Nutrient turnover at the hypoxic boundary: flux measurements and model representation for the bottom water environment of the Gulf of Riga, Baltic Sea*

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Abstract

Experimental studies of intact sediment cores from the Gulf of Riga, Baltic Sea, were conducted to estimate the response of sediment nutrient fluxes to various near-bottom water oxygen conditions. The experiment was performed in the laboratory using a batch-mode assay type system on the sediment cores held at 4°C and oxygen concentrations maintained at 1, 2, 3, 4 and 5 mg l^{-1}. The results from the experiment were subsequently used to optimise the fit of the sediment denitrification sub-model of the Gulf of Riga basin. Sediment-water fluxes of phosphate were low and directed out of the sediments under all treatments, demonstrating a general decreasing tendency with increasing near-bottom water oxygen concentration. The sediment-water fluxes of ammonium and nitrate + nitrite demonstrated opposing trends: ammonium fluxes decreased whereas nitrate + nitrite fluxes increased with rising near-bottom water oxygen concentration. The modelled fluxes agreed well with the measured ones, with correlation coefficients of 0.75, 0.63 and 0.88 for ammonium, nitrate + nitrite and phosphate fluxes respectively. The denitrification rate in sediments was simulated at oxygen concentrations from -2 to 10 mg l^{-1}. At oxygen concentrations < 2 mg l^{-1} the modelled denitrification was sustained by nitrate transport from water overlying the sediments. With increasing oxygen concentrations the simulated denitrification switched from the process fuelled by nitrates originating from the overlying water (D_w) to one sustained by nitrates originating from the coupled sedimentary nitrification – denitrification (D_n). D_n reached its maximum at an oxygen concentration of 5 mg l^{-1}.

1. Introduction

Industrial and agricultural development has resulted in enhanced loads of nitrogen and phosphorus over the last 100 years, causing marine ecosystems to deteriorate (e.g. Nixon et al. 1995). Semi-enclosed marine regions, such as the Baltic Sea (e.g. Witek et al. 2003), and its sub-areas with large terrestrial loads, such as the Gulf of Riga (e.g. Yurkovskis et al. 1993), are particularly impacted by elevated nutrient levels. Most of the increase in riverine nutrient loads to the Baltic Sea occurred before the 1970s (Stålnacke et al. 1999), although annual increases of approximately 5% and 2–3% for nitrate and phosphate, respectively, have been estimated for the period 1970–1990 (Rahm & Danielson 2001). Similarly, the negative effects of anthropogenic nutrient loading from urban and agricultural sources were evident already in the 1950s in the Gulf of Riga (Ojaveer 1995). Thereafter, the deterioration of the Gulf of Riga environment accelerated in the 1970s and 1980s (Ojaveer 1995), reaching a peak in 1990 (HELCOM 2010). Since then, nitrogen inputs have decreased but phosphorus has continued to increase (HELCOM 2013).

One of the most conspicuous and environmentally significant effects of environmental deterioration is the establishment of hypoxia and anoxia in

near-bottom waters in deep areas (Diaz & Rosenberg 2008). Furthermore, recent findings indicate that hypoxic conditions significantly affect coastal zones as well (Conley et al. 2011), mostly because of the combination of increased inputs of nutrients from the land and higher respiration rates caused by elevated water temperatures (Carstensen et al. 2014). As discussed by e.g. Zillén et al. (2008), anoxic and hypoxic conditions alter nutrient biogeochemical cycles, leading to increased phosphorus release from the sediments and reduced nitrogen losses through bacteria-mediated denitrification (Conley et al. 2011, Meier et al. 2012, Hietanen et al. 2012, Jäntti & Hietanen 2012). Enhanced phosphorus availability fuels primary production, in particular by diazotrophic cyanobacteria, subsequently increasing the oxygen demand for the decomposition of organic matter to an extent where oxygen depletion restricts nitrification and thus limits denitrification, as a result blocking the natural cycle of nitrogen removal via dinitrogen gas (Hietanen et al. 2012, Jäntti & Hietanen 2012). These distortions and internal feedbacks in nutrient biogeochemical cycling have been suggested as maintaining eutrophication (Conley et al. 2011) and should also be relevant to the Gulf of Riga, where denitrification is the major pathway of nitrogen removal and sediment-water fluxes represent the largest phosphorus supply to the water column (Savchuk 2002, Müller-Karulis & Aigars 2011).

Given the importance of oxygen as a driver of biogeochemical reactions, a number of studies worldwide and in the Baltic Sea have been conducted to investigate process alterations caused by the transition from oxic to anoxic conditions. However, systems like the Gulf of Riga, where bottom waters exhibit various degrees of hypoxia (1–6 mg l^{-1}) during the summer thermal stratification but never reach anoxic conditions, have been less well studied. Owing to global climate change and the subsequent strengthening of thermal stratification (Graham et al. 2008), there is a growing possibility of more frequent and prolonged periods of hypoxia in the near-bottom waters of the Gulf of Riga and similar shallow ecosystems of the Baltic Sea. Although various models for the Baltic Sea ecosystem have been developed in recent years (e.g. Eilola et al. 2009, Savchuk & Wulff 2009, Müller-Karulis & Aigars 2011), which successfully hindcast changes in nutrient and oxygen concentrations as well as primary production, few direct observations on major nutrient fluxes are available to validate individual model processes.

Even though a variety of model approaches exist, ranging from fully mechanistic diagenetic models to simple empirical parameterisations (see e.g. the review by Fennel et al. 2008), current Baltic Sea biogeochemical models mainly use bulk formulations to describe nutrient fluxes at the sediment-water interface. To capture the denitrification dynamics in the

Gulf of Riga, where sediments can be subject to both temporal hypoxia as well as high nitrate concentrations, a model parameterisation is needed that takes into account the fact that the nitrate required for denitrification is either derived from the nitrification of mineralised ammonium within the sediments by coupled nitrification – denitrification (Vanderborght et al. 1977, Jenkins & Kemp 1984) or is provided by diffusion from the overlying water column (Vanderborght & Billen 1975). In the current study, therefore, we have not only assessed the potential consequences of hypoxia on the biogeochemical cycle in the Gulf of Riga by studying nutrient flux dynamics under various oxygen conditions; we have also used the experimental results to adjust the representation of sediment-water fluxes of nitrogen and phosphorus in a biogeochemical model of the Gulf of Riga.

