Temporal and spatial variations in benthic nitrogen cycling in a temperate macro-tidal coastal ecosystem: Observation and modeling

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ARTICLE INFO
Keywords:
DIN
DON fluxes
Diatom blooms
Hypoxia/anoxia
Monitoring station
Reactive transport model
Sediments

ABSTRACT
We used field observations, laboratory measurements and a reactive transport model (RTM) to investigate temporal and spatial variations in benthic nitrogen (N) cycling in the eutrophic temperate macro-tidal Vilaine Bay (VB). A time series of benthic flux measurements and pore-water profiles of dissolved inorganic N (DIN: ammonium, nitrate, nitrite) and dissolved organic N (DON) was conducted at a single station between April and September 2015 (six times). A spatial investigation of the benthic fluxes was performed in July 2016 at this station and three other stations in the VB. All measurements were accompanied by a large panel of physical, chemical and biological descriptors in the water column. In 2015, benthic ammonium fluxes at the monitoring station varied between 75 μmol m⁻² h⁻¹ in spring and were less than 10 μmol m⁻² h⁻¹ in summer. The benthic DON fluxes co-varied with the ammonium fluxes, ranging from 100 μmol m⁻² h⁻¹ in spring to zero in summer. In the summer of 2016, a phytoplankton bloom occurred and as a result the benthic ammonium and DON fluxes reached higher values than in the spring of 2015, accompanied by bottom water hypoxia at one measured station. Benthic nitrate and nitrite fluxes varied between −10 (towards the sediments) and 22 μmol m⁻² h⁻¹ and were explained by the bottom water concentration and nitrification rates. After fitting the existing pore-water profiles, the applied RTM correctly simulated the temporal and spatial variations in the benthic DIN fluxes and predicted that a large part of the deposited organic matter (OM) is remineralized aerobically at the sediment-water interface (SWI). The overall results showed a synthetic pattern of benthic N cycling in the VB, based on the occurrence of diatom blooms as the main source of OM in the sediments. The rapid decomposition of this deposited diatom material at the SWI releases large amounts of ammonium and DON to the water column and rapidly consumes oxygen at the sediment surface. When blooms occur in summer, their decomposition can be followed by hypoxia/anoxia in the bottom water. When blooms are absent, benthic N fluxes are weak and mainly fed by the diffusion from the pore-water. By integrating the present results in a 3D ecological model, it should be possible to more accurately predict the development of bottom water hypoxia in the VB.

1. Introduction

Coastal areas are among the world’s most vulnerable ecosystems to anthropogenic pressures (Turner et al., 2003), particularly to nitrogen and phosphorus pollution which leads to eutrophication (Le Moal et al., 2019). The most visible aspect of anthropogenic marine eutrophication...
is the mass accumulation of macroalgae on the coast (Smetacek and Zingone, 2013) and phytoplankton blooms (Carstensen et al., 2015). In shallow coastal ecosystems with water bodies exhibiting a residence time of at least several days, senescent phytoplankton blooms can be deposited at the sediment-water interface (SWI) representing a significant amount of oxidizable organic matter (OM) (Smetacek, 1980; Taguchi, 1982). When dead phytoplankton cells decompose, this sometimes results in the depletion of dissolved oxygen (O$_2$) in bottom waters (Cloern, 2001; Kemp et al., 2005) with a subsequent impact on the ecosystem’s structure and function (Gray et al., 2002).

Nitrogen (N) is the key limiting nutrient in many coastal marine environments (Paerl, 2018). In shallow coastal ecosystems, benthic OM remineralization can represent a significant source of N in the water column, helping to maintain eutrophication (Fisher et al., 1982). During algal decomposition in sediment, OM undergoes microbially-mediated biogeochemical transformations, resulting in dissolved organic N (DON) intermediates and dissolved inorganic N (DIN) end products. These can either escape as a benthic flux across the SWI or undergo further transformation in the pore-water (Herbert, 1999; Burdige, 2001). Ammonium (NH$_4^+$) can be transformed into nitrite (NO$_2^-$) and nitrate (NO$_3^-$) under oxic conditions through nitrification (Ward, 2008). Under anoxic conditions, DIN (NH$_4^+$, NO$_2^-$, NO$_3^-$) can be eliminated as N$_2$ gas through denitrification and/or anammox (Thamdrup and Dalsgaard, 2002; Devol, 2015). The dissimilatory NO$_3^-$ reduction to NH$_4^+$ (DNRA) competes with denitrification for NO$_3^-$ and tends to retain N in the system (Giblin et al., 2013). The dynamics and competition between these processes govern dissolved N recycling variations and amplitudes at the SWI (Blackburn and Henriksen, 1983; Hulth et al., 2005).

Mechanisms that control benthic N cycling are complex, often site-specific and depend on several factors. These factors include: ambient nutrient concentrations in the water column (Hensen et al., 1998; Khalil et al., 2018), the amount and quality of the deposited OM (Ardnt et al., 2013; Ait Ballagh et al., 2021), sediment characteristics (Blackburn and Henriksen, 1983), bottom water O$_2$ concentrations (Glud, 2008), temperature (Banta et al., 1995) and intensity of the sediment bioturbation (Aller and Aller, 1998), which all vary seasonally. Benthic N cycling can be highly variable over time in coastal ecosystems undergoing phytoplankton blooms (Jensen et al., 1990). In their global synthesis, Boynton et al. (2018) pointed out the lack of time series measurements for a rigorous evaluation of seasonal and inter-annual variability of oxygen and nutrient exchanges across the SWI in estuarine and coastal ecosystems. More generally, temporal and spatial variations of benthic DIN and DON fluxes in relation with the water column composition, especially phytoplankton biomass and sediment characteristics.

This study aims to investigate the key factors controlling the temporal and spatial variations of benthic N fluxes at the SWI of a macro-tidal coastal bay threatened with eutrophication (i.e., increased phytoplankton biomass). Time-and-space-based field measurement campaigns were accompanied by a large panel of physical, chemical and biological descriptors in the water column. Temporal and spatial datasets were interpreted using a steady-state early diagenetic reactive transport model in order to obtain a general summarized outline of the key processes governing temporal and spatial variations of the benthic N fluxes in the VB.

2. Material and methods

2.1. Study site

The Vilaine Bay (VB) is a shallow macro-tidal coastal bay under direct influence of the Loire and Vilaine rivers (Fig. 1, see Ratmaya et al., 2019 for a detailed description of the riverine nutrient inputs). The VB has a total area of 220 km$^2$, with a depth varying between 10 and 15 m depending on the tidal amplitude between 4 and 6 m. Water circulation is characterized by low tidal and residual currents, driven mainly by tides, winds and river flows (Lazure and Jégou, 1998). The water residence time in the bay varies between 10 and 20 days depending on the season and can exceed 30 days during calm periods (Chapelle, 1991). The VB is one of the European Atlantic coastal ecosystems most sensitive to eutrophication (Ménèsguen et al., 2019), and has some of the highest concentrations of chlorophyll a (Chl a) in French coastal waters (Gohin, 2011). In the VB, eutrophication materializes in phytoplankton blooms, characterized by diatom dominance (Ratmaya et al., 2019). The occurrence of phytoplankton blooms in this area is predominantly controlled by the magnitude and timing of river floods (Guillaud et al., 2008) and is simulated using a coupled pelagic biogeochemical and 3D hydrodynamic model (ECOMARS3D; Ménèsguen et al., 2019). Oxygen depletion in bottom waters following phytoplankton blooms is frequently observed (Rossignol-Strick, 1985; Iffrem, 2015). Therefore, the onset of hypoxia/anoxia in the VB is probably related to the timing of the phytoplankton blooms induced by river floods. Sediments in the VB are dominated by silt (>80%), with silty sediments mainly in the north-western part of the bay, silty fine sand sediments in the eastern and north-eastern part of Dumet Island, and rocky substrates (gravel) in the southern part between Dumet Island and Piriac shelf (Le Bris and Gémarc, 1996).

