al*. 2008, Kauppi *et al.* 2017). Large differences in bioirrigation between these siblings are observed. Generally, *M. viridis* and *M. neglecta* dig deep unbranched mucus-lined burrows down to 25–35 cm (Essink and Kleef 1988, Quintana *et al*. 2011) while *M. arctia* digs more shallow burrows down to eight cm (Hietanen *et al*. 2007). However, all three species dig considerably deeper than other macrofaunal species in the Baltic Sea (Karlson *et al.* 2011). Thereby they change ventilation rates and redox conditions for most sediments with consequences for P dynamics (Kristensen *et al.* 2011). It is suggested that the colonisation by *M. neglecta* has resulted in an oxidation of previously hypoxic/anoxic sediments in both Stockholm archipelago (Karlsson *et al.* 2010) and the eastern Gulf of Finland (Maximov *et al.* 2014). It is suggested that these worms may help reducing the release of P from the sediment also in a longer time perspective (Norkko *et al*. 2012).

The present study is part of a mesocosm experiment which has been carried out with reoxygenation of natural, previously anoxic sediments collected in the Stockholm archipelago. Bonaglia *et al*. (2013) aimed to follow how reoxygenation and bioirrigation by *Marenzelleria* affected the retention of N, P and dissolved silica (DSi) in this sediment-bottom water complex. They used microsensor profiling and determined oxygen consumption rates by individuals. The present work focuses on the effects of the above mentioned treatments, but measured in the mesocosms during several weeks of exposure in flow-through conditions. Since Fe^{2+} and Mn^{2+} (hereafter called Fe(II) and Mn(II)) are assumed to play crucial roles in the P retention process being able to form oxyhydroxides that can sorb DIP and precipitate (Mortimer 1941), their roles were studied in both mesocosm water and sediment. Comparisons are made between the mesocosms flushed with hypoxic and those with oxic water, as well as with the mesocosms flushed with oxic

water with and without bioturbation by the polychaete *M. arctia*.

Material and methods

Sediment boxcores were collected from Kanholmsfjärden, which is a 35 km^2 large bay in the Stockholm archipelago. It is connected to the Baltic Proper (Landsort Deep) via several deep channels and this exchange dominates its hydrography. Long stagnation periods with a low circulation of deep-water through the channels have led to periods of hypoxia and even anoxia in the deeper parts of the bay. During the last five years preceding this experiment anoxic conditions with high concentrations of hydrogen sulphide (H_2S) have been prevalent in the bottom water (Lücke 2013).

Sediment handling and experimental setup

The aim was to analyse the fluxes in three different treatments with four mesocosm replicates per treatment. These treatments were: (1) hypoxic water treatment (HY), (2) normoxic water treatment (NO) and (3) normoxic water treatment with added *Marenzelleria arctia* (NOB).

Sampling of sediments was made on 7 June 2011. The organic-rich hypoxic muddy sediments were collected with a Jonasson-Olausson box corer from Kanholmsfjärden at 105 m depth (59°20.1814´N, 18°46.2680´E). On board, the sediments were immediately transferred from the corer to 12 transparent acrylic boxes (20 × 20 × 50 cm). Each box was sealed with a baseplate and a detachable lid. They were filled with bottom water collected with a Niskin water sampler and transported to the Askö Laboratory, Stockholm University. *In situ* water temperature was 4.7 °C, salinity 9.3 PSU and oxygen (O_2) < 5 µM.

The experiment had two phases. The first represented a stabilisation and acclimatisation (start 7 June). All mesocosms were kept in cold storage (~5 °C) to allow the sediment to stabilise and acclimatise for 48 days. During this period no new water was added and the oxygen level was kept hypoxic (~20 µM O_2) in all 12 mesocosms. No macrofauna was observed in either of them. The mesocosms were thereafter (25 Aug.) transferred to an experimental hall and immersed in a temperature controlled bath where each mesocosm was connected with tubings through their lids for incoming and outgoing water. The rather long acclimatising period should guarantee the same starting conditions for all mesocosms in the experiment but in the light of e.g. the results of Ekeroth *et al.* (2016) one may expect some changes in both the degradation process over time and the P fluxes during this period. Water flow was regulated with peristaltic pumps allowing an average water renewal time of 25.5 ± 2.3 h. The incoming water was sand-filtered natural seawater pumped from 20m depth in the bay in vicinity of the laboratory. The salinity was approximately the same as at the sampling site. Eight of the twelve mesocosms were supplied with natural oxic water (NO, O_2 ~300 µM). The remaining four mesoscoms were supplied with hypoxic water (HY, $O_2 \leq 50$ µM). The latter was obtained by circulating the incoming water and bubbling it with nitrogen gas (N_2). This was regulated by using a digital-controlled N_2 valve connected to an oxygen optod (dTRANS O2 01, JUMO). The mesocosms were circulated with NO or HY water during an acclimatisation period of almost four weeks in order to establish an oxic surface sediment layer in the oxygenated mesocosms. This could result in an increase in DIP storage in the sediments which could be released under reduced conditions. However, this was not investigated in present study. The mean oxygen concentration in the water were 90 ± 73, 352 ± 73 and 300 ± 76 µM for HY, NO and NOB respectively. Each mesocosm was continuously mixed with a stirrer placed under its lid. The mixing rate was kept sufficiently high to allow the water column to mix without causing noticeable resuspension. For more details about the experimental setup *see* Bonaglia *et al.* (2013).