2. Material and methods

2.1. Study area

The Gulf of Riga is a semi-enclosed sub-basin of the Baltic Sea with maximum and mean depths of 62 and 20 m respectively (Yurkovskis et al. 1993). Water exchange with the Baltic Sea occurs through the Irbe Strait in the north-west and the Suur Strait in the north, which are both sufficiently shallow to restrict the water exchange to the low saline surface water of the Baltic Proper. The surface water circulation in the Gulf is predominantly oriented anticlockwise (Reigstad et al. 1999). Freshwater is supplied mainly by the major rivers entering the southern and eastern parts of the Gulf (Tamminen & Seppälä 1999).

The bottom sediments in the Gulf of Riga are dominated by fine material (< 0.01 mm) at depths exceeding 27 m. Its main sediment accumulation zone is located at depths > 40 m, so accumulation bottoms are found mostly in the southern and south-western parts of the Gulf (Carman et al. 1996). The current study was carried out in a sediment accumulation area in the southern Gulf of Riga, at monitoring station 119 (depth 42 m; 57°18′N; 23°51′E) (Figure 1). The total carbon and total nitrogen concentrations in the surface sediments in this area are 5.1 and 0.5 mmol g^{-1} dry weight respectively.

Considerable seasonal variations of temperature and oxygen concentration are characteristic of the near-bottom water of the Gulf of Riga. During autumn and winter the water column is well mixed (Berzinsh 1980, Omstedt & Axell 2003). Vertical temperature gradients begin to develop during spring and the water column remains thermally stratified throughout summer and early autumn. As a result, near-bottom oxygen concentrations in the central part of the Gulf generally increase until the
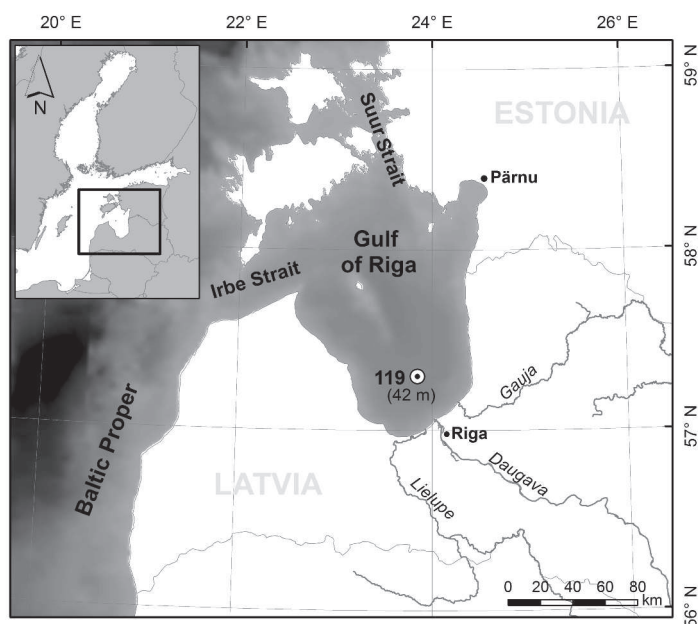
Figure 1. Location of the sampling site in the Gulf of Riga

onset of thermal stratification in spring as a function of temperature-controlled solubility. Thereafter, near-bottom water oxygen concentrations gradually decrease as a result of oxygen consumption at the sediment-water interface, while oxygen advection from the water surface is inhibited by thermal stratification.

The average annual freshwater runoff (39.8 km^3 y^{-1}) constitutes almost 10% of the Gulf of Riga's volume (Yurkovskis et al. 1993) and contributes to the water column stratification.

2.2. Sampling and sediment incubation

Sediment cores were collected aboard the Latvian navy ship A 90 'Varonis' using a modified Kajak type gravity corer (Blomqvist & Abrahamsson 1985) equipped with Plexiglas tubes (diameter 8 cm, length 50 cm). Cores for the experiments were collected between September 2007 and August 2009 during 5 cruises in late summer – early winter in order to represent the autumn period of minimum oxygen conditions. The cores ($n = 8$) contained approximately 20 cm of sediments with ca 20 cm of overlying water. Samples were transported to the laboratory in an insulated box and maintained in darkness at 4°C for 24 h. Thereafter the overlying water

volume was gently replaced by bottom water collected 1–1.5 m above the seafloor at the sampling site in parallel to the sediment cores.

Nitrogen and phosphorus flux measurements. For flux measurements we used a batch-mode assay type system (Nielsen 1992) to measure sediment-water nutrient fluxes at varying oxygen concentrations in the overlying water. The collected sediment cores were incubated in darkness at 4°C with water oxygen concentrations maintained at 1, 2, 3, 4 and 5 mg l^{-1} ($n = 4$ for each treatment). Each incubation run also contained reference sediment cores ($n = 4$), where the oxygen concentration in the sediments overlying the water was maintained at 10 mg l^{-1}, which simulated oxygen saturation conditions in the near-bottom water. For convenience, the incubations are further referred to, according to the oxygen concentrations in the sediments overlying the water, as treatments 1, 2, 3, 4, 5 and 10. In parallel with the sediment cores, core liners ($n = 2$) containing only bottom water were incubated at the same oxygen levels. In all experiments, the oxygen concentration in the water overlying the sediments was adjusted by bubbling N$_2$ through it. Thereafter, the cores were closed for the experiment. The nutrient concentrations were measured prior to and after the incubation period. The overlying water was continuously stirred gently. Every 48 h the overlying water of sediments was removed for chemical analysis and replaced with fresh unfiltered bottom water, which contained a small amount of organic material and was kept in the dark at a low temperature. The 48 h period was chosen to ensure that the nutrient concentration changes in the overlying water were larger than the uncertainty of the analytical methods used (nitrate + nitrite (NO$_x^-$) 5.6%, NH$_4^+$ 16.5%, PO$_4^{3-}$ 6.8%). Altogether, measurements for flux calculations were made 8–10 times over the incubation period. The fluxes (μmol m^{-2} h^{-1}) were then calculated according to the methodology presented by Dalsgaard et al. (2011), i.e. from concentration differences using the results from the last 8 incubation periods:

$$\text{Flux} = \frac{(C_a - C_b)V}{At} \times 100, \tag{1}$$

where C_b and C_a – the nutrient concentrations before and after incubation (μmol l^{-1}) respectively, V – overlying water volume (l), A – area of water sediment interface in the core (cm^2), and t – incubation time (h).