2.2. Sampling strategy

2.2.1. Water column

The water quality in the VB is monitored regularly as part of the French National Observation Network for Phytoplankton and Hydrology (REPHY, Belin et al., 2020) and Water Framework Directive (WFD) at two monitoring stations, Nord Dumet (ND) and Ouest Loscolo (OL; Fig. 1). Surface water at the ND Station has been monitored monthly (at 1 m below the surface) since 2008 as part of REPHY and WFD for the nutrient and Chl a concentrations, and phytoplankton composition. This station also benefits from an instrumented buoy (MOLIT), deployed since 2008 to monitor the temperature, salinity, dissolved oxygen and turbidity in surface and bottom waters with an hourly frequency. Surface waters at the OL station has been monitored bi-monthly since 1996 for phytoplankton, nutrients and physical parameters (temperature, salinity, dissolved oxygen) as part of REPHY and WFD.

2.2.2. Sediment

The year 2015 was devoted to a temporal study and involved renewing measurements and experiments at a single station on six dates between April and September and by alternating periods of strong
(spring) and weak (neap) tides in order to take tidal variations into account. The ND monitoring station (St. A, Fig. 1) was chosen for its high frequency monitoring of physicochemical parameters.

Close to 30 stations spread over the whole bay were sampled in April 2016 to assess the spatial distribution of the sediment granulometry (grain size, porosity, density), organic carbon ($C_{org}$), total nitrogen (TN), biogenic silica (BSi) and Chl a contents in the first 5 cm of the sediments. Spatial variations of the benthic fluxes were measured at four stations (including the ND monitoring station) selected among those sampled in April 2016. All four campaigns were grouped together over a short period to minimize temporal variations (July 18th to 28th).

2.3. Data acquisition

2.3.1. River discharge

River discharge data were extracted from the French hydrologic “Banque Hydro” database (http://www.banquehydro.eaufrance.fr/, access: May 20, 2016). Daily discharge data were available at the Montjean-sur-Loire gauging station for the Loire River and at the Rieux gauging station for the Vilaine River.

2.3.2. Water column

Physicochemical (temperature, salinity and dissolved oxygen), phytoplankton and nutrient data from the ND and OL monitoring stations were used to provide a hydrological context for the benthic N flux studied in 2015 and 2016. Additional samples were taken bimonthly at the ND station in bottom waters (1 m above the bottom) from March to October 2015 for the nutrient and Chl a analyses. Physicochemical data at the ND station were obtained from the MOLIT buoy, and were validated and published in SEANOE (Retho et al., 2020). Water samples for the DIN and DON analyses were filtered using syringe fitted filters (CA membrane 0.2 μm Sartorius®) and stored at −20 °C for analysis. The pore-water was extracted by centrifugation at 3360g for 20 min at in situ temperature. The pore-water was filtered using syringe fitted filters (CA membrane 0.2 μm Sartorius®) and stored at −20 °C for the DIN and DON analyses. An aliquot of the sediment remaining after the pore-water was collected for each layer was frozen for the $C_{org}$ and TN analyses.

The second triplicate of the sediment cores was used for the sediment physical property analysis. For the grain size analysis, an aliquot of the wet sediment samples from each layer was stored in a plastic bottle containing a mixture of one third ethanol and two thirds distilled water to prevent microbial activity. Another aliquot of wet sediment of known volume and weight was dried (45 °C, 5d) for the density and porosity analysis. For another triplicate of the sediment cores, the top first cm was sliced and frozen for the sediment Chl a analysis.

One sediment core was used to measure the vertical profiles of the dissolved O$_2$ at the SWI and in the sediment using a miniaturizedClark-type oxygen sensor (Unisense OX500®) coupled with a picocammeter (Unisense PA2000®) and a micromanipulator (Unisense MM33®) at room temperature. The position of the SWI was determined visually from the O$_2$ microprofile according to Lansard et al. (2008), by adjusting the SWI position to the steepest O$_2$ concentration gradient.

For the spatial study carried out in April 2016, the samples of the first 5 cm of the sediments for the physical property analysis were lost and therefore are not presented here.

2.3.4. Benthic DIN and DON fluxes

For each sampling date and station, approximately 80 L of bottom water was collected using a peristaltic pump for laboratory incubation experiments. When collecting bottom water samples, the light intensity was also measured at 0.5 m above the bottom using a Li-COR Spherical Underwater Quantum Sensor. Benthic fluxes were measured using the sediment core incubation technique. For each experiment, duplicate sediment cores were incubated at in situ temperature and light conditions in a thermo-regulated water bath with one duplicate wrapped with tin foil to avoid light exposure. Two additional cores, containing only bottom water (blank cores), were incubated in order to verify changes in the concentration in the overlying water. Each tube was carefully sealed with a cap equipped with a stirring rod (Fig. S1). The overlying water was gently stirred while avoiding sediment resuspension. During incubation, a probe was used to monitor O$_2$ in the overlying water in order to make sure that O$_2$ concentrations did not drop below 20% of the initial sampling values (Dalsgaard et al., 2000). The overlying water was sampled five to six times during the 20–24 h incubation period. Water samples were immediately filtered using syringe fitted filters (CA membrane 0.2 μm Sartorius®) and stored at −20 °C for analysis. The
sampled volume (50 mL) was replaced with the same volume from a reserve tank containing unfiltered bottom water. Fluxes were calculated from the change in concentrations over the incubation time after a correction for dilution due to replacing the overlying water and possible changes in the blank cores. Only significant slopes (linear regression, \( p < 0.05 \)) were taken into account, otherwise the fluxes were considered to be zero. Finally, the results from light and dark measurements (\( n = 4 \)) were pooled because there was no significant difference between both treatments (Mann-Whitney, \( p > 0.05 \)). At the end of incubation, sediments were fixed using 10% formalin for the macrofauna counts and changes in the blank cores. Only significant slopes (linear regression, correction for dilution due to replacing the overlying water and possible from the change in concentrations over the incubation time after a

2.3.5. Potential nitrification and NO\(_3^−\) reduction

Potential nitrification step 1 (NH\(_4^+\) oxidation to NO\(_2^-\)) rates were measured by incubating slurries containing sodium chloride (NaClO\(_3\)) in order to inhibit NO\(_2^-\) oxidation (Bianchi et al., 1994; Gilbert et al., 1997). Fresh sediments (30 g) from the 0–2 cm layer were mixed homogeneously with 1 L of filtered bottom water (CA membrane 0.2 μm Sartorius®) in polycarbonate bottles. A control triplicate of bottles contained untreated slurries only. Two mL of NaClO\(_3\) (10 mM) was added to one triplicate of bottles. No substrate was added. Slurries were incubated for 20–24 h in the dark at in situ temperature, with loosely fitted caps to ensure oxic conditions. Each slurry was subsampled every 4 h, and subsamples were centrifuged (3920 g, 15 min). The supernatant was sampled, fixed with 50 μL HgCl\(_2\) (60 g L\(^{-1}\)) and stored at 4 °C while awaiting NO\(_2^-\) analysis. The rates were calculated using a linear regression of the change in NO\(_2^-\) concentrations over time. Only significant slopes (linear regression, \( p < 0.05 \)) were taken into account, otherwise the rates were considered to be zero.