The worms were collected in Kanholmsfjärden (2 Sep.) at 55 m depth (59°20.3701´N, 18°45.3815´E), just above the halocline (O_2 ~260 µM, salinity 7.4 PSU), using a van Veen grab sampler. The sediment grabs were sieved directly on ship through a 0.5 mm mesh and ca. 1000 individuals were collected, placed in cooled

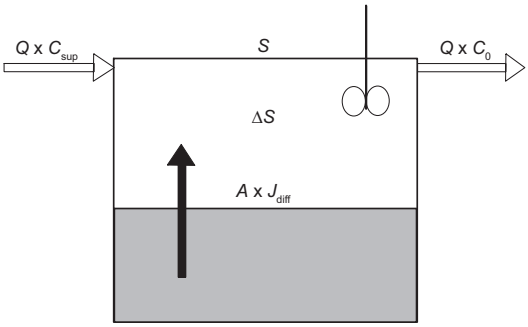

Fig. 1. Experimental configuration of the through-flow mesocosms. Open arrows denote water supply and discharge, *Q*. The element concentration in supply and water column is C_{sup} and C_0, respectively. J_{diff} represents the diffusive specific flux over sediment–water interface with cross area *A*. *S* stands for net system source/sink and ΔS represents the unaccounted sources/sinks required to balance the system. The water mass was continuously mixed as indicated by symbol in the upper right corner.

and aerated containers with natural seawater and transported to the Askö laboratory. A sub-sample of 10 specimens was sent to Rostock University (Germany) and identified as *Marenzelleria arctia* using DNA analyses following Bastrop and Götting (2006). The worms were added to four of the oxygenated mesocosms (21 Sep.). The density was 80 worms per mesocosm. This is equivalent to 2000 specimen m^{-2}, corresponding to a natural population density in the Baltic proper (Villnäs and Norkko 2011). The worms were retrieved in the end of the experiment. No notable mortality (< 10%) was observed, indicating good conditions for the worms.

Sampling and analysis of DIP, Fe and Mn

DIP, Fe(II) and Mn(II) were sampled in the incoming water (i.e. in the well-mixed water tanks), in the middle of the mesocosm water columns and in the sediment pore water (Fig. 1). This was done using DGT passive samplers (Davison and Zhang 1994, Zhang *et al*. 1995) following Krom *et al.* (2002). A DGT probe is composed of a filter (of thickness 0.135 mm), a diffusive hydrogel (0.8 mm) and a resin gel (0.4 mm). The filter (mesh size 0.45 μm) will prevent small particles to penetrate the diffusive hydrogel while ions pass through both filter and diffusive hydrogel before they are trapped by the resin. The hydrogel has a known diffusivity for each ion. Based on the amount of ions sorbed by the binding gel, duration of exposure, geometry of sampler and diffusivity of each element (adjusted for temperature), the concentration outside the diffusion gel can be estimated. As the binding gel accumulates elements over time, this method enables detection of even very low concentrations (Davison and Zhang 2012). The DGT probes used for sampling in the water column had circular gel discs of radius 10 mm. Those for sediment were similar, but in the form of exposed oblong rectangles (150 × 18 mm) enabling to obtain vertical profiles of DIP and metals in sediment by cutting the DGT samplers into slices after exposure. Before inserting them into the sediment, the pore water samplers were degassed for at least one day with N_2 in a container with water of salinity similar to the supply. This was made in order to eliminate O_2 in the gel. The sediment samplers were carefully pressed into the sediment to ensure good contact between sediment and diffusion gel. The DGT technique generally requires a reasonably well mixed water mass to keep the concentration unaltered outside the diffusive gel. Hence, the sediment probes were left in sediment for 24–29 hours to minimise the effect of ion depletion in their surroundings as the ions lost to the sampler could only be replaced by a slow diffusive ion transport from the adjacent sediment (Harper *et al*. 1998, Zhang *et al*. 1995). After exposure the sediment samples were carefully retrieved from the sediment, washed in Milli-Q water and then sliced using Teflon™ coated razor blades to minimise metal contamination. The uppermost 1.5 cm slice reflected the deepest part of the water column. The following three slices were cut to 0.5 cm thickness each and the rest of the gel in 1cm thick slices.

Two types of DGT probes were used, one for cations (i.e. Fe(II) and Mn(II)) and one for anions (DIP). The DGT samplers for Fe(II) and Mn(II) as well as DIP in water mass were deployed two weeks before the end of the experiment (7 Nov.). Thereafter they were retrieved after which the sediment DGT samples were deployed. This was done next day (> 24 hours)

and analysed. The passive sediment samplers were extracted and analysed according to the standard protocols USEPA 200.7 (ICP-AES) and 200.8 (ICP-SFMS). The resin gels were digested in 1 M nitric acid for cations and in 0.25 M sulphuric acid for anions. Fe(II) and Mn(II) were analysed using an ICP-MS (NexION 300D, PerkinElmer). DIP was measured spectrophotometrically using a Bran+Luebbe Autoanalyzer 3 following their manual for analysis of DIP in seawater. Reference material, blanks and spiked samples were analysed to identify interferences and contamination sources. The pore water concentration was calculated according to Davison and Zhang (1994) taking the elution efficiency of the actual gel for the specific ions into consideration. The water column samples were analysed by a commercial laboratory (ALS Scandinavia) using the same technique.