Nutrient concentrations in the overlying water were determined according to Grasshoff et al. (1983), e.g. ammonium (NH$_4^+$) and phosphate (PO$_4^{3-}$) were measured by the indophenol blue and molybdenum blue methods respectively. The sum of nitrate and nitrite (NO$_x^-$) was determined by reacting nitrite with an azo dye after the reduction of nitrate to nitrite in a copper-coated cadmium column. Nitrite was determined by reaction with

an azo dye and nitrate was determined as the difference between nitrite and the sum of nitrate and nitrite. Super-pure distilled water obtained from a Millipore water purification system was used for the experiment. Oxygen (O_2) concentrations were measured with a WTW Oxi 340i oximeter with a CellOx 325 sensor, calibrated using the Winkler titration method. All laboratory analyses were performed in an accredited laboratory (ISO/IEC 17025). To determine the significance between the nutrient flux results at each O_2 concentration, a one-way ANOVA test with a subsequent post-hoc Tukey test was performed.

2.3. Sediment model

To capture the denitrification dynamics in the Gulf of Riga, where sediments can be subject to both temporal hypoxia and high nitrate concentrations, we developed a simple bulk model that describes coupled nitrification – denitrification (D_n) as well as denitrification based on nitrate diffusion from the water column (D_w). Both processes are simulated depending on the O_2 concentrations in the overlying bottom water and the bulk organic matter mineralisation rate in the sediments.

We mimicked the nitrogen (N) transformation pathways in the bottom sediments by first estimating the potential denitrification rate. This is equal to the electron acceptor demand for the mineralisation of sediment organic matter exceeding the diffusion-limited supply of O_2. If the nitrification rate is faster than the potential denitrification rate, the simulated denitrification rate is equal to the potential denitrification rate and excess nitrate is released to the water column (Figure 2, right-hand panel). If the potential denitrification rate is higher than the nitrification rate, we assumed that in addition to D_n the nitrate from sediments overlying the water diffuses into the sediment and is denitrified (Figure 2, left-hand panel). Both the nitrification rate as well as the potential denitrification rate depend on the bottom water O_2 concentration. The NH_4^+ produced as a result of organic matter mineralisation and which is not nitrified to NO_3^- is released to the water column. The biogeochemical pathways of nitrogen in the sediment model are shown schematically in Figure 2.

In the sediment model the release of PO_4^{3-} from the sediments to the water column is provided by organic phosphorus mineralisation. The fraction of the mineralised phosphorus is adsorbed to sediment particles but the rest is instantly released to the water column. In this study, this pathway was simplified by excluding the desorption process.

The model equations and parameter values are described in detail in Appendices A and B.
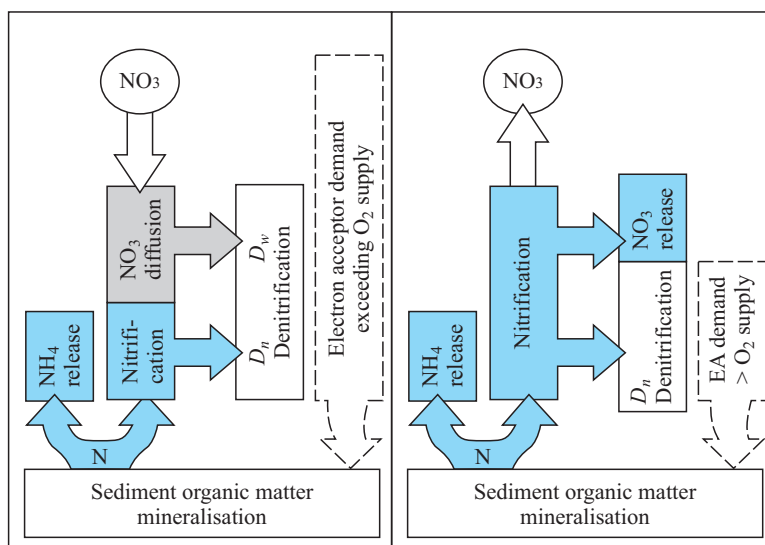
Figure 2. Biogeochemical pathways of nitrogen in the modified Gulf of Riga sediment model. The light blue arrows and boxes show the fate of nitrogen produced by the mineralisation of sediment organic matter. The dashed box represents the part of the electron acceptor demand required to match the organic matter mineralisation rate, which exceeds the oxygen supply to the sediments. This electron acceptor (EA) demand is covered by denitrification or by other electron acceptors. When the electron acceptor demand exceeds nitrification, nitrate diffuses into the sediments and is denitrified (D_w, left-hand panel). When nitrification exceeds the electron acceptor demand, only coupled denitrification (D_n) occurs and excess NO_3 is released into the water column

Model calibration and validation. Calibration of the new N flux model and a simplified version of P flux model presented by Müller-Karulis & Aigars (2011) against median PO_4^{3-}, NO_x^- and NH_4^+ flux measurements was performed using a simulated annealing routine (SANN) in statistical analysis software R v.3.0.2.