Potential NO\(_3^-\) reduction rates were measured using flow-through reactor methods (Laverman et al., 2006). For each experiment, duplicate sediment layers (0–2 cm) were placed in Plexiglas® rings (4.2 cm inner diameter, 2 cm height). A 0.2 μm pore size PVDF (Durapore®) membrane filter and a glass fiber backing filter (1.2 mm thickness, 4.7 cm diameter) were placed at both ends of the ring, and the resulting sediment reactor cell was enclosed by two Plexiglas® caps with in/outflow channels. Reactor cells were fed with a saline solution containing NO\(_3^-\) (salinity 33, 4500 μM KNO\(_3\)) using a peristaltic pump (Gilson Minipuls®) at a constant flow rate (2 mL h\(^{-1}\)). The saline NO\(_3^-\) containing the input solution was bubbled with N\(_2\) for about 10 min to exchange and replace the existing gas phase creating an anoxic solution. Samples were collected from the outflow of the reactors every 4–6 h during 20–24 h. Reduction rates were determined from the difference in the NO\(_3^-\) concentrations at the inflow and outflow, multiplied by the flow rate and normalized by the volume of the reactor.

The measured potential NO\(_3^-\) reduction rates (NRR) were corrected for in situ temperature using the Arrhenius equation (eq. (1)) and fitted to the Michaelis-Menten rate expression (eq. (2))

\[
\text{Pot.NRR} = \frac{\text{Pot.NRR}_\text{T}}{Q_{10}}
\]

\[
R = \frac{\text{Pot.NRR} \times [\text{NO}_3^-]}{k_{\text{NO}_3} + [\text{NO}_3^-]} \tag{2}
\]

where Pot.NRR\(_T\) is the potential NRR corrected with in situ temperature \( T \), Pot.NRR\(_T\) is the potential NRR measured at laboratory temperature \( T_l \), \( Q_{10} = 2.5 \) (Laverman et al., 2006); \( k_{\text{NO}_3} \) is the affinity constant of NO\(_3^-\) for denitrification (see Table S2), and [NO\(_3^-\)] is the average measured NO\(_3^-\) concentrations in the first 2 cm of sediment.

2.3.6. Analytical methods

Sediment grain size was measured using the laser diffraction technique (Malvern 2000) on wet sediment samples. Density and porosity were calculated from the weight loss after drying. Sediment C\(_{org}\) and TN concentrations were measured on freeze-dried sediment using a Thermo Scientific™ elemental analyzer after eliminating inorganic carbon using phosphoric acid (Cawet, 1975). The BSI content was determined via the alkaline extraction method using 0.1 M sodium carbonate (Na\(_2\)CO\(_3\)) at 85 °C (DeMaster, 1981). The extract was analyzed as dissolved silica (DSI). NH\(_4^+\), NO\(_3^-\), NO\(_2^-\) and DSI concentrations were measured using a segmented flow colorimetric analysis according to Aminot and Kerouel (2007). NO\(_3^-\) and NO\(_2^-\) concentrations in the water column were reported as the sum of NO\(_3^-\) + NO\(_2^-\). Total dissolved N (TDN) concentrations were analyzed using the persulfate oxidation method according to Raimbault et al. (1999) after NH\(_4^+\) removal (Burdige and Zheng, 1998). DON concentrations were determined from the difference between TDN and DIN. Chl a concentrations in the water column were measured using spectrophotometry according to Aminot and Kerouel (2004). Sediment Chl a concentrations were extracted from freeze-dried sediment according to Lorenzen (1967) after an extraction with 90% acetone and ultrasonication for 5 min (Sundbäck et al., 1996). Microscopic observations of the phytoplankton and/or microagal dominant species in the sediment surface were conducted on Lugol-fixed samples collected from the uppermost mm of sediments.

2.3.7. Data analysis

If not stated otherwise, measurements are reported here as the average ± standard error: triplicate cores for the potential nitrification-denitrification rates and Chl a in the sediment surface, and four replicate cores for the benthic fluxes. Variations in the C\(_{org}\), TN, DIN and DON concentration profiles between sampling dates and depths were analyzed using a non-parametric Kruskal-Wallis test. The inter-variable relationship was tested using a linear regression. Spearman’s rank correlation was used to analyze the relationship between benthic macrofauna density, N transformation rates and benthic N fluxes for the temporal study carried out in 2015. Bottom water turbidity and O\(_2\) concentrations were also added to take the potential influence of sediment resuspension on benthic N transformation into account. For all tests, the level of significance was set to \( p < 0.05 \), and these tests were performed using the STATGRAPHIC CENTURION software (Statgraphics Technologies Inc., Version XVIII, Released, 2018). The spatial distributions of C\(_{org}\), TN, BSI and Chl a in the first 5 cm of sediment were visualized using the Ocean Data View software. Automatic weighted-average gridding was used to spatially interpolate the data (Schlitzer, 2002).

2.4. Reactive transport model

2.4.1. Model description

A one-dimensional steady state reactive transport model (RTM) was applied to the dataset mainly to simulate sediment-water DIN fluxes, as well as DIN concentrations in the pore-water and to quantify N transformation process rates. This present study focuses on the sediment N cycle by integrating a newly developed N reaction network as developed by Akbarzadeh et al. (2018). DON benthic flux modeling was limited to only calculating the diffusive fluxes.

2.4.2. Reactions

This model combines general organic matter (OM) oxidation reactions with N transformation processes. Five principal reactions in the sediment N cycle are considered: ammonification, nitrification, denitriﬁcation, dissimilatory NO\(_3^-\) reduction to NH\(_4^+\) (DNRA) and anammox (Table S1). NH\(_4^+\) production (ammonification) occurs by aerobic respiration, denitrification, DNRA, dissimilatory iron reduction and sulfate reduction. Nitrification is modeled as a two-step process: NH\(_4^+\) (step 1) and NO\(_2^-\) (step 2) oxidation, respectively. Anaerobic processes (denitrification, DNRA, anammox, Fe(OH)\(_3\) and SO\(_4^{2-}\) reduction) are prevented by the presence of O\(_2\) using an inhibition term (\( F_{\text{in}} \)). Denitrification and DNRA are modeled as a one-step process of OM oxidation
using NO$_3^-$, with N$_2$ and NH$_4^+$ production, respectively, as the ultimate end result. The fraction of the NO$_3^-$ reduction by denitrification and DNRA is assumed to be a fixed value. A term $F_{\text{DNRA}}$ is added to distribute the fraction of NO$_3^-$ reduction between two pathways (Canavan et al., 2007; Akbarzadeh et al., 2018), and the fraction of NO$_3^-$ reduced by denitrification is defined as 1 minus (–) $F_{\text{DNRA}}$ (Table S1). The $F_{\text{DNRA}}$ value was adjusted by testing a series of values (5, 10, 25, 50, 75, 90, 95%) to obtain the fit of the NH$_4^+$ fluxes. The retained value was 5% (see Supplement).

2.4.3. Boundary conditions and reaction parameters

NH$_4^+$, NO$_3^-$, NO$_2^-$ and O$_2$ concentrations measured in the bottom water were set as the upper boundary conditions (Table S2). This model considers two pools of organic matter: a labile pool (abbreviated as OM1) and a less labile pool (abbreviated as OM2), as well as the following N species: NH$_4^+$, NO$_3^-$, NO$_2^-$, NO$_4^-$, NO$_2^-$. Additional chemical species include dissolved O$_2$, sulfate (SO$_4^{2-}$), dissolved iron (Fe$^{2+}$) and iron hydroxides (Fe(OH)$_3$). For solid species, deposition fluxes at the SWI were imposed. Measured benthic fluxes for the NH$_4^+$ and O$_2$ pore-water profiles were used to constrain the depositional fluxes of OM, whereas the depositional fluxes of OM2 were adjusted to best reproduce the NH$_4^+$ and NO$_3^-$ pore-water profiles. A CN ratio of 10 was assumed for OM1 according to the measured average CN molar ratio sediment surface (Table S3), while that of OM2 was assumed to be poorer in N (C:N = 15). The lower boundary conditions of all chemical species were set to zero concentration gradients.