Water content (WC) in sediment was determined by drying the sediment slices at 105 °C for 24 hours and then calculating the relative weight loss. Four sediment cores were used for WC, one each for HY and NO and two for NOB. WC was then used to calculate sediment porosity.

Statistical analysis

The concentration data relating to Fe(II), Mn(II) and DIP in the water column as well as in the pore water with the three treatments were analysed using one-way analysis of variance (ANOVA) with treatment as a fixed factor. With the relatively large number of observations and the lack of outliers in the data, the central limit theorem motivates the use of the parametric ANOVA for testing differences in mean values. If there was a significant difference, the treatments were compared using post-hoc Tukey's test for all pairwise combinations of treatments to determine which treatment(s) that were significantly different from each other. The level of significance was set to 5% for all tests.

Pore water fluxes

The diffusive flux, J_{diff}, in muddy sediment can be estimated from Fick's First Law taking porosity (φ) and tortuosity (θ^2) into consideration (Boudreau 1997):

$$J_{diff} = -\frac{D}{\theta^2}\frac{\partial C}{\partial z} \quad (1)$$

where D is the molecular diffusivity for the dissolved substance in water adjusted for ambient temperature. The porosity, φ, was estimated using the sediment water content (WC). $\partial C/\partial z$ represents the vertical concentration gradient. Since the sediments had generally been anoxic for more than four years, HY and NO treatments were assumed to be without macrofauna (no macrofauna was observed as mentioned above). Finally, θ^2 is a measure of the actual diffusion pathway in sediment. Boudreau and Meysman (2006) have suggested an empirical relationship for θ^2 based on porosity for muddy sediments:

$$\theta^2 = \left[1 + \frac{32}{9\pi}\left(1-\varphi\right)\right]^2 \quad (2)$$

The specific diffusive flux across the sediment–water surface is approximatively (Mort *et al.* 2010):

$$J_{diff} = -\frac{\varphi D}{\theta^2}\frac{\left(C_0 - C_1\right)}{\Delta z_1/2} \quad (3)$$

where C_0 and C_1 are the mesocosm water and mean pore water concentrations in the uppermost sediment layer, and Δz_1 is the layer thickness. Mean microelectrode profiles of O_2 (*see* Appendix) suggest an oxygen sediment penetration thickness of 0.5 to 2.8 mm. The assumption that C_0 is representative for the concentration at the interface will probably lead to a slight overestimation of the diffusive flux as a viscous sublayer probably influenced by bioturbation/bioirrigation in the NOB case will develop at the sediment–water interface.

Net mesocosm change of DIP and Fe(II) and Mn(II)

A simple through-flow mesocosm model based on concentrations in supply (C_{sup}) and discharge (C_0) was used based on inflow, Q, which equals outflow (Fig. 1). The change in mass flux, S, represented the net sink or source of the system:

$$S = (C_0 - C_{sup})Q \quad (4)$$

The diffusive sediment-to-water flux, Eq. 3 for HY and NO, combined with S enabled an estimate of the net impact of other sinks or sources:

$$S = A \times J_{diff} + \Delta S \quad (5)$$

where A denotes the sediment area and ΔS comprises the difference between total net sink/source (S) and the diffusive flux ($A \times J_{diff}$). This was estimated for HY and NO treatments, but not for NOB as the impact of bioirrigation was unknown.

Results

Water column concentrations

In Table 1 water concentrations of Fe(II), Mn(II) and DIP are presented together with the inflow ditto. These results present a good representation of dissolved concentrations in the water column in flow-through conditions and the effect on the three treatments during an exposure time of 13 days.

There was a significant difference in Fe(II) mean concentrations between the three treatments (ANOVA: $F_{2,33} = 17.63$, $p < 0.001$). They differed significantly between all treatments, with the highest concentrations in NOB. The $Fe(II)_{NOB}$ concentrations were significantly higher than $Fe(II)_{NO}$ (Tukey's test: $q_s = 5.95$, $p < 0.001$) and $Fe(II)_{HY}$ (Tukey's test: $q_s = 3.70$, $p = 0.002$). $Fe(II)_{HY}$ was also higher than $Fe(II)_{NO}$ (Tukey's test: $q_s = 3.08$, $p = 0.015$). To summarise: $Fe(II)_{NOB} > Fe(II)_{HY} > Fe(II)_{NO}$.

For Mn(II), the three treatments were significantly different (ANOVA: $F_{2,33} = 33.37$, $p < 0.001$). The average Mn(II) concentration was significantly higher in NOB than in the other two treatments (Tukey's test: $q_s = 7.04$ and $q_s = 7.10$ for NO and HY, respectively, both $p < 0.001$). However, there was no significant difference between $Mn(II)_{HY}$ and $Mn(II)_{NO}$ (Tukey's test: $q_s = 0.06$, $p = 0.901$). To summarise: $Mn(II)_{NOB} > Mn(II)_{HY} = Mn(II)_{NO}$.