3. Results

3.1. Sediment incubation experiments and modelled dynamics of nutrients in the Gulf of Riga sediments

The average fluxes of PO_4^{3-} (42–115 μmol m^{-2} d^{-1}) were always directed out of the sediments. Although PO_4^{3-} fluxes tended to decrease with increasing O_2 concentration in the near-bottom water, they exhibited no significant differences (ANOVA; $p < 0.01$) among treatments, most likely due to the substantial variability of fluxes within the treatments (Figure 3).
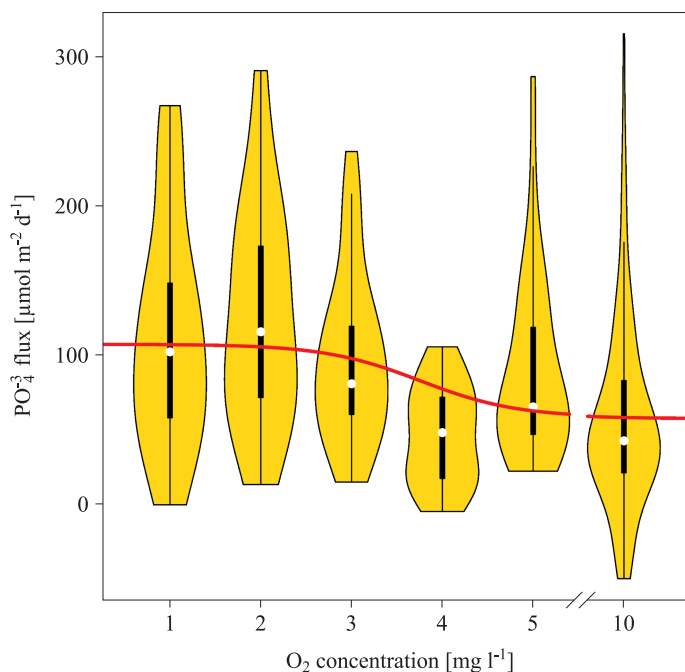
Figure 3. PO_4^{3-} fluxes at the sediment-water interface in incubations with O_2 concentrations of 1–5 and 10 mg l^{-1}, shown as a kernel density plot, and the modelled PO_4^{3-} flux (red line)

The simulated values of PO_4^{3-} flux (Figure 3) are in good agreement with the median values of the experimental data set and show nearly constant maximum values (105–106 μmol PO_4^{3-} m^{-2} d^{-1}) at an O_2 concentration range of 1–2 mg l^{-1} and a smooth decline with increasing O_2 concentrations, reaching the lowest fluxes (57 μmol PO_4^{3-} m^{-2} d^{-1}) at oxygen concentrations in the range between 5 and 10 mg l^{-1}.

Sediment-water fluxes of NH_4^+ are always positive and exhibit large variability within and among O_2 treatments, ranging on average from 1800 μmol m^{-2} d^{-1} at an O_2 concentration of 2 mg l^{-1} to 140 μmol m^{-2} d^{-1} at an O_2 concentration of 10 mg l^{-1} (Figure 4). At this latter O_2 concentration the observed fluxes vary between −734 and 528 μmol NH_4^+ m^{-2} d^{-1} (the highest observation is treated as an outlier) with 90 μmol NH_4^+ m^{-2} d^{-1} as the median value. Although there is no significant difference in NH_4^+ fluxes between treatments 1 and 3, the significant differences between treatments 2 and 3 (ANOVA; $p < 0.01$) and 3 and 4 (ANOVA; $p < 0.01$) clearly demonstrate increasing NH_4^+ fluxes when O_2 concentrations are < 4 mg l^{-1}. Larger oxygen concentrations do not result in a further decrease of NH_4^+ fluxes, however.
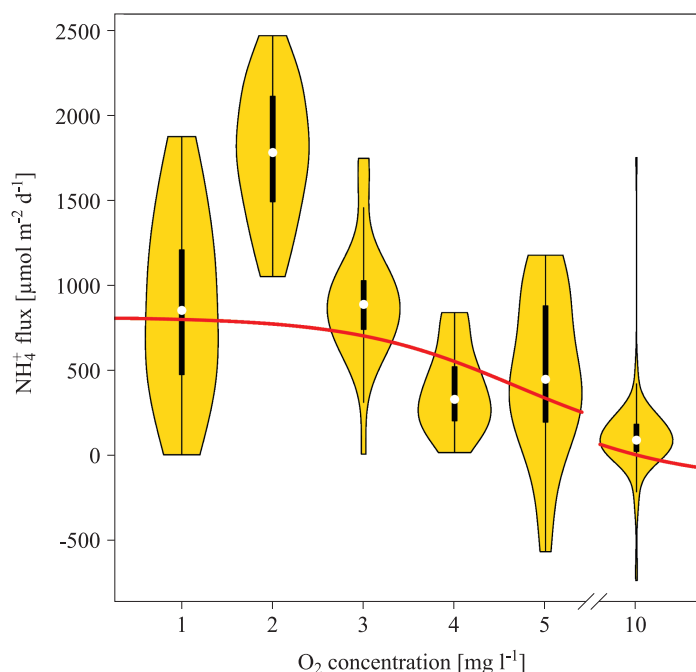
Figure 4. NH_4^+ fluxes at the sediment-water interface in incubations with O_2 concentrations of 1–5 and 10 mg l^{-1}, shown as a kernel density plot, and the modelled NH_4^+ flux (red line)

The modelled NH_4^+ fluxes (Figure 4) show a smooth decline with increasing concentration, reaching the lowest value (2.3 μmol NH_4^+ m^{-2} d^{-1}) at an O_2 concentration of 10 mg l^{-1}. The model fits the data well at low (1 mg l^{-1}) and intermediate to high (≥ 4 mg l^{-1}) O_2 concentrations, but does not correspond with the high fluxes observed at an O_2 concentration of 2 mg l^{-1}, which vary between 1051 and 2467 μmol NH_4 m^{-2} d^{-1}.