The reaction rate parameters detailed in Table S3 were obtained following a common procedure in the early diagenetic modeling (e.g., Wang and VanCappellen, 1996; Canavan et al., 2006; Dale et al., 2011; Akbarzadeh et al., 2018). Values were either taken directly from the literature or adjusted by trial and error to obtain global fits of the model to the DIN fluxes was considered to be negligible (<5% of the NH$_4^+$ and NO$_3^-$ fluxes) and therefore they were not included in the sensitivity analysis.

3. Results

3.1. Hydrological conditions in 2015 and 2016

During both studied periods (April–September 2015 and July 2016), the seasonal variations of the physico-chemical parameters in the water column at both monitoring stations in the VB essentially depended on climatic conditions and freshwater inputs from the Loire and Vilaine rivers (Figs. 2 and S2). The water column temperature varied between 10 °C in March and 21 °C in July with temporary stratifications of several degrees in summer. The water column O$_2$ concentrations exhibited opposite variations to those observed for temperature. The lowest bottom water O$_2$ concentration value, close to the hypoxia threshold (63 μM, Middelburg and Levin, 2009; Zhang et al., 2010), was detected at St. B in July 2016 (96 μM, Table S2). Discharges from the Loire and Vilaine rivers displayed similar variations in 2015 with a flood...
in May, while 2016 was characterized by a flood from the Loire River in early June. Within one week after flooding, the surface water in the VB displayed drops in salinity below 28, coinciding with the peaks of \(\text{NO}_3^- + \text{NO}_2^-\) concentrations (>60 \(\mu\)M). Aside from these peaks, the surface and bottom water \(\text{NO}_3^- + \text{NO}_2^-\) concentrations were ~20 \(\mu\)M in spring and they gradually decreased in June to reach levels below 1 \(\mu\)M. With regards to all four stations studied in July 2016, the highest \(\text{NO}_3^- + \text{NO}_2^-\) concentration was recorded at St. B (Table S2). \(\text{NH}_4^+\) concentrations remained below 2 \(\mu\)M in the surface water. Peaks were recorded in the bottom water in May 2015 (>5 \(\mu\)M) and in June 2016 (>3 \(\mu\)M), decreasing gradually below 1 \(\mu\)M in July. In 2016, the highest \(\text{NH}_4^+\) and minimum \(\text{O}_2\) concentrations were found at St. B (Table S2). Chl \(a\) concentrations in the surface water peaked (>15 \(\mu\)g L\(^{-1}\)) in March and May in 2015 and in June 2016 corresponding to diatom blooms. Small peaks (~5 \(\mu\)g L\(^{-1}\)) of diatom blooms were observed in August 2015 and October 2016 (see Retho, 2019 for additional information). For both studied periods, DON concentrations at the ND station varied around 7 \(\mu\)M throughout the year in both the surface and bottom waters (not shown).

3.2. Sediment characteristics

The sediment grain size distribution at the ND monitoring station was dominated by very fine particles (<63 \(\mu\)m) and remained constant with depth regardless of the sampling date (Fig. S3). At three stations sampled in July 2016, this distribution was dominated by a very fine fraction (<63 \(\mu\)m) at St. B, a coarse fraction (>100 \(\mu\)m) at St. C and gravel at St. D (Fig. S4). Sediment porosity and dry density varied slightly with the depth (0.85–0.79 and 2.96–2.90, respectively) and sampling dates (0.80–0.82 and 2.60–2.96, respectively) at the ND
station, and displayed spatial variations according to the grain size distribution (Figs. S5 and S6). Sediment $C_{\text{org}}$ and TN concentrations at the ND monitoring station were not significantly different according to the date and depth ($p > 0.05$), with median values of 1168 (~1.6% DW) and 120 μmol g$^{-1}$ (~0.2% DW) for $C_{\text{org}}$ and TN, respectively (Fig. 3a and b). The median of the C:N molar ratio varied between 9.2 in the first top cm and 10.8 at depth (Fig. 3c). $C_{\text{org}}$, TN and BSi concentrations at the sediment surface (5 cm) ranged respectively from 221 to 2,095, 25 to 233, and 10–215 μmol g$^{-1}$ and were higher in the north-western part of the bay than in the south-eastern part (Fig. S7).

At the ND monitoring station in 2015, the Chl $a$ content in the first cm of sediment slightly increased from 8.9 ± 1.4 μg g$^{-1}$ in April to 11.9 ± 1.5 μg g$^{-1}$ in June (Fig. 2d), it decreased in August (4.6 ± 0.3 μg g$^{-1}$) and then slightly increased in September (8.7 ± 0.9 μg g$^{-1}$). The highest values in April and June were found subsequent to spring diatom blooms. Benthic Chl $a$ displayed a spatial variation similar to that of $C_{\text{org}}$, TN and BSi (Fig. S7), with the highest concentration observed at St. B (Fig. 2h). Microscopic observations of the sediment surface in 2015 revealed abundant benthic diatoms (Pleurosigma sp., Navicula spp., Nitzschia spp.) and organic debris in April and June, while there was less organic debris, some phytoplanktonic (Thalassiosira sp.) and tycho-planktonic (Paralia sp.) diatoms and many empty cells in August and September (Fig. S9). Overall, on average, the macrofauna density in the incubated sediment cores of the ND monitoring station in 2015 were <1500 ind. m$^{-2}$, dominated by Nucula nitidosa (a small bivalve), Amphiura filiformis (a brittle star) and Sternaspis scutata (polychaeta) (Table S8). No significant correlations were observed between the benthic macrofauna density and benthic N transformation rates, and measured N fluxes (Table S9).

### 3.3. Oxygen and dissolved N pore-water profiles

Irrespective of the sampling date, the $O_2$ concentration decreased rapidly within the first 2 mm and was undetectable below this depth (Fig. 4a). In 2015, pore-water $NH_4^+$ concentrations at the ND station showed positive concentration gradients in the first 5 cm (Fig. 4b) and nearly constant values around 300 μM below 5 cm, except in two cores (June 24th and August 5th with a value exceeding 1200 μM). $NH_4^+$ concentration profiles did not show any significant differences between sampling dates ($p > 0.05$). In 2015, pore-water DON concentrations at the ND station were higher than those in the bottom water, with no significant difference between sampling dates ($p > 0.05$, Fig. S8a). Steep positive concentration gradients were observed in the top 1 cm, which became weaker in the layer below. The global mean pore-water DON concentration was higher than that of $NH_4^+$ in the first 5 cm layer and lower below (Fig. S8b). Pore-water $NO_3^-$ concentrations at the ND
station displayed negative concentration gradients in April 2015 (Fig. 4c). Peaks of NO$_3^-$ were observed in the top first 0.5 cm from June to September 2015, with a high value up to 12 μM on August 5th. Pore-water NO$_2^-$ concentrations were low (<2 μM). Peaks of NO$_2^-$ maxima were generally observed in the first 1 cm, which decreased gradually below (Fig. 4d).

