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

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## 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), France. 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  $\mu\text{mol m}^{-2} \text{h}^{-1}$  in spring and were less than 10  $\mu\text{mol m}^{-2} \text{h}^{-1}$  in summer. The benthic DON fluxes co-varied with the ammonium fluxes, ranging from 100  $\mu\text{mol m}^{-2} \text{h}^{-1}$  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 -31 (towards the sediments) and 22  $\mu\text{mol m}^{-2} \text{h}^{-1}$  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.

### Highlights

► The temporal and spatial variations of benthic N cycling in a eutrophic macro-tidal bay are studied using field measurements and the reactive transport model. ► Benthic N flux variations depend on the phytoplankton-derived organic matter input. ► Rapid mineralization of organic matter at the sediment-water interface controls benthic N cycling dynamics and sediment oxygen consumption. ► Organic matter decomposition can be followed by bottom water hypoxia when blooms occur in the summer.

**Keywords** : DIN, DON fluxes, diatom blooms, hypoxia/anoxia, monitoring station, reactive transport model, sediments

## 53 1. Introduction

54 Coastal areas are among the world's most vulnerable ecosystems to anthropogenic  
55 pressures (Turner et al., 2003), particularly to nitrogen and phosphorus pollution which leads to  
56 eutrophication (Le Moal et al., 2019). The most visible aspect of anthropogenic marine  
57 eutrophication is the mass accumulation of macroalgae on the coast (Smetacek and Zingone, 2013)  
58 and phytoplankton blooms (Carstensen et al., 2015). In shallow coastal ecosystems with water  
59 bodies exhibiting a residence time of at least several days, senescent phytoplankton blooms can be  
60 deposited at the sediment-water interface (SWI) representing a significant amount of oxidizable  
61 organic matter (OM) (Smetacek, 1980; Taguchi, 1982). When dead phytoplankton cells  
62 decompose, this sometimes results in the depletion of dissolved oxygen ( $O_2$ ) in bottom waters  
63 (Cloern, 2001; Kemp et al., 2005) with a subsequent impact on the ecosystem's structure and  
64 function (Gray et al., 2002).

65 Nitrogen (N) is the key limiting nutrient in many coastal marine environments (Paerl,  
66 2018). In shallow coastal ecosystems, benthic OM remineralization can represent a significant  
67 source of N in the water column, helping to maintain eutrophication (Fisher et al., 1982). During  
68 algal decomposition in sediment, OM undergoes microbially-mediated biogeochemical  
69 transformations, resulting in dissolved organic N (DON) intermediates and dissolved inorganic N  
70 (DIN) end products. These can either escape as a benthic flux across the SWI or undergo further  
71 transformation in the pore-water (Herbert, 1999; Burdige, 2001). Ammonium ( $NH_4^+$ ) can be  
72 transformed into nitrite ( $NO_2^-$ ) and nitrate ( $NO_3^-$ ) under oxic conditions through nitrification  
73 (Ward, 2008). Under anoxic conditions, DIN ( $NH_4^+$ ,  $NO_3^-$ ,  $NO_2^-$ ) can be eliminated as  $N_2$  gas  
74 through denitrification and/or anammox (Thamdrup and Dalsgaard, 2002; Devol, 2015). The  
75 dissimilatory  $NO_3^-$  reduction to  $NH_4^+$  (DNRA) competes with denitrification for  $NO_3^-$  and tends  
76 to retain N in the system (Giblin et al., 2013). The dynamics and competition between these  
77 processes govern dissolved N recycling variations and amplitudes at the SWI (Blackburn and  
78 Henriksen, 1983; Hulth et al., 2005).

79 Mechanisms that control benthic N cycling are complex, often site-specific and depend on  
80 several factors. These factors include: ambient nutrient concentrations in the water column  
81 (Hensen et al., 1998; Khalil et al., 2018), the amount and quality of the deposited OM (Arndt et  
82 al., 2013; Ait Ballagh et al., 2021), sediment characteristics (Blackburn and Henriksen, 1983),  
83 bottom water  $O_2$  concentrations (Glud, 2008), temperature (Banta et al., 1995) and intensity of the  
84 sediment bioturbation (Aller and Aller, 1998), which all vary seasonally. Benthic N cycling can  
85 be highly variable over time in coastal ecosystems undergoing phytoplankton blooms (Jensen et  
86 al., 1990). In their global synthesis, Boynton et al. (2018) pointed out the lack of time series

87 measurements for a rigorous evaluation of seasonal and inter-annual variability of oxygen and  
88 nutrient exchanges across the SWI in estuarine and coastal ecosystems. More generally, temporal  
89 and spatial variations of benthic DIN and DON fluxes in relation with the water column  
90 composition, especially chlorophyll *a* (Chl *a*) concentrations as an indicator of phytoplankton  
91 biomass, still need to be investigated.

92 Numerical models are now widely used to simulate phytoplankton blooms and possible  
93 hypoxia (or anoxia) under the influence of various nutrient sources and to forecast scenarios of  
94 nutrient load reduction for oligotrophication purposes (Ménesguen et al., 2018). Using an  
95 ecological model coupled with an early diagenetic model, Soetaert and Middelburg (2009) and  
96 Gürevin et al. (2017) have shown how important it is to take benthic nutrient loads into account in  
97 order to rehabilitate eutrophic coastal ecosystems. Sedimentary biogeochemical processes must be  
98 considered when assessing risks of hypoxia caused by the sedimentation of phytoplankton blooms  
99 (Testa et al., 2014). It is therefore essential to understand and quantify how shallow coastal  
100 ecosystems accumulate, recycle and eliminate nutrients, especially at the SWI.

101 Multi-component reactive transport models (RTMs) have been widely used to estimate  
102 solute exchange rates at the SWI and biogeochemical processes in both marine and freshwater  
103 sediments (Wang and VanCappellen, 1996; Bohlen et al., 2011; Akbarzadeh et al., 2018), but few  
104 of these models have been used to simultaneously explore temporal and spatial variations (Paraska  
105 et al., 2014). The challenge remains to use a single model (e.g., same reaction parameter values)  
106 that could accurately simulate benthic N fluxes and biogeochemical processes as a function of the  
107 water column composition, especially phytoplankton biomass and sediment characteristics.

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

## 115 **2. Material and methods**

### 116 *2.1. Study site*

117 The Vilaine Bay (VB) is a shallow macro-tidal coastal bay under direct influence of the  
118 Loire and Vilaine rivers (Fig. 1, see Ratmaya et al., 2019 for a detailed description of the riverine  
119 nutrient inputs). The VB has a total area of 220 km<sup>2</sup>, with a depth varying between 10 and 15 m  
120 depending on the tidal amplitude between 4 and 6 m. Water circulation is characterized by low

121 tidal and residual currents, driven mainly by tides, winds and river flows (Lazure and Jegou, 1998).  
122 The water residence time in the bay varies between 10 and 20 days depending on the season and  
123 can exceed 30 days during calm periods (Chapelle, 1991). The VB is one of the European Atlantic  
124 coastal ecosystems most sensitive to eutrophication (Ménesguen et al., 2019), and has some of the  
125 highest concentrations of chlorophyll *a* (Chl *a*) in French coastal waters (Gohin, 2011). In the VB,  
126 eutrophication materializes in phytoplankton blooms, characterized by diatom dominance  
127 (Ratmaya et al., 2019). The occurrence of phytoplankton blooms in this area is predominantly  
128 controlled by the magnitude and timing of river floods (Guillaud et al., 2008) and is simulated  
129 using a coupled pelagic biogeochemical and 3D hydrodynamic model (ECOMARS3D;  
130 Ménesguen et al., 2019). Oxygen depletion in bottom waters following phytoplankton blooms is  
131 frequently observed (Rossignol-Strick, 1985; Ifremer, 2015). Therefore, the onset of  
132 hypoxia/anoxia in the VB is probably related to the timing of the phytoplankton blooms induced  
133 by river floods. Sediments in the VB are dominated by silt (> 80%), with silty sediments mainly  
134 in the north-western part of the bay, silty fine sand sediments in the eastern and north-eastern part  
135 of Dumet Island, and rocky substrates (gravels) in the southern part between Dumet Island and  
136 Piriac shelf (Le Bris and Glémarec, 1996).

## 137 2.2. *Sampling strategy*

### 138 2.2.1. *Water column*

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

### 149 2.2.2. *Sediment*

150 The year 2015 was devoted to a temporal study and involved renewing measurements and  
151 experiments at a single station on six dates between April and September and by alternating periods  
152 of strong (spring) and weak (neap) tides in order to take tidal variations into account. The ND

153 monitoring station (St. A, Fig. 1) was chosen for its high frequency monitoring of physicochemical  
154 parameters.

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

### 161 2.3. *Data acquisition*

#### 162 2.3.1. *River discharge*

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

#### 167 2.3.2. *Water column*

168 Physicochemical (temperature, salinity and dissolved oxygen), phytoplankton and nutrient  
169 data from the ND and OL monitoring stations were used to provide a hydrological context for the  
170 benthic N flux studied in 2015 and 2016. Additional samples were taken bimonthly at the ND  
171 station in bottom waters (1 m above the bottom) from March to October 2015 for the nutrient and  
172 Chl *a* analyses. Physicochemical data at the ND station were obtained from the MOLIT buoy, and  
173 were validated and published in SEANOE (Retho et al., 2020). Water samples for the DIN and  
174 DON analyses were filtered using syringe fitted filters (CA membrane 0.2  $\mu$ m Sartorius<sup>®</sup>) and  
175 stored at -20°C.

#### 176 2.3.3. *Sediment core sampling and treatments*

177 For each sampling date, 20 undisturbed cores were collected by scuba divers using  
178 Plexiglas<sup>®</sup> tubes (9 cm inner diameter; 30 cm height). Each core contained approximately 15 cm  
179 of sediment with 1 L of overlying water. Upon collection, all sediment cores were transported to  
180 the laboratory within 2 h.

181 For two sets of the triplicate sediment cores, the top first 15 cm were sliced into 10  
182 horizontal layers in a glove box filled with N<sub>2</sub> (1 cm intervals for 0-6 cm, 2 cm intervals for 6-12  
183 cm, and 3 cm intervals for 12-15 cm). The first triplicate of the sediment cores was used to extract



184 the pore-water. For each layer, the pore-water was extracted by centrifugation at 3360 g for 20  
185 minutes at in situ temperature. The pore-water was filtered using syringe fitted filters (CA  
186 membrane 0.2  $\mu\text{m}$  Sartorius<sup>®</sup>) and stored at -20°C for the DIN and DON analyses. An aliquot of  
187 the sediment remaining after the pore-water was collected for each layer was frozen for the C<sub>org</sub>  
188 and TN analyses.

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

195 One sediment core was used to measure the vertical profiles of the dissolved O<sub>2</sub> at the SWI  
196 and in the sediment using a miniaturized Clark-type oxygen sensor (Unisense OX500<sup>®</sup>) coupled  
197 with a picoammeter (Unisense PA2000<sup>®</sup>) and a micromanipulator (Unisense MM33<sup>®</sup>) at room  
198 temperature. The position of the SWI was determined visually from the O<sub>2</sub> microprofile according  
199 to Lansard et al. (2008), by adjusting the SWI position to the steepest O<sub>2</sub> concentration gradient.

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

#### 202 2.3.4. *Benthic DIN and DON fluxes*

203 For each sampling date and station, approximately 80 L of bottom water was collected  
204 using a peristaltic pump for laboratory incubation experiments. When collecting bottom water  
205 samples, the light intensity was also measured at 0.5 m above the bottom using a Li-COR Spherical  
206 Underwater Quantum Sensor. Benthic fluxes were measured using the sediment core incubation  
207 technique. For each experiment, duplicate sediment cores were incubated at in situ temperature  
208 and light conditions in a thermo-regulated water bath with one duplicate wrapped with tin foil to  
209 avoid light exposure. Two additional cores, containing only bottom water (blank cores), were  
210 incubated in order to verify changes in the concentration in the overlying water. Each tube was  
211 carefully sealed with a cap equipped with a stirring rod (Fig. S1). The overlying water was gently  
212 stirred while avoiding sediment resuspension. During incubation, a probe was used to monitor O<sub>2</sub>  
213 in the overlying water in order to make sure that O<sub>2</sub> concentrations did not drop below 20% of the  
214 initial sampling values (Dalsgaard et al., 2000). The overlying water was sampled five to six times  
215 during the 20 to 24 h incubation period. Water samples were immediately filtered using syringe



216 fitted filters (CA membrane 0.2  $\mu\text{m}$  Sartorius®) and stored at  $-20^{\circ}\text{C}$  for analysis. The sampled  
217 volume (50 mL) was replaced with the same volume from a reserve tank containing unfiltered  
218 bottom water. Fluxes were calculated from the change in concentrations over the incubation time  
219 after a correction for dilution due to replacing the overlying water and possible changes in the  
220 blank cores. Only significant slopes (linear regression,  $p < 0.05$ ) were taken into account, otherwise  
221 the fluxes were considered to be zero. Finally, the results from light and dark measurements ( $n =$   
222 4) were pooled because there was no significant difference between both treatments (Mann-  
223 Whitney,  $p > 0.05$ ). At the end of incubation, sediments were fixed using 10% formalin for the  
224 macrofauna counts and identification.

### 225 2.3.5. *Potential nitrification and $\text{NO}_3^-$ reduction*

226 Potential nitrification step 1 ( $\text{NH}_4^+$  oxidation to  $\text{NO}_2^-$ ) rates were measured by incubating  
227 slurries containing sodium chlorate ( $\text{NaClO}_3$ ) in order to inhibit  $\text{NO}_2^-$  oxidation (Bianchi et al.,  
228 1994; Gilbert et al., 1997). Fresh sediments (30 g) from the 0-2 cm layer were mixed  
229 homogeneously with 1 L of filtered bottom water (CA membrane 0.2  $\mu\text{m}$  Sartorius®) in  
230 polycarbonate bottles. A control triplicate of bottles contained untreated slurries only. Two mL of  
231  $\text{NaClO}_3$  (10 mM) was added to one triplicate of bottles. No substrate was added. Slurries were  
232 incubated for 20 to 24 h in the dark at in situ temperature, with loosely fitted caps to ensure oxic  
233 conditions. Each slurry was subsampled every 4 h, and subsamples were centrifuged (3920 g, 15  
234 min). The supernatant ( $\sim 10$  mL) was sampled, fixed with 50  $\mu\text{L}$   $\text{HgCl}_2$  (60 g  $\text{L}^{-1}$ ) and stored at  $4^{\circ}\text{C}$   
235 while awaiting  $\text{NO}_2^-$  analysis. The rates were calculated using a linear regression of the change in  
236  $\text{NO}_2^-$  concentrations over time. Only significant slopes (linear regression,  $p < 0.05$ ) were taken  
237 into account, otherwise the rates were considered to be zero.

238 Potential  $\text{NO}_3^-$  reduction rates were measured using flow-through reactor methods  
239 (Laverman et al., 2006). For each experiment, duplicate sediment layers (0-2 cm) were placed in  
240 Plexiglas® rings (4.2 cm inner diameter; 2 cm height). A 0.2  $\mu\text{m}$  pore size PVDF (Durapore®)  
241 membrane filter and a glass fiber backing filter (1.2 mm thickness, 4.7 cm diameter) were placed  
242 at both ends of the ring, and the resulting sediment reactor cell was enclosed by two Plexiglas®  
243 caps with in/outflow channels. Reactor cells were fed with a saline solution containing  $\text{NO}_3^-$   
244 (salinity 33, 4500  $\mu\text{M}$   $\text{KNO}_3$ ) using a peristaltic pump (Gilson Minipuls®) at a constant flow rate  
245 (2 mL  $\text{h}^{-1}$ ). The saline  $\text{NO}_3^-$  containing the input solution was bubbled with  $\text{N}_2$  for about 10 minutes  
246 to exchange and replace the existing gas phase creating an anoxic solution. Samples were collected  
247 from the outflow of the reactors every 4-6 h during 20 to 24 h. Reduction rates were determined

248 from the difference in the  $\text{NO}_3^-$  concentrations at the inflow and outflow, multiplied by the flow  
 249 rate and normalized by the volume of the reactor.

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

$$252 \text{ Pot. NRR}_T = \frac{\text{Pot. NRR}_{Tl}}{Q_{10}^{\left(\frac{Tl-T}{10}\right)}} \quad (1)$$

$$253 R = \frac{\text{Pot. NRR}_T * [\text{NO}_3^-]}{k_{NO} + [\text{NO}_3^-]} \quad (2)$$

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

### 258 2.3.6. Analytical methods

259 Sediment grain size was measured using the laser diffraction technique (Malvern 2000) on  
 260 wet sediment samples. Density and porosity were calculated from the weight loss after drying.  
 261 Sediment  $C_{\text{org}}$  and TN concentrations were measured on freeze-dried sediment using a Thermo  
 262 Scientific™ elemental analyzer after eliminating inorganic carbon using phosphoric acid (Cauwet,  
 263 1975). The BSi content was determined via the alkaline extraction method using 0.1 M sodium  
 264 carbonate ( $\text{Na}_2\text{CO}_3$ ) at 85°C (DeMaster, 1981). The extract was analyzed as dissolved silica (DSi).  
 265  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and DSi concentrations were measured using a segmented flow colorimetric  
 266 analysis according to Aminot and K  rouel (2007).  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations in the water  
 267 column were reported as the sum of  $\text{NO}_3^- + \text{NO}_2^-$ . Total dissolved N (TDN) concentrations were  
 268 analyzed using the persulfate oxidation method according to Raimbault et al. (1999) after  $\text{NH}_4^+$   
 269 removal (Burdige and Zheng, 1998). DON concentrations were determined from the difference  
 270 between TDN and DIN. Chl  $a$  concentrations in the water column were measured using  
 271 spectrophotometry according to Aminot and K  rouel (2004). Sediment Chl  $a$  concentrations were  
 272 extracted from freeze-dried sediment according to Lorenzen (1967) after an extraction with 90%  
 273 acetone and ultrasonication for 5 minutes (Sundb  ck et al., 1996). Microscopic observations of the  
 274 phytoplankton and/or microalgae dominant species in the sediment surface were conducted on  
 275 Lugol-fixed samples collected from the uppermost mm of sediments.

### 276 2.3.7. Data analysis

277 If not stated otherwise, measurements are reported here as the average  $\pm$  standard error:  
278 triplicate cores for the potential nitrification-denitrification rates and Chl *a* in the sediment surface,  
279 and four replicate cores for the benthic fluxes. Variations in the  $C_{org}$ , TN, DIN and DON  
280 concentration profiles between sampling dates and depths were analyzed using a non-parametric  
281 Kruskal-Wallis test. The inter-variable relationship was tested using a linear regression.  
282 Spearman's rank correlation was used to analyze the relationship between benthic macrofauna  
283 density, N transformation rates and benthic N fluxes for the temporal study carried out in 2015.  
284 Bottom water turbidity and  $O_2$  concentrations were also added to take the potential influence of  
285 sediment resuspension on benthic N transformation into account. For all tests, the level of  
286 significance was set to  $p < 0.05$ , and these tests were performed using the STATGRAPHIC  
287 CENTURION software (Statgraphics Technologies Inc., Version XVIII, Released 2018). The  
288 spatial distributions of  $C_{org}$ , TN, BSi and Chl *a* in the first 5 cm of sediment were visualized using  
289 the Ocean Data View software. Automatic weighted-average gridding was used to spatially  
290 interpolate the data (Schlitzer, 2002).