The DIP concentrations were relatively similar in the different treatments, although some significant differences occurred (ANOVA: $F_{2,33} = 14.90$, $p < 0.001$). The average DIP concentration with NO was significantly lower than in both HY and NOB (Tukey's test: $q_s = 5.32$, $p < 0.001$ and $q_s = 3.65$, $p = 0.002$, respectively). DIP_{HY} and DIP_{NOB} were, however, not significantly different from each other (Tukey's test: $q_s = 1.67$, $p = 0.229$). To summarise: $DIP_{NOB} = DIP_{HY} > DIP_{NO}$

Table 1. Concentrations of dissolved Fe, Mn and DIP (μmol l^{-1}) in the water columns. Concentrations are given as mean ± standard deviation (n = 4). HY = hypoxic water treatment, NO = normoxic water treatment, NOB = normoxic water treatment with added *M. arctia*.

Element	HY	NO	NOB
Fe(II)	0.02 ± 0.01	0.01 ± 0.00	0.07 ± 0.02
Mn(II)	2.12 ± 0.65	1.91 ± 0.91	9.45 ± 1.70
DIP	0.31 ± 0.70	0.17 ± 0.10	0.27 ± 0.03

Pore water concentrations and profiles

For average pore water profiles for Fe(II), Mn(II) and DIP mean concentrations were calculated for each depth interval in respective treatments (Fig. 2). There were significant differences between the treatments for all three elements taken the sediment depth into account (ANOVA: $F_{Fe\ 2,187} = 13.72$, $F_{Mn\ 2,187} = 11.70$, $F_{DIP\ 2,116} = 12.19$, all $p < 0.001$).

$Fe(II)_{NOB}$ had a marked maxima a few cm below the sediment surface followed by low and almost constant concentrations in the deeper parts (Fig. 2a). This was seen also for $Fe(II)_{NO}$, but less pronounced. $Fe(II)_{HY}$ lacked such peaks. The mean $Fe(II)_{NOB}$ concentrations were significantly higher than for the other two treatments (Tukey's test: $q_s = 4.16$ and $q_s = 4.83$, for NOB *vs*. NO and HY respectively, both $p < 0.001$), while the latter two were not significantly different (Tukey's test: $q_s = 0.63$, $p = 0.805$). To summarise: $Fe(II)_{NOB} > Fe(II)_{HY} = Fe(II)_{NO}$.

The Mn(II) profiles had less distinct peaks than the corresponding Fe(II) (Fig. 2b). Their maxima were found further down in the sediments with decreasing levels toward the deeper

parts. Except for the surface layers, Mn(II) concentrations were higher in NO than in HY and NOB. In the deepest parts, the concentrations were similar irrespective of treatment. $Mn(II)_{HY}$ had generally significantly lower mean concentrations and less pronounced maxima than for both $Mn(II)_{NOB}$ and $Mn(II)_{NO}$ (Tukey's test: q_s = 4.83, $p < 0.001$ and $q_s = 3.28$, $p = 0.004$, respectively). There was no significant difference between the latter two (Tukey's test: $q_s = 1.51$, $p = 0.287$). To summarise: $Mn(II)_{HY} < Mn(II)_{NOB} = Mn(II)_{NO}$.

DIP pore water profiles increased downwards with depth for all three treatments (Fig. 2c). The deepest parts were all characterised by weak gradients. The results for DIP_{NOB} showed that the concentrations were significantly higher than for DIP_{HY} (Tukey's test: $q_s = 2.5$, $p = 0.038$) as well as DIP_{NO} (Tukey's test: $q_s = 5.26$, $p < 0.001$). There was no significant difference between DIP_{HY} and DIP_{NOB} (Tukey's test: $q_s = 2.07$, $p = 0.103$). To summarise: $DIP_{NO} = DIP_{HY} < DIP_{NOB}$.

The increasing DIP porewater concentrations downwards usually indicate an accumulation due to organic matter remineralisation and reductive dissolution of iron minerals in the sediments. Fe(II) showed distinct production peaks except $Fe(II)_{HY}$, which only indicated a weak increase close to the sediment surface. (The corresponding Mn(II) maxima extended over almost the entire investigated sediment columns). The metal concentrations decreased above and below the peaks, indicating both a diffusive transport away from the zones as well as internal sinks. The sometimes large subsurface peaks of Fe and Mn were observed without pronounced phosphate peaks. The corresponding peaks in Fe(II):DIP ratios (Fig. 3) supported these findings, this ratio was substantial only in the NOB case. This was notable as reduction of Fe and Mn oxides are generally assumed the main mode of phosphate regeneration.