In contrast to NH_4^+, NO_x^- fluxes are mostly directed into the sediments, although, like NH_4^+, these fluxes exhibit a considerable variability within and among treatments, ranging on average from -390 μmol m^{-2} d^{-1} at an O_2 concentration of 1 mg l^{-1} to 85 μmol m^{-2} d^{-1} at an O_2 concentration of 10 mg l^{-1} (Figure 5). The variation of NO_x^- fluxes at different O_2 concentrations is most likely caused by more intensive denitrification at O_2 concentrations of 3 and 5 mg l^{-1}. However, this statement cannot be scientifically sound, given the available NO_x^- flux data. The results indicate that an increase in O_2 concentration from 1 to 3 mg l^{-1} has no apparent effect on NO_x^- fluxes, but a near-bottom water O_2 concentration of 4 to 5 mg l^{-1} switches the flux direction from positive to negative. At the same time, it should be mentioned that although NO_x^-
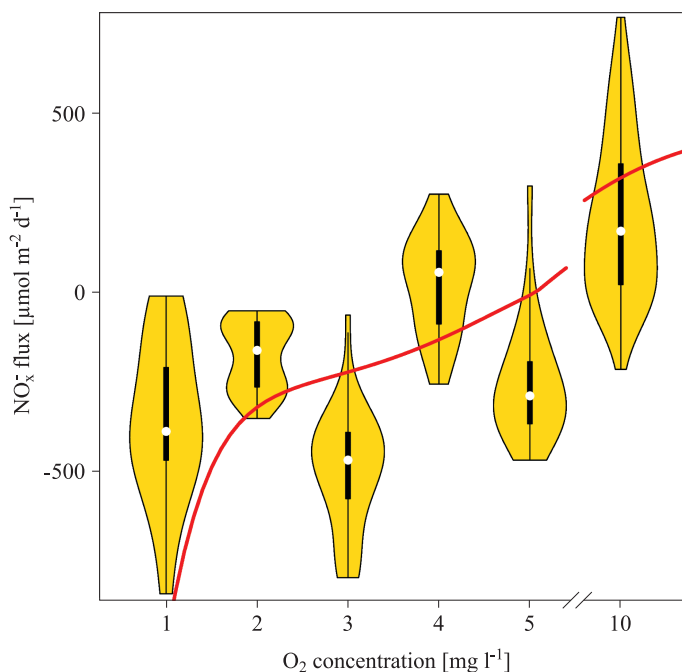
Figure 5. NO_x^- fluxes at the sediment-water interface in incubations with O_2 concentrations of 1–5 and 10 mg l^{-1}, shown as a kernel density plot, and the modelled NO_x^- flux (red line)

fluxes differ significantly (ANOVA; $p < 0.01$) between treatments 1–3 and 4, the NO_x^- fluxes observed in treatment 5 do not differ significantly from those observed in treatments 1–3.

The modelled NO_x^- fluxes, like the measured ones, increase with O_2 concentration (Figure 5). However, the modelled fluxes are lower than those observed under low O_2 conditions and, because of their smooth increase, slightly overestimate fluxes under sub-oxic conditions. The modelled fluxes achieve the highest values at O_2 concentrations of 10 mg l^{-1} and above (319 μmol NO_x^- m^{-2} d^{-1}). Also, the observed NO_x^- flux reaches a maximum at an O_2 concentration of 10 mg l^{-1}, where it varies between -309 and 765 μmol NO_x^- m^{-2} d^{-1} with a median value of 169 μmol NO_x^- m^{-2} d^{-1}.

3.2. Model-data fit

We used model-data correlation coefficients (Pearson's R) to determine the agreement between the modelled and the median values from the experimental data set of nutrient fluxes. The percentage difference between the modelled and the observed experimental data (Table 1) was used to

Table 1. Relative deviation [%] and correlation between the simulated and the median observed experimental NH_4^+, NO_x^- and PO_4^{3-} [μmol m^{-2} d^{-1}] fluxes at each oxygen concentration [mg l^{-1}]

O_2 concentration	NH_4^+	NO_x^-	PO_4^{3-}
1	−6.31	153.88	−3.79
2	−56.62	98.19	−16.76
3	−20.90	−52.42	6.43
4	67.28	−339.29	26.92
5	−25.08	−97.19	−32.18
10	−97.44	87.84	−6.73
Correlation coefficient (R)	**0.75**	**0.63**	**0.88**

determine the variation of the modelled data from the observed experimental data at each O_2 treatment used in the incubation experiment.

The correlation coefficients show that there is good agreement between the dynamics of the modelled values and the median values of the observed experimental fluxes of nutrients ($R = 0.75$, 0.63, and 0.88 for NH_4^+, NO_x^- and PO_4^{3-} respectively). The relative deviation shows that the modelled nutrient fluxes tend to be lower than the observed experimental values with the exception of the NH_4^+ flux at $O_2 = 4$ mg l^{-1}, the NO_x^- flux at $O_2 = 1$, 2 and 10 mg l^{-1} and the PO_4^{3-} flux at $O_2 = 3$ and 4 mg l^{-1}.

3.3. Simulated denitrification

The calibrated denitrification model was extrapolated to anoxic conditions, using 'negative oxygen' concentrations (Fonselius 1969) to show the degree of anoxia. 'Negative oxygen' is equivalent to the amount of oxygen needed to oxidise the end products of anaerobic organic matter oxidation pathways like hydrogen sulphide or reduced forms of manganese and iron. At O_2 concentrations < -2 mg l^{-1} the simulated NO_3^- flux is directed into the sediments where it is instantly denitrified, while the NH_4^+ flux remains constant and no coupled nitrification-denitrification occurs (Figure 6). The first notable changes in the N flux are evident at O_2 concentrations > -2 mg l^{-1}, when both D_w and the amount of NO_3^- flux directed into the sediments start to decrease. This process becomes more rapid in a hypoxic environment, whereas the NH_4^+ flux shows a smooth decline and D_n increases. As the O_2 concentration increases above 2 mg l^{-1}, the denitrification pathway gradually switches from D_w to D_n, which reaches its highest flux at an O_2 concentration of 5 mg l^{-1}. Meanwhile, NH_4^+ continues to decrease as a result of nitrification, which leads to a further increase in NO_3^- fluxes.
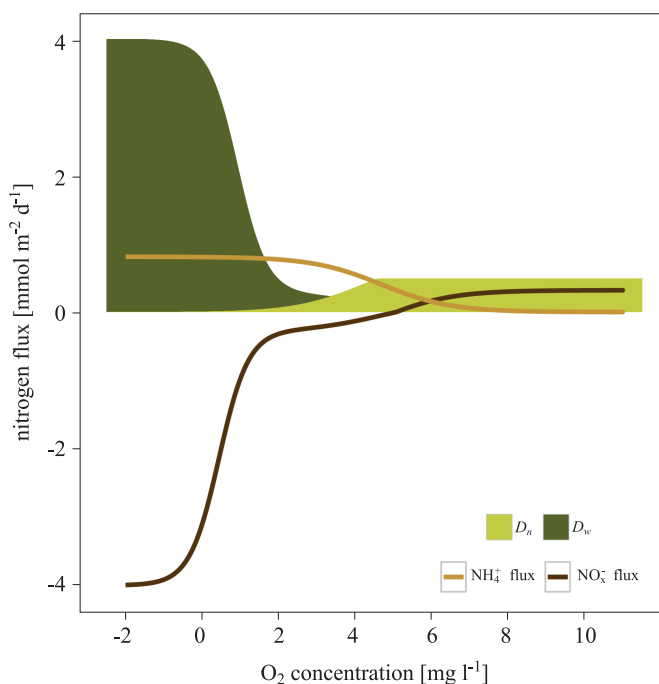
Figure 6. The modelled nitrogen fluxes and model-based denitrification rates in the sediments of the Gulf of Riga; D_n – coupled nitrification-denitrification, D_w – denitrification from water