## 291 2.4. Reactive transport model

### 292 2.4.1. Model description

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

### 298 2.4.2. Reactions

299 This model combines general organic matter (OM) oxidation reactions with N  
300 transformation processes. Five principal reactions in the sediment N cycle are considered:  
301 ammonification, nitrification, denitrification, dissimilatory  $NO_3^-$  reduction to  $NH_4^+$  (DNRA) and  
302 anammox (Table S1).  $NH_4^+$  production (ammonification) occurs by aerobic respiration,  
303 denitrification, DNRA, dissimilatory iron reduction and sulfate reduction. Nitrification is modeled  
304 as a two-step process:  $NH_4^+$  (step 1) and  $NO_2^-$  (step 2) oxidation, respectively. Anaerobic processes  
305 (denitrification, DNRA, anammox,  $Fe(OH)_3$  and  $SO_4^{2-}$  reduction) are prevented by the presence  
306 of  $O_2$  using an inhibition term ( $F_{In}$ ). Denitrification and DNRA are modeled as a one-step process  
307 of OM oxidation using  $NO_3^-$ , with  $N_2$  and  $NH_4^+$  production, respectively, as the ultimate end result.  
308 The fraction of the  $NO_3^-$  reduction by denitrification and DNRA is assumed to be a fixed value. A  
309 term  $F_{DNRA}$  is added to distribute the fraction of  $NO_3^-$  reduction between two pathways (Canavan

310 et al., 2007; Akbarzadeh et al., 2018), and the fraction of  $\text{NO}_3^-$  reduced by denitrification is defined  
 311 as 1 minus (-)  $F_{DNRA}$  (Table S1). The  $F_{DNRA}$  value was adjusted by testing a series of values (5, 10,  
 312 25, 50, 75, 90, 95%) to obtain the fit of the  $\text{NH}_4^+$  fluxes. The retained value was 5% (see  
 313 Supplement).

#### 314 2.4.3. Boundary conditions and reaction parameters

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

326 The reaction rate parameters detailed in Table S3 were obtained following a common  
 327 procedure in the early diagenetic modeling (e.g., Wang and VanCappellen, 1996; Canavan et al.,  
 328 2006; Dale et al., 2011; Akbarzadeh et al., 2018). Values were either taken directly from the  
 329 literature or adjusted by trial and error to obtain global fits of the model to the DIN pore-water  
 330 profiles and benthic flux datasets. For further details about the original model and examples of  
 331 applications, see Canavan et al. (2006), Couture et al. (2010), Torres et al. (2015) and Akbarzadeh  
 332 et al. (2018).

#### 333 2.4.4. Transport

334 Solid chemical species in the simulated sediment column are transported by the sediment  
 335 advective velocity and particle mixing due to bioturbation, while solute chemical species are  
 336 additionally transported by molecular diffusion and bioirrigation. The change in concentration for  
 337 solute (eq. 3) and solid (eq. 4) species is described in the following mass conservation equations:

$$338 \quad \emptyset \frac{\partial(C_d)}{\partial t} = \emptyset \frac{\partial^2(D_b C_d)}{\partial x^2} + \emptyset \frac{\partial^2(D_s C_d)}{\partial x^2} - \emptyset \omega_d \frac{\partial(C_d)}{\partial x} + \emptyset \alpha(C_{d0} - C_d) + \emptyset \sum R_d = 0 \quad (3)$$

$$339 \quad (1 - \emptyset) \rho \frac{\partial(C_s)}{\partial t} = (1 - \emptyset) \rho \frac{\partial^2(D_b C_s)}{\partial x^2} - (1 - \emptyset) \rho \omega_s \frac{\partial(C_s)}{\partial x} + (1 - \emptyset) \rho \sum R_s = 0 \quad (4)$$

340 where  $C_d$  and  $C_s$  are the solute and solid species concentrations respectively,  $D_b$  is the bioturbation  
341 coefficient ( $\text{cm}^2 \text{yr}^{-1}$ ),  $D_s$  is the molecular diffusion coefficient ( $\text{cm}^2 \text{yr}^{-1}$ ),  $\alpha$  is the bioirrigation  
342 coefficient ( $\text{yr}^{-1}$ ),  $\rho$  is the sediment dry density ( $\text{g cm}^{-3}$ ),  $\omega_d$  and  $\omega_s$  are the advective or burial  
343 velocities of the pore-water and solids, respectively ( $\text{cm yr}^{-1}$ ),  $\emptyset$  is the sediment porosity, and  $R_d$   
344 and  $R_s$  are the reaction rates for the solute and solid species, respectively. The  $D_s$  values for all  
345 solute species included in the model were corrected with the bottom water temperature and  
346 sediment porosity for each measurement according to Boudreau (1997). The  $D_s$  of DON was  
347 estimated using the empirical relationship between the free solution diffusion coefficient ( $D_o$ ) and  
348 molecular weight (MW) for various organic compounds at  $25^\circ\text{C}$  in distilled water reported by  
349 Burdige et al. (1992), assuming a fixed average MW of 2500 Daltons. The obtained values were  
350 then corrected for the in situ temperature using the Stoke-Einstein equation and transformed to  $D_s$   
351 after correction for sediment porosity (Boudreau, 1997). Bioturbation and bioirrigation were  
352 described in the model by a coefficient with values that decrease with depth (Table S4).

#### 353 2.4.5. Modelling strategy

354 The model was run to steady state ( $\partial C/\partial t = 0$ ), although we are aware that coastal sediments  
355 are a more transient environment than shelf or deep-sea sediments. The steady state assumption  
356 was based on the calculation of diffusion time-scales of solutes calculated from the modified  
357 Einstein-Smoluchowski equation (Jørgensen and Revsbech, 1985). If these time-scales are smaller  
358 than the elapsed time between two campaigns, it can be assumed that the system has re-equilibrated  
359 to the new condition and can be treated in a pseudo steady state. The diffusion time-scales and  
360 residence time of DIN ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) were estimated over the first 2 cm sediment layer, where  
361 the exchange of DIN between the sediment and overlying water occurs most actively. They vary  
362 from 1 to 3 days (Table S5) and from 2 to 7 days (Table S6) for the diffusion time-scales and  
363 residence time, respectively, and were lower than the elapsed time between two campaigns  
364 (8-15 d). The diffusion time-scales and residence time for DON were approximately six to eight  
365 times greater than those for DIN (Tables S5, S6). A detailed description of the diffusion time-scale  
366 calculation is provided in the Supplement.

#### 367 2.4.6. Spatial simulation

368 Benthic DIN fluxes measured in July 2016 were simulated using the same fixed parameter  
369 values as in 2015 (Tables S3, S4).

#### 370 2.4.7. Sensitivity analyses

371 The RTM was also used as a sensitivity tool to identify the main factors (e.g., parameter  
372 set, forcing functions) that exert the most effect on benthic DIN fluxes (e.g., increase, decrease or  
373 direction change). The set of parameters tested were those related to environmental factors and  
374 suspected to have the largest effect on SWI DIN exchanges. These include the depositional fluxes  
375 of OM1, its reactivity ( $k_1$  OM1), the proportion of OM1 and OM2, the C:N ratio of OM1,  
376 bioturbation (Db), bioirrigation ( $\alpha$ ) in addition to the bottom water concentration of  $O_2$  and  $NO_3^-$   
377 (Table S7). A stepwise approach was applied by manually changing the parameter values  
378 individually and observing the model response on the  $NH_4^+$  and  $NO_3^-$  fluxes. The model was run  
379 by imposing each change in these values one by one for each sampling date of the temporal study  
380 in 2015. No combination effects between the parameters were tested in the sensitivity analysis of  
381 this present study. The response was calculated as a percentage of change in the  $NH_4^+$  and  $NO_3^-$   
382 fluxes with regard to the best fits (baseline model). The contribution of  $NO_2^-$  to the DIN fluxes  
383 was considered to be negligible (< 5% of the  $NH_4^+$  and  $NO_3^-$  fluxes) and therefore they were not  
384 included in the sensitivity analysis.

### 385 **3. Results**

#### 386 *3.1. Hydrological conditions in 2015 and 2016*

387 During both studied periods (April-September 2015 and July 2016), the seasonal variations  
388 of the physico-chemical parameters in the water column at both monitoring stations in the VB  
389 essentially depended on climatic conditions and freshwater inputs from the Loire and Vilaine rivers  
390 (Figs. 2, S2). The water column temperature varied between 10°C in March and 21°C in July with  
391 temporary stratifications of several degrees in summer. The water column  $O_2$  concentrations  
392 exhibited opposite variations to those observed for temperature. The lowest bottom water  $O_2$   
393 concentration value, close to the hypoxia threshold (63  $\mu M$ , Middelburg and Levin, 2009; Zhang  
394 et al., 2010), was detected at St. B in July 2016 (96  $\mu M$ , Table S2). Discharges from the Loire and  
395 Vilaine rivers displayed similar variations in 2015 with a flood in May, while 2016 was  
396 characterized by a flood from the Loire River in early June. Within one week after flooding, the  
397 surface water in the VB displayed drops in salinity below 28, coinciding with the peaks of  
398  $NO_3^- + NO_2^-$  concentrations (> 60  $\mu M$ ). Aside from these peaks, the surface and bottom water  
399  $NO_3^- + NO_2^-$  concentrations were ~20  $\mu M$  in spring and they gradually decreased in June to reach  
400 levels below 1  $\mu M$ . With regards to all four stations studied in July 2016, the highest  $NO_3^- + NO_2^-$   
401 concentration was recorded at St. B (Table S2).  $NH_4^+$  concentrations remained below 2  $\mu M$  in the  
402 surface water. Peaks were recorded in the bottom water in May 2015 (> 5  $\mu M$ ) and in June 2016  
403 (> 3  $\mu M$ ), decreasing gradually below 1  $\mu M$  in July. In 2016, the highest  $NH_4^+$  and minimum  $O_2$   
404 concentrations were found at St. B (Table S2). Chl *a* concentrations in the surface water peaked



405 (> 15  $\mu\text{g L}^{-1}$ ) in March and May in 2015 and in June 2016 corresponding to diatom blooms. Small  
 406 peaks ( $\sim 5 \mu\text{g L}^{-1}$ ) of diatom blooms were observed in August 2015 and October 2016 (see Retho,  
 407 2019 for additional information). For both studied periods, DON concentrations at the ND station  
 408 varied around 7  $\mu\text{M}$  throughout the year in both the surface and bottom waters (not shown).

### 409 3.2. Sediment characteristics

410 The sediment grain size distribution at the ND monitoring station was dominated by very  
 411 fine particles ( $< 63 \mu\text{m}$ ) and remained constant with depth regardless of the sampling date  
 412 (Fig. S3). At three stations sampled in July 2016, this distribution was dominated by a very fine  
 413 fraction ( $< 63 \mu\text{m}$ ) at St. B, a coarse fraction ( $> 100 \mu\text{m}$ ) at St. C and gravel at St. D (Fig. S4).  
 414 Sediment porosity and dry density varied slightly with the depth (0.85-0.79 and 2.96-2.90,  
 415 respectively) and sampling dates (0.80-0.82 and 2.60-2.96, respectively) at the ND station, and  
 416 displayed spatial variations according to the grain size distribution (Figs. S5, S6). Sediment  $C_{\text{org}}$   
 417 and TN concentrations at the ND monitoring station were not significantly different according to  
 418 the date and depth ( $p > 0.05$ ), with median values of 1,168 ( $\sim 1.6\%$  DW) and 120  $\mu\text{mol g}^{-1}$  ( $\sim 0.2\%$   
 419 DW) for  $C_{\text{org}}$  and TN, respectively (Figs. 3a, 3b). The median of the C:N molar ratio varied  
 420 between 9.2 in the first top cm and 10.8 at depth (Fig. 3c).  $C_{\text{org}}$ , TN and BSi concentrations at the  
 421 sediment surface (5 cm) ranged respectively from 221 to 2,095, 25 to 233, and 10 to 215  $\mu\text{mol g}^{-1}$   
 422 and were higher in the north-western part of the bay than in the south-eastern part (Fig. S7).

423 At the ND monitoring station in 2015, the Chl *a* content in the first cm of sediment slightly  
 424 increased from  $8.9 \pm 1.4 \mu\text{g g}^{-1}$  in April to  $11.9 \pm 1.5 \mu\text{g g}^{-1}$  in June (Fig 2d), it decreased in August  
 425 ( $4.6 \pm 0.3 \mu\text{g g}^{-1}$ ) and then slightly increased in September ( $8.7 \pm 0.9 \mu\text{g g}^{-1}$ ). The highest values  
 426 in April and June were found subsequent to spring diatom blooms. Benthic Chl *a* displayed a  
 427 spatial variation similar to that of  $C_{\text{org}}$ , TN and BSi (Fig. S7), with the highest concentration  
 428 observed at St. B (Fig. 2h). Microscopic observations of the sediment surface in 2015 revealed  
 429 abundant benthic diatoms (*Pleurosigma* sp., *Navicula* spp., *Nitzschia* spp.) and organic debris in  
 430 April and June, while there was less organic debris, some phytoplanktonic (*Thalassiosira* sp.) and  
 431 tychoplanktonic (*Paralia* sp.) diatoms and many empty cells in August and September (Fig. S9).  
 432 Overall, on average, the macrofauna density in the incubated sediment cores of the ND monitoring  
 433 station in 2015 were  $< 1,500 \text{ ind. m}^{-2}$ , dominated by *Nucula nitidosa* (a small bivalve), *Amphiura*  
 434 *filiformis* (a brittle star) and *Sternaspis scutata* (polychaeta) (Table S8). No significant correlations  
 435 were observed between the benthic macrofauna density and benthic N transformation rates, and  
 436 measured N fluxes (Table S9).

### 437 3.3. Oxygen and dissolved N pore-water profiles



438 Irrespective of the sampling date, the O<sub>2</sub> concentration decreased rapidly within the first  
439 2 mm and was undetectable below this depth (Fig. 4a). In 2015, pore-water NH<sub>4</sub><sup>+</sup> concentrations  
440 at the ND station showed positive concentration gradients in the first 5 cm (Fig. 4b) and nearly  
441 constant values around 300 μM below 5 cm, except in two cores (June 24<sup>th</sup> and August 5<sup>th</sup> with a  
442 value exceeding 1200 μM). NH<sub>4</sub><sup>+</sup> concentration profiles did not show any significant differences  
443 between sampling dates ( $p > 0.05$ ). In 2015, pore-water DON concentrations at the ND station  
444 were higher than those in the bottom water, with no significant difference between sampling dates  
445 ( $p > 0.05$ , Fig. S8a). Steep positive concentration gradients were observed in the top 1 cm, which  
446 became weaker in the layer below. The global mean pore-water DON concentration was higher  
447 than that of NH<sub>4</sub><sup>+</sup> in the first 5 cm layer and lower below (Fig. S8b). Pore-water NO<sub>3</sub><sup>-</sup>  
448 concentrations at the ND station displayed negative concentration gradients in April 2015 (Fig.  
449 4c). Peaks of NO<sub>3</sub><sup>-</sup> were observed in the top first 0.5 cm from June to September 2015, with a high  
450 value up to 12 μM on August 5<sup>th</sup>. Pore-water NO<sub>2</sub><sup>-</sup> concentrations were low (< 2 μM). Peaks of  
451 NO<sub>2</sub><sup>-</sup> maxima were generally observed in the first 1 cm, which decreased gradually below  
452 (Fig. 4d).

#### 453 3.4. Dissolved N fluxes at the SWI

454 NH<sub>4</sub><sup>+</sup> fluxes measured at the ND station in 2015 varied between  $36 \pm 22 \mu\text{mol m}^{-2} \text{h}^{-1}$  in  
455 April and  $50 \pm 19 \mu\text{mol m}^{-2} \text{h}^{-1}$  in June (Fig. 5a), and were 10 times lower in August and September  
456 ( $5.3 \pm 4.5 \mu\text{mol m}^{-2} \text{h}^{-1}$ ). Maximum NH<sub>4</sub><sup>+</sup> fluxes were found after spring blooms, as observed for  
457 the sediment Chl *a* content (Fig. 2d). The calculated diffusive NH<sub>4</sub><sup>+</sup> fluxes, based on pore-water  
458 concentration gradients in the first cm measured in 2015, were approximately 50% of the measured  
459 fluxes, with little variation over time (Table S6). In 2016, NH<sub>4</sub><sup>+</sup> fluxes were three times higher  
460 than those measured in June 2015 and displayed spatial variation, with maximum values observed  
461 at St. A and St. B. NH<sub>4</sub><sup>+</sup> fluxes measured at the ND station in 2015 were positively correlated to  
462 the Chl *a* content in the first cm sediment layer ( $r = 0.82$ ,  $p < 0.05$ , Fig. 6a). Benthic DON fluxes  
463 measured at the ND station in 2015 had similar values and displayed a temporal variation similar  
464 to those of NH<sub>4</sub><sup>+</sup> (Fig. 5b), with which they were positively correlated ( $r = 0.82$ ,  $p < 0.05$ , Fig. 6b).  
465 DON fluxes were close to zero in August and September. In 2016, the DON fluxes were in the  
466 same order of magnitude as those measured in 2015. Diffusive DON fluxes represented  
467 approximately 10% of the measured DON fluxes in spring and were higher in summer than in  
468 spring, with little variation over the sampling dates (Table S6). At the ND station, NO<sub>3</sub><sup>-</sup> fluxes  
469 were directed towards the sediments in April 2015, with an average rate of  $-17 \pm 5 \mu\text{mol m}^{-2} \text{h}^{-1}$   
470 (Fig. 5c), coinciding with high NO<sub>3</sub><sup>-</sup> concentrations in the bottom water (Fig. 2c). For the rest of  
471 the studied period, NO<sub>3</sub><sup>-</sup> was released from the sediments except in August 2015 when the values

472 were close to zero ( $< 0.1 \mu\text{mol m}^{-2} \text{h}^{-1}$ ). The release of  $\text{NO}_3^-$  represented approximately 25% of the  
473  $\text{NH}_4^+$  fluxes. In 2016, the measured  $\text{NO}_3^-$  fluxes varied between the stations, with a flux towards  
474 the sediments particularly at St. B (Fig. 5c), coinciding with high bottom water  $\text{NO}_3^-$   
475 concentrations (Table S2). The measured  $\text{NO}_2^-$  fluxes remained below  $5.0 \mu\text{mol m}^{-2} \text{h}^{-1}$ , maximum  
476 values were observed in June and September in 2015 and there was a flux towards the sediments  
477 at St. B in 2016 (Fig. 5d). For all benthic flux values, there was no significant difference between  
478 measurements during spring and neap tides (Mann-Whitney,  $p > 0.05$ ).

### 479 3.5. *Potential nitrification and $\text{NO}_3^-$ reduction rates*

480 In 2015, the potential rates of nitrification measured at the ND station increased from April  
481 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 ( $14.0 \pm$   
482  $2.5 \mu\text{mol N m}^{-2} \text{h}^{-1}$ ) and September ( $12.0 \pm 1.3 \mu\text{mol N m}^{-2} \text{h}^{-1}$ ) to values comparable to those in  
483 April (Table 2). The potential nitrification rates measured in July 2016 were lower than those  
484 measured in 2015. The potential  $\text{NO}_3^-$  reduction rates measured in 2015 increased from April ( $52.4$   
485  $\pm 6.6 \mu\text{mol N m}^{-2} \text{h}^{-1}$ ) to their maximum values in June ( $119.0 \pm 24.8 \mu\text{mol N m}^{-2} \text{h}^{-1}$ ; Table 2).

### 486 3.6. *Model outputs*

#### 487 3.6.1. *Organic matter mineralization and N transformation rates*

488 Aerobic respiration was the major pathway of labile OM (OM1) mineralization (Table 1),  
489 with rates displaying similar temporal and spatial variations to those for OM1 depositional fluxes  
490 (Table S2). Aerobic respiration represented up to 75% of the total rates. The anaerobic OM  
491 mineralization pathway was dominated by  $\text{SO}_4^{2-}$  reduction, with the highest value at St. B in 2016.  
492 The reduction of  $\text{NO}_3^-$  and  $\text{Fe}(\text{OH})_3$  activities was less significant ( $\sim 10\%$  of the total rates for both  
493 processes). The modeled nitrification rates (step 1) were similar to the measured potential rates  
494 and displayed similar temporal and spatial variations (Table 2). In 2015, the model-predicted  
495 denitrification rates revealed a temporal variation contrary to the measured potential rates and  
496 model-predicted nitrification rates, with the highest rates in April decreasing over the studied  
497 period. In 2016, St. B displayed the highest denitrification rates. Adjusting the  $F_{\text{DNRA}}$  value to 5%  
498 of all of the reduced  $\text{NO}_3^-$  resulted in the best fit of the  $\text{NH}_4^+$  fluxes. When values higher than 5%  
499 were tested, this resulted in an overestimation of the  $\text{NH}_4^+$  fluxes (Fig. S10). The anammox rates  
500 were quantitatively low ( $< 0.2 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) compared to the other N transformation processes  
501 with little variation over time and between stations.