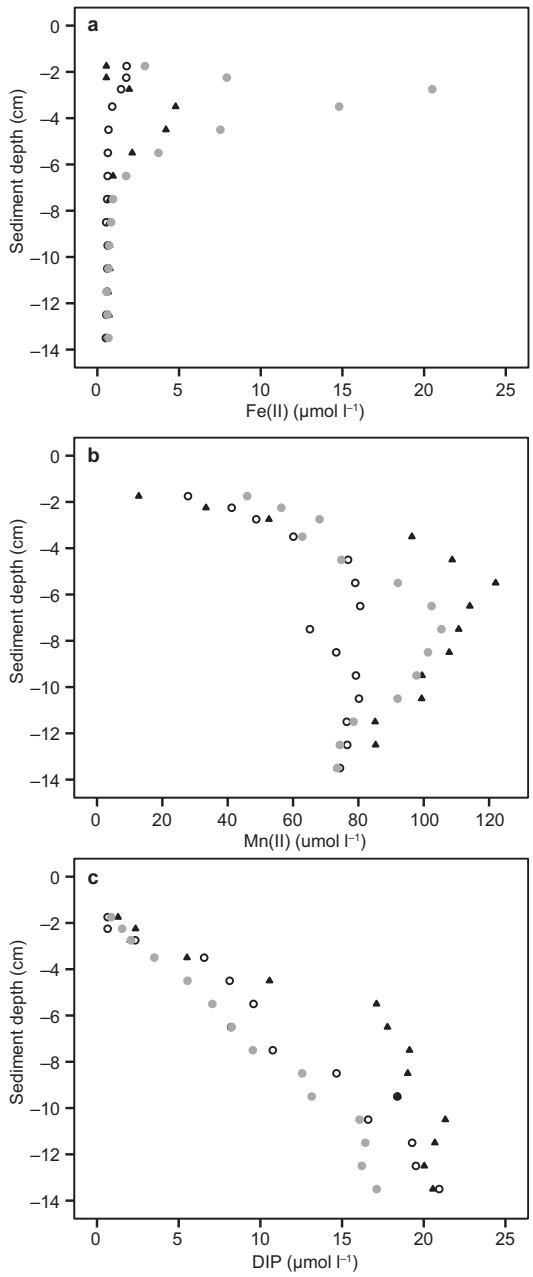

Fig. 2. Mean pore water concentrations of (**a**) Fe(II), (**b**) Mn(II) and (**c**) DIP. ○ = hypoxic water treatment (HY), ▲ = normoxic water treatment (NO), ● = normoxic water treatment with added *M. arctia* (NOB).

Input-output analysis and pore water fluxes

Water content varied between 80%–91% (HY: 82.7%–88.9%, NO: 79.9%–88.3%, NOB: 80.1%–91.3%) with generally higher percentage closer to the sediment surface. Mean diffusive pore water fluxes for HY and NO were calculated from concentration gradients, molecular

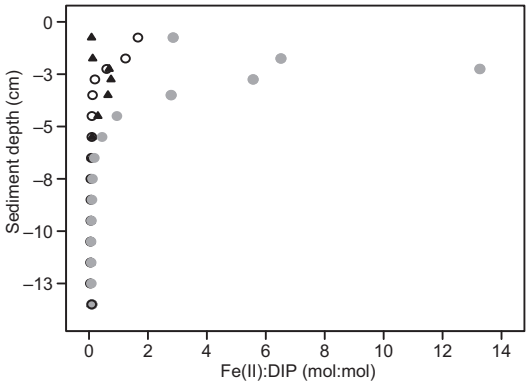

Fig. 3. Mean Fe(II):DIP ratio (mol:mol) profiles in the pore water. ○ = hypoxic water treatment (HY), ▲ = normoxic water treatment (NO), ● = normoxic water treatment with added *M. arctia* (NOB).

diffusivity and porosity. Bioirrigation and bioturbation caused by *M. arctia* is not included (*see* Material and methods).

Input-output analysis based on mean water supply and discharge and their measured concentrations gave the net source/sink in each mesocosm type. Net Fe(II) sinks were found for HY and NO treatment. Corresponding sinks for DIP were linked to NO and NOB (Table 2). Further, the Mn source term in NOB treatment was almost five times as large as for the other treatments. Its concentration was at least two orders of magnitude higher than the corresponding Fe and DIP ones.

The diffusive flux (J_{diff}) based on Fick's First Law and molecular diffusivity is presented in Table 2. It was always directed out from sediment. The diffusive fluxes for Fe(II), Mn(II) and DIP were lowest in NO treatment. The difference between the net mass flux change in the through-flow system and the diffusive efflux from sediment based on molecular diffusivity was denoted ΔS (Table 2). Note that the standard deviation was large for all estimates indicating substantial variations in concentration and source/sink within respective mesocosm.

Discussion

Concentrations in the water column and pore water

Concentrations of Fe(II), Mn(II) and DIP in the water column of the mesocosms were higher than in the incoming seawater (supply water). The average Fe(II) and DIP concentrations in the supply water are in the same range as reported by e.g. Turnewitsch and Pohl (2010) at similar water depths in the central Baltic proper (Table 1). For Mn(II) the concentrations in the mesocosm water were several orders of magni-

Table 2. Results from in- and output analysis of Fe(II), Mn(II) and DIP. Numbers are given as mean ± standard deviation (μmol m^{-2} d^{-1}, n = 4). HY = hypoxic water treatment, NO = normoxic water treatment, NOB = normoxic water treatment with added *M. arctia*. $C_{sup} \times Q$ and $C_0 \times Q$ represent concentrations in supply respectively in discharge times the water flow (Q). S, $A \times J_{diff}$, and ΔS denote through-flow mass change, diffusive sediment–water flux and additional internal source/sink respectively (*see* Fig. 1). N.b. ΔS was not calculated for NOB.