3.4. Dissolved N fluxes at the SWI

NH$_4^+$ fluxes measured at the ND station in 2015 varied between 36 ± 22 μmol m$^{-2}$ h$^{-1}$ in April and 50 ± 19 μmol m$^{-2}$ h$^{-1}$ in June (Fig. 5a), and were 10 times lower in August and September (5.3 ± 4.5 μmol m$^{-2}$ h$^{-1}$). Maximum NH$_4^+$ fluxes were found after spring blooms, as observed for the sediment Chl a content (Fig. 2d). The calculated diffusive NH$_4^+$ fluxes, based on pore-water concentration gradients in the first cm measured in 2015, were approximately 50% of the measured fluxes, with little variation over time (Table S6). In 2016, NH$_4^+$ fluxes were three times higher than those measured in June 2015 and displayed spatial variation, with maximum values observed at St. A and St. B. NH$_4^+$ fluxes measured at the ND station in 2015 were positively correlated to the Chl a content in the first cm sediment layer ($r = 0.82$, $p < 0.05$, Fig. 6a). Benthic DON fluxes measured at the ND station in 2015 had similar values and displayed a temporal variation similar to those of NH$_4^+$ (Fig. 5b), with which they were positively correlated ($r = 0.82$, $p < 0.05$, Fig. 6b). DON fluxes were close to zero in August and September. In 2016, the DON fluxes were in the same order of magnitude as those measured in 2015. Diffusive DON fluxes represented approximately 10% of the measured DON fluxes in spring and were higher in summer than in spring, with little variation over the sampling dates (Table S6). At the ND station, NO$_3^-$ fluxes were directed towards
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the sediments in April 2015, with an average rate of $-17 \pm 5 \mu\text{mol m}^{-2}\text{h}^{-1}$ (Fig. 5c), coinciding with high NO$_3^-$ concentrations in the bottom water (Fig. 2c). For the rest of the studied period, NO$_3^-$ was released from the sediments except in August 2015 when the values were close to zero ($<0.1 \mu\text{mol m}^{-2}\text{h}^{-1}$). The release of NO$_3^-$ represented approximately 25% of the NH$_4^+$ fluxes. In 2016, the measured NO$_3^-$ fluxes varied between the stations, with a flux towards the sediments particularly at St. B (Fig. 5c), coinciding with high bottom water NO$_3^-$ concentrations (Table S2). The measured NO$_2^-$ fluxes remained below 5.0 μmol m$^{-2}$h$^{-1}$, maximum values were observed in June and September in 2015 and there was a flux towards the sediments at St. B in 2016 (Fig. 5d). For all benthic flux values, there was no significant difference between measurements during spring and neap tides (Mann-Whitney, p > 0.05).

3.5. Potential nitrification and NO$_3^-$ reduction rates

In 2015, the potential rates of nitrification measured at the ND station increased from April to June ($11.5 \pm 0.4$ to $28.0 \pm 2.9 \mu\text{mol N m}^{-2}\text{h}^{-1}$) and then decreased afterwards in August ($14.0 \pm 2.5 \mu\text{mol N m}^{-2}\text{h}^{-1}$) and September ($12.0 \pm 1.3 \mu\text{mol N m}^{-2}\text{h}^{-1}$) to values comparable to those in April (Table 2). The potential nitrification rates measured in
July 2016 were lower than those measured in 2015. The potential NO$_3^-$ reduction rates measured in 2015 increased from April (52.4 ± 6.6 μmol N m$^{-2}$ h$^{-1}$) to their maximum values in June (119.0 ± 24.8 μmol N m$^{-2}$ h$^{-1}$; Table 2).

3.6. Model outputs

3.6.1. Organic matter mineralization and N transformation rates

Aerobic respiration was the major pathway of labile OM (OM1) mineralization (Table 1), with rates displaying similar temporal and spatial variations to those for OM1 depositional fluxes (Table S2). Aerobic respiration represented up to 75% of the total rates. The anaerobic OM mineralization pathway was dominated by SO$_4^{2-}$ reduction, with the highest value at St. B in 2016. The reduction of NO$_3^-$ and Fe(OH)$_3$ activities was less significant (~10% of the total rates for both processes). The modeled nitrification rates (step 1) were similar to the measured activities was less significant (~10% of the total rates for both processes).

The modeled nitrification rates (step 1) were similar to the measured potential rates and displayed similar temporal and spatial variations (Table 2). In 2015, the model-predicted denitrification rates revealed a temporal variation contrary to the measured potential rates and model-predicted nitrification rates, with the highest rates in April decreasing over the studied period. In 2016, St. B displayed the highest denitrification rates. Adjusting the $F_{DNRA}$ value to 5% of all of the reduced NO$_3^-$ resulted in the best fit of the NH$_4^+$ fluxes. When values higher than 5% were tested, this resulted in an overestimation of the NH$_4^+$ fluxes (Fig. S10). The anammox rates were quantitatively low (<0.2 μmol m$^{-2}$ h$^{-1}$) compared to the other N transformation processes with little variation over time and between stations.

3.6.2. Modeled pore-water profiles and benthic fluxes

The reactive transport model reproduced a good fit for most O$_2$ and DIN pore-water concentration profiles at the ND station in 2015 (Fig. 4). However, some discrepancies were observed, such as the O$_2$ and NH$_4^+$ profiles on August 5th and September 8th, as well as the NO$_3^-$ peak on June 24th. For both studied periods (2015 and 2016), the simulated NH$_4^+$ and NO$_3^-$ fluxes showed a good fit with the measured fluxes (Fig. 5), with differences still observed within the standard error of the measured values: 4.9, 0.6 and 9.9 μM m$^{-2}$ h$^{-1}$ for NO$_3^-$, NO$_2^-$ and NH$_4^+$ fluxes, respectively.

3.6.3. Sensitivity analysis

The sensitivity analysis showed that the OM1 pool input had the largest effect on the magnitude of the NH$_4^+$ fluxes for each sampling date (Fig. 7). NH$_4^+$ fluxes increased with the increase in OM1 input and decreased with changes in the proportion of the OM pool, which corresponded to decreased OM1 fluxes by a factor of 3–4. Minor effects on the NH$_4^+$ fluxes were observed (<10%) for the other scenarios of change in the environmental factor-related model parameters (Fig. 7). For the NO$_3^-$ fluxes, changes in the bottom water NO$_3^-$ concentrations and the anoxic condition were the main factors influencing flux magnitude and direction (Fig. 8). In April, NO$_3^-$ sediment inward fluxes were increased by increasing the bottom water NO$_3^-$ concentrations and by eliminating O$_2$ from the bottom water (Fig. 8a and b). In June, August and September (Fig. 8c–f), benthic NO$_3^-$ fluxes reverted from outward to inward when the bottom water O$_2$ was set to zero and the bottom water NO$_3^-$ concentrations were increased.

4. Discussion

4.1. OM deposition fluxes and diageneric pathways

Temporal and spatial variations of the benthic dissolved N fluxes in Vilaine Bay (VB) are mainly explained by OM remineralization at the SWI. The model accurately simulated temporal and spatial variations in benthic fluxes by setting high rates of OM decomposition in the upper sediment layer and by essentially varying the input of labile OM (OM1), which constitutes the main fraction (~80%) of the total OM depositional flux. This proportion of OM1 is comparable to that obtained by a modeling study carried out on the Rhone River delta sediments (Pastor et al., 2011; Ait Ballagh et al., 2021), and suggests that most OM inputs into the sediment surface in the VB consists of labile matter. This fraction is characterized in the model by the first-order decomposition rate constant, with this value (16 yr$^{-1}$) falling within the range of those values (3-33 yr$^{-1}$) reported in Westrich and Berner (1984) from incubation experiments using fresh planktonic material. The decomposition rate constant of OM2 (0.1 yr$^{-1}$) lies in the range of those values reported in the literature (see Paraska et al., 2014; Ait Ballagh et al., 2021), which may correspond to degraded algal cells, containing organic acids and lipids, with a lower degradability than fresh planktonic material (Cowie

Table 1

Model-predicted OM decomposition rates through the different pathways for OM1 and OM2 (in parentheses). All values are in μmol C m$^{-2}$ h$^{-1}$.