#### 502 3.6.2. *Modeled pore-water profiles and benthic fluxes*

503 The reactive transport model reproduced a good fit for most O<sub>2</sub> and DIN pore-water  
504 concentration profiles at the ND station in 2015 (Fig. 4). However, some discrepancies were  
505 observed, such as the O<sub>2</sub> and NH<sub>4</sub><sup>+</sup> profiles on August 5<sup>th</sup> and September 8<sup>th</sup>, as well as the NO<sub>3</sub><sup>-</sup>  
506 peak on June 24<sup>th</sup>. For both studied periods (2015 and 2016), the simulated NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> fluxes  
507 showed a good fit with the measured fluxes (Fig. 5), with differences still observed within the  
508 standard error of the measured values: 4.9, 0.6 and 9.9 μM m<sup>-2</sup> h<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> fluxes,  
509 respectively.

### 510 3.6.3. Sensitivity analysis

511 The sensitivity analysis showed that the OM1 pool input had the largest effect on the  
512 magnitude of the NH<sub>4</sub><sup>+</sup> fluxes for each sampling date (Fig. 7). NH<sub>4</sub><sup>+</sup> fluxes increased with the  
513 increase in OM1 input and decreased with changes in the proportion of the OM pool, which  
514 corresponded to decreased OM1 fluxes by a factor of 3-4. Minor effects on the NH<sub>4</sub><sup>+</sup> fluxes were  
515 observed (< 10%) for the other scenarios of change in the environmental factor-related model  
516 parameters (Fig. 7). For the NO<sub>3</sub><sup>-</sup> fluxes, changes in the bottom water NO<sub>3</sub><sup>-</sup> concentrations and the  
517 anoxic condition were the main factors influencing flux magnitude and direction (Fig. 8). In April,  
518 NO<sub>3</sub><sup>-</sup> sediment inward fluxes were increased by increasing the bottom water NO<sub>3</sub><sup>-</sup> concentrations  
519 and by eliminating O<sub>2</sub> from the bottom water (Figs. 8a, 8b). In June, August and September (Figs.  
520 8c-8f), benthic NO<sub>3</sub><sup>-</sup> fluxes reverted from outward to inward when the bottom water O<sub>2</sub> was set to  
521 zero and the bottom water NO<sub>3</sub><sup>-</sup> concentrations were increased.

## 522 4. Discussion

### 523 4.1. OM deposition fluxes and diagenetic pathways

524 Temporal and spatial variations of the benthic dissolved N fluxes in Vilaine Bay (VB) are  
525 mainly explained by OM remineralization at the SWI. The model accurately simulated temporal  
526 and spatial variations in benthic fluxes by setting high rates of OM decomposition in the upper  
527 sediment layer and by essentially varying the input of labile OM (OM1), which constitutes the  
528 main fraction (~80%) of the total OM depositional flux. This proportion of OM1 is comparable to  
529 that obtained by a modeling study carried out on the Rhone River delta sediments (Pastor et al.,  
530 2011; Ait Ballagh et al., 2021), and suggests that most OM inputs into the sediment surface in the  
531 VB consists of labile matter. This fraction is characterized in the model by the first-order  
532 decomposition rate constant, with this value (16 yr<sup>-1</sup>) falling within the range of those values (3-  
533 33 yr<sup>-1</sup>) reported in Westrich and Berner (1984) from incubation experiments using fresh  
534 planktonic material. The decomposition rate constant of OM2 (0.1 yr<sup>-1</sup>) lies in the range of those

535 values reported in the literature (see Paraska et al., 2014; Ait Ballagh et al., 2021), which may  
536 correspond to degraded algal cells, containing organic acids and lipids, with a lower degradability  
537 than fresh planktonic material (Cowie et al., 1992; Komada et al., 2013). The deposition fluxes of  
538 OM1 in this study ( $275\text{-}1,800 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ ) are in the range of those reported from  
539 anthropogenic impacted estuarine and coastal waters, such as the Aulne and Elorn estuaries ( $840\text{-}$   
540  $3,580 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ ; Khalil et al., 2018), Rhône River delta ( $260\text{-}5,475 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ ; Pastor et  
541 al., 2011), and Loch Creran sea ( $73\text{-}1,060 \mu\text{mol cm}^{-2} \text{yr}^{-1}$ ; Brigolin et al., 2009). The highest OM1  
542 deposition flux values in the VB (Tables S2) correspond to the maximum Chl *a* contents measured  
543 in the sediment surface (Fig. 2), suggesting that this OM has a plant origin (Szymczak-Żyła et al.,  
544 2011).

545 The gradual decrease of  $\text{O}_2$  and low  $\text{O}_2$  penetration depth suggest rapid  $\text{O}_2$  consumption  
546 related to OM degradation (Pastor et al., 2011; Rabouille et al., 2021). This is consistent with our  
547 model results, which indicate that OM, especially the OM1 pool, was decomposed primarily at the  
548 sediment surface using  $\text{O}_2$  (Table 1). The difference between the measured and modeled  $\text{O}_2$   
549 penetration depth on August 5<sup>th</sup> and September 8<sup>th</sup> (Fig. 4a) could not be explained by the  
550 limitation of the OM input; if this is the case, the  $\text{NH}_4^+$  fluxes would be underestimated by the  
551 model. We ascribe this discrepancy to the effects of temperature on microbial metabolism related  
552 to the lack of temperature control during the sediment core  $\text{O}_2$  profiling in summer, which may  
553 have increased  $\text{O}_2$  consumption and OM mineralization (Glud et al., 1994; Mogg et al., 2017). In  
554 the model, the remaining OM1 and OM2 pool was essentially mineralized through the reduction  
555 of  $\text{SO}_4^{2-}$  (Table 1). This relatively high contribution of  $\text{SO}_4^{2-}$  reduction, compared to  $\text{NO}_3^-$  and  
556  $\text{Fe}(\text{OH})_3$ , is in agreement with the high availability of  $\text{SO}_4^{2-}$  at the upper boundary condition  
557 relative to  $\text{NO}_3^-$  and  $\text{Fe}(\text{OH})_3$  availability (Canfield, 1993). The contribution to OM decomposition  
558 by  $\text{SO}_4^{2-}$  reduction increases with increasing OM deposition fluxes and particularly when the  
559 bottom water  $\text{O}_2$  concentration decreases close to the hypoxia level, as was the case at St. B in the  
560 summer of 2016. This rapid oxic OM mineralization at the SWI plays a critical role in controlling  
561 the bottom water  $\text{O}_2$  concentrations as well as benthic nutrient recycling.

#### 562 4.2. *Benthic N transformations: dominance of aerobic processes*

563 The temporal (and spatial) variations in the benthic fluxes and pore-water concentrations  
564 of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are consistent with those in the process rates and comparable to those reported  
565 in coastal ecosystems subjected to seasonality with regards to the  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations  
566 in the water column (Jensen et al., 1990; Kemp et al., 1990; Kitidis et al., 2017). The negative  
567 concentration gradients of  $\text{NO}_3^-$  in April 2015, due to large  $\text{NO}_3^-$  concentrations in the water

568 column, are in agreement with inward sediment fluxes, which can be attributed to  $\text{NO}_3^-$  uptake via  
569 denitrification (Jorgensen and Sorensen, 1988). These inward sediment  $\text{NO}_3^-$  fluxes seem  
570 proportional to the  $\text{NO}_3^-$  concentrations in the bottom water. The shift in the  $\text{NO}_3^-$  flux direction  
571 in June 2015 appears to be the result of increasing nitrification, as shown by the  $\text{NO}_3^-$  concentration  
572 peaks in the upper 0.5 cm sediment layer and the bottom water  $\text{NO}_3^-$  depletion (Jensen et al., 1990),  
573 and is in agreement with the measured potential nitrification rates. The temporal and spatial co-  
574 variations between the measured potential nitrification and  $\text{NO}_2^-$  fluxes, as well as the peaks of  
575  $\text{NO}_2^-$  in the first 1 cm oxic sediment layer, emphasize the role of nitrification in benthic  $\text{NO}_2^-$   
576 production (Mordy et al., 2010).

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

599 4.3. *Importance of DON in benthic N cycling*

600 The DON pore-water concentrations in the VB sediments are within the same range as the  
601 DIN (mainly  $\text{NH}_4^+$ ) concentrations and are in the same order of magnitude as those reported in the  
602 Chesapeake Bay (Burdige and Zheng, 1998) and the St. Lawrence estuary (Alkhatib et al., 2013).  
603 The concentration gradients in the DON pore-water profiles were lower than those of  $\text{NH}_4^+$  below  
604 a depth of 2 cm (Fig. S7), suggesting that DON below this sediment layer may largely consist of  
605 refractory compounds slowly producing  $\text{NH}_4^+$  in the pore-water (Burdige, 2001; Burdige et al.,  
606 2016). The absence of a temporal variation in the DON pore-water profiles indicates that DON  
607 cycling in the pore-water, as for  $\text{NH}_4^+$  (see below), is relatively independent of seasonal events in  
608 the water column, particularly fresh OM inputs from phytoplankton blooms (Hansen and  
609 Blackburn, 1992). The positive concentration gradients in the upper 1 cm layer imply DON  
610 production and release to the overlying water by diffusion (Alkhatib et al., 2013). However, the  
611 weak concentration gradient in the DON pore-water profiles below a depth of 2 cm and much  
612 higher DON diffusion time-scales and residence time than those of DIN converge to explain low  
613 diffusive DON fluxes (see the Supplementary Material). As observed for  $\text{NH}_4^+$  (see below),  
614 temporal variations in the diffusive DON fluxes did not reflect large fluctuations in the measured  
615 fluxes via incubation.

616 The benthic DON fluxes measured in the VB represent up to 50% of the dissolved N fluxes  
617 (Fig. 5). Although data on benthic DON flux measurements remain scarce in the literature, it  
618 appears that their values become truly quantifiable only after the sedimentation of fresh OM  
619 (Burdige and Komada, 2002; Eyre and Ferguson, 2002). Parallel temporal and spatial variations  
620 in the benthic DON and  $\text{NH}_4^+$  fluxes infer that DON was released during OM degradation in the  
621 sediment surface. Our measurements confirm those of Hansen and Blackburn (1992), showing that  
622 the addition of diatom material to the sediment during laboratory experiments leads to a release of  
623 DON to the overlying water, as significant as that of  $\text{NH}_4^+$ . However, the importance of DON  
624 fluxes in benthic N cycling dynamics remains understudied in early diagenetic modeling studies  
625 (Paraska et al., 2014). This omission of DON in the RTM is likely related to the uncertainty in  
626 estimating its diffusion coefficient (Alperin et al., 1999; Alkhatib et al., 2013), as well as to the  
627 scarcity of data concerning benthic DON fluxes and pore-water concentrations (Boynton et al.,  
628 2018). Given the significance of DON release in this study, the integration of DON in the RTM  
629 may constitute an improvement in order to better estimate the role of this compound in the benthic  
630 N budget.

631 4.4. *Phytoplankton-derived OM mineralization at the SWI as the main driver of benthic N fluxes*



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

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

650 Benthic macrofauna rework sediments, favoring their homogenization and oxygenation,  
651 and accelerating the remineralization of sedimentary OM (Shull, 2019). The excretion of dissolved  
652 N by benthic macrofauna can also contribute to the enrichment of pore- water and overlying waters  
653 with  $\text{NH}_4^+$  and DON (Gardner et al., 1993; Yamamuro and Koike, 1998). Among the three main  
654 taxa observed in the incubated cores, *Amphiura filiformis* and *Sternaspis scutata* may favor  
655 biodiffusion, whereas *Nucula nitidosa* is instead considered to be a surficial modifier (Queiros et  
656 al., 2013). Although the densities of these three species are moderate in the VB (Le Bris and  
657 Glémarec, 1996; Ehrhold et al., 2008), they probably enhanced sedimentary OM recycling (Follum  
658 and Gray, 1987). The exceptionally high  $\text{NH}_4^+$  concentrations in two cores (June 24<sup>th</sup> and  
659 August 5<sup>th</sup>), found also for phosphate and silicate (Ratmaya, 2018), could be explained by  
660 heterogeneities linked to macrofaunal activity. However, no significant correlations between  
661 macrofauna density and benthic N transformation rates or N fluxes were found. Additionally, the  
662 low bioturbation and bioirrigation coefficients used in the model were sufficient to adjust benthic  
663 DIN fluxes, which may indicate the minor influence of benthic macrofaunal activities on benthic  
664 N cycling. Although the contribution of benthic macrofauna to benthic dissolved N fluxes could



665 not be quantified in this study, it probably represents a limited part of the fluxes from the sediment  
666 to the water column, but this still needs to be confirmed.

667 The mineralization of OM in the sediment leads to a build-up of  $\text{NH}_4^+$  in the sediment pore-  
668 water resulting in the benthic efflux of  $\text{NH}_4^+$  (Herbert, 1999; Schulz, 2006). The absence of a  
669 significant change in the  $\text{NH}_4^+$  pore-water profiles during the temporal study carried out in 2015  
670 agrees with the lack of temporal variations in diffusive  $\text{NH}_4^+$  fluxes, implying that a large part of  
671 deposited OM is decomposed at the sediment surface before integrating the sediment column, as  
672 suggested by Rabouille et al. (2021) for the Louisiana shelf. Relatively low diffusive  $\text{NH}_4^+$  fluxes  
673 compared to the measured fluxes confirms that significant  $\text{NH}_4^+$  production took place through  
674 aerobic OM mineralization at the SWI in contact with the bottom water. This pattern is consistent  
675 with the relatively low  $C_{\text{org}}$  values (1.6% DW) of the VB sediments, compared to other eutrophic  
676 coastal ecosystems, such as Kiel Bight (3.0-5.0% DW; Balzer et al., 1986) and Aarhus Bay (2.5-  
677 3.8% DW; Dale et al., 2008).

678 In shallow coastal environments, sediment resuspension due to tides, swells and wind may  
679 influence benthic fluxes of dissolved substances (Boynton et al., 2018). The absence of a  
680 significant difference between benthic flux measurement values during spring and neap tides  
681 suggests the minor influence of tidal cycles on SWI DIN and DON exchanges. Sanford et al.  
682 (1991) reported that tides had a minor influence on sediment resuspension in the Chesapeake Bay  
683 compared to strong wind episodes. In the VB, large sediment resuspension occurs generally in  
684 winter in relation with strong hydrodynamic conditions, e.g., during winter storms where several  
685 centimeters of sediment can be resuspended (Goubert et al., 2010). This is reflected by the constant  
686 depth profiles of granulometry,  $C_{\text{org}}$  and TN (Bunke et al., 2019). Moreover, sediment resuspension  
687 in the VB is often accompanied by high turbidity values in the bottom waters (>100 NTU, Retho  
688 et al. 2020). Nevertheless, turbidity values measured at the ND station during the study period  
689 remained low (<10 NTU). The persistence of the concentration gradient for the dissolved  
690 compounds in the pore-water suggests that sediments have not undergone strong resuspension  
691 during the study period. In addition, we did not find any significant correlation between bottom  
692 water turbidity and benthic N transformation rates or N fluxes (Table S9).

693 Different types of OM can be deposited in the VB sediments from external sources. The  
694 riverine input of particulate OM is limited due to efficient recycling in the Loire estuary (Relexans  
695 et al., 1988) and the presence of a dam in the Vilaine estuary (Traini et al., 2015). Phytoplankton  
696 from oceanic waters may not be substantial due to lower biomass than in the VB (Ratmaya et al.,  
697 2019). The positive correlation between the measured  $\text{NH}_4^+$  fluxes and sediment Chl *a*

698 concentrations in the VB (Fig. S10a) indicates that benthic  $\text{NH}_4^+$  fluxes are dependent on the  
699 sedimentation of the phytoplankton (Cowan and Boynton, 1996). This has been shown previously  
700 for different coastal ecosystems such as Aarhus Bay (Jensen et al., 1990) and San Francisco Bay  
701 (Caffrey, 1995). The observations in the water column and sediment surface, together with the  
702 BSi,  $C_{\text{org}}$  and TN content in the top first five cm of the sediment confirm that diatom blooms are  
703 the main source of OM to the VB sediments, with the north-western part as the favored deposition  
704 area (Le Bris and Glémarec, 1996; Ehrhold, 2014).

705 Diatom blooms in the VB are predominantly driven by nutrient inputs associated with  
706 floods from the Loire and Vilaine rivers (Figs. 2, S2). After blooms appear, the deposited diatom-  
707 derived OM is mostly mineralized aerobically at the SWI within 2-3 weeks and recycled directly  
708 to the water column as dissolved inorganic ( $\text{NH}_4^+$ ) and organic N (Fig. 9a). When blooms are  
709 absent, benthic dissolved N fluxes decrease and may be supported essentially by a diffusion from  
710 the deeper sediment layer, especially for DIN (Fig. 9b). For both situations, the diffusion of DON  
711 from a deeper sediment layer is very low, implying that DON is instead gradually mineralized to  
712  $\text{NH}_4^+$  in the pore-water. In addition, decomposition of the deposited phytoplanktonic material can  
713 rapidly consume  $\text{O}_2$  at the sediment surface (within hours to several days) and can be followed by  
714  $\text{O}_2$  depletion in the bottom water, especially during summer. This pattern may also be valid for  
715 other coastal ecosystems with similar characteristics as the VB, as was reported in oxic sediments  
716 from the North Sea (De Borger et al., 2021) and in the seasonally hypoxic sediments of the northern  
717 Gulf of Mexico (Rabouille et al., 2021). The overall results lead to conclude that temporal and  
718 spatial variations of the benthic DIN and DON fluxes in the VB depend predominantly on the  
719 sedimentation of the diatom blooms rather than on the composition of the sediment column itself.

#### 720 4.5. *Ecological implication of benthic DIN fluxes compared to riverine inputs*

721 DIN constitute the limiting nutrient of eutrophication during summer in the VB (Ratmaya  
722 et al., 2019). One can wonder how sedimentary and riverine sources contribute to summer DIN  
723 budget of the VB. These DIN flux data can be used to give a rough estimate of the role played by  
724 sediments in this budget for two different summer scenarios, low water and flood situations in  
725 2015 and 2016 respectively. Benthic DIN fluxes measured in summer 2015 (June-September) at  
726 the ND station brings around 225 t N to the VB water column, when extrapolated to the surface of  
727 the muddy area ( $\sim 40\%$  of the total area, 220  $\text{km}^2$ , Ehrhold, 2014). For the same period, the Loire  
728 delivers around 820 t N by applying a dilution of 20-fold at its outlet, while the Vilaine carried up  
729 to 1,120 t N to the VB water column. For this low water scenario, benthic DIN inputs therefore  
730 represent around 15% of the riverine inputs. For the summer flood scenario in 2016, benthic DIN

731 inputs (~360 t N) represent up to 30% of DIN riverine inputs, estimated for 430 t N from the  
732 Vilaine and 930 t N from the Loire by applying the same dilution. This higher contribution of  
733 benthic DIN source during the summer flood scenario is related to the higher benthic DIN  
734 recycling due to higher OM inputs to the sediment surface compared to low water scenario. Despite  
735 its uncertainty, this rough estimate suggest that sediments constitute a non-negligible source of  
736 DIN to the VB water column, aggravating the effect of riverine DIN inputs. The use of a 3D  
737 ecological model (Ménésguen et al., 2019), that takes hydrodynamics into account is required to  
738 better estimate the contribution of each DIN source to the VB water column.