Flux	Treatment	Fe(II)	Mn(II)	DIP
$C_{sup} \times Q$	HY	6.1 ± 0.1	1.6 ± 0.0	35.5 ± 0.8
	NO	3.1 ± 0.2	0.9 ± 0.1	63.8 ± 4.0
	NOB	3.0 ± 0.2	0.9 ± 0.1	65.0 ± 3.4
$C_0 \times Q$	HY	3.4 ± 2.4	465.1 ± 148.0	70.0 ± 20.6
	NO	1.5 ± 0.4	464.1 ± 222.0	39.9 ± 24.7
	NOB	15.4 ± 3.9	2204.1 ± 400.0	62.9 ± 11.2
S	HY	–2.7 ± 2.4	463.5 ± 148.0	34.5 ± 17.5
	NO	–1.6 ± 0.5	463.2 ± 222.0	–23.9 ± 22.4
	NOB	12.4 ± 3.9	2203.2 ± 400.0	–2.1 ± 8.5
$A \times J_{diff}$	HY	14.6 ± 16.4	202.3 ± 180.5	18.1 ± 11.8
	NO	4.3 ± 3.0	98.5 ± 40.2	11.8 ± 7.8
ΔS	HY	17.3 ± 16.8	261.2 ± 159.0	16.4 ± 16.5
	NO	–5.9 ± 3.5	364.7 ± 191.9	–35.7 ± 19.0

tude higher than in the supply water. This supply water concentration was, however, slightly lower than those found previously (Turnewitsch and Pohl 2010). In the normoxic water the DIP concentration (DIP_{NO}) was equal to that of the supply water, while in the two other treatments (DIP_{HY} and DIP_{NOB}) the concentrations were higher in the mesocosm water. This lower concentration in DIP_{NO} is probably a result of an oxidation of Fe(II) and Mn(II) to oxyhydroxides, which can sorb and precipitate DIP and thereby lower DIP in the water column (Mortimer 1941). There must be other Fe sinks/sources in the mesocosms, such as sorption of Fe to the side walls, particle-bound $Fe(OH)_3$ or colloids (e.g. Egger *et al*. 2015) to account for the difference between net change in the through-flow fluxes and calculated diffusive flux from sediment. These pools are, however, not in focus in present work. The addition of *M. arctia* resulted in a drastic increase of both Fe(II) and Mn(II) and a weak retention of DIP. The latter is probably a result of more reduced conditions in porewater caused by stimulated degradation of organic matter and increased ventilation of porewater due to bioturbation and bioirrigation (Kristensen 2000).

The average Fe(II) peak in sediment indicates a suboxic zone of maximum Fe reduction for the two oxic treatments (NO and NOB; Fig. 2a). This region separates an upper oxic layer from a deeper sulphidic one (Hensen *et al.* 2006), H_2S data for present experiment are shown in Bonaglia *et al*. (2013). For HY this zone might have been too close to the sediment surface to be captured with the relatively low resolution of the sediment sampling. Microelectrode profiles in these sediments suggest an oxidised upper layer of about a few mm from sediment surface (Bonaglia *et al.* 2013: fig A1). The $Fe(II)_{NOB}$ peak was located closer to the surface than the one for $Fe(II)_{NO}$. The Mn(II) profiles (Fig. 2b) had less pronounced peaks compared to Fe(II) and were found deeper down in the sediment with substantial concentrations even relatively deep down. This zonation, with Mn(II) peaks found below the Fe(II) peaks, contrasts with the assumption of a "redox ladder" based on the higher redox potential required for Mn(II) oxidation compared to Fe(II) (Froelich *et al*. 1979, Thamdrup *et al*. 1994). The reason for present pattern is unknown, but since the DGT probe gel was sliced and analysed for Fe and Mn simultaneously for each layer by the ICP-MS spectrometer, the resulting profiles should reflect the real distribution of Fe(II) and Mn(II).

There are multiple pathways for oxidation and reduction of Fe and Mn (Van Cappellen and Wang 1996). The above mentioned reduction zone produces Fe(II) and Mn(II) by degradation of organic matter and reduction of their respective oxides. Both may be exported upwards where they may re-oxidise in the overlaying sediment or in the water column. In present set up, the oxygen penetration zone in the surface sediment was only a few mm as mentioned above. In the sulphidic zone, below the reduction zone, sinks like FeS and pyrite are expected (Rickard 1997, Krom *et al.* 2002). This should lead to a decrease in Fe(II) with depth (Van Cappellen and Wang 1996), as was also noticed in present study. A marked decrease was also noticed but deeper down for Mn(II) in all treatments indicating Mn(II) sinks. These Mn(II) sinks may be caused when Mn precipitates as carbonate or adsorbs to clay minerals, carbonates or metal oxides in the sediment (Middelburg *et al.* 1987, Aller 1994).

Fe(II) plays an important role in the oxidation of sulphide to sulphate (Jörgensen and Nelson 2004). Further, in a mesocosm experiment, Kristensen *et al*. (2011) found that "*M. viridis* stimulated sulphate reduction at the expense of aerobic respiration". Much of the ventilation of the blind-end burrows are supposed to occur by percolation of the return water to the sediment surface, increasing the transport of solutes to the water column (Quintana *et al.* 2007). This may cause both enhanced benthic O_2 consumption and increased Fe(II) efflux, as is indicated in present NOB (*see* also Jørgensen and Nelson 2004, Bonaglia *et al.* 2013).