4. Discussion

4.1. Nutrient pattern on the sediment-water interface

Phosphorus release from sediments under hypoxic and anoxic conditions has been extensively studied worldwide (e.g. Ingall & Jahnke 1994, 1997) as well as in the Baltic Sea (e.g. Koop et al. 1990, Gunnars & Blomqvist 1997, Conley et al. 2002). The results of these studies exhibit certain variations in critical oxygen concentrations at which phosphorus release from sediments is enhanced. As concluded by Koop et al. (1990) bottom water oxygen concentrations $> 1\,\mathrm{mg\,l^{-1}}$ are associated with small and variable phosphorus fluxes, whereas below this level flux rates increase and are generally positive. At the same time, the observations by e.g. Jensen et al. (1995) and Gunnars & Blomqvist (1997) indicate the enhanced release of phosphorus from sediments at bottom water oxygen concentrations as high as $2\,\mathrm{mg\,l^{-1}}$. This is also supported by the oxygen concentration and DIP relationships given by Conley et al. (2002). At the same time, the experimental results of the current study (Figure 3) show a positive phosphorus efflux at all oxygen concentrations tested, though never reaching the values (329–885 μmol-P

m^{-2} d^{-1}) observed under anoxic conditions from non-laminated sediments by Koop et al. (1990). Sediments in the Baltic Sea, as in other water bodies, have a certain natural capacity to adsorb phosphorus under oxic conditions (Carman & Wulff 1989). The amount of currently adsorbed phosphorus is dependent on sediment characteristics and environmental conditions. The adsorbed phosphorus can be released if the environmental conditions shift from oxic to anoxic (e.g. Koop et al. 1990, Gunnars & Blomqvist 1997, Conley et al. 2002). However, release from or accumulation in the sediments under oxic or hypoxic conditions is presumably controlled by the interaction between the oxygen supply to the sediment-water interface and the intensity of organic material mineralisation, which consumes oxygen. In our study the supply of oxygen to the sediment-water interface appeared to be sufficient to sustain the mineralisation of organic material and to prevent a massive release of phosphorus even at the lowest oxygen concentrations tested (1 mg l^{-1}). At the same time, the enhanced release of phosphorus from sediments under low oxygen conditions suggests that phosphate released during mineralisation exceeded the equilibrium sorption capacity of the sediments.

It has been argued that only very low (< 1 mg l^{-1}) near-bottom water oxygen concentrations limit nitrification and consequently denitrification (e.g. Tuominen et al. 1998). The results of our study (Figures 4 and 5) indicate a decrease of nitrification activity already at higher oxygen concentrations, with a sharp activity drop at 2 mg O_2 l^{-1}, where the NH_4^+ flux increased by ca 108% compared to > 2 mg O_2 l^{-1}. A similar effect was observed in experiments where fresh organic material was added to simulate sedimentation of the phytoplankton spring bloom (e.g. Jensen et al. 1990, Conley & Johnstone 1995). In the case of the spring phytoplankton bloom deposition Jensen et al. (1990) argues strongly that the influx of NO_x^- into the sediments is due to the suppression of nitrification resulting from an oxygen deficit in sediments, which in turn is related to increased microorganism activity in response to the deposition of fresh organic material. As a result, diffusion from the water is the predominant NO_x^- source for denitrification.

Furthermore, several studies suggest a higher ammonium efflux from sediments under hypoxic conditions, e.g. Chesapeake Bay (Kemp et al. 1990), the Louisiana shelf (McCarthy et al. 2008) and Danish coastal systems (Conley et al. 2007) due not only to suppressed nitrification efficiency, but also to elevated levels of the dissimilatory nitrate reduction to ammonium (DNRA). DNRA has also been called a 'short circuit in the biological N cycle' (Cole & Brown 1980), since it allows the direct transformation of NO_3^- and NO_2^- to NH_4^+ (Rütting et al. 2011). In

our study the NH_4^+ accumulation rate at 2 mg O_2 l^{-1} (Figure 4) was higher than that given by the model; it is not clear whether this is a sign of nitrification limitation or the start-up of DNRA. Instead of NH_4^+ utilisation by nitrification and its subsequent contribution to denitrification, the NH_4^+ is effluxed out of the sediments, indicating the production of bioavailable forms of N under hypoxic conditions. It is clear that the presence of one of these competing processes cannot be explained solely by nutrient measurements.

It should also be mentioned that several authors have concluded that a decrease in bottom water O_2 concentration might even stimulate denitrification by shortening the physical distance between NO_x^- production and reduction zones (Stockenberg & Johnstone 1997, Hietanen & Kuparinen 2008). However, according to long-term observations by Kristensen (2000), persistently hypoxic bottom water conditions and high O_2 consumption within the sediment surface decrease NO_x^- supplies and consequently hamper denitrification.