## 739 **5. Conclusion and perspectives**

740 The cross-interpretation of the field observations, laboratory measurements and modeling  
741 approach indicate that OM inputs from diatom blooms are the key factor controlling benthic N  
742 cycling in the VB. The rapid decomposition of the deposited diatom material at the SWI may be  
743 followed by the depletion of the O<sub>2</sub> concentration in the bottom water, especially when blooms  
744 occur in summer. Using the same fixed model parameters, the RTM can be used to interpret both  
745 the time series and the spatial dataset for the benthic N cycle as a function of the OM deposition  
746 rate and the sedimentary environments. The dynamics of the DON fluxes still need to be  
747 investigated before they can be integrated into the RTM. The interpolation of benthic DIN flux  
748 measurement to the surface area of the VB, suggests that sediments represent a non-negligible  
749 source of DIN compared to riverine inputs.

750 In order to obtain a seasonal and spatial description of the biogeochemical processes in  
751 both the sediment and water column, the results presented in this study must be integrated into a  
752 3D ecological model (see Ménésguen et al., 2019 for ECOMARS3D model). Our key results  
753 provide the dataset to parameterize the sediment biogeochemical processes (e.g., nutrient  
754 transformation, elimination, and/or immobilization) in the ecological model. This integration will  
755 improve the ecological model in order to more accurately predict the sequence of river floods,  
756 phytoplankton blooms, sedimentation, benthic mineralization and bottom water hypoxia in the  
757 VB.

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1164 **Figure captions**

1165 **Fig. 1** Location of the study area. The off-shore limit of the Vilaine Bay is indicated by a dashed  
 1166 line. The bathymetry (GEBCO bathymetry data in Ocean Data View) is displayed using the colors  
 1167 corresponding to the scale on the right of the graph. The sampling location of the sediment cores  
 1168 is indicated by red circles, the Nord Dumet monitoring station for the temporal study carried out  
 1169 from April to September 2015 and St. A, B, C, & D for the spatial study carried out in July 2016.  
 1170 The green squares correspond to the REPHY monitoring stations. The black dots are the spatial  
 1171 sampling points of the superficial sediments in April 2016.

1172 **Fig. 2** Variations in the salinity and river discharge (Loire and Vilaine) (a, e), temperature and  
 1173 dissolved O<sub>2</sub> (b, f), NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (c, g), Chl *a* in the water column and sediment surface  
 1174 (d, h), at the Nord Dumet monitoring station (St. A) in 2015 (left) and 2016 (right) from January  
 1175 to December. Dashed-dotted horizontal line (panels b & f): hypoxia threshold (63 μM; Middelburg  
 1176 and Levin, 2009; Zhang et al., 2010). Vertical lines: dates of the sediment investigations. ST and  
 1177 NT: spring and neap tides. Color symbols: Chl *a* concentration in the first top cm of the sediment  
 1178 ( $n = 3$ ).

1179 **Fig. 3** Depth profiles of the organic carbon, C<sub>org</sub> (a), total nitrogen, TN (b) and C:N ratios (c) for  
 1180 the triplicate sediment cores at the Nord Dumet monitoring station (St. A) for the temporal study  
 1181 from April to September 2015. No measurements were taken on April 15<sup>th</sup>.

1182 **Fig. 4** Modeled (red curves) and measured (symbols) pore-water concentration profiles of O<sub>2</sub> (a),  
 1183 NH<sub>4</sub><sup>+</sup> (b), NO<sub>3</sub><sup>-</sup> (c) and NO<sub>2</sub><sup>-</sup> (d) in the temporal study from April to September 2015 conducted at  
 1184 the Nord Dumet monitoring station (St. A). The symbols correspond to the results from the  
 1185 triplicate sediment cores for the nutrients and the O<sub>2</sub> measurements. Dashed lines: sediment-water  
 1186 interface (SWI).

1187 **Fig. 5** Measured and simulated NH<sub>4</sub><sup>+</sup> (a), DON (b), NO<sub>3</sub><sup>-</sup> (c) and NO<sub>2</sub><sup>-</sup> (d) fluxes across the SWI  
 1188 in the Vilaine Bay during the temporal study carried out from April to September 2015 conducted  
 1189 at the Nord Dumet monitoring station (St. A, left) and the spatial study carried out in July 2016  
 1190 (right). The error bars represent the standard error of the mean ( $n = 4$ ). There were no model  
 1191 simulations for the DON fluxes.

1192 **Fig. 6** Relationship between the measured NH<sub>4</sub><sup>+</sup> fluxes and Chl *a* content (a), NH<sub>4</sub><sup>+</sup> and DON  
 1193 fluxes (b) for the temporal study carried out in 2015. The equation and the regression line were  
 1194 obtained from linear regression.

1195 **Fig. 7** Model sensitivity analysis showing the response of the benthic NH<sub>4</sub><sup>+</sup> fluxes during the  
 1196 temporal study carried out from April to September 2015 (a-f) to different scenarios of change in  
 1197 environmental factor-related model parameters. The response was calculated as a percentage of  
 1198 change in the NH<sub>4</sub><sup>+</sup> fluxes with regard to the baseline simulation (zero dashed line). The factors  
 1199 lying furthest from the zero dashed line are those causing the greatest change in the NH<sub>4</sub><sup>+</sup> fluxes.  
 1200 Anoxic: zero bottom water O<sub>2</sub> concentrations; BW NO<sub>3</sub><sup>-</sup> = 10x [100x]: increase in the bottom  
 1201 water NO<sub>3</sub><sup>-</sup> concentrations by 10 fold or 100 fold for August and September; OM1 2x [3x]:  
 1202 increase in the deposition of OM1 by 2 fold (or 3x for August); OM1 <=> OM2: inverting the  
 1203 proportion of OM1 and OM2; k1 OM1 = 2x: increase in the rate constant for the aerobic oxidation  
 1204 of OM1 by 2 fold); k1 OM1 = 1/2 x decrease in the rate constant for the aerobic oxidation of OM1  
 1205 by one-half; C/N OM1 = 106/16: imposed change in the C/N ratio compared to that in living  
 1206 phytoplankton i.e., Redfield ratio; Db = 10x: increase in the bioturbation coefficient by 10 fold; α  
 1207 = 10x: increase in the bioirrigation coefficient by 10 fold.

1208 **Fig. 8** Model sensitivity analysis showing the response of the benthic  $\text{NO}_3^-$  fluxes during the  
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1210 environmental factor-related model parameters. The response was calculated as a percentage of  
1211 change in the  $\text{NO}_3^-$  fluxes with regard to the baseline simulation (zero dashed line). The factors  
1212 lying furthest from the zero dashed line are those causing the greatest change in the  $\text{NO}_3^-$  fluxes.  
1213 Anoxic: zero bottom water  $\text{O}_2$  concentrations; BW  $\text{NO}_3^- = 10x$  [100x]: increase in the bottom water  
1214  $\text{NO}_3^-$  concentrations by 10 fold or 100 fold for August and September; OM1 2x [3x]: increase in  
1215 the deposition of OM1 by 2 fold (or 3x for August); OM1  $\rightleftharpoons$  OM2: inverting the proportion of  
1216 OM1 and OM2;  $k_1$  OM1 = 2x: increase in the rate constant for the aerobic oxidation of OM1 by  
1217 2 fold);  $k_1$  OM1 = 1/2 x decrease in the rate constant for the aerobic oxidation of OM1 by one-  
1218 half; C/N OM1 = 106/16: imposed change in the C/N ratio compared to that in living  
1219 phytoplankton i.e., Redfield ratio;  $D_b = 10x$ : increase in the bioturbation coefficient by 10 fold;  $\alpha$   
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1221 **Fig. 9** Summary diagram of the benthic N fluxes in the Vilaine Bay for two distinct situations: (a)  
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1225 DON stand for dissolved inorganic and organic N, respectively. The different arrow sizes indicate  
1226 the magnitude of the OM input for each pool, as well as its recycling into DIN (mostly  $\text{NH}_4^+$ ) and  
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1228 each pathway (aerobic and anaerobic), estimated from the model rate constants of OM1 and OM2  
1229 (Table S3) and the residence time of solutes (Table S6). Where the DON diffusion from pore-water  
1230 is questioned, this is indicated by a question mark.

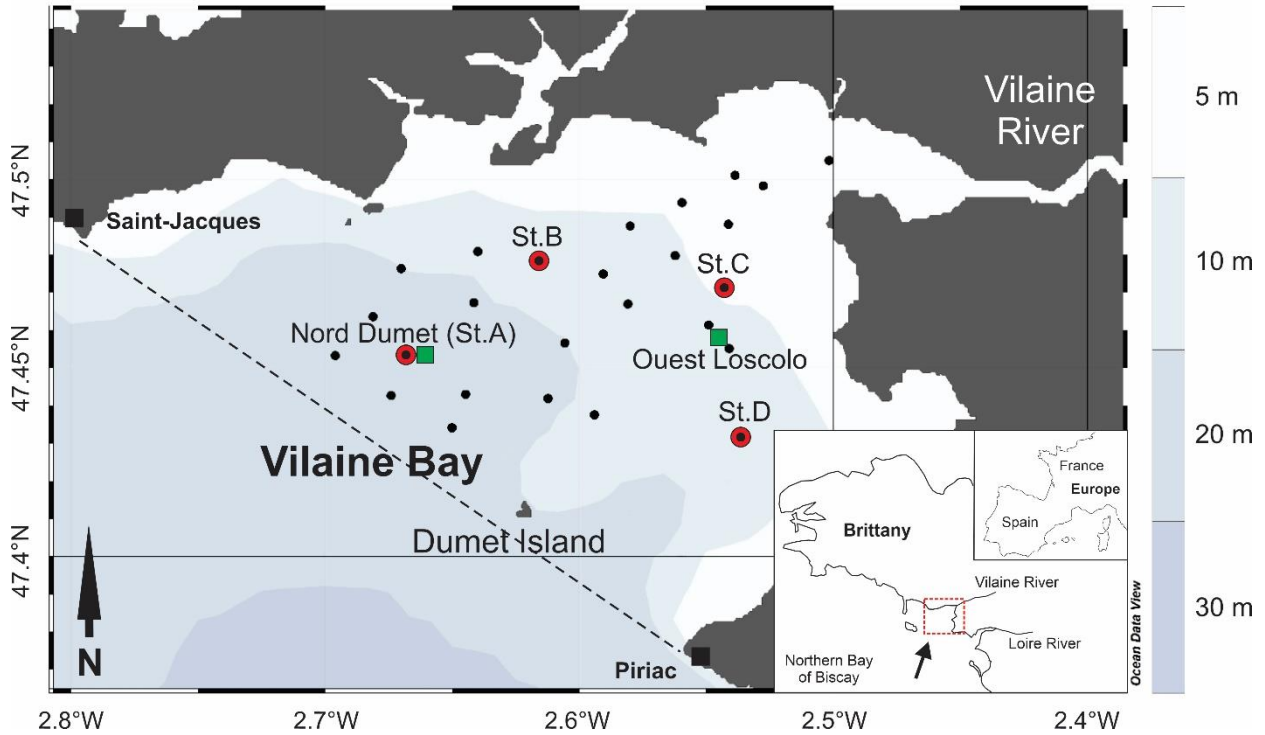
1231 **Table captions**

1232 **Table 1** Model-predicted OM decomposition rates through the different pathways for OM1 and  
1233 OM2 (in parentheses). All values are in  $\mu\text{mol C m}^{-2} \text{ h}^{-1}$

1234 **Table 2** Model-predicted depth-integrated N transformation rates derived from a model  
1235 simulation. The measured potential nitrification step 1 and  $\text{NO}_3^-$  reduction rates are indicated in  
1236 parentheses (mean  $\pm$  SE). All values are in  $\mu\text{mol N m}^{-2} \text{ h}^{-1}$ .



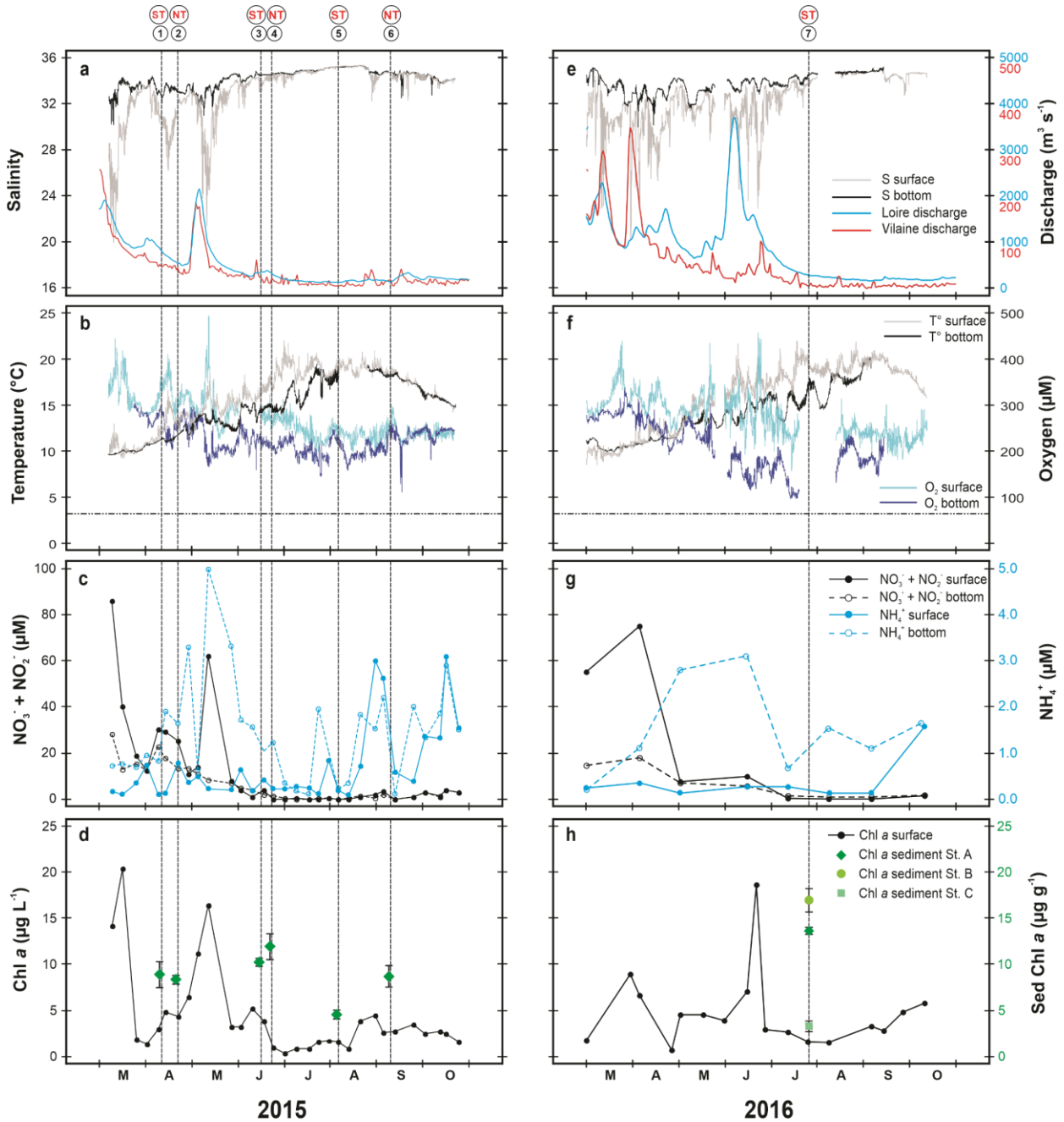
1237 **Fig. 1** Location of the study area. The off-shore limit of the Vilaine Bay is indicated by a dashed  
 1238 line. The bathymetry (GEBCO bathymetry data in Ocean Data View) is displayed using the colors  
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 1243 sampling points of the superficial sediments in April 2016.



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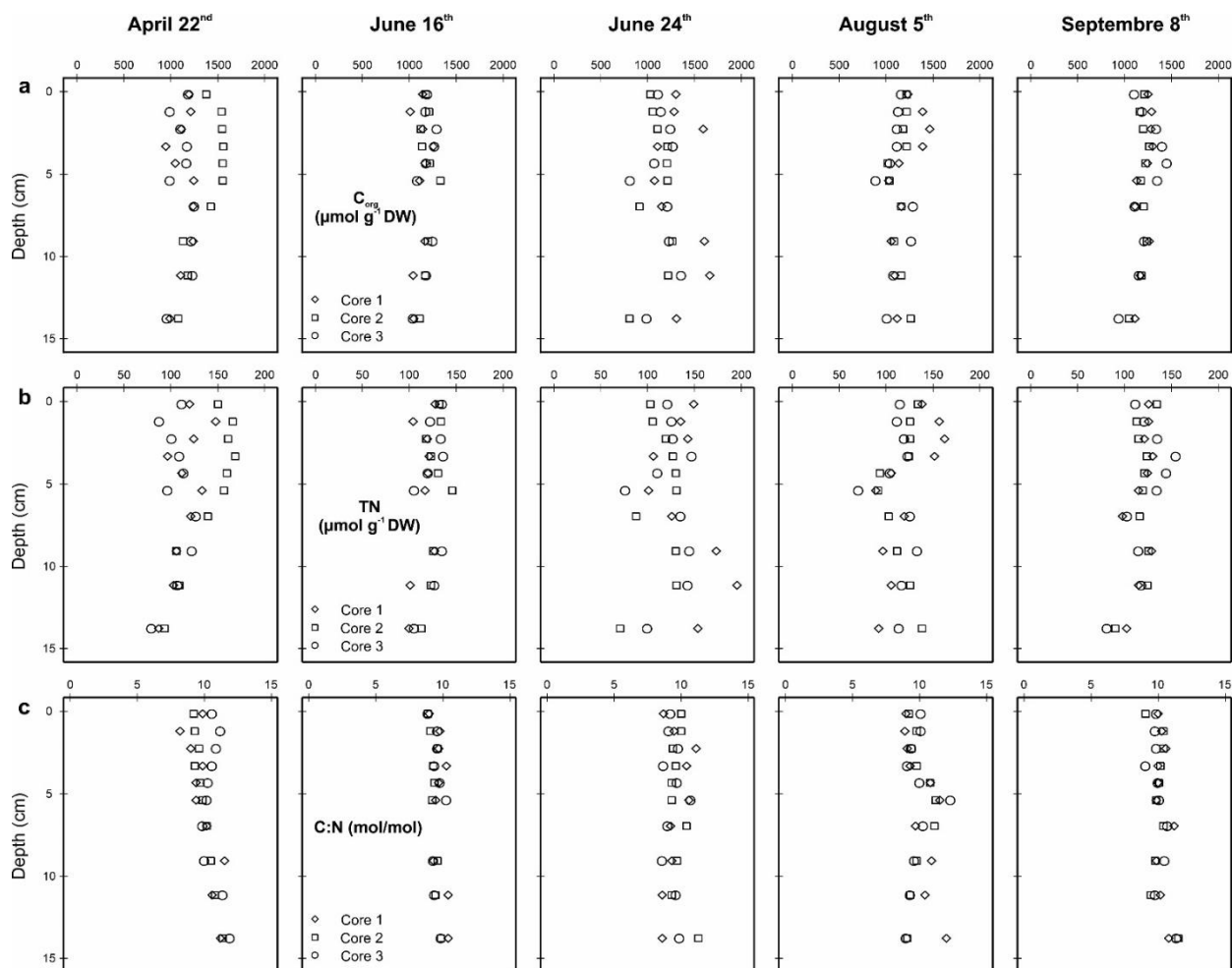
1246 **Fig. 2** Variations in the salinity and river discharge (Loire and Vilaine) (a, e), temperature and  
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 1248 (d, h), at the Nord Dumet monitoring station (St. A) in 2015 (left) and 2016 (right) from January  
 1249 to December. Dashed-dotted horizontal line (panels b & f): hypoxia threshold (63 μM; Middelburg  
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 1251 NT: spring and neap tides. Color symbols: Chl *a* concentration in the first top cm of the sediment  
 1252 ( $n = 3$ ).