<table>
<thead>
<tr>
<th>Processes</th>
<th>April 15th</th>
<th>April 22nd</th>
<th>June 16th</th>
<th>June 24th</th>
<th>August 5th</th>
<th>September 8th</th>
<th>St. A</th>
<th>St. B</th>
<th>St. C</th>
<th>St. D</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>475.8 (3.9)</td>
<td>566.4 (4.9)</td>
<td>605.8 (5.9)</td>
<td>629.7 (5.3)</td>
<td>261.3 (9.1)</td>
<td>343.3 (6.7)</td>
<td>1307.9 (9.3)</td>
<td>1164.4 (3.9)</td>
<td>862.6 (9.3)</td>
<td>298.9 (3.1)</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>45.5 (1.1)</td>
<td>36.5 (1.0)</td>
<td>23.1 (0.7)</td>
<td>19.7 (0.5)</td>
<td>12.9 (1.6)</td>
<td>17.8 (1.1)</td>
<td>2.6 (0.1)</td>
<td>49.0 (0.5)</td>
<td>4.0 (0.1)</td>
<td>41.0 (1.1)</td>
</tr>
<tr>
<td>Fe(OH)$_3$</td>
<td>21.3 (1.5)</td>
<td>21.6 (1.8)</td>
<td>20.9 (1.7)</td>
<td>20.7 (1.4)</td>
<td>18.1 (0.7)</td>
<td>19.7 (3.5)</td>
<td>21.1 (1.2)</td>
<td>20.9 (0.6)</td>
<td>20.7 (1.8)</td>
<td>23.1 (2.0)</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>111.5 (23.8)</td>
<td>98.7 (26.8)</td>
<td>133.5 (40.4)</td>
<td>168.5 (44.8)</td>
<td>19.0 (30.5)</td>
<td>43.0 (32.4)</td>
<td>354.1 (82.4)</td>
<td>723.1 (69.0)</td>
<td>235.2 (85.0)</td>
<td>120.0 (39.7)</td>
</tr>
<tr>
<td>Total</td>
<td>654.1 (30.5)</td>
<td>663.2 (34.7)</td>
<td>783.3 (48.7)</td>
<td>838.6 (52.2)</td>
<td>311.3 (48.1)</td>
<td>423.7 (43.9)</td>
<td>1685.8 (93.0)</td>
<td>1957.5 (73.9)</td>
<td>1126.4 (96.3)</td>
<td>446.2 (44.9)</td>
</tr>
</tbody>
</table>

*a* Sum of the denitrification and DNRA rates (see section 2.4.2. and Table S1).

*b* Total rates of all OM decomposition pathways.
et al., 1992; Komada et al., 2013). The deposition fluxes of OM1 in this study (275–1800 μmol cm⁻² yr⁻¹) are in the range of those reported from anthropogenic impacted estuarine and coastal waters, such as the Aulne and Elorn estuaries (840–3580 μmol cm⁻² yr⁻¹; Khalil et al., 2018), Rhône River delta (260–5475 μmol cm⁻² yr⁻¹; Pastor et al., 2011), and Loch Creran sea (73–1060 μmol cm⁻² yr⁻¹; Brigolin et al., 2011).

Table 2

Model-predicted depth-integrated N transformation rates derived from a model simulation. The measured potential nitrification step 1 and NO₃⁻ reduction rates are indicated in parentheses (mean ± SE). All values are in μmol N m⁻² h⁻¹.

<table>
<thead>
<tr>
<th>Processes</th>
<th>April 15th</th>
<th>April 22nd</th>
<th>June 16th</th>
<th>June 24th</th>
<th>August 5th</th>
<th>September 8th</th>
<th>St. A</th>
<th>St. B</th>
<th>St. C</th>
<th>St. D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrification 1</td>
<td>18.4 (11.5)</td>
<td>19.1 (16.7)</td>
<td>29.2 (20.0)</td>
<td>24.2 (28.0 ± 2.9)</td>
<td>20.8 (14.0 ± 2.5)</td>
<td>27.5 (12.0 ± 1.3)</td>
<td>3.1 (7.3 ± 0.7)</td>
<td>0.4 (0.0 ± 0.0)</td>
<td>7.3 (2.8 ± 0.7)</td>
<td>6.6 (2.2 ± 0.7)</td>
</tr>
<tr>
<td>Nitrification 2</td>
<td>17.7 ± 0.4</td>
<td>28.6 (60.7 ± 8.8)</td>
<td>18.1 (73.6 ± 8.2)</td>
<td>15.4 (119.0 ± 24.8)</td>
<td>20.5 (26.8 ± 2.0)</td>
<td>37.6 (na)</td>
<td>3.6 (na)</td>
<td>5.5 (na)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Denitrification</td>
<td>35.5 (52.4)</td>
<td>28.6 (60.7)</td>
<td>18.1 (73.6)</td>
<td>15.4 (119.0 ± 24.8)</td>
<td>20.5 (26.8 ± 2.0)</td>
<td>37.6 (na)</td>
<td>3.6 (na)</td>
<td>5.5 (na)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DNRA</td>
<td>1.17 ± 0.8</td>
<td>0.94 ± 0.6</td>
<td>0.60 ± 0.51</td>
<td>0.37 ± 0.07</td>
<td>0.48 ± 1.24</td>
<td>1.24 (na)</td>
<td>0.12 (na)</td>
<td>0.11 (na)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anammox</td>
<td>0.08 ± 0.04</td>
<td>0.10 ± 0.06</td>
<td>0.06 ± 0.06</td>
<td>0.08 ± 0.07</td>
<td>0.04 ± 0.04</td>
<td>0.06 ± 0.03</td>
<td>0.03 ± 0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Model sensitivity analysis showing the response of the benthic NH₄⁺ fluxes during the temporal study carried out from April to September 2015 (a–f) to different scenarios of change in environmental factor-related model parameters. The response was calculated as a percentage of change in the NH₄⁺ fluxes with regard to the baseline simulation (zero dashed line). The factors lying furthest from the zero dashed line are those causing the greatest change in the NH₄⁺ fluxes. Anoxic: zero bottom water O₂ concentrations; BW NO₃⁻ = 10x [100x]: increase in the bottom water NO₃⁻ concentrations by 10 fold or 100 fold for August and September; OM1 2x [3x]: increase in the deposition of OM1 by 2 fold (or 3x for August); OM1 ≤ OM2: inverting the proportion of OM1 and OM2; k1 OM1 = 2x: increase in the rate constant for the aerobic oxidation of OM1 by 2 fold); k1 OM1 = 1/2 x decrease in the rate constant for the aerobic oxidation of OM1 by one-half; C/N OM1 = 106/16: imposed change in the C/N ratio compared to that in living phytoplankton i.e., Redfield ratio; Db = 10x: increase in the bioturbation coefficient by 10 fold; α = 10x: increase in the bioirrigation coefficient by 10 fold.
The highest OM1 deposition flux values in the VB (Table S2) correspond to the maximum Chl a contents measured in the sediment surface (Fig. 2), suggesting that this OM has a plant origin (Szymczak-Zyła et al., 2011). The gradual decrease of O2 and low O2 penetration depth suggest rapid O2 consumption related to OM degradation (Pastor et al., 2011; Rabouille et al., 2021). This is consistent with our model results, which indicate that OM, especially the OM1 pool, was decomposed primarily at the sediment surface using O2 (Table 1). The difference between the measured and modeled O2 penetration depth on August 5th and September 8th (Fig. 4 a) could not be explained by the limitation of the OM input; if this is the case, the NH4+ fluxes would be underestimated by the model. We ascribe this discrepancy to the effects of temperature on microbial metabolism related to the lack of temperature control during the sediment core O2 profiling in summer, which may have increased O2 consumption and OM mineralization (Glud et al., 1994; Mogg et al., 2017). In the model, the remaining OM1 and OM2 pool was essentially mineralized through the reduction of SO4^2- (Table 1). This relatively high contribution of SO4^2- reduction, compared to NO3^- and Fe(OH)3, is in agreement with the high availability of SO4^2- at the upper boundary condition relative to NO3^- and Fe(OH)3 availability (Canfield, 1993). The contribution to OM decomposition by SO4^2- reduction increases with increasing OM deposition fluxes and particularly when the bottom water O2 concentration decreases close to the hypoxia level, as was the case at St. B in the summer of 2016. This rapid oxic OM mineralization at the SWI plays a critical role in controlling the bottom water O2 concentrations as well as benthic nutrient recycling.