4.2. Modelled data fit to experimental observations

Biogeochemical models that include simulation of sediment phosphorus transformation and flux (e.g. Savchuk & Wulff 2009, Eilola et al. 2009) show a clear pattern of reducing PO_4^{3-} flux out of sediments with increasing oxygen concentration and thus increasing PO_4^{3-} adsorption in sediments. This pattern is also reproduced in our model. Figure 3 demonstrates stable simulated flux rates of phosphate under hypoxic conditions, a smooth decline under oxygenated conditions and stable low flux rates at high oxygen concentrations, which is in good agreement with the median values of the observed experimental fluxes. Such dynamics of the simulated and the observed phosphate flux in response to oxygen conditions from the sediments to the overlying water has been observed by e.g. Koop et al. (1990) and Mort et al. (2010).

The simulation of ammonium generated from organic matter is split into pathways of nitrification of ammonium, which intensifies with increasing oxygen concentration, and the release of ammonium to the water column. The deep parts of the Baltic Sea, such as the Gotland Deep and the Gdańsk Deep, are on occasion characterised by anoxic sediments. Under such conditions nitrification is highly dependent on the dynamics of the redoxcline, which determines the mixing of ammonium-rich waters with oxygenated ones (Hietanen et al. 2012). In the Gulf of Riga, long-term average and minimal oxygen concentrations rarely reach hypoxic levels and never anoxic levels (Müller-Karulis & Aigars 2011). Furthermore, organic nitrogen mineralisation in the Gulf of Riga delivers large amounts of

ammonium (Henriksen & Kemp 1988, Tuominen et al. 1998, Savchuk 2002). Therefore, both ammonium and oxygen supplies should be appropriate for continuous nitrification. However, despite the suitable conditions for nitrification and the reasonable correlation between the simulated and observed ammonium fluxes (Table 1), the dynamics of observed ammonium and thus its modelling approach contains some issues that need clarification, for example, the high observed experimental values of NH_4^+ flux at an O_2 concentration of 2 mg l^{-1} (Figure 4). This oxygen concentration marks the borderline between hypoxic and oxygenated conditions, as well as the oxygen level needed to sustain most animal life (Hansson et al. 2011). According to Henriksen & Kemp (1988), the higher observed ammonium flux at oxygen concentrations of 2 mg l^{-1} may be related to the less efficient activity of nitrifying bacteria, which are outcompeted by heterotrophic bacteria at low oxygen concentrations. Moreover, McCarthy et al. (2008) indicate that the hypoxia threshold provides good conditions for dissimilatory nitrate reduction to ammonium (DNRA). The findings of these authors, as well as the 108% higher NH_4^+ flux at oxygen concentrations of 2 mg l^{-1} as compared to ammonium fluxes at lower and higher concentrations (Figure 4), lead us to the conclusion that studies of DNRA and the processes driving it in the Gulf of Riga should be undertaken and that the biogeochemical model should be expanded to include DNRA.

Compared to the previously reported results of the biogeochemical model of the Gulf of Riga (Müller-Karulis & Aigars 2011), the simulation of the nitrate flux has been improved in the current study. Here, the simulated nitrate flux increases with oxygen concentration. It is formed as the sum of nitrate diffusion, which marks the nitrate inflow in sediments from the overlying water and thus D_w, and the portion of nitrified nitrate that escapes denitrification, which represents the outward flux from sediments. Although the experimental results vary and do not show a steady increase in NO_x^- with increasing oxygen concentrations, the general increasing trend in NO_x^- flux is evident and agrees with the conventional sediment nitrogen flux modelling approach (Eilola et al. 2009, Savchuk & Wulff 2009, Müller-Karulis & Aigars 2011). Although the correlation and variance between the simulated and observed NO_x^- fluxes is not as good as for PO_4^{3-} and NH_4^+ (Table 1), the simulations nonetheless agree reasonably well with observations.

4.3. Denitrification model

The experimental data used for the sediment model calibration and denitrification measurement results in the Gulf of Riga indicate that a substantial part of denitrification is provided by the diffusion of nitrate

from the water column into the bottom sediments. To accommodate this pathway, the parameterisation of denitrification in the biogeochemical model of the Gulf of Riga has been modified and is described in detail in Appendix A.

Denitrification in the Gulf of Riga based on the previous version of the denitrification model (Müller-Karulis & Aigars 2011) indicates average denitrification rates of 0.90 mmol N m^{-2} d^{-1} for the period 1973–2000, which agree well with the results of this study. Furthermore, the average denitrification rates simulated in this study are in the same range as the rates reported for other areas of the Baltic Sea (e.g. Deutsch et al. 2010). This indicates that the improved denitrification model enables the mass balance and the results of its new parameters – nitrate diffusion and both denitrification pathways – to be estimated accurately.

The denitrification sustained by the nitrate flux from the overlying water of the sediments is about 0.99 mmol N m^{-2} d^{-1} at an O$_2$ concentration of 1 mg l^{-1} (Figure 6). The simulated nitrogen flux shows that denitrification from water switches to coupled nitrification – denitrification at an oxygen concentration of 5 mg l^{-1}, when nitrification starts generating enough nitrate for denitrification, sustaining a maximum denitrification rate of 0.49 mmol N m^{-2} d^{-1}. Such conditions at the sediment-water interface can be observed in winter and early spring. Coupled nitrification – denitrification then removes up to 65% of NO$_x{}^-$ generated by nitrification. This amount of denitrified NO$_x$ is in agreement with the model results obtained by Kiirikki et al. (2006), which indicate that coupled nitrification – denitrification is mostly a seasonal process that occurs under oxygenated conditions.

5. Summary and conclusions

The improved sediment sub-model presented in this paper can be implemented in the biogeochemical model of the Gulf of Riga. Its simulated nutrient fluxes show good agreement with the observed experimental results, and it is capable of simulating nitrogen transformation fluxes that concur with observations from the Gulf of Riga and other Baltic Sea areas.