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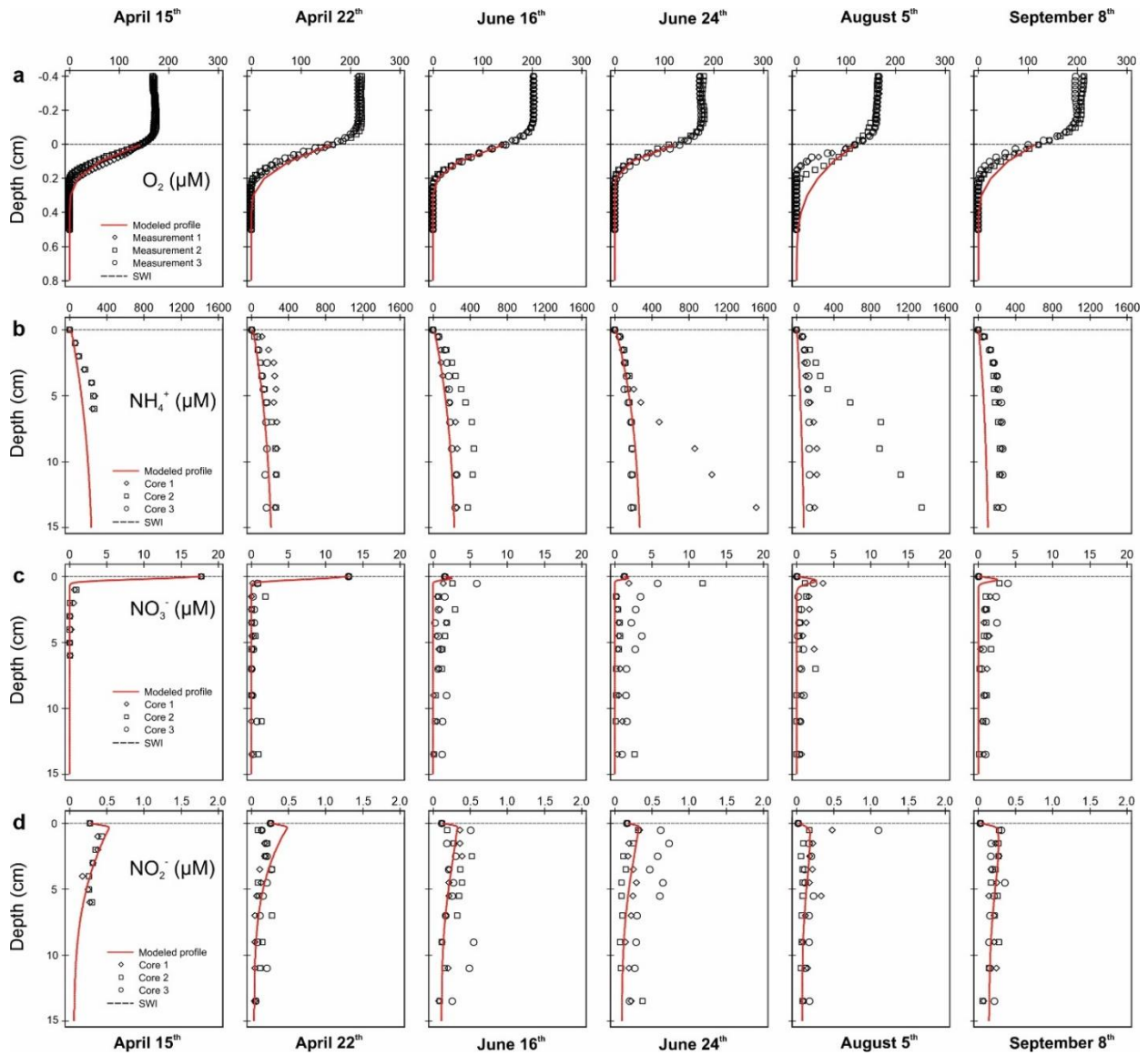
1255 **Fig. 3** Depth profiles of the organic carbon,  $C_{org}$  (a), total nitrogen, TN (b) and C:N ratios (c) for  
 1256 the triplicate sediment cores at the Nord Dumet monitoring station (St. A) for the temporal study  
 1257 from April to September 2015. No measurements were taken on April 15<sup>th</sup>.



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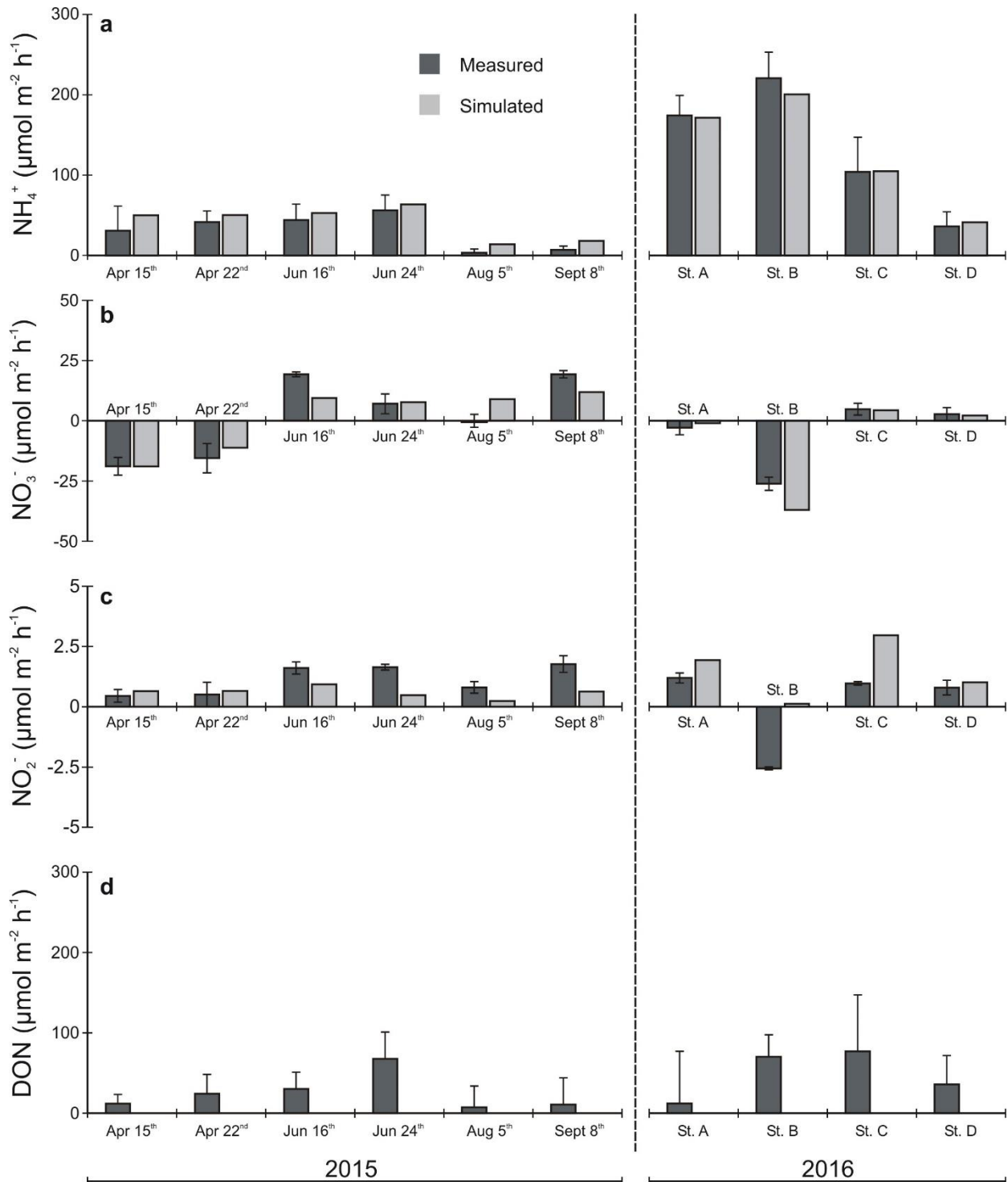
1260 **Fig. 4** Modeled (red curves) and measured (symbols) pore-water concentration profiles of O<sub>2</sub> (a),  
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 1262 the Nord Dumet monitoring station (St. A). The symbols correspond to the results from the  
 1263 triplicate sediment cores for the nutrients and the O<sub>2</sub> measurements. Dashed lines: sediment-water  
 1264 interface (SWI).



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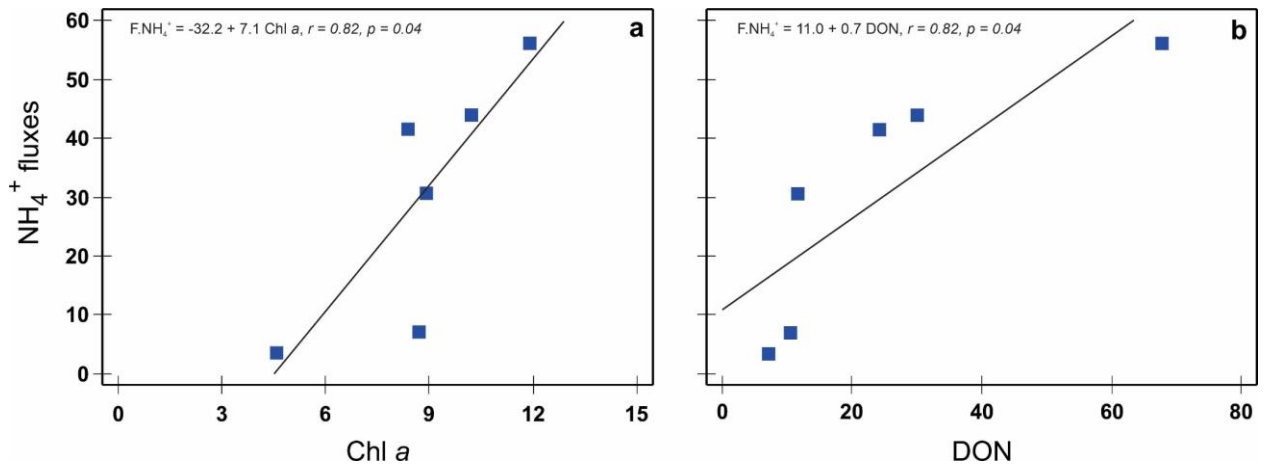
1267 **Fig. 5** Measured and simulated  $\text{NH}_4^+$  (a), DON (b),  $\text{NO}_3^-$  (c) and  $\text{NO}_2^-$  (d) fluxes across the SWI  
 1268 in the Vilaine Bay during the temporal study carried out from April to September 2015 conducted  
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 1270 (right). The error bars represent the standard error of the mean ( $n = 4$ ). There were no model  
 1271 simulations for the DON fluxes.



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1274 **Fig. 6** Relationship between the measured  $\text{NH}_4^+$  fluxes and Chl *a* content (a),  $\text{NH}_4^+$  and DON  
1275 fluxes (b) for the temporal study carried out in 2015. The equation and the regression line were  
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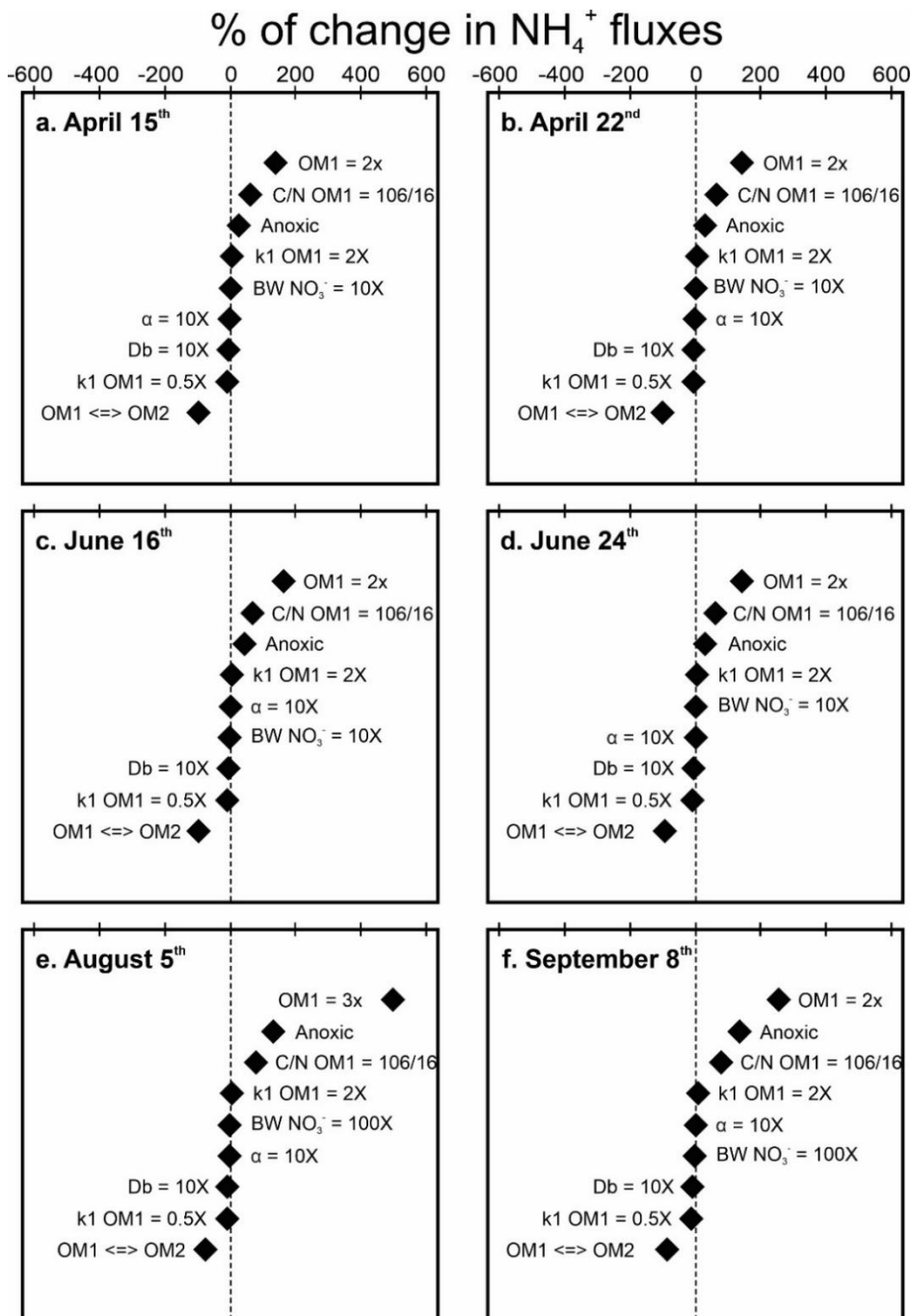


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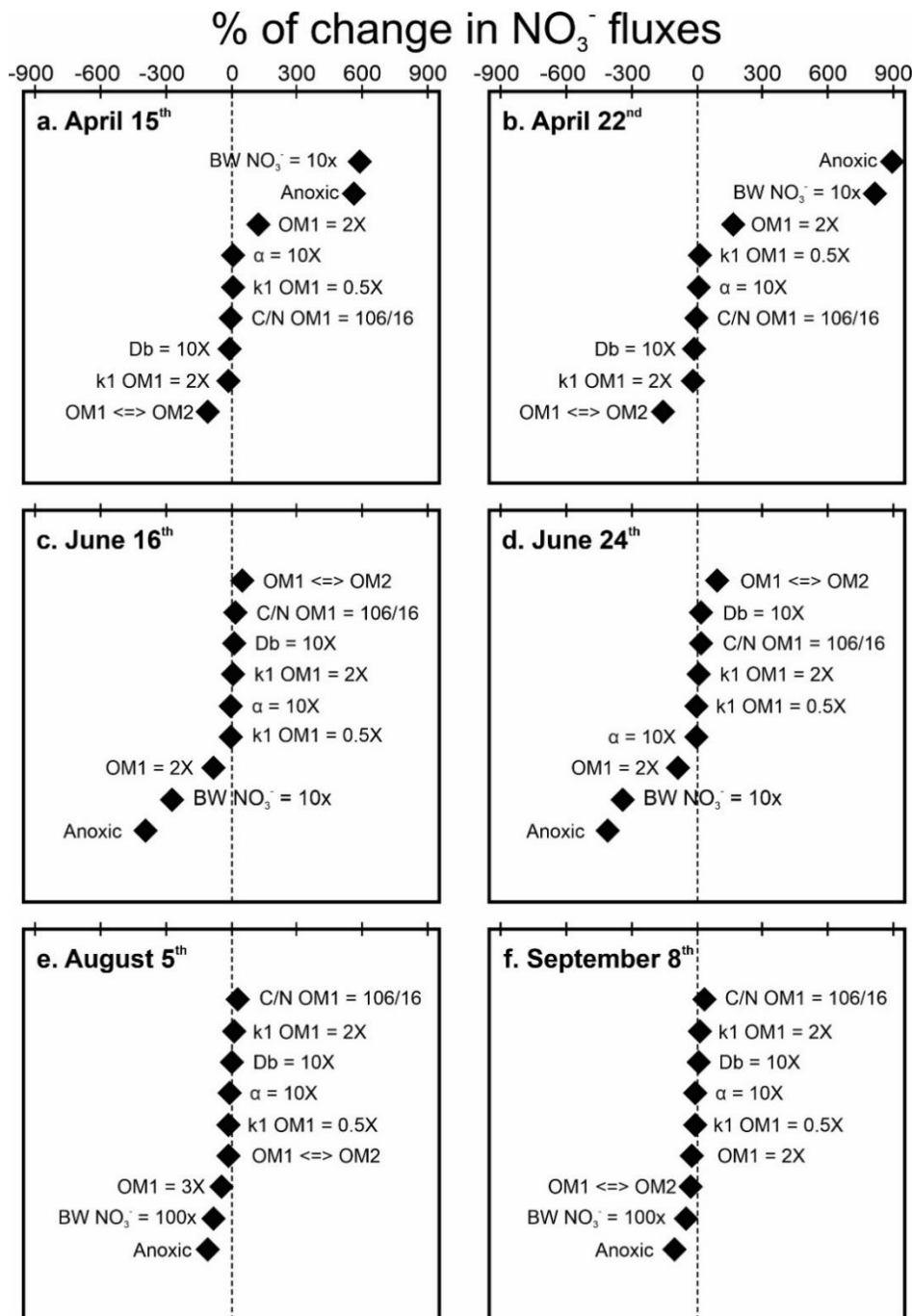