4.2. Benthic N transformations: dominance of aerobic processes

The temporal (and spatial) variations in the benthic fluxes and pore-water concentrations of NO3^- and NO2^- are consistent with those in the
process rates and comparable to those reported in coastal ecosystems subject to seasonality with regards to the $\text{NO}_3^-$ and $\text{NO}_2^-$ concentrations in the water column (Jensen et al., 1990; Kemp et al., 1990; Kitidis et al., 2017). The negative concentration gradients of $\text{NO}_3^-$ in April 2015, due to large $\text{NO}_3^-$ concentrations in the water column, are in agreement with inward sediment fluxes, which can be attributed to $\text{NO}_3^-$ uptake via denitrification (Jorgensen and Sorensen, 1988). These inward sediment $\text{NO}_3^-$ fluxes seem proportional to the $\text{NO}_3^-$ concentrations in the bottom water. The shift in the $\text{NO}_3^-$ flux direction in June 2015 appears to be the result of increasing nitrification, as shown by the $\text{NO}_3^-$ concentration peaks in the upper 0.5 cm sediment layer and the bottom water $\text{NO}_3^-$ depletion (Jensen et al., 1990), and is in agreement with the measured potential nitrification rates. The temporal and spatial co-variations between the measured potential nitrification and $\text{NO}_2^-$ fluxes, as well as the peaks of $\text{NO}_3^-$ in the first 1 cm oxic sediment layer, emphasize the role of nitrification in benthic $\text{NO}_2^-$ production (Mordy et al., 2010).

Nitrification measurements using the slurry incubation of the first two cm of sediment were taken without limiting O$_2$ and by adding substrate ($\text{NH}_4^+$). The good fit between the modeled nitrification rates (step 1) and measurements confirms that the conditions were largely aerobic during OM decomposition. The maximum nitrification rates in June suggest that nitrification is dependent on the $\text{NH}_4^+$ produced from OM remineralization (Herbert, 1999). With regards to denitrification, the model-predicted values were much lower than the potential rates measured without limitation of substrate ($\text{NO}_3^-$), implying that denitrification was limited by the availability of $\text{NO}_3^-$ (Middelburg et al., 1996; Laverman et al., 2012). Apart from the $\text{NO}_3^-$ supply from the water column in April 2015, $\text{NO}_3^-$ availability in the sediments was controlled by the nitrification efficiency and therefore by OM remineralization, suggesting that denitrification was closely coupled to nitrification (Risgaard-Petersen, 2003). This also explains the low nitrification/denitrification rate values in August 2015 coinciding with the lowest OM decomposition rates (Tables 1 and 2). The low model-predicted DNRA rates are consistent with the potential $\text{NO}_3^-$ reduction experiments showing little $\text{NH}_4^+$ production, suggesting that the $\text{NO}_3^-$ reduction activity was dominated by denitrification (Laverman et al., 2012). Anammox activity is generally low in eutrophic coastal waters (Bonaglia et al., 2014), which is, in our case, likely related to the low availability of $\text{NO}_2^-$ in pore-water (Dalsgaard et al., 2005). These low DNRA values and anammox rates are comparable to the observations made in oxygenated surface sediments from the Gulf of Finland (Jantti et al., 2011). This dominance of aerobic processes in the benthic N cycle (i.e., coupled nitrification-denitrification), as for aerobic OM mineralization, suggests that the transformation of N in the VB occurs mainly in the uppermost centimeter of the sediments.

4.3. Importance of DON in benthic N cycling

The DON pore-water concentrations in the VB sediments are within the same range as the DIN (mainly $\text{NH}_4^+$) concentrations and are in the same order of magnitude as those reported in the Chesapeake Bay (Burdige and Zheng, 1998) and the St. Lawrence estuary (Alkhathib et al., 2013). The concentration gradients in the DON pore-water profiles were lower than those of $\text{NH}_4^+$ below a depth of 2 cm (Fig. S7), suggesting that DON below this sediment layer may largely consist of refractory compounds slowly producing $\text{NH}_4^+$ in the pore-water (Burdige, 2001; Burdige et al., 2016). The absence of a temporal variation in the DON pore-water profiles indicates that DON cycling in the pore-water, as for $\text{NH}_4^+$ (see below), is relatively independent of seasonal events in the water column, particularly fresh OM inputs from phytoplankton blooms (Hansen and Blackburn, 1992). The positive concentration gradients in the upper 1 cm layer imply DON production and release to the overlying water by diffusion (Alkhathib et al., 2013). However, the weak concentration gradient in the DON pore-water profiles below a depth of 2 cm and much higher DON diffusion time-scales and residence time than those of DIN converge to explain low diffusive DON fluxes (see the Supplementary Material). As observed for $\text{NH}_4^+$ (see below), temporal variations in the diffusive DON fluxes did not reflect large fluctuations in the measured fluxes via incubation.

The benthic DON fluxes measured in the VB represent up to 50% of the dissolved N fluxes (Fig. 5). Although data on benthic DON flux measurements remain scarce in the literature, it appears that their values become truly quantifiable only after the sedimentation of fresh OM (Burdige and Komada, 2002; Eyre and Ferguson, 2002). Parallel temporal and spatial variations in the benthic DON and $\text{NH}_4^+$ fluxes infer that DON was released during OM degradation in the sediment surface. Our measurements confirm those of Hansen and Blackburn (1992), showing that the addition of diatom material to the sediment during laboratory experiments leads to a release of DON to the overlying water, as significant as that of $\text{NH}_4^+$. However, the importance of DON fluxes in benthic N cycling dynamics remains understudied in early diagenetic modeling studies (Paraska et al., 2014). This omission of DON in the RTM is likely related to the uncertainty of estimating its diffusion coefficient (Alperin et al., 1999; Alkhathib et al., 2013), as well as to the scarcity of data concerning benthic DON fluxes and pore-water concentrations (Boynton et al., 2018). Given the significance of DON release in this study, the integration of DON in the RTM may constitute an improvement in order to better estimate the role of this compound in the benthic N budget.

4.4. Phytoplankton-derived OM mineralization at the SWI as the main driver of benthic N fluxes

The benthic $\text{NH}_4^+$ fluxes measured in the VB showed strong temporal and spatial variations, with values lying within the range of those reported in other coastal ecosystems (Boynton et al., 2018). The exchange of $\text{NH}_4^+$ at the SWI can be influenced by several processes, in particular: consumption by benthic primary producers, benthic macrofauna activities, diffusive exchanges between the pore-water and overlying water and direct release from the decomposition of OM that was deposited at the SWI. These processes largely depend on hydrodynamic conditions (water aeration, sediment resuspension, etc.) and OM inputs (production at the SWI and sedimentation).

Primary producers that develop at the SWI (e.g., macroalgae and microphytobenthos) can assimilate $\text{NH}_4^+$ produced in the sediment and affect its exchange between the sediment and overlying water (Sundbäck et al., 2006). In the VB, the presence of macroalgae is limited to the rocky bottom and to the edge and foreshore, both representing less than 10% of the total surface area of the bay (Ehrhold, 2014). Microphytobenthos and particularly benthic diatoms can develop when sufficient light reaches the sediment surface (Miller et al., 1996). The absence of a significant difference between benthic flux measurement values under light and dark conditions in our experiment suggests that microphytobenthos had a minor contribution to the benthic fluxes. The high water column turbidity in the VB (Tessier et al., 2011), which limits microphytobenthos development (Mangan et al., 2020), may explain this hypothesis.