The denitrification model can be used as a useful tool to envisage NO$_x{}^-$ pathways for denitrification in the muddy sediments of the Gulf of Riga without time-consuming laboratory measurements of denitrification. Both the simulated and measured NO$_x{}^-$ flux patterns reflect a gradual replacement of D_w by D_n in the O$_2$ concentration range of 1–4 mg l^{-1} and D_n prevalence when the O$_2$ concentration exceeds 4 mg l^{-1} (Figures 5 and 6). However, the variability of the measured NO$_x{}^-$ fluxes, including shifts between influx and efflux, at higher O$_2$ concentrations indicates the co-existence of both NO$_x{}^-$ pathways for denitrification; this is in good

agreement with recent denitrification field measurements (Aigars et al. 2013, under review), thus limiting the model's scope of application.

Since the experimental results of this study do not cover evidently anoxic conditions, the improved denitrification model should be used with caution, particularly because under sulphidic conditions, microbial denitrification shifts from sediment heterotrophic to water column chemolithotrophic, as reported by e.g. Hietanen et al. (2012) and Dalsgaard et al. (2013).

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Appendix A. Model description

The mineralisation rate of sediment organic matter m_c is described as a first-order process depending on bottom water temperature T and sediment organic nitrogen concentration NS, converted into carbon equivalents via a constant carbon/nitrogen ratio r_{CN} assumed for the sediments:

$$m_c = r_{CN} \times NS \times a_{mN} \times e^{b_{mn} \times T}. \tag{1}$$

The fraction of mineralised organic carbon σ that is oxidised using terminal electron acceptors other than oxygen increases from $1 - a_d$ to 1 with declining bottom water oxygen concentrations OX:

$$\ddot{a} = 1 - \frac{a_d}{1 + e^{-b_d \times (OX - c_d)}}. \tag{2}$$

The potential denitrification rate d_p, assuming that the entire electron acceptor demand not covered by oxygen is provided by denitrification, is then given by

$$d_p = 0.8 \times \sigma \times r_{CN} \times m_c, \tag{3}$$

where the factor 0.8 expresses the fact that the oxidation of 1 mol organic carbon at oxidation number 0 requires the denitrification of 0.8 mol NO_3^-.

The nitrification rate n_x of ammonium released by the mineralisation of sediment organic matter increases with bottom water oxygen concentration until all the ammonium generated is nitrified:

$$n_x = \frac{m_c}{r_{CN}} \times \frac{1}{1 + e^{-a_x(b_x - OX)}}. \tag{4}$$

If the potential denitrification rate d_p exceeds the nitrification rate n_x, nitrate diffuses into the sediments depending on the nitrate deficit given by $d_p - n_x$, the nitrate concentration in the overlying water NO and the diffusion resistance parameter k. All the nitrate diffusing into the sediment is denitrified (d_w):

$$d_w = \begin{cases} (d_p - n_x) \times \dfrac{NO}{k + NO}, & d_p \geq n_x, \\ 0, & d_p < n_x \end{cases}. \tag{5}$$

Coupled denitrification d_n is limited by nitrification and the potential denitrification rate:

$$d_n = \begin{cases} n_x, & d_p \geq n_x \\ d_p, & d_p < n_x \end{cases}. \tag{6}$$

The total denitrification rate d_t is the sum of coupled denitrification d_n and the denitrification of water column nitrate d_w:

$$d_t = d_w + d_n. \tag{7}$$

If nitrification exceeds the total denitrification rate, nitrate is released into the water column at rate w_{NO}:

$$w_{NO} = \begin{cases} n_x - d_t, & n_x \geq d_t \\ 0, & n_x < d_t \end{cases}. \tag{8}$$

Similarly, all ammonium from the mineralisation of sediment organic matter that is not nitrified is released into the water column at rate w_{NH}:

$$w_{NH} = \frac{m_c}{r_{CN}} - n_x. \tag{9}$$

Mineralisation of sediment organic phosphorus is described in the same way as for sediment organic nitrogen – a first-order process dependent on bottom water temperature and sediment organic phosphorus concentration:

$$m_{CP} = r_{CP} \times PS \times a_m \times e^{b_m \times T}. \tag{10}$$

Furthermore, the regenerated PO_4 is split into two pathways. Part of the generated PO_4 is adsorbed to the sediments and increases with oxygen concentration:

$$p_{ads} = \frac{q_{bP}}{1 + e^{-a_{bP}(b_{bP} - OX)}}. \tag{11}$$

Regenerated PO_4 that is not adsorbed is released to the water column at a rate that is inversely proportional to the oxygen concentration:

$$w_{PO} = (1 - p_{ads}) \frac{m_{cP}}{r_{CP}}. \tag{12}$$

Appendix B. Model parameters

Parameter	Units	Value	Description
T	$^\circ$C	4	Bottom water temperature
NS	mmol m^{-2}	2357	Organic nitrogen concentration in bottom sediments
r_{CN}	mol mol^{-1}	10.8	Carbon – nitrogen ratio in sediment organic matter
a_{mN}	mmol m^{-2} day^{-1}	0.0003	Organic nitrogen mineralisation rate constant
b_{mN}	$^\circ$C^{-1}	0.035	Temperature constant for organic nitrogen mineralisation
a_d	dimensionless	0.93	Fraction of organic carbon oxidised by O_2 at high oxygen conditions
b_d	(mg l^{-1})$^{-1}$	2.61	Oxygen slope for potential denitrification
c_d	mg l^{-1}	0.44	Oxygen offset for potential denitrification
a_x	dimensionless	5.15	Oxygen slope for nitrification
b_x	mg l^{-1}	1.10	Oxygen offset for nitrification
k	mol m^{-3}	8.62	Nitrate diffusion resistance
PS	mmol m^{-2}	285	Organic phosphorus concentration in bottom sediments
r_{CP}	mol mol^{-1}	106	Carbon – phosphorus ratio in sediment organic matter
a_{mP}	mmol m^{-2} day^{-1}	0.00036	Organic phosphorus mineralisation rate constant
b_{mP}	$^\circ$C^{-1}	0.0102	Temperature constant for organic phosphorus mineralisation
q_{bP}	dimensionless	0.459	Maximum fraction of generated PO$_4$ adsorbed
a_{bP}	dimensionless	7.031	Oxygen slope for PO$_4$ adsorption
b_{bP}	mg l^{-1}	1.87	Oxygen offset for PO$_4$ adsorption