1279 **Fig. 7** Model sensitivity analysis showing the response of the benthic  $\text{NH}_4^+$  fluxes during the  
 1280 temporal study carried out from April to September 2015 (a-f) to different scenarios of change in  
 1281 environmental factor-related model parameters. The response was calculated as a percentage of  
 1282 change in the  $\text{NH}_4^+$  fluxes with regard to the baseline simulation (zero dashed line). The factors  
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 1284 Anoxic: zero bottom water  $\text{O}_2$  concentrations;  $\text{BW NO}_3^- = 10x$  [100x]: increase in the bottom water  
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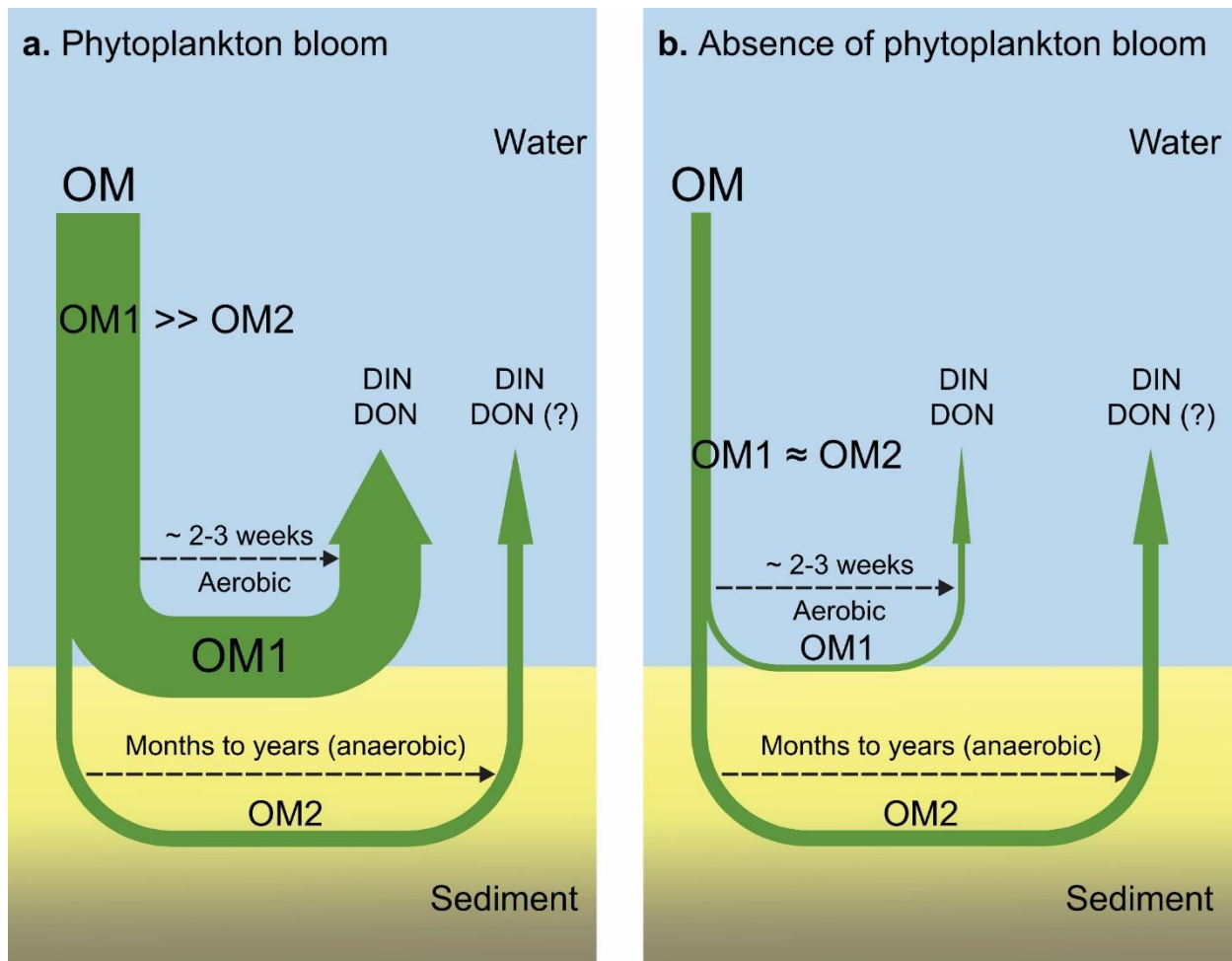
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1293 **Fig. 8** Model sensitivity analysis showing the response of the benthic  $\text{NO}_3^-$  fluxes during the  
 1294 temporal study carried out from April to September 2015 (a-f) to different scenarios of change in  
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 1311 DON stand for dissolved inorganic and organic N, respectively. The different arrow sizes indicate  
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 1313 DON. The horizontal dashed lines are meant to approximately illustrate the OM turnover time for  
 1314 each pathway (aerobic and anaerobic), estimated from the model rate constants of OM1 and OM2  
 1315 (Table S3) and the residence time of solutes (Table S6). Where the DON diffusion from pore-water  
 1316 is questioned, this is indicated by a question mark.



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1319 **Table 1** Model-predicted OM decomposition rates through the different pathways for OM1 and OM2 (in parentheses). All values are in  $\mu\text{mol C m}^{-2} \text{h}^{-1}$

Processes	April 15 <sup>th</sup>	April 22 <sup>nd</sup>	June 16 <sup>th</sup>	June 24 <sup>th</sup>	August 5 <sup>th</sup>	September 8 <sup>th</sup>	St. A	St. B	St. C	St. D
O <sub>2</sub>	475.8 (3.9)	506.4 (4.9)	605.8 (5.9)	629.7 (5.3)	261.3 (9.1)	343.3 (6.7)	1,307.9 (9.3)	1,164.4 (3.9)	862.6 (9.3)	298.9 (3.1)
NO <sub>3</sub> <sup>-</sup> <sup>a</sup>	45.5 (1.1)	36.5 (1.0)	23.1 (0.7)	19.7 (0.5)	12.9 (1.6)	17.8 (1.1)	2.6 (0.1)	49.0 (0.5)	4.6 (0.1)	4.1 (0.1)
Fe(OH) <sub>3</sub>	21.3 (1.5)	21.6 (1.8)	20.9 (1.7)	20.7 (1.4)	18.1 (6.7)	19.7 (3.5)	21.1 (1.2)	20.9 (0.6)	20.7 (1.8)	23.1 (2.0)
SO <sub>4</sub> <sup>2-</sup>	111.5 (23.8)	98.7 (26.8)	133.5 (40.4)	168.5 (44.8)	19.0 (30.5)	43.0 (32.4)	354.1 (82.4)	723.1 (69.0)	238.5 (85.0)	120.0 (39.7)
Total <sup>b</sup>	654.1 (30.5)	663.2 (34.7)	783.3 (48.7)	838.6 (52.2)	311.3 (48.1)	423.7 (43.9)	1,685.8 (93.0)	1,957.5 (73.9)	1,126.4 (96.3)	446.2 (44.9)

<sup>a</sup> Sum of the denitrification and DNRA rates (see section 2.4.2. and Table S1).

<sup>b</sup> Total rates of all OM decomposition pathways.

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1323 **Table 2** Model-predicted depth-integrated N transformation rates derived from a model simulation. The measured potential nitrification step 1 and  
 1324  $\text{NO}_3^-$  reduction rates are indicated in parentheses (mean  $\pm$  SE). All values are in  $\mu\text{mol N m}^{-2} \text{h}^{-1}$ .

Processes	April 15 <sup>th</sup>	April 22 <sup>nd</sup>	June 16 <sup>th</sup>	June 24 <sup>th</sup>	August 5 <sup>th</sup>	September 8 <sup>th</sup>	St. A	St. B	St. C	St. D
Nitrification 1	18.4 (11.5 $\pm$ 0.4)	19.1 (16.7 $\pm$ 0.6)	29.2 (20.0 $\pm$ 1.6)	24.2 (28.0 $\pm$ 2.9)	20.8 (14.0 $\pm$ 2.5)	27.5 (12.0 $\pm$ 1.3)	3.1 (7.3 $\pm$ 0.7)	0.4 (0.0 $\pm$ 0.0)	7.3 (2.8 $\pm$ 0.6)	6.6 (2.2 $\pm$ 0.7)
Nitrification 2	17.7	18.3	28.2	23.7	20.5	26.8	1.1	2.0	5.4	5.5
Denitrification	35.5 (52.4 $\pm$ 6.6)	28.6 (60.7 $\pm$ 8.8)	18.1 (73.6 $\pm$ 8.2)	15.4 (119.0 $\pm$ 24.8)	11.2 (na)	14.5 (na)	2.0 (na)	37.6 (na)	3.6 (na)	3.2 (na)
DNRA	1.17	0.94	0.60	0.51	0.37	0.48	0.07	1.24	0.12	0.11
Anammox	0.08	0.10	0.06	0.06	0.08	0.07	0.04	0.06	0.03	0.05

1325

1326 **Supplementary materials**1327 **Temporal and spatial variations in benthic nitrogen cycling in a temperate macro-tidal**  
1328 **coastal ecosystem: observation and modeling**

1329  
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1348 **Table S1** Reaction network and rate formulation used in the model.

Description	Reaction formulation <sup>a</sup>	Rate expression <sup>b, c</sup>
Aerobic respiration	$OM + xO_2 + (2z-y)HCO_3^- \rightarrow yNH_4^+ + zHPO_4^{2-} + (x-y+2z)CO_2 + (x-y+2z)H_2O$	$R1 = k1 [OM] \cdot \frac{[O_2]}{[O_2] + kO} \cdot F_T$
Denitrification	$OM + 0.8xNO_3^- \rightarrow 0.4xN_2 + yNH_4^+ + 0.8xNO_2^- + zHPO_4^{2-} + (0.8x+y-2z)HCO_3^- + (0.2x-y+2z)CO_2 + (0.6x-y+2z)H_2O$	$R2 = k2 [OM] \cdot \frac{[NO_3^-]}{[NO_3^-] + kNO} \cdot \frac{kinO}{[O_2] + kinO} \cdot 1 - F_{DNRA} \cdot F_T$
DNRA	$OM + 0.5xNO_3^- \rightarrow (0.5x+y)NH_4^+ + (0.5xNO_2^-) + zHPO_4^{2-} + (y-2z)HCO_3^- + (x-y+2z)CO_2 + (0.5x-y+2z)H_2O$	$R3 = k2 [OM] \cdot \frac{[NO_3^-]}{[NO_3^-] + kNO} \cdot \frac{kinO}{[O_2] + kinO} \cdot F_{DNRA} \cdot F_T$
Nitrification step 1	$NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O$	$R4 = k_{nit1} \cdot \frac{[NH_4^+]}{[NH_4^+] + kmNH4ao} \cdot \frac{[O_2]}{[O_2] + kmO2ao} \cdot F_T$
Nitrification step 2	$NO_2^- + 0.5O_2 \rightarrow NO_3^-$	$R5 = k_{nit2} \cdot \frac{[NO_2^-]}{[NO_2^-] + khNIT} \cdot \frac{[O_2]}{[O_2] + kHO} \cdot F_T$
Anammox	$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$	$R6 = k_{anx} \cdot \frac{[NH_4^+]}{[NH_4^+] + khNH4} \cdot \frac{[NO_2^-]}{[NO_2^-] + khNO} \cdot \frac{kinO}{[O_2] + kinO} \cdot F_T$

1349 <sup>a</sup>  $OM = x(CH_2O)_{org} + y(NH_3)_{org} + z(H_3PO_4)_{org}$ , where x, y, z represent the CNP ratios,1350 <sup>b</sup>  $F_{DNRA}$  = fraction of the total nitrate reduction occurring via DNRA (5%),1351 <sup>c</sup>  $F_T$  = temperature correction for the rates.  $F_T = \frac{K_1 \cdot \exp(\gamma_1 \cdot (T - T_1))}{1 + K_1 \cdot \exp(\gamma_1 \cdot (T - T_1) - K_1)} \cdot \frac{K_2 \cdot \exp(\gamma_2 \cdot (T_2 - T))}{1 + K_2 \cdot \exp(\gamma_2 \cdot (T_2 - T) - K_2)}$ , where  $T_1$  and  $T_2$  are the lower and upper temperature for the OM decay, respectively;1352  $K_1$  and  $K_2$  are the coefficient rates for the lower and upper temperature, respectively;  $\gamma_1$  and  $\gamma_2$  are the temperature rate multipliers for  $T_1$  and  $T_2$ , respectively (see Cole and

1353 Wells, 2006 for details).

1354 **Table S2** Boundary conditions used in the model.

Parameters	Apr 15 <sup>th</sup>	Apr 22 <sup>nd</sup>	Jun 16 <sup>th</sup>	Jun 24 <sup>th</sup>	Aug 5 <sup>th</sup>	Sep 8 <sup>th</sup>	St. A	St. B	St. C	St. D	Unit	Sources
2015 (Nord Dumet monitoring station/St. A)							2016					
<i>Solutes</i>												
O <sub>2</sub>	142 (84%)	161 (95%)	142 (82%)	120 (75%)	118 (93%)	114 (101%)	198 (80%)	96 (37%)	170 (70%)	198 (79%)	μM	I
NO <sub>3</sub> <sup>-</sup>	17.7	13.1	1.60	1.30	0.07	0.04	0.37	6.82	0.20	0.47	μM	I
NO <sub>2</sub> <sup>-</sup>	0.27	0.26	0.12	0.17	0.03	0.03	0.04	0.73	0.00	0.06	μM	I
NH <sub>4</sub> <sup>+</sup>	1.90	3.30	1.03	1.23	0.21	0.09	0.80	4.40	1.80	1.61	μM	I
Fe <sup>2+</sup>	0	0	0	0	0	0	0	0	0	0	μM	I
SO <sub>4</sub> <sup>2-</sup> <sup>a</sup>	28	28	28	28	28	28	28	28	28	28	mM	M
<i>Solids</i>												
OM1	600	600	700	750	275	375	1,500	1,800	1,000	400	μmol C cm <sup>-2</sup> yr <sup>-1</sup>	M
OM2	150	150	170	180	120	120	300	300	300	150	μmol C cm <sup>-2</sup> yr <sup>-1</sup>	M
Fe(OH) <sub>3</sub>	75	75	75	75	75	75	75	75	75	75	μmol cm <sup>-2</sup> yr <sup>-1</sup>	M

1355 Solute concentrations were obtained from the measurements. Solid fluxes were constrained from the model fitting (see Methods). <sup>a</sup>The SO<sub>4</sub><sup>2-</sup> concentration was constrained from  
1356 the measured salinity. Sources: **M**, constrained by the model fitting; **I**, independently determined from the field data.

1357 **Table S3** Reaction parameter values used in the model.

Parameters	Apr 15 <sup>th</sup>	Apr 22 <sup>nd</sup>	Jun 16 <sup>th</sup>	Jun 24 <sup>th</sup>	Aug 5 <sup>th</sup>	Sep 8 <sup>th</sup>	St. A	St. B	St. C	St. D	Unit	Source	Ref.	Description
2015 (Nord Dumet monitoring station/St. A)							2016							
<i>Fixed</i>														
C:N OM1	10	10	10	10	10	10	10	10	10	10		M		C:N ratio for OM1
C:N OM2	15	15	15	15	15	15	15	15	15	15		M		C:N ratio for OM2
k <sub>O</sub>	5	5	5	5	5	5	5	5	5	5	μM	L	2, 4, 5	Limitation of O <sub>2</sub> for aerobic oxidation
k <sub>NO</sub>	5	5	5	5	5	5	5	5	5	5	μM	L	2, 4, 5	Limitation of NO <sub>3</sub> <sup>-</sup> for denitrification
k <sub>mNH4ao</sub>	5	5	5	5	5	5	5	5	5	5	μM	L	1	Limitation of NH <sub>4</sub> <sup>+</sup> for nitrification step 1
k <sub>mO2ao</sub>	5	5	5	5	5	5	5	5	5	5	μM	L	1	Limitation of O <sub>2</sub> for nitrification step 1
k <sub>hNIT</sub>	1	1	1	1	1	1	1	1	1	1	μM	L	1	Limitation of NO <sub>2</sub> <sup>-</sup> for nitrification step 2
k <sub>HO</sub>	5	5	5	5	5	5	5	5	5	5	μM	L	1	Limitation of O <sub>2</sub> for nitrification step 2
k <sub>hno</sub>	1	1	1	1	1	1	1	1	1	1	μM	L	3	Limitation of NO <sub>2</sub> <sup>-</sup> for anammox
k <sub>hnh</sub>	1	1	1	1	1	1	1	1	1	1	μM	L	3	Limitation of NH <sub>4</sub> <sup>+</sup> for anammox
k <sub>inO</sub>	6	6	6	6	6	6	6	6	6	6	μM	L	6	Inhibition of O <sub>2</sub> for anoxic processes
k <sub>1</sub> OM1	16	16	16	16	16	16	16	16	16	16	yr <sup>-1</sup>	M		Rate constant for aerobic oxidation of OM1
k <sub>1</sub> OM2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	yr <sup>-1</sup>	M		Rate constant for aerobic oxidation of OM2
k <sub>2</sub> OM1	5	5	5	5	5	5	5	5	5	5	yr <sup>-1</sup>	M		Rate constant for denitrification and DNRA of OM1
k <sub>2</sub> OM2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	yr <sup>-1</sup>	M		Rate constant for denitrification and DNRA of OM2
<i>Adjusted</i>														
k <sub>nit</sub> 1	90	80	180	180	100	190	20	5	50	60	μmol cm <sup>-3</sup> yr <sup>-1</sup>	M		Maximum rate for nitrification step 1
k <sub>nit</sub> 2	200	195	550	550	400	540	30	50	190	150	μmol cm <sup>-3</sup> yr <sup>-1</sup>	M		Maximum rate for nitrification step 2
k <sub>anx</sub>	0.03	0.05	0.02	0.02	0.04	0.02	0.02	0.02	0.02	0.02	μmol cm <sup>-3</sup> yr <sup>-1</sup>	M		Maximum rate for anammox
<i>Measured</i>														
Ø	0.83	0.84	0.88	0.85	0.85	0.82	0.87	0.92	0.59	0.40	cm <sup>3</sup> cm <sup>-3</sup>	I		Sediment porosity
ρ	2.89	2.49	3.26	2.74	3.08	3.06	2.71	4.45	2.50	1.93	g cm <sup>-3</sup>	I		Sediment density
T°	11.1	11.9	14.4	14.9	17.9	17.8	16.5	13.8	17.3	15.8	°C	I		Bottom water temperature

1358 The sources of the parameter values are indicated by the following codes: **M**, constrained by the model fitting; **I**, independently determined from the field data, **L**, literature value,  
1359 with references given as follows: 1. Ward (1986); 2. Wang and VanCappellen (1996); 3. Dalsgaard and Thamdrup (2002); 4. Canavan et al. (2006); 5. Dale et al. (2016); 6.  
1360 Akbarzadeh et al. (2018).

1361 **Table S4** Model parameter values for the transport processes that were invariable within the season  
 1362 and sampling station.

Parameters	Value	Description	Unit	Sources
Db	3	Bioturbation coefficient at $x < 2$ cm	$\text{cm}^2 \text{yr}^{-1}$	M
	1.5	Bioturbation coefficient at $2 \text{ cm} \leq x \leq 4$ cm	$\text{cm}^2 \text{yr}^{-1}$	M
	0.3	Bioturbation coefficient at $4 \text{ cm} \leq x \leq 7$ cm	$\text{cm}^2 \text{yr}^{-1}$	M
	$0.1 * (1 - \exp(x - 20))$	Bioturbation coefficient at $x > 7$ cm	$\text{cm}^2 \text{yr}^{-1}$	M
$\alpha$	3	Bioirrigation coefficient at $x < 2$ cm	$\text{yr}^{-1}$	M
	1.5	Bioirrigation coefficient at $2 \text{ cm} \leq x \leq 4$ cm	$\text{yr}^{-1}$	M
	0.3	Bioirrigation coefficient at $4 \text{ cm} \leq x \leq 7$ cm	$\text{yr}^{-1}$	M
	$0.1 * (1 - \exp(x - 20))$	Bioirrigation coefficient at $x > 7$ cm	$\text{yr}^{-1}$	M
$\omega$	0.5	Burial velocity	$\text{cm yr}^{-1}$	M

1363 See Table S2 for the source indications

1364

1365 **Characteristic time-scales for the sediment processes**1366 *1. Diffusion time-scale*

1367 Diffusion time-scales calculated from the modified Einstein-Smoluchowski equation (Jørgensen  
1368 and Revsbech, 1985):

$$1369 \quad t_{DIFF} = z^2 / 2D_s \quad \text{eq. 1}$$

1370 where  $t_{DIFF}$  is the diffusion time-scales (d),  $z$  is the characteristic length (cm), and  $D_s$  is the diffusion  
1371 coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), corrected with the bottom water temperature and sediment porosity for each  
1372 measurement. The diffusion time-scale was calculated for the upper 2 cm layer, where the  
1373 exchange between the sediment and overlying water occurs most actively.

1374 **Table S5** Diffusion time-scales for  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON over the first 2 cm sediment layer.