The oxic condition in the water columns enables a shift from Fe(II) to Fe(III) and Fe-oxyhydroxide formation thereby enabling DIP sorption. The shift from a minor Fe_{NO} retention to a substantial source for Fe_{NOB} with still a retention of P suggests an excess of reducible Fe over P in the NOB case.

In the present study, Mn(II) has a strong internal source in all treatments. This is in agreement with Slomp *et al*. (1997) who found that Mn(II)

may leak even through oxidised sediment surfaces and into overlying oxic or hypoxic water. Mn(II) has a slow oxidation compared to Fe(II) even if it may be catalysed by surfaces and/or microorganisms (De Schamphelaire *et al*. 2007). Tebo (1991) showed that released Mn(II) may remained unoxidised for a week in oxic open-ocean conditions. This is much longer than the supply water turnover of approximately one day in our mesocosms. Nevertheless, high Mn(II) concentrations occurred in the mesocosms´ water columns, especially for NOB. The latter is emphasised in the measured O_2 fluxes into the sediment surface in our companion paper (Bonaglia *et al.* 2013: fig. 3) where the presence of *M. arctia* doubled the oxygen consumption in the sediment compared to NO. This may explain the high Mn(II) concentrations observed in the water column (Table 1), while Fe(II) probably precipitates as Fe-oxyhydroxides (Davison 1993).

The concentration of DIP increased with sediment depth without pronounced peaks for all treatments. This suggests more efficient sinks above the suboxic layer than in the deeper one. The linear increase of DIP down to the end of the burrows (Bonaglia *et al.* 2013) seems reasonable with regard to the bioirrigation of the worms. The decrease in DIP retention in NOB compared to NO (*see* Table 2) is probably due to an increased O_2 consumption which may explain the shift from a marked Fe efflux in NOB to a minor retention in NO. The incubations by Bonaglia *et al.* (2013) shows the opposite trend where the benthic DIP retention increased by a factor four compared to NO. The present throughflow flux estimates were based on an average over 24–29 hours (the exposure time for DGT) while the incubation in Bonaglia *et al*. (2013) continued for six hours after capping before the porewater sampling. The different results in net fluxes obtained may be an effect of the different procedures used for flux calculations.

Sources and sinks

Redox conditions can explain the DIP mobilisation in the hypoxic treatment and the retention in the normoxic treatment. DIP has high diffusive fluxes and net sources for HY, as well as low diffusive fluxes and strong net sinks for NO (Table 2). This is in accordance to what occurs in the Baltic Proper deep bottoms (Stigebrandt *et al.* 2014). The weak retention observed in NOB is in line with what could be expected from the previously mentioned increased sulphide flux towards the upper sediment layers caused by bioirrigation (Jørgensen and Nelson 2004, Kristensen *et al*. 2011). On a mesocosm level HY gave a net mean DIP mobilisation of 34.5 ± 17.5 μmol P m^{-2} d^{-1} while NO resulted in a net retention of –23.9 ± 22.4 μmol P m^{-2} d^{-1}. NOB, on the other hand, resulted in at most a weak DIP retention of –2.1 ± 8.5 μmol P m^{-2} d^{-1}. However, the large standard deviations make the estimates uncertain.

It has recently been estimated that the present large-scale net DIP efflux from anoxic bottoms in the Baltic Proper is ~2.3 g P m^{-2} yr^{-1} based on budget estimates (Stigebrandt *et al.* 2014). This flux decreased to 0.5 and 0.8 g P m^{-2} yr^{-1} under oxic and hypoxic conditions respectively. Hence, present mean net mesocosm flux for HY of 0.4 g P m^{-2} yr^{-1} is reasonable. Fickian diffusive sediment DIP fluxes in present experiment were, on average, 0.16 and 0.10 g P m^{-2} yr^{-1} for HY and NO respectively. Bolałek (1992), Hille *et al.* (2005), Mort *et al.* (2010) and Jilbert *et al.* (2011) presented fluxes in the range of 0.1–5.5 g P m^{-2} yr^{-1} using Baltic pore water concentration gradients in sediment, molecular diffusion and Fick's First Law. Also Karlson *et al.* (2007) reported low fluxes in the range 0.4–0.5 g P m^{-2} yr^{-1} using benthic chamber measurements with anoxic sediments from Kanholmsfjärden. Hence, present DIP estimates are in the lower range of these estimates under hypoxic and oxic conditions.

Bioirrigation effects of *Marenzelleria*

The presence of *M. arctia* resulted in burrow digging and pumping of water to flush out excrements and debris, but also pumping for their respiration. Kristensen (2000) and Kristensen *et al.* (2011) found that burrow-dwelling fauna could enhance the capacity for bulk benthic metabolism up to a factor three. This should lead to enhanced degradation of OM and increased DIP production. These results agree with present results

and those of Ekeroth *et al.* (2016). They found insignificant effects of DIP retention in their mesocosm experiment under similar conditions and probably using the same sibling of *Marenzelleria* as in present study. They also cited other experimental studies which report similar effects of bioturbation by *Marenzelleria* spp. on DIP retention (Karlson *et al.* 2005, Urban-Malinga *et al*. 2013) which confirm our observed lack of enhanced DIP retention by *M. arctia*. Bonaglia *et al*. (2013), on the other hand, found a slight increase in DIP retention by bioturbation.