Benthic macrofauna rework sediments, favoring their homogenization and oxygenation, and accelerating the remineralization of sedimentary OM (Shull, 2019). The excretion of dissolved N by benthic macrofauna can also contribute to the enrichment of pore-water and overlying waters with $\text{NH}_4^+$ and DON (Gardner et al., 1993; Yamamuro and Koike, 1998). Among the three main taxa observed in the incubated cores, Amphitrite filiformis and Seramaspis scutata may favor biodiffusion, whereas Nucula nitidosa is instead considered to be a surficial modifier (Queiros et al., 2013). Although the densities of these three species are moderate in the VB (Le Bris and Glemarec, 1996; Ehrhold et al., 2008), they probably enhanced sedimentary OM recycling (Follum and Gray, 1987). The exceptionally high $\text{NH}_4^+$ concentrations in two cores (June 24th and August 5th), found also for phosphate and silicate (Ratmaya, 2018), could be explained by heterogeneities linked to macrofaunal
activity. However, no significant correlations between macrofauna density and benthic N transformation rates or N fluxes were found. Additionally, the low bioturbation and bioirrigation coefficients used in the model were sufficient to adjust benthic DIN fluxes, which may indicate the minor influence of benthic macrofaunal activities on benthic N cycling. Although the contribution of benthic macrofauna to benthic dissolved N fluxes could not be quantified in this study, it probably represents a limited part of the fluxes from the sediment to the water column, but this still needs to be confirmed.

The mineralization of OM in the sediment leads to a build-up of NH$_4^+$ in the sediment pore-water resulting in the benthic efflux of NH$_4^+$ (Herbert, 1999; Schulz, 2006). The absence of a significant change in the sediment pore-water suggests that sediments have not undergone strong resuspension during the study period. In addition, we did not find any significant correlation between bottom water turbidity and benthic N transformation rates or N fluxes (Table S9).

Different types of OM can be deposited in the VB sediments from external sources. The riverine input of particulate OM is limited due to efficient recycling in the Loire estuary (Relexans et al., 1988) and the presence of a dam in the Vilaine estuary (Traini et al., 2015). Phytoplankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton from oceanic waters may not be substantial due to lower plankton. Aarhus Bay (Jensen et al., 1990) and San Francisco Bay (Caffrey, 1995). The observations in the water column and sediment surface, together with the BSI, C$_{org}$ and TN content in the top first five cm of the sediment confirm that diatom blooms are the major source of OM to the VB sediments, with the north-western part as the favored deposition area (Le Bris and Glemarec, 1996; Ehrhold, 2014).

Diatom blooms in the VB are predominantly driven by nutrient inputs associated with floods from the Loire and Vilaine rivers (Figs. 2 and S2). After blooms appear, the deposited diatom-derived OM is mostly mineralized aerobically at the SWI within 2–3 weeks and recycled directly to the water column as dissolved inorganic (NH$_4^+$) and organic N (Fig. 9a). When blooms are absent, benthic dissolved N fluxes decrease and may be supported essentially by a diffusion from the deeper sediment layer, especially for DIN (Fig. 9b). For both situations, the diffusion of DON from a deeper sediment layer is very low, implying that DON is instead gradually mineralized to NH$_4^+$ in the pore-water. In addition, decomposition of the deposited phytoplanktonic material can rapidly consume O$_2$ at the sediment surface (within hours to several days) and can be followed by O$_2$ depletion in the bottom water, especially during summer. This pattern may also be valid for other coastal ecosystems with similar characteristics as the VB, as was reported inoxic sediments from the North Sea (De Borger et al., 2021) and in the seasonally hypoxic

**Fig. 9.** Summary diagram of the benthic N fluxes in the Vilaine Bay for two distinct situations: (a) in the presence of a phytoplanktonic bloom and (b) in the absence of a phytoplanktonic bloom, based on field observations, laboratory measurements and a modeling study. The terms OM1 and OM2 are used to distinguish between a labile and a less labile pool of organic matter input. DIN and DON stand for dissolved inorganic and organic N, respectively. The different arrow sizes indicate the magnitude of the OM input for each pool, as well as its recycling into DIN (mostly NH$_4^+$) and DON. The horizontal dashed lines are meant to approximately illustrate the OM turnover time for each pathway (aerobic and anaerobic), estimated from the model rate constants of OM1 and OM2 (Table S3) and the residence time of solutes (Table S6). Where the DON diffusion from pore-water is questioned, this is indicated by a question mark.
sediments of the northern Gulf of Mexico (Rabouille et al., 2021). The overall results lead to conclude that temporal and spatial variations of the benthic DIN and DON fluxes in the VB depend predominantly on the sedimentation of the diatom blooms rather than on the composition of the sediment column itself.

4.5. Ecological implication of benthic DIN fluxes compared to riverine inputs

DIN constitute the limiting nutrient of eutrophication during summer in the VB (Ratmaya et al., 2019). One can wonder how sedimentary and riverine sources contribute to summer DIN budget of the VB. These DIN flux data can be used to give a rough estimate of the role played by sediments in this budget for two different summer scenarios, low water flux data can be used to give a rough estimate of the role played by riverine sources contribute to summer DIN budget of the VB. These DIN inputs to the sediment surface compared to low water scenario. Despite its uncertainty, this rough estimate suggest that sediments constitute a non-negligible source of DIN to the VB water column, aggravating the effect of riverine DIN inputs. The use of a 3D ecological model (Ménèsquen et al., 2019), that takes hydrodynamics into account is required to better estimate the contribution of each DIN source to the VB water column.

5. Conclusion and perspectives

The cross-interpretation of the field observations, laboratory measurements and modeling approach indicate that OM inputs from diatom blooms are the key factor controlling benthic N cycling in the VB. The rapid decomposition of the deposited diatom material at the SWI may be followed by the depletion of the O₂ concentration in the bottom water, especially when blooms occur in summer. Using the same fixed model parameters, the RTM can be used to interpret both the time series and the spatial dataset for the benthic N cycle as a function of the OM deposition rate and the sedimentary environments. The dynamics of the DON fluxes still need to be investigated before they can be integrated into the RTM. The interpolation of benthic DIN flux measurement to the surface area of the VB, suggests that sediments represent a non-negligible source of DIN compared to riverine inputs.

In order to obtain a seasonal and spatial description of the biogeochemical processes in both the sediment and water column, the results presented in this study must be integrated into a 3D ecological model (see Ménèsquen et al., 2019 for ECOMARSSD model). Our key results provide the dataset to parameterize the sediment biogeochemical processes (e.g., nutrient transformation, elimination, and/or immobilization) in the ecological model. This integration will improve the ecological model in order to more accurately predict the sequence of river floods, phytoplankton blooms, sedimentation, benthic mineralization and bottom water hypoxia in the VB.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This study was funded by The Loire-Brittany Water Agency (AELB). We thank IFREMER-LER/MPL staff, especially the head of the laboratory Nathalie Cochenne-Laureau, Karine Collin, Jean-François Bouget, Michaël Retho, Noëmie Delaplanque, Thibault Dinet and Gwenael Bellec for the technical contributions. We would also like to thank the IFREMER DYNECO/PELAGOS staff: Agnes Youenou, Florian Caraced, Sophie Schmitt, Julien Quéré and Clémence Caule for assistance during the laboratory measurements. We thank Ludovic Helias, Ludovic Boucher, Sébastien Petton for assistance during the field sampling. We thank Philippe Rosa and Anthony Le Bris for the pigment analysis and Lourenço Ribeiro for the taxonomic analysis of the microalgae in the benthic samples. We thank Vincent Soulhier, Tiffenn Neveu, Valérie Le Cadre, Mathieu Mombreun and Evelyne Goubert for assistance to analyze the sediment physical properties. We thank Sara Mullin for proofreading the English and correcting the English content. The authors acknowledge IFREMER and the Regional Council of the Région des Pays de la Loire for providing funding for the PhD of W. Ratmaya. The authors thank Chen-Tung Arthur Chen for editing the manuscript. Our grateful acknowledgements also go to three anonymous reviewers for their constructive comments and suggestions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.car.2022.104649.

References