Date	$D_s \text{ NH}_4^+$	$D_s \text{ NO}_3^-$	$D_s \text{ DON}^*$	$t_{DIFF} \text{ NH}_4^+$	$t_{DIFF} \text{ NO}_3^-$	$t_{DIFF} \text{ DON}$
	(x $10^{-6} \text{ cm}^2 \text{ s}^{-1}$ )			(d)		
April 15 <sup>th</sup> .	1.4	1.4	0.17	1.6	1.7	13.2
April 22 <sup>nd</sup>	1.4	1.4	0.18	1.6	1.6	13.2
June 16 <sup>th</sup>	1.5	1.5	0.19	1.5	1.5	12.4
June 24 <sup>th</sup>	1.6	1.5	0.19	1.5	1.5	12.5
August 5 <sup>th</sup>	1.7	1.6	0.21	1.4	1.4	11.3
September 8 <sup>th</sup>	1.7	1.6	0.21	1.4	1.4	11.1

1375  $t_{DIFF}$  = the diffusion time-scale;  $D_s$  = the diffusion coefficient. \*The  $D_s$  of DON was estimated using the empirical  
1376 relationship between the free solution diffusion coefficient ( $D_o$ ) and the molecular weight (MW) for the various  
1377 organic compounds at 25°C in distilled water reported by Burdige et al. (1992), assuming a fixed average MW of 2500  
1378 Daltons. The obtained values were then corrected for in situ temperature using the Stoke-Einstein equation and  
1379 translated to  $D_s$  after correction for sediment porosity (Boudreau, 1997).

1380 *2. Residence time of the solutes*

1381 The residence time of the solutes at steady-state can be calculated by dividing the stock of the  
1382 solutes by the flux of these solutes.

$$1383 \quad t_{RES} = \text{Stock} / \text{DifFlux} \quad \text{eq. 2}$$

1384 where  $t_r$  is the residence time of the solutes (d), *Stock* is the average stock of the solutes over the  
1385 first 2 cm sediment layer ( $\mu\text{mol m}^{-2}$ ), and *DifFlux* is the diffusive fluxes of the solutes  
1386 ( $\mu\text{mol m}^{-2} \text{ d}^{-1}$ ).

1387 **Table S6** Residence time of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON over the first 2 cm sediment layer.

Date	Stock			DifFlux			$t_{RES}$		
	$\text{NH}_4^+$	$\text{NO}_3^-$	DON	$\text{NH}_4^+$	$\text{NO}_3^-$	DON	$\text{NH}_4^+$	$\text{NO}_3^-$	DON
	( $\mu\text{mol m}^{-2}$ )			( $\mu\text{mol m}^{-2} \text{ d}^{-1}$ )			(d)		
April 15 <sup>th</sup> .	3,138	376	7,473	427	-247	148	7.4	1.5	50
April 22 <sup>nd</sup>	3,699	294	8,156	541	-99	157	6.8	3.0	52
June 16 <sup>th</sup>	3,487	130	6,471	518	17	175	6.7	7.5	37
June 24 <sup>th</sup>	2,858	198	9,469	439	44	225	6.5	4.5	42
August 5 <sup>th</sup>	3,384	84	6,322	589	21	193	5.7	4.1	33
September 8 <sup>th</sup>	3,795	113	6,916	567	22	212	6.7	5.2	33

1388 \* Diffusive fluxes calculated from the concentration gradient at the SWI using Fick's first law of diffusion (Boudreau,  
1389 1997; Schulz, 2006)

1390 **Sensitivity analysis**

1391 The sensitivity analysis was carried out by imposing changes in the model boundary  
 1392 condition (Table S3) and parameter values (Table S2 & S4) for each sampling date. The  
 1393 contribution of  $\text{NO}_2^-$  to the DIN fluxes was considered negligible ( $< 5\%$  of the  $\text{NH}_4^+$  and  $\text{NO}_3^-$   
 1394 fluxes) and therefore it not included in the sensitivity analysis. A stepwise approach was applied  
 1395 by manually changing the parameter values individually (Table S7) and observing the model  
 1396 response on the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  fluxes. The model was run by imposing each change in these  
 1397 values one by one for each sampling date. A combination effect between the parameters was not  
 1398 tested in the sensitivity analysis in the present study. The response was calculated as a percentage  
 1399 of change in the  $\text{NH}_4^+$  and  $\text{NO}_3^-$  fluxes with regard to best fits (baseline model).

1400 **Table S7** List of tested parameters for the sensitivity analysis.

Parameters	Description
Anoxic	Bottom water $\text{O}_2$ concentrations are equal to zero
BW $\text{NO}_3^- = 10\text{x}$ (100x)	Increase in the bottom water $\text{NO}_3^-$ 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 $\Leftrightarrow$ OM2	Inversing the proportion of OM1 and OM2
$k_1$ OM1 = 2x	Increase in the rate constant for the aerobic oxidation of OM1 by 2 fold
$k_1$ 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
$\alpha = 10\text{x}$	Increase in the bioirrigation coefficient by 10 fold

1401



1402 **Table S8** Density of macrofauna in the incubated sediment cores ( $n = 6$ ) of the temporal study  
 1403 carried out at the ND monitoring station in 2015.

Taxa / Species names	Apr 15 <sup>th</sup>	Apr 22 <sup>nd</sup>	Jun 16 <sup>th</sup>	Jun 24 <sup>th</sup>	Aug 5 <sup>th</sup>	Sep 8 <sup>th</sup>
<b>Crustacea</b>						
<i>Asthenognathus atlanticus</i>	1	2				
<i>Philocheras bispinosus bispinosus</i>			1			
<b>Echinoderms</b>						
<i>Acrocnida brachiata</i>	1				1	
<b><i>Amphiura filiformis</i></b>	6	6	4	22		6
<i>Labidoplax digitata</i>					2	
<i>Leptopentacta elongata</i>			1	2	2	
<i>Synaptidae</i>						
<b>Molluscs</b>						
<i>Abra nitida</i>			1		2	1
<i>Corbula gibba</i>		1				
<i>Kurtiella bidentata</i>	5		1	3		4
<i>Nassarius pygmaeus</i>					1	1
<b><i>Nucula nitidosa</i></b>	27	27	15	24	3	5
<i>Philine aperta</i>				1	2	
<i>Spisula solida</i>	1					
<i>Turritella communis</i>				1	1	
<b>Annelids</b>						
<i>Aphelochaeta</i>						1
<i>Chaetozone</i>						1
<i>Glycera unicornis</i>	1					1
<i>Heteromastus filiformis</i>		2				6
<i>Labioleanira yhleni</i>	1	4	2	2	1	
<i>Magelona</i>			1		4	
Maldanidae		1	1	4	1	
<i>Malmgrenia lilianae</i>	3	1		3		
<i>Nephtys</i>	1	1				
<i>Pholoe baltica</i>			1	1		
<b><i>Sternaspis scutata</i></b>	5	3	5	1	8	
<b>Cnidaria</b>						
<i>Edwardsidae</i>					1	
<i>Halcapa</i>						
<i>Virgularia</i>					1	4
<b>Others</b>						
<i>Nemertea</i>		2	1			1
<i>Phoronidien</i>		1				1
<sup>a</sup> Average value (Ind. m <sup>-2</sup> )	1354	1328	886	1667	781	833

1404 \* Sediment core surface area = 64 cm<sup>2</sup>; <sup>a</sup> Average value for 6 sediment cores

1405 Table S9. Spearman's rank correlations between benthic macrofauna density, N transformation  
 1406 rates, benthic N fluxes bottom water turbidity and O<sub>2</sub> concentration for the temporal study in 2015  
 1407 ( $n = 6$ ). Asterisks designate significant correlations (\*\*\*  $p < 0.001$ , \*\*  $p < 0.01$ , \*  $p < 0.05$ ).

	NTF1	NTF2	DNF	DNRA	ANX	AMF	F.NO <sub>3</sub> <sup>-</sup>	F.NH <sub>4</sub> <sup>+</sup>	Fauna	Turb	Oxy
NTF1	1.00										
NTF2	1.00***	1.00									
DNF	-0.49	-0.49	1.00								
DNRA	-0.49	-0.49	1.00***	1.00							
ANX	-0.79	-0.79	0.26	0.26	1.00						
AMF	0.26	0.26	0.43	0.43	-0.53	1.00					
F.NO <sub>3</sub> <sup>-</sup>	0.89*	0.89*	-0.71	-0.71	-0.53	-0.20	1.00				
F.NH <sub>4</sub> <sup>+</sup>	0.23	0.23	0.46	0.46	-0.58	0.99*	-0.23	1.00			
Fauna	-0.31	-0.31	0.66	0.66	-0.18	0.77	-0.66	0.81	1.00		
Turb	-0.90*	-0.90*	0.64	0.64	0.72	-0.12	-0.90*	-0.09	0.29	1.00	
Oxy	-0.03	-0.03	-0.41	-0.41	0.31	-0.93*	0.41	-0.90*	-0.75	-0.13	1.00

1408 NTF1: Nitrification step 1; NTF2: Nitrification step 2; DNF: Denitrification; ANX: Anammox; AMF:  
 1409 Ammonification; F.NO<sub>3</sub><sup>-</sup>: NO<sub>3</sub><sup>-</sup> fluxes; F.NH<sub>4</sub><sup>+</sup>: NH<sub>4</sub><sup>+</sup> fluxes; Fauna: Macrofauna density; Turb & Oxy: bottom water  
 1410 turbidity (NTU) and oxygen concentration (μM) respectively.  
 1411

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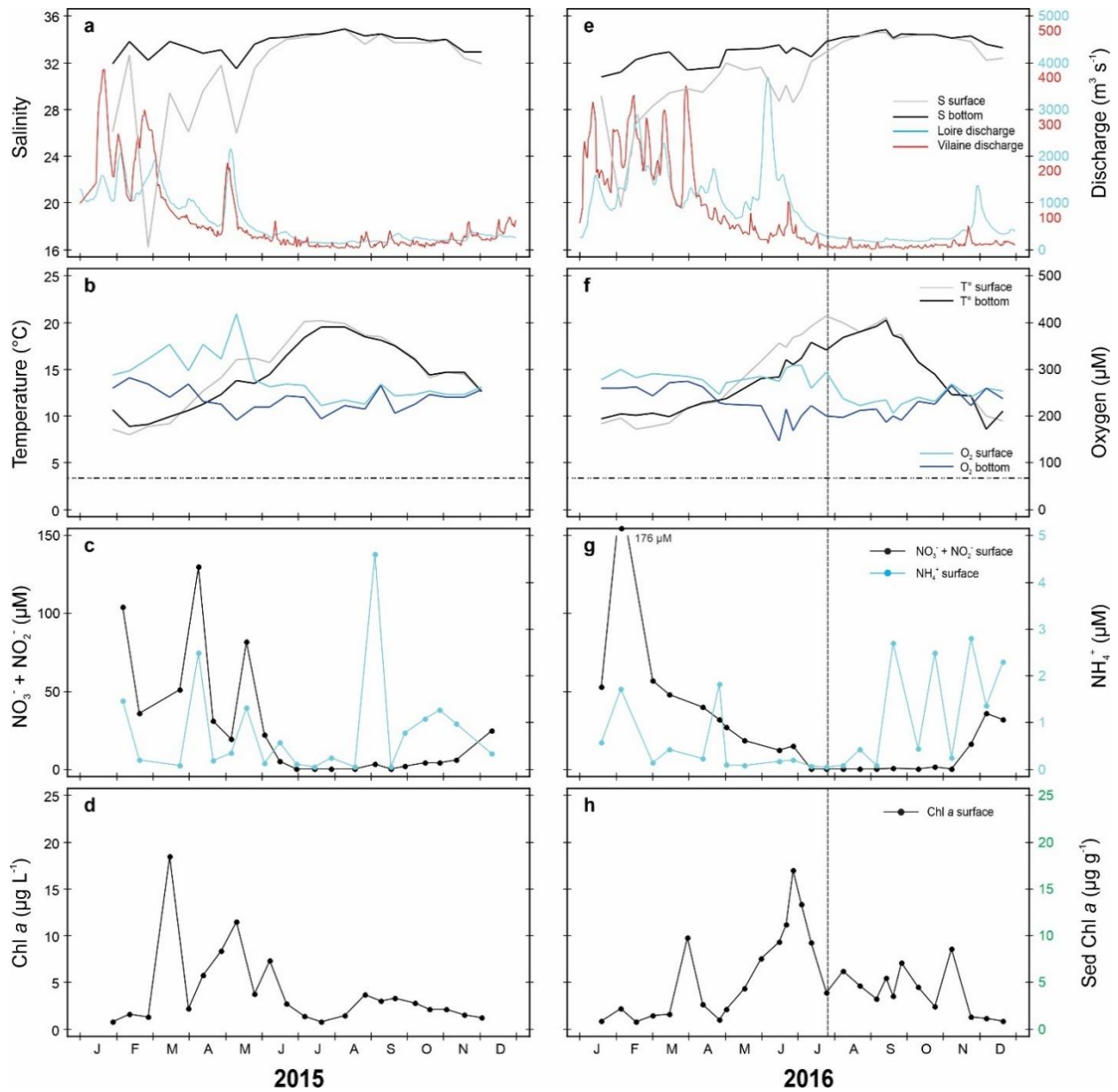
1448 **Fig. S1** Sediment core incubations for measuring benthic DIN and DON fluxes in the laboratory.  
1449 Two triplicates were incubated in dark and the light conditions, respectively; a control core without  
1450 sediment was used to monitor the evolution of the overlying water itself.



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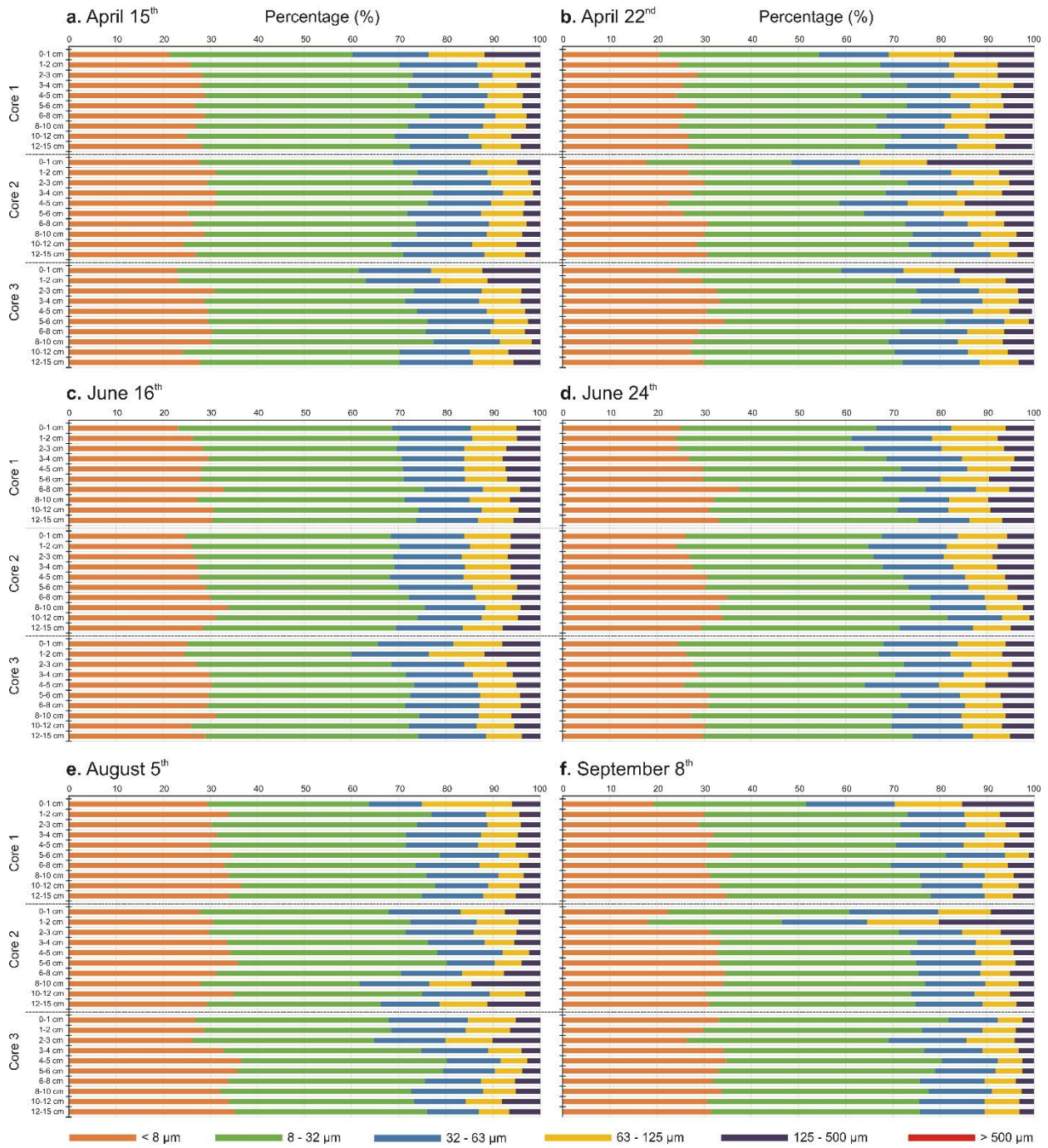
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1453 **Fig. S2** Variations in the salinity and river discharge (Loire and Vilaine) (a, e), temperature and  
 1454 dissolved O<sub>2</sub> (b, f), NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (c, g), Chl *a* in the water column and sediment surface  
 1455 (d, h), at the Ouest Loscolo monitoring station in 2015 (left) and 2016 (right) from January to  
 1456 December. Dashed-dotted horizontal line (panels a & e): hypoxia threshold (63 μM; Middelburg  
 1457 and Levin, 2009; Zhang et al., 2010). Vertical lines: dates of the sediment investigations.



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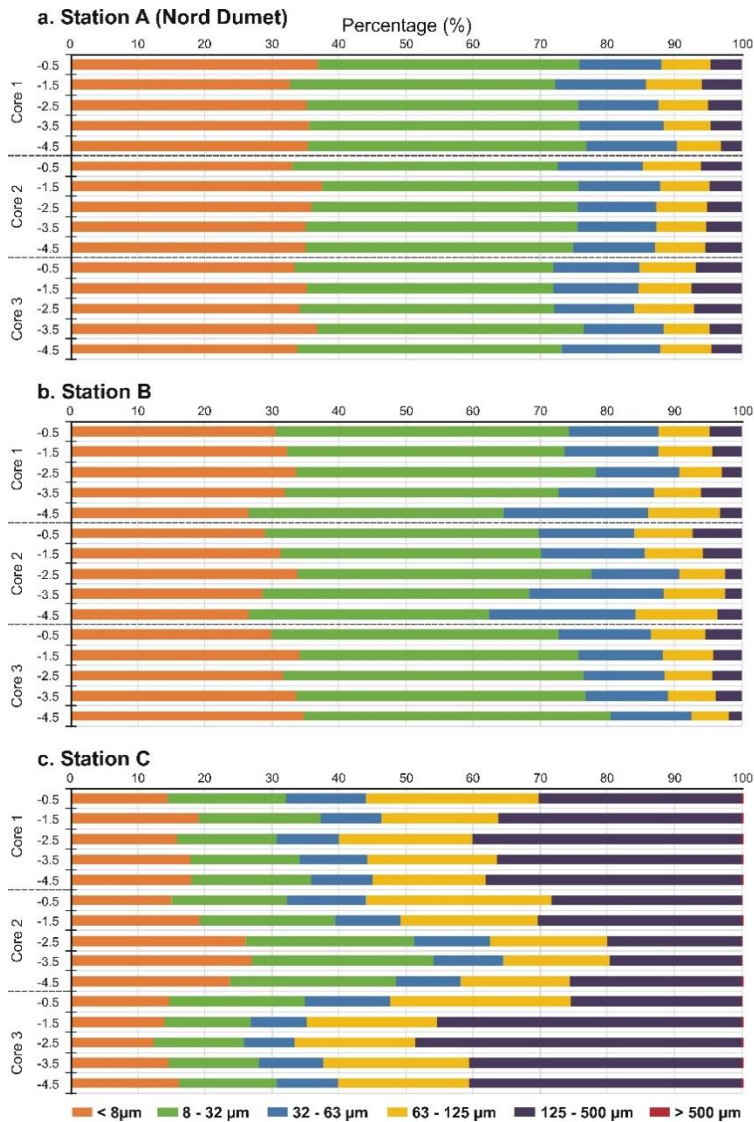
1460 **Fig. S3** Depth profile of the grain size distribution at the Nord Dumet monitoring station (St. A)  
 1461 in triplicate sediment cores for the temporal study from April to September 2015. The y-axis  
 1462 represents each section of the sediment layers in the triplicate cores.