Norkko *et al*. (2012) regarded the invasive polychaetes as efficient oxidisers of reduced sediments and thus they should enhance the P retention process. This was based on an advanced reaction-transport model simulating the impact of a seasonal hypoxia including the effects of bioirrigation by *Marenzelleria* spp. After a five-year simulated acclimatisation period, the polychaetes were introduced and the model was run for ten years. The first year was characterised by a P efflux out of the sediment. Thereafter P retention started to grow up to a quasi-steady state during the rest of the period with a successive increase in the retention capacity for P as a result of oxidation of the sediment by bioirrigation. In the present study, in Bonaglia *et al*. (2013) study, as well as in Ekeroth *et al*. (2016) the mesocosm experiments were running for just a few months, which may explain why the retention probably had not fully developed. Nevertheless the model results for the first year are more or less in line with present results. This is valid also for Bonaglia *et al*. (2013) and Ekeroth *et al.* (2016). Hence it seems justified to believe that the present study gives a fair description of the impact of *M. arctia* on the P retention under the beginning of the re-oxygenation process. It also highlights that longer term experiments and more flux measurements *in situ* are needed to understand the long-term role of *Marenzelleria* for P retention.

Conclusions

The adding of *M. arctia* to oxic sediments led to a lower retention capacity for DIP compared to normoxic conditions without bioturbation. Hence, the bioturbation and bioirrigation activities of the polychaetes did not further increase the sequestration of DIP as was hypothesised. At the same time and in the same sediments the Fe(II) leakage strongly increased in the bioturbated sediments. The already large Mn(II) efflux increased further under the same conditions. This strong mobilisation of Fe(II) and Mn(II) is probably an affect of bioirrigation, which is known to increase organic matter degradation and decrease DIP retention by Fe oxides in sediment. MnO_2 oxidation of Fe(II) in sediment is supposed to play a significant role.

The present experiment was run for seven weeks. A long-term advection-reaction might cause a change from insignificant phosphate efflux (in line with present results) to a long-term P retention state. These temporal aspects suggest that longer mesocosm studies are needed in combination with measurements *in situ* to account for temporal and seasonal variations. Such information is important in the light of large-scale geoengineering projects with the goal of counteracting eutrophication and decreasing the current spreading of hypoxic bottom areas in the Baltic proper.

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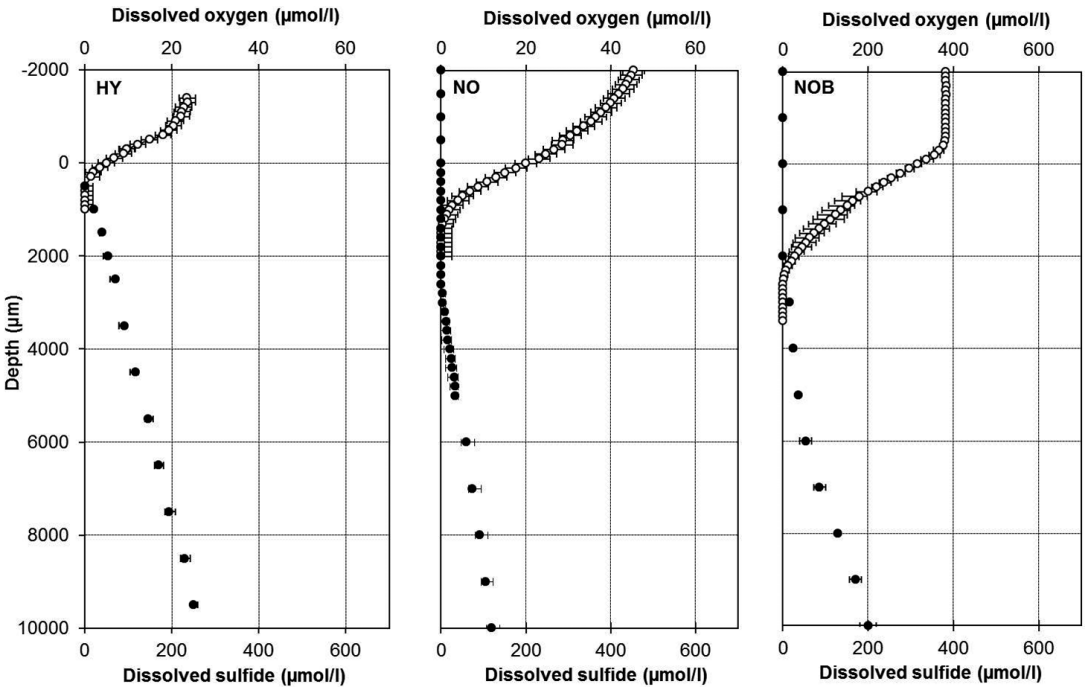

Appendix. Microelectrode profiles of dissolved oxygen (○) and total dissolved sulphide (●). HY = hypoxic water treatment, NO = normoxic water treatment, NOB = normoxic water treatment with added *M. arctia*. Profiles are given as mean ± SD. From Bonaglia *et al.* 2013 (reproduced with permission form the copyright holder).