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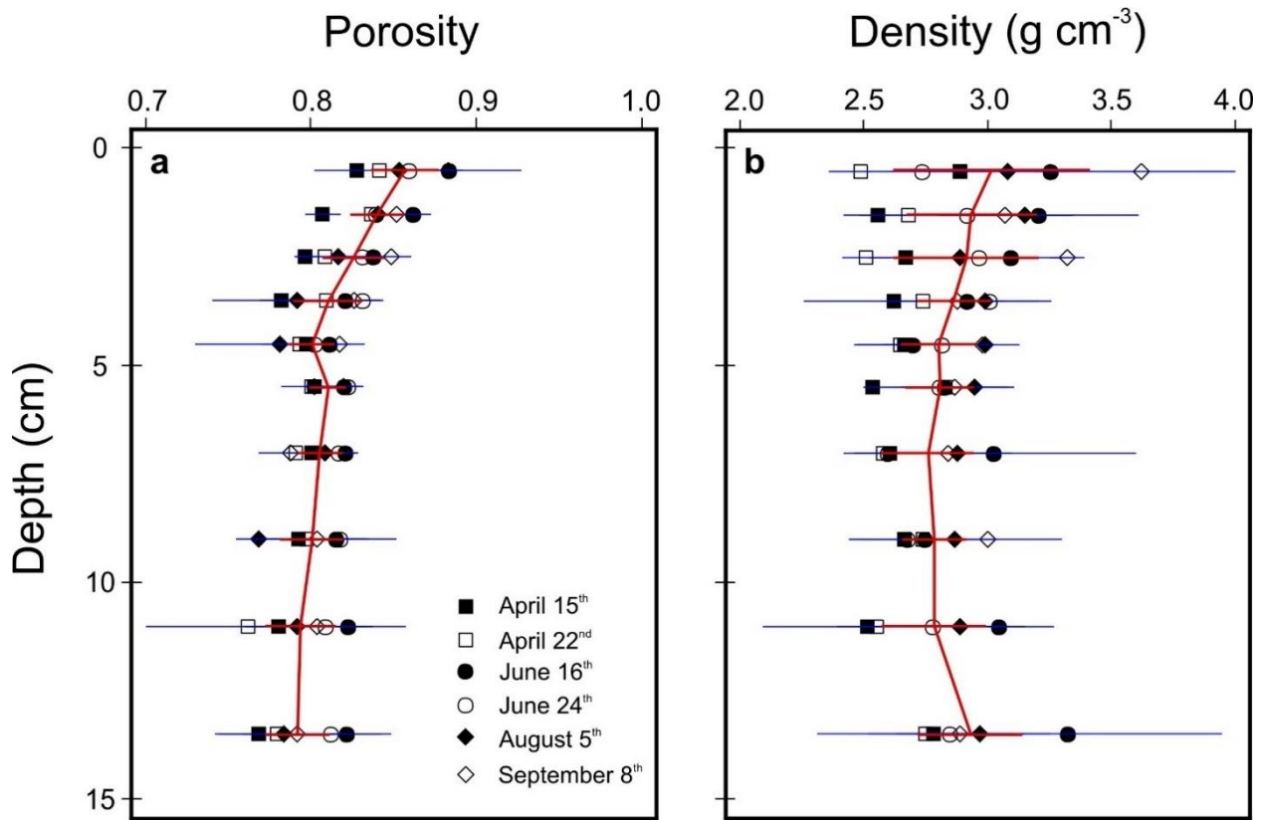


1465 **Fig. S4** Depth profile of the grain size distribution in the triplicate sediment cores at Station A, B  
 1466 & C for the spatial study carried out in July 2016. The y-axis represents each section of the  
 1467 sediment layers in the triplicate cores. Right panel: image of a sediment core sampled at Station  
 1468 D. There was no analysis of the grain size distribution for Station D.



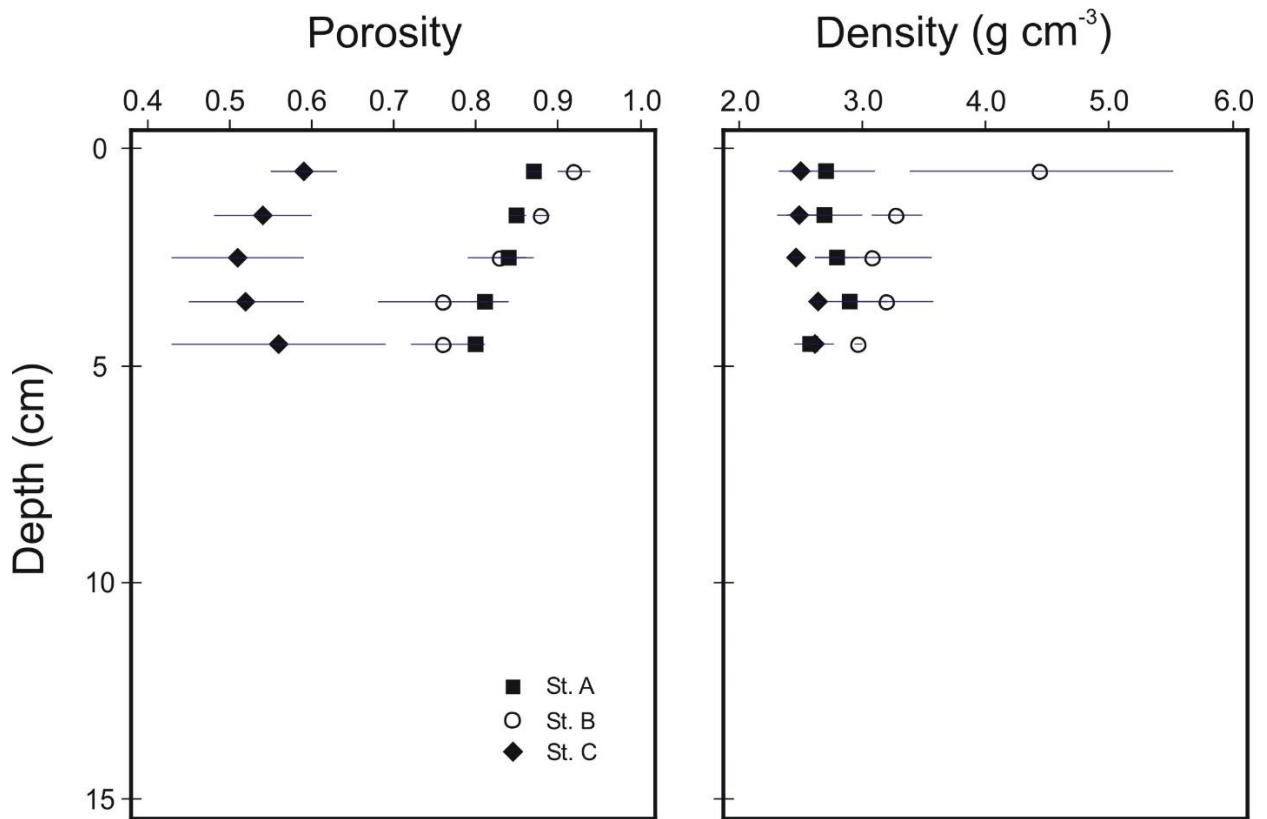
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1471 **Fig. S5** Depth profiles of the sediment porosity (a) and density (b) at the Nord Dumet monitoring  
 1472 station (St. A) for the temporal study carried out from April to September 2015. The solid  
 1473 horizontal lines are the standard error of the triplicate sediment cores. The red curves are the  
 1474 average of all values with the standard error ( $n = 60$ ).



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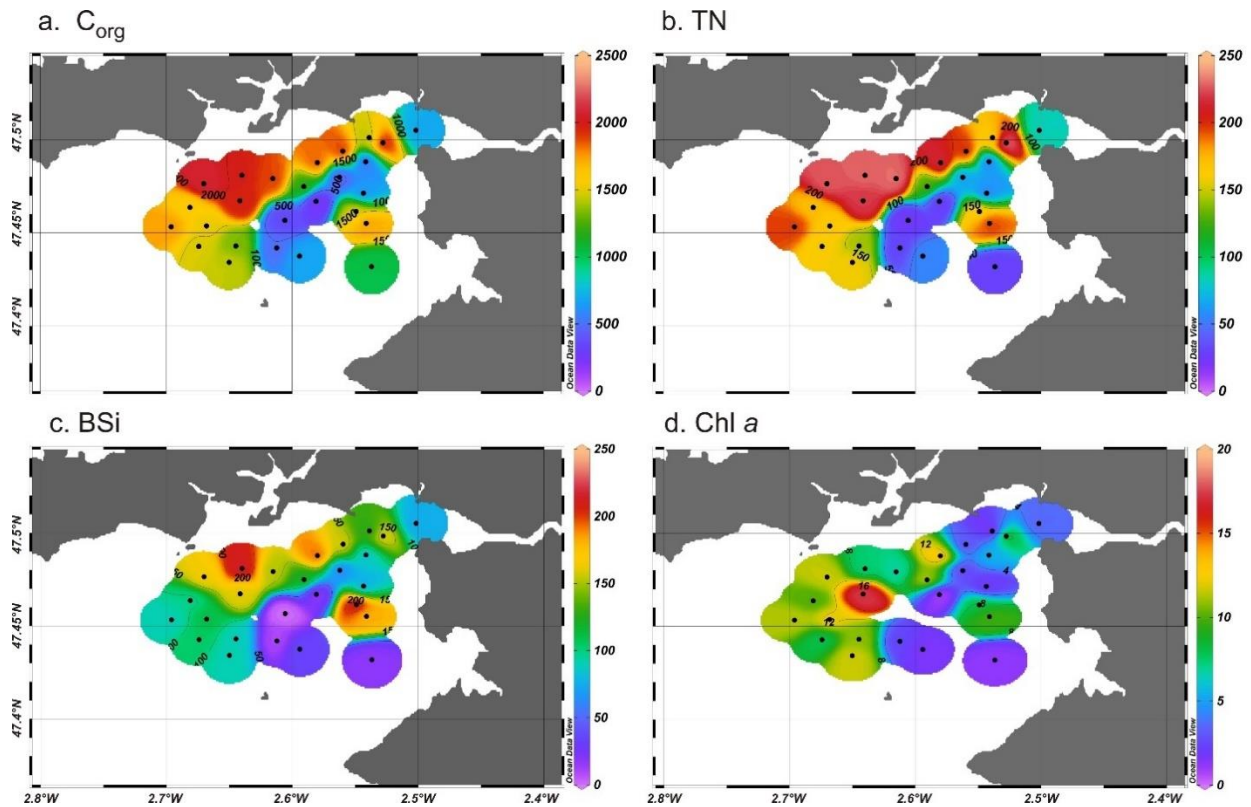
1477 **Fig. S6** Depth profiles of the sediment porosity (a) and density (b) at Station A, B & C for the  
 1478 spatial study carried out in July 2016. The solid horizontal lines are the standard error of the  
 1479 triplicate sediment cores. Note: there was no measurement for Station D (gravel).



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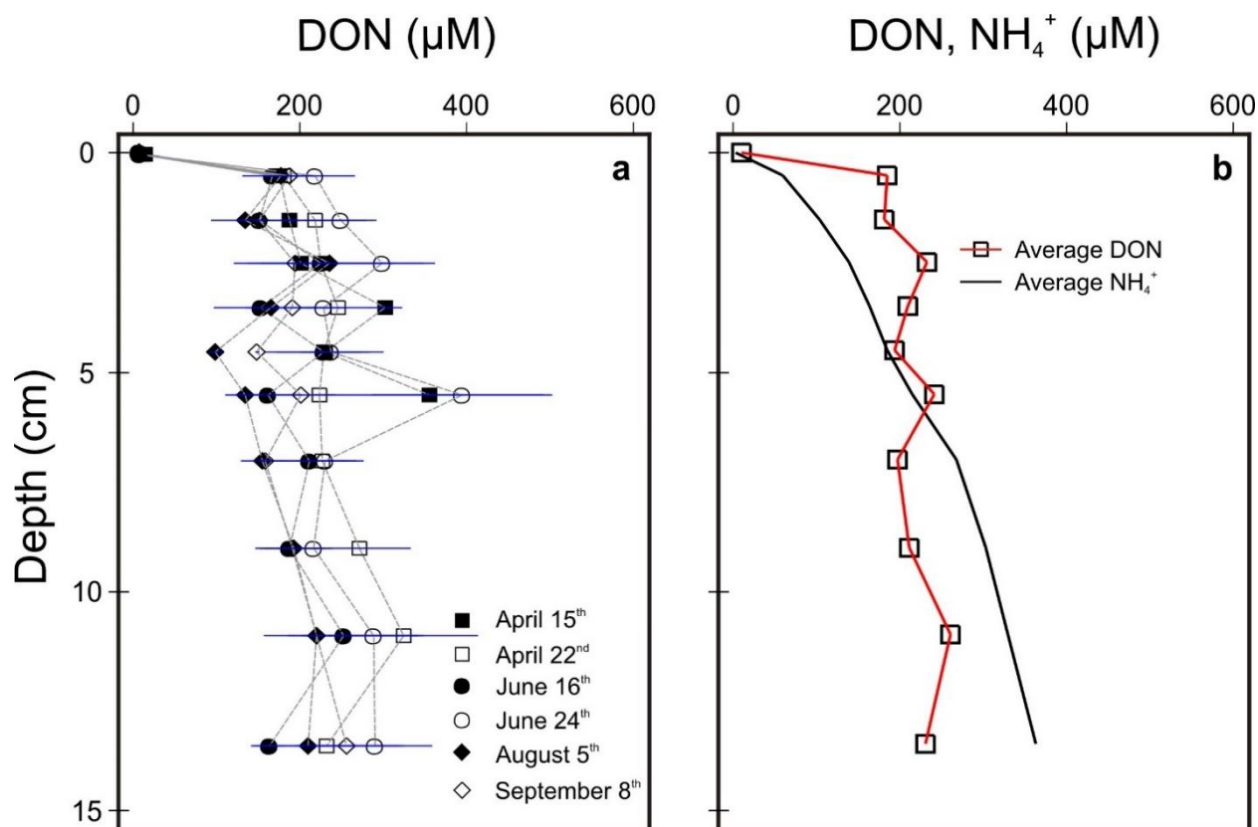
1482 **Fig. S7**  $C_{org}$ , total N, BSi (in  $\mu\text{mol g}^{-1}$ ) and Chl  $a$  (in  $\mu\text{g g}^{-1}$ ) concentrations at the sediment surface  
1483 (5 cm and 1 cm for Chl  $a$ ) in April 2016. The data were interpolated using an automatic weighted-  
1484 average gridding with the Ocean Data View software.



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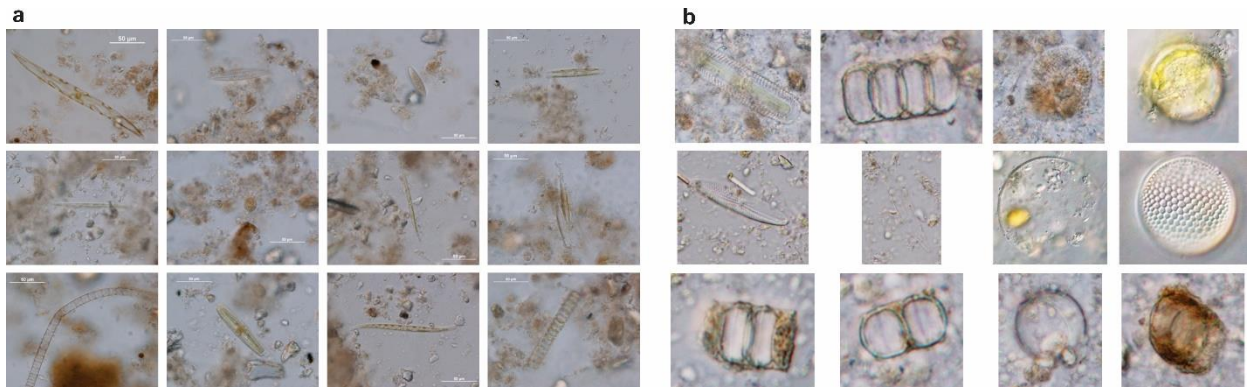
1487 **Fig. S8** DON depth profiles at the Nord Dumet monitoring station (St. A) for the temporal study  
 1488 carried out from April to September 2015 (a) and global average of the measured DON and  $\text{NH}_4^+$   
 1489 values (b). The solid horizontal lines are the standard error of the triplicate sediment cores.



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1492 **Fig. S9** Microscopic observation of microalgae cells on the surface sediment at the Nord Dumet  
1493 monitoring station (St. A) during the period of study from April to June (a) and from August to  
1494 September (b) 2015.



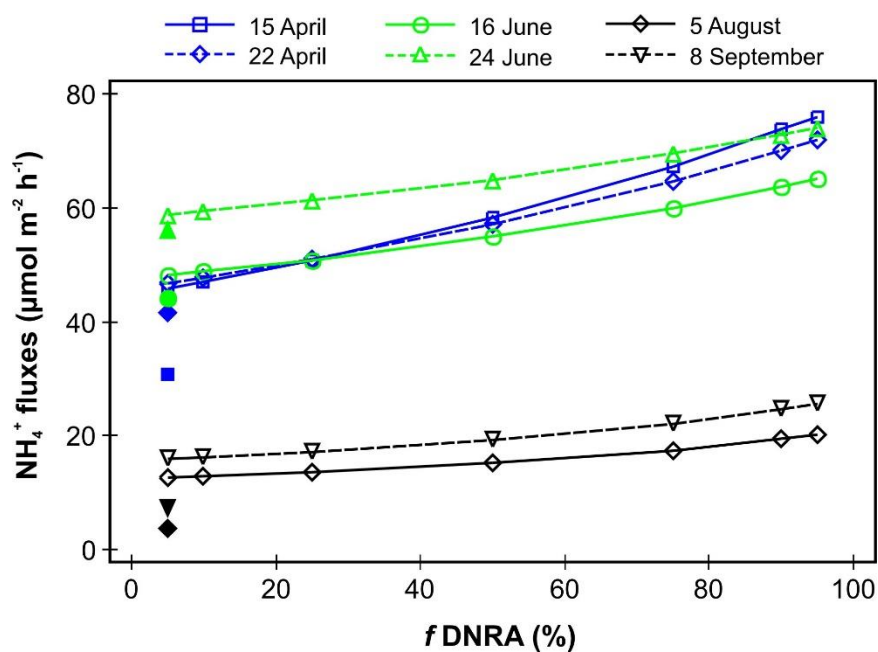
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1498 **Fig. S10** Modeled  $\text{NH}_4^+$  fluxes in 2015 across the SWI as a function of the various  $f\text{DNRA}$  values.  
1499 Sampling dates are represented by the various colored lines with color symbols. Solid symbols  
1500 represent the  $\text{NH}_4^+$  fluxes measured at the Nord Dumet station.



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- The temporal and spatial variations of benthic N cycling in a eutrophic macro-tidal bay are studied using field measurements and the reactive transport model
- Benthic N flux variations depend on the phytoplankton-derived organic matter input
- Rapid mineralization of organic matter at the sediment-water interface controls benthic N cycling dynamics and sediment oxygen consumption
- Organic matter decomposition can be followed by bottom water hypoxia when blooms occur in the summer

**Declaration of interests**

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: