

1 Effects of global climate change and organic pollution on nutrient cycling in marine sediments

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4 Carlos Sanz-Lázaro^{1,2*}, Thomas Valdemarsen¹ & Marianne Holmer¹

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6 ¹Department of Biology, University of Southern Denmark, Campusvej 55, 5230 Odense,

7 Denmark

8 ²Present address: Departamento de Ciencias del Mar y Biología Aplicada, Universidad de

9 Alicante, P.O. Box 99, E-03080 Alicante, Spain.

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11 *Corresponding author:

12 E-mail: carsanz@ua.es, carsanzla@gmail.com

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14 Running title: Climate warming effect on nutrient cycling

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16

17 Abstract

18 Increasing ocean temperature due to climate change is an important anthropogenic driver of
19 ecological change in coastal systems, where sediments play a major role in nutrient cycling. Our
20 ability to predict ecological consequences of climate change is enhanced by simulating real
21 scenarios. Based on predicted climate change scenarios, we tested the effect of temperature and
22 organic pollution on nutrient release from coastal sediments to the water column in a mesocosm
23 experiment. PO_4^{3-} release rates from sediments followed the same trends as organic matter
24 mineralization rates, and increased linearly with temperature and were significantly higher under
25 organic pollution than under non-polluted conditions. NH_4^+ release only increased significantly
26 when the temperature rise was above 6°C , and was significantly higher in organic polluted
27 compared to non-polluted sediments. Nutrient release to the water column was only a fraction
28 from the mineralized organic matter, suggesting PO_4^{3-} retention and NH_4^+ oxidation in the
29 sediment. Bioturbation and bioirrigation appeared to be key processes responsible for this
30 behaviour. Considering that the primary production of most marine basins is N-limited, the
31 excess release of NH_4^+ at a temperature rise > 6 degrees could enhance water column primary
32 productivity, which may lead to the deterioration of the environmental quality. Climate change
33 effects are expected to be accelerated in areas affected by organic pollution.

Eliminado: especially when the interactions among drivers may not be just additive

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35 Keywords: eutrophication, global warming, nitrogen, organic matter enrichment, phosphorus, sea
36 water temperature.

37 1. Introduction

38 Ocean temperature rise due to climate change is considered among the most severe
39 anthropogenic drivers of ecological change in marine systems, especially in coastal areas
40 (Halpern et al. 2008). Sea surface temperature (SST) in marine systems is expected to rise 0.2°C
41 per decade (IPCC 2007), but in relatively enclosed and shallow coastal areas, such as the Baltic
42 Sea, temperature has risen much more rapidly (1°C in last decade; ~~(Mackenzie and Schiedek~~
43 ~~2007; Belkin 2009)~~ and similar rises are expected for the next decades (Doscher and Meier 2004).
44 In these areas, heterotrophic processes in sediments prevail due to the generally low availability
45 of light in the seabed due to eutrophication and high input of labile organic matter (Conley et al.
46 2009).

Eliminado: Belkin 2009;

47 Coastal areas are climate-sensitive systems (IPCC 2007) that play an important role in the
48 mineralization of organic matter (OM) (Middelburg et al. 1997). During mineralization, organic
49 phosphorous (P) and nitrogen (N) are transformed into inorganic forms (PO_4^{3-} and NH_4^+ ,
50 respectively). OM is mineralized mainly by microbial processes, which are strongly influenced
51 by temperature (Robador et al. 2009). Consequently, climate change may affect nutrient
52 regeneration rates in coastal ecosystems.

Código de campo cambiado

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53 PO_4^{3-} can be sequestered in the sediment by adsorption to ferric (oxy)hydroxides forming
54 solid ferrous phosphates (Jorgensen 1983). Sulfides resulting from sulfate reduction may
55 mobilize PO_4^{3-} by reducing ferric oxyhydroxides (Roden and Edmonds 1997) and by dissolving
56 Fe minerals containing PO_4^{3-} (Gachter and Muller 2003). Despite the complex interactions
57 among the Fe, S and P pools, PO_4^{3-} release to the water column is mainly dependent on the redox
58 conditions in the sediment surface, where oxidized Fe keep PO_4^{3-} immobilized. Thus seasonal
59 increases in sediment metabolic rates due to temperature rise may lead to reduced conditions in

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Eliminado: anoxic

60 the sediment surface, resulting in PO_4^{3-} release during summer (Jensen et al. 1995;Cowan and
61 Boynton 1996). Mineralized N is mainly released to the water column as NH_4^+ (Jorgensen 1983).
62 NH_4^+ can be further transformed into NO_3^- and NO_2^- , through nitrification, and end up as N_2
63 through denitrification or anammox (Thamdrup 2012). In contrast to NH_4^+ , NO_3^- and NO_2^- , N_2
64 exits the biological N-cycle. Consequently, **denitrification** results in N removal from the
65 ecosystem preventing eutrophication (Thamdrup and Dalsgaard 2008). Marine coastal sediments
66 play a major role in supporting primary productivity of the water column by supplying a large
67 part of the nutrient demand for phytoplankton (Nixon 1981;Kelly et al. 1985). Increases in sea
68 water temperature and input of OM to the sediment, are both expected to stimulate the release of
69 inorganic nutrients from the sediment to the water column, which may in turn stimulate primary
70 productivity. Nutrient increase above a certain threshold may lead to algal blooms and
71 subsequent hypoxic/anoxic events, resulting in the deterioration of ecological status (Gray et al.
72 2002).

Eliminado: ;Jensen et al. 1995

Eliminado: and need to be fixed again so it can be available again for primary producers

Eliminado: N_2 production

Eliminado: ;Nixon 1981

73 Coastal areas gather the greatest human population densities in the world, resulting in
74 high anthropogenic pressure on coastal ecosystems. Thus, many coastal areas are subject to
75 multiple stressors (Halpern et al. 2008) such as different kinds of pollution and global warming.
76 Among the different types of pollution, organic pollution, also know as organic enrichment, is
77 one of the most common in densely populated coastal areas (Islam and Tanaka 2004). As for
78 temperature, organic enrichment enhances sediment metabolism, mainly by stimulating
79 anaerobic pathways and especially sulphate reduction (Valdemarsen et al. 2009). This effect is
80 magnified when **organic pollution and temperature rise co-occur** (Sanz-Lazaro et al. 2011b).

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81 Our ability to predict the ecological consequences of climate change is enhanced by
82 simulating realistic future scenarios. Hence, it is important to conduct experiments to elucidate

83 not only the effects of individual drivers of ecological change but also the interactions among
84 them, especially when the interactions among these drivers are not just additive (Falkenberg et
85 al. 2013). Despite the current concern of global change, scarce research effort has been taken on
86 understanding how temperature rise affect the cycling of N and P in coastal sediments
87 (Alsterberg et al. 2012). In fact, the accuracy of predictive biogeochemical models related to the
88 effect of climate change on the coastal eutrophication is restrained due to limited knowledge
89 (Meier et al. 2011).

90 The aim of this work is to examine the effects of temperature rise and organic enrichment
91 on sediment nutrient release derived from heterotrophic processes. We used a mesocosm
92 approach and hypothesized that temperature rise due to climate change increases PO_4^{3-} and NH_4^+
93 release from the sediments as a consequence of increased metabolic rates. We expected an
94 increase of the release of nutrients with temperature, with a more marked effect in organic
95 enriched than in non-organic enriched sediments, due to stimulation of anaerobic processes
96 resulting in PO_4^{3-} and NH_4^+ release.

97

98

99 2. Materials and methods

100

101 This experiment is the second part of a study. The results on carbon and sulphur cycles are
102 presented in Sanz-Lázaro et al. (2011b), where detailed information on the methods it is given.

103

104 2.1. Collection of sediment and polychaetes

105 The sediment used for experiments was well sorted, organic poor, Fe-rich sand [0.4 %DW
106 particulate organic carbon (POC), 125 $\mu\text{mol cm}^{-3}$ reactive Fe and 220 μm average grain size]
107 collected [at 1 m depth](#) in Fænø Sund, Denmark (for further details seeValdemarsen et al. 2009).
108 The macrofaunal organism used for experiments was the polychaete *Nereis diversicolor*, which
109 was chosen based on its ability to bioirrigate surface sediment and influence microbial reaction
110 rates (Kristensen 2000;Mermillod-Blondin et al. 2004). *N. diversicolor* was collected from
111 Fællesstrand in the outer part of Odense Fjord, Denmark.

112

113 2.2. Experimental setup

114 Sediment was split into either control (-OM) or organically enriched sediment (+OM).
115 Enrichment was performed by adding 92 g labile OM [finely ground fish feed, Ecolife, Dansk
116 Ørredfoder with 49.4% DW POC, 8.1% DW total nitrogen organic N (TN), 0.9% DW total P
117 (TP)] to 20 L of sediment. The enrichment corresponded to 26 mol POC m^{-2} , which is
118 comparable to the annual OM deposition at fish or mussel farms (Callier et al. 2006;Holmer et al.
119 2007;Sanz-Lazaro et al. 2011a).

120 Sediment was packed into 36 core liners (8 cm internal diameter; i.d., 35 cm sediment
121 depth) which were distributed in three tanks maintained at 16, 22 or 26°C containing 65 L GF/F-
122 filtered seawater from Fænø Sund with a salinity of 17 psu. Each tank contained 6 cores of each
123 -OM and +OM, sediment. The 16°C treatment was chosen as the reference level of present mean
124 SST for summer months in temperate areas of the Baltic Sea (Kristensen 1993;Holmer and
125 Kristensen 1996). The 22°C and 26°C treatments were chosen as SST climate change scenarios
126 in 60 and 100 years based on SST temperature rise observed in the last decades (Mackenzie and

127 Schiedek 2007;Belkin 2009) and expected raises (Doscher and Meier 2004) (1°C per decade in
128 both cases).

129 The sediment in the cores was left 3 days to compact and acclimitize. Then three *N.*
130 *diversicolor* were added to each core to simulate the natural density (Delefosse et al. 2012). The
131 time of polychaete addition was assumed the beginning of the experiment (t = 0). *N. diversicolor*
132 bioirrigation rates were previously reported in Sanz-Lázaro et al. (2011b). They were calculated
133 based on Br⁻-addition experiments and were on average 13-24 L m⁻² d⁻¹ in the different
134 treatments. There were no significant (p < 0.05) effects of temperature or of OM enrichment on
135 bioirrigation rates and all cores were bioirrigated to 6–8 cm depth (Sanz-Lazaro et al. 2011b).
136 Bioirrigation rates in the present experiment were similar to the bioirrigation measured
137 previously for other polychaetes (Quintana et al. 2013) and within the range of the bioirrigation
138 performed by natural macrofaunal communities (Valdemarsen et al. 2010).

Con formato: Español (España
- alfab. internacional)

139 Additionally, six cores with 5 cm i.d. were also filled with –OM and +OM sediment to
140 determine initial element pools in the sediment. Cores were closed at the bottom with rubber
141 stoppers and ~20 cm sediment was added, leaving a 10-12 cm headspace above the sediment.
142 During the experiment the water in each tank was kept aerated and changed regularly. The cores
143 were kept submerged and in darkness throughout the experiment (25-39 days). More specific
144 details can be found in Sanz-Lázaro et al. (2011b).

Eliminado: conditions

145
146 2.3. Nutrient fluxes

147 NH₄⁺ and PO₄³⁻ fluxes between sediment and water were measured every 2-4 days during the
148 first 2 weeks and every week during the rest of the experiment. During flux measurements, the
149 water column of each sediment core was sampled and cores were closed with rubber stoppers.

150 Incubations were ended after 3-5 h (-OM) or 1-2 h (+OM), where the rubber stoppers were
151 removed and the water column was sampled again. All samples were GF/F-filtered, transferred
152 to 20 mL plastic vials and frozen (-20°C).

153

154 2.4. Sectioning of cores

155 The three 5 cm i.d. sediment cores of each sediment type (-OM and +OM) were initially
156 sectioned ($t = 0$; henceforth referred to as initial cores) and the remaining cores from every
157 temperature treatment were sectioned at the end of the experiment (henceforth, final cores).

158 Cores were sectioned into 1 cm ~~slices~~ to 2 cm depth and into 2 cm slices to 16 cm depth. Every
159 sediment slice was homogenized and subsampled for different analysis. One subsample from
160 each sediment slice was used to measure reactive Fe and phosphate bound to reactive Fe. A
161 subsample of sediment was used for TP measurement. The remaining sediment from each slice
162 was used to determine TN, sediment density and water content. All analytical methods are
163 described below. Since temperature has a strong stimulatory effect on microbial reaction rates,
164 the duration of the temperature treatments varied to prevent porewater sulfate depletion and a
165 shift in sediment metabolism towards methanogenesis. Thus, the sectioning of the sediments at
166 16, 22 and 26°C was performed after 39, 32 and 25 days, respectively.

Eliminado: slices

167

168 2.5. Sediment metabolic rates

169 C mineralization rates were estimated as time-integrated TCO_2 sediment-water column flux
170 divided by the experiment duration as described in Sanz-Lázaro *et al.* (2011b). Average C
171 mineralization was 85 ± 7 , 138 ± 15 and 257 ± 24 $\text{mmol m}^{-2} \text{d}^{-1}$ in -OM cores at 16, 22 and 26°C,

172 respectively, and 355 ± 21 , 486 ± 43 and 775 ± 43 mmol m⁻² d⁻¹ in the +OM cores for 16, 22 and
173 26°C, respectively.

174

175 2.6. Analyses

176 NH₄⁺ and PO₄³⁻ were analyzed spectrophotometrically on a Lachat QuikChem 8500
177 autoanalyzer. Reactive Fe was extracted on ~0.2 g of sediment subsamples with 5 ml of 0.5 M
178 HCl shaken for 30 min. Then samples were centrifuged for 5 min (3000 rpm, ca. 1000 × g) and
179 GF/F filtered. The supernatant was analyzed by the ferrozine method (Stookey 1970). Fe (II) was
180 determined on the untreated extract while total Fe [Fe(II)+Fe(III)] was determined after
181 reduction with hydroxylamine (Lovley and Phillips 1987). Fe (III) was determined as the
182 difference between total Fe and Fe(II). PO₄³⁻ in HCl extracts was also analyzed
183 spectrophotometrically after addition of Molybdate reagent (Koroleff 1983) to get a measure of
184 Fe-bound P. Total P was determined on combusted sediment subsamples (520°C, 2 h), which
185 were boiled in 1 M HCl for 1 h. The supernatant was analyzed for PO₄³⁻ as described above. TN
186 was determined on a Carlo Erba CHN EA1108 elemental analyzer according to Kristensen and
187 Andersen (1987). Sediment density was determined gravimetrically by weighing a known
188 volume of sediment using cut off syringes. Water content was measured as weight loss after
189 drying (105°C, >12 h).

190

191 2.7. Data analysis

192 Significant differences in the content of solid phase nutrients were tested by pair-wise t-tests.
193 Comparisons were done between initial -OM and +OM cores, and between initial and each final
194 treatment within each sediment type (-OM and +OM).

195 Average nutrient efflux rates were estimated as time-integrated nutrient effluxes divided
196 by the experiment duration. To compare the trends of the time-integrated effluxes between –OM
197 and +OM treatments along temperature we did regression models considering temperature the
198 continuous covariate and OM enrichment as a fixed factor. According to the data on the trends of
199 the time-integrated effluxes with increasing temperature we hypothesized different regression
200 models. We used the second order Akaike Information Criterion (AICc) to choose the best
201 model, since it is a good compromise between fitting and complexity of the model and it is
202 recommended when the sample size is relatively low (Burnham and Anderson 2002). In all
203 regressions temperature was centered at 26°C, so intercepts showed mean values of effluxes at
204 this temperature. The significance of the regression coefficients was tested by ANOVA.
205 Homocedasticity was checked using Levene’s test and normality with p-p plots. Analyses were
206 run in R (v. 2.15.0) and linear regressions were implemented using the *lm* function (R
207 Development Core Team 2012). All data were reported as mean ± standard error (SE) and
208 statistical tests were conducted with a significance level of $\alpha = 0.05$.

209 ~~We calculated the~~ molar ratio of C:N:P in the added OM based on its composition. ~~We~~
210 ~~calculated the~~ molar C:N:P ratio in the sediment based on POC, TN and TP content in
211 unenriched and enriched sediment. ~~We estimated~~ C:N:P ratios of organic matter being
212 mineralized based on TCO₂, NH₄⁺ and PO₄³⁻ effluxes. C and TCO₂ effluxes were reported in
213 Sanz-Lázaro *et al.* (2011b).

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216 3. RESULTS

217

218 3.1. P in sediment

219 TP concentration in initial -OM and +OM sediment was 50.8 ± 3.2 and $51.2 \pm 0.3 \mu\text{mol cm}^{-3}$,
220 respectively. Depth-integrated (0-16 cm) TP thus amounted to 8.2 ± 0.5 and $8.2 \pm 0.1 \text{ mol m}^{-2}$ in
221 initial -OM and +OM cores, respectively (Table 1). The initial enrichment with fish feed should
222 have resulted in 0.4 mol m^{-2} higher TP in +OM cores than -OM cores (4.7 % of the TP in the
223 sediment), but this was not evident from our measurements probably due to high variability
224 between subsamples. Hence, there were no detectable differences in the TP content between
225 initial -OM and +OM cores ($p > 0.05$). Additionally, there were no significant differences on TP
226 content between the initial and each final treatment within each sediment type (-OM and +OM).
227 Depth-integrated (0-16 cm) Fe-bound P corresponded to 2.5 ± 0.1 and $2.1 \pm 0.2 \text{ mol m}^{-2}$ in initial
228 -OM and +OM sediment, respectively. By the end, Fe-bound P ranged between 2.1 ± 0.2 and 2.6
229 $\pm 0.3 \text{ mmol m}^{-2}$ in -OM cores, and between 2.0 ± 0.2 and $2.6 \pm 0.3 \text{ mmol m}^{-2}$ in +OM cores
230 (Table 2).

231

232 3.2. N in sediment

233 PON concentration in initial -OM and +OM sediment was 47.5 ± 2.4 and $61.4 \pm 1.6 \mu\text{mol cm}^{-3}$,
234 respectively. Thus depth-integrated (0-16 cm) PON was 7.7 ± 0.4 and $9.8 \pm 0.3 \text{ mol m}^{-2}$ in initial
235 -OM and +OM cores, respectively (Table 1). The enrichment resulted in significantly higher
236 PON in +OM cores ($p < 0.05$). Additionally, there were no significant differences on PON content
237 between the initial and each final treatment within each sediment type (-OM and +OM). The
238 initial enrichment with fish feed should have resulted in extra 3.6 mol m^{-2} (46.8 % of the PON
239 concentration in the sediment), which was close to the measured enrichment (28.6 % of the PON
240 in the sediment).

241
242 3.3. Fe in sediment
243 Depth-integrated (0-16 cm) pools of reactive Fe (III) were 2.5 ± 0.1 and 2.3 ± 0.2 mol m⁻² in
244 initial -OM and +OM sediment, respectively. After the experiment, the pools of reactive Fe (III)
245 were 2.0 ± 0.3 , 1.8 ± 0.1 and 2.3 ± 0.5 mmol m⁻² in -OM cores at 16, 22, and 26°C, respectively,
246 and 1.9 ± 0.2 , 2.5 ± 0.3 and 2.3 ± 0.5 mmol m⁻² in +OM cores at 16, 22, and 26°C (Table 2). Fe
247 (III) concentration was high in the first cm of the sediment being 32.9 ± 8.0 , 35.5 ± 4.3 and 25.1
248 ± 5.6 $\mu\text{mol cm}^{-3}$ in -OM cores at 16, 22, and 26°C, respectively, and 12.7 ± 3.6 , 24.0 ± 6.9 and
249 28.5 ± 6.2 $\mu\text{mol cm}^{-3}$ in +OM cores at 16, 22, and 26°C (Fig. 1).

250
251 3.4. Nutrient release
252 PO₄³⁻ efflux showed a similar temporal pattern in the different treatments: an increase in the first
253 days, a peak at intermediate stages and then decreasing effluxes towards the end (Fig. 2). The
254 peaks of PO₄³⁻ efflux were stimulated by OM enrichment and temperature. In -OM cores PO₄³⁻
255 efflux ranged from -0.3 to 0.3, -0.4 to 0.8 and -0.2 to 0.7 mmol m⁻² d⁻¹ at 16, 22 and 26°C,
256 respectively. In + OM cores PO₄³⁻ efflux ranged from -0.2 to 1.0, -0.2 to 1.9 and 0.0 to 1.4 mmol
257 m⁻² d⁻¹ at 16, 22 and 26°C, respectively.

258 Average PO₄³⁻ efflux over the whole experiment was 1.7 ± 1.2 , 3.5 ± 1.7 and 4.3 ± 1.1
259 mmol m⁻² in -OM cores at 16, 22, and 26°C, respectively. In +OM cores total PO₄³⁻ effluxes
260 were 6.6 ± 1.2 , 11.4 ± 2.0 and 13.2 ± 1.8 mmol m⁻² in +OM cores at 16, 22, and 26°C,
261 respectively, corresponding to 4.2, 7.6 and 9.3 % of the total P added in fish feed (Table 1).
262 Average PO₄³⁻ efflux showed a linear increasing trend along temperature in both -OM and +OM
263 cores (Fig 3a). The AICc showed that PO₄³⁻ effluxes were best fitted with a linear regression

264 (Table A1). The regression analysis showed that average PO_4^{3-} efflux increased linearly with
265 temperature ($p < 0.05$) in -OM and +OM cores. There were significant differences between -OM
266 and +OM treatments at 26°C ($p < 0.05$) and the significant interaction term of the regression
267 ($p < 0.05$) indicated a steeper temperature response in +OM compared to -OM treatments (Table
268 3).

269 The overall trend of NH_4^+ -efflux was similar to PO_4^{3-} -efflux. NH_4^+ effluxes increased at
270 the beginning, peaked and then decreased towards the end (Fig. 2). The range of the NH_4^+
271 effluxes was stimulated by both organic enrichment and temperature. In -OM cores NH_4^+ efflux
272 ranged from -12.5 to 27.8, -20.7 to 35.8 and -16.2 to 54.6 $\text{mmol m}^{-2} \text{d}^{-1}$ at 16, 22 and 26°C ,
273 respectively. In +OM cores NH_4^+ efflux ranged from 0.0 to 58.8, 0.0 to 60.0 and 3.1 to 55.6
274 $\text{mmol m}^{-2} \text{d}^{-1}$ at 16, 22 and 26°C , respectively.

275 Average NH_4^+ efflux over the whole experiment was 217 ± 48 , 112 ± 58 and 339 ± 106
276 mmol m^{-2} in -OM cores at 16, 22, and 26°C , respectively. Total NH_4^+ effluxes in +OM cores
277 were 559 ± 113 , 525 ± 102 and 577 ± 132 mmol m^{-2} at 16, 22, and 26°C , corresponding to 17.9,
278 17.4 and 20.1 % of N added in fish feed (Table 1). The trend of average NH_4^+ -effluxes over the
279 whole experiment was not as clear as for PO_4^{3-} effluxes (Fig. 3b). NH_4^+ effluxes were clearly
280 stimulated at 26°C in both sediment types, however. According to the AICc, the trend of NH_4^+
281 efflux over temperature was best fitted with an exponential regression (Table A1). The
282 regression analysis showed significant increasing NH_4^+ effluxes with temperature following an
283 exponential trajectory ($p < 0.05$) in both -OM and +OM sediment. There were significant
284 differences between -OM and +OM treatments at 26°C ($p < 0.05$). The interaction term of the
285 regression did not show significant differences. Thus, NH_4^+ efflux in -OM and +OM cores
286 followed a similar trend with temperature although at different ranges (Table 3).

287

288 3.5. C:N:P ratios

289 The C:N, C:P and N:P ratios of the added OM were 5.2, 21.3 and 4.1, respectively. C:N ratios in
290 the initial -OM and +OM sediment were 12.7 and 11.6, respectively. The ratios among C, N and
291 P at the end of the experiment were calculated based on CO_2 , NH_4^+ and PO_4^{3-} effluxes. In -OM
292 cores, C:N, C:P and N:P ranged 13.3 - 25.3, 656 - 988 and 25.9 - 65.3, respectively, while in +
293 OM cores, C:N, C:P and N:P ranged 21.6 - 26.8, 1157 - 1866 and 43.7 - 86.5, respectively
294 (Table 4).

295

296

297 4. Discussion

298 Our results show that temperature rise resulted in different trends of sediment
299 nutrient release of PO_4^{3-} and NH_4^+ under both organic and non-organic enrichment conditions.
300 While sediment PO_4^{3-} release followed a linear trend with increasing temperature, the NH_4^+
301 release from sediment show exponential trends, notably increasing when temperature increments
302 were above 6°C.

303 4.1. PO_4^{3-} release

304 The measured PO_4^{3-} effluxes at 16°C were within the range of effluxes measured in coastal
305 sediments in the Baltic Sea (Sundby et al. 1992; Jensen et al. 1995). PO_4^{3-} effluxes increased
306 linearly with temperature in both -OM and +OM treatments, but the slope of the regression was
307 significantly steeper in +OM cores compared to -OM cores. This suggests that the temperature
308 dependent increase in PO_4^{3-} effluxes is enhanced by OM enrichment. The temperature effect on
309 PO_4^{3-} release was comparable to the temperature effect on total C-metabolism in both organic

Eliminado: natural

310 enriched and non-organic enriched conditions (Sanz-Lazaro et al. 2011b). Thus, a 10°C rise lead
311 to 4.3 and 3.4 times stimulated PO_4^{3-} -efflux of in -OM and +OM cores, respectively, while this
312 temperature rise stimulated TCO_2 -efflux 3.0 and 2.2 times in -OM and +OM cores, respectively.
313 This indicated that PO_4^{3-} release occurred in proportion to total sediment metabolism. However,
314 the release of PO_4^{3-} was much lower than that of TCO_2 , as indicated by C:P ratios above 600 in
315 all treatments. This was far below the C:P ratio in the sediment (11.6 and 13.5 for -OM and
316 +OM treatments, respectively) and the C:P ratio in the added OM (21.3), suggesting that organic
317 P was either less labile compared to organic C or that inorganic PO_4^{3-} was retained in the
318 sediment to a larger extent than C. For each temperature, we estimated the mineralized OM out
319 of the added OM by subtracting the TCO_2 production in the +OM treatments to the TCO_2
320 production in the -OM treatments. We found that 55-77% of the added OM was mineralized,
321 whereas P efflux only corresponded to 4.2-9.3 % of the added P (Table 2). Taking into account
322 that the added OM (fish feed) is highly labile, our data suggest PO_4^{3-} retention in the sediment,
323 which could be associated with adsorption to oxidized forms of Fe (Jensen et al. 1995).

Eliminado: OM

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324 P-retention in marine sediments is controlled by the pools of P, Fe and S in the sediment,
325 interactions between these pools and the sediment redox-conditions (Roden and Edmonds
326 1997; Gachter and Muller 2003). Generally, in sediments with an oxic surface layer, oxidized Fe
327 acts as a lid for PO_4^{3-} , which is adsorbed to ferric Fe preventing its release to the water column
328 (Rozan et al. 2002). All the treatments maintained a considerable pool of oxidized Fe(III) (1.8 to
329 2.5 mol m^{-2}), in the same range as measured at the beginning of the experiment (2.3 to 2.5 mol
330 m^{-2}) indicating that the PO_4^{3-} retention capacity of the sediment was maintained despite elevated
331 temperature and organic enrichment. Similarly, levels of PO_4^{3-} bound to Fe (III) showed low
332 variation between initial and final cores. The oxic conditions of the sediment surface were

Eliminado: mobilization

333 maintained in all treatments despite metabolism enhancement and subsequent increase in
334 sulphide production, which was especially notable in the +OM treatments. The continuous
335 oxygenation of surface sediment due to *N. diversicolor* bioturbation and bioirrigation (Sanz-
336 Lazaro et al. 2011b) was probably critical for maintaining and oxic sediment surface with high
337 Fe(III) concentrations, since dramatically stimulated sediment metabolism are expected to
338 notably diminish the Fe(III) pool of the sediment in the absence of macrofauna (Valdemarsen et
339 al. 2009). All these results suggest that the capacity of the sediment to retain PO_4^{3-} was
340 maintained despite high metabolic rates due to organic enrichment and elevated temperatures.

341 The PO_4^{3-} retention may be diminished in sediments with a low pool of Fe(III) (Rozañ et
342 al. 2002) and/or with no bioturbating macrofauna (Bartoli et al. 2009). Hence under such
343 conditions the PO_4^{3-} efflux could be much higher than measured in this experiment. A longer
344 experiment could also have resulted in decreased PO_4^{3-} retention, because of exhaustion of the
345 binding sites of PO_4^{3-} with Fe (III) (Jorgensen 1996). Nevertheless, the capacity of the sediment
346 to retain PO_4^{3-} is notable considering that the amount of OM added in this experiment
347 corresponded to the total OM deposited on the seabed below fish farms during a year, and that
348 the OM added has a high reactivity, which implies that most of the OM is mineralized initially.
349 Thus, marine sediment can act as a relevant sink of P, even under severe scenarios of
350 temperature rise and organic enrichment, as long as it has a large enough pool of Fe and the
351 macrofauna keeps the surface of the sediment under oxic conditions.

352

353 4.2. NH_4^+ release

354 Rates of NH_4^+ -effluxes at 16°C were within the range reported from previous laboratory
355 experiments at similar conditions with non-enriched or enriched sediment (Valdemarsen et al.

356 2009;Valdemarsen et al. 2010). The 1-3 times temperature stimulation of NH_4^+ -efflux were in
357 the same range observed in sediments from coastal areas (i.e. temperature rise ca. 10°C during
358 summer resulted in one- to four-fold increases in NH_4^+ -efflux) (Kristensen 1993). As with PO_4^{3-} ,
359 the release rates of NH_4^+ were always higher in +OM cores than in -OM treatments for a given
360 temperature, highlighting that OM enrichment had a stimulatory effect on NH_4^+ release. This was
361 expected since high NH_4^+ -release is often observed in sediments enriched with labile organic
362 matter (Christensen et al. 2000;Valdemarsen et al. 2012). NH_4^+ release was not stimulated by
363 temperature between $16\text{-}22^\circ\text{C}$, but above 22°C NH_4^+ release increased exponentially in both -
364 OM and +OM treatments. The notable increase of NH_4^+ release at a temperature increment of
365 10°C in both -OM and +OM treatments, could led us to speculate that the efficiency of NH_4^+
366 oxidizing pathways is lowered at high temperatures, nevertheless the data of C:N ratios pointed
367 to an opposite hypothesis.

368 The C:N ratio of the added OM was 5.2, whereas the C:N ratios of the sediment OM at
369 the beginning of the experiment was close to 12 in both -OM and +OM cores. The C:N ratios of
370 C and N release during the experiment were always higher than the C:N ratios of the sediment
371 OM, in particular at high temperature rise (C:N ratios of C and N release were 25.3 and 25.0 for
372 a temperature increment of 6°C , 15.1 and 26.8 for a temperature increment of 10°C , in -OM and
373 +OM cores, respectively). This suggests that part of the mineralized N is not released to the
374 water column as NH_4^+ , but transformed into other N compounds. NH_4^+ could be nitrified in the
375 oxidized surface sediment or in *N. divericolor* burrows, and subsequently reduced to N_2 via
376 anammox or denitrification (Thamdrup 2012). Previous studies show that both denitrification
377 and anammox are stimulated by increasing temperatures (Nowicki 1994;Alsterberg et al.
378 2012;Canion et al. 2013) and by availability of OM (Nowicki 1994;Thamdrup and Dalsgaard

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2005;

379 2002;[Engstrom et al. 2005](#)) which supports the data from this experiment. Nevertheless,
380 evidence based on NO_3^- and NO_2^- data should be needed to confirm this hypothesis. Despite so,
381 NH_4^+ is mostly the dominating form of dissolved inorganic N effluxing from organic enriched
382 sediments ([Christensen et al. 2000](#);[Holmer et al. 2003](#)), while coupled nitrification-denitrification
383 rarely exceeds $1\text{-}2\text{ mmol m}^{-2}\text{ d}^{-1}$ in marine sediments ([Middelburg et al. 1996](#)). We are therefore
384 confident that the NH_4^+ release rates can act as a proxy for total inorganic N release to the water
385 column.

386 Despite that bioturbation and bioirrigation by macrofauna promotes OM mineralization,
387 in the present experiment, both PO_4^{3-} and NH_4^+ effluxes were below the expected levels of the
388 mineralized organic matter. In the case of PO_4^{3-} , this can be explained by the PO_4^{3-} retention
389 capacity of the sediment that is promoted by macrofauna activity ([Bartoli et al. 2009](#)). In the case
390 of NH_4^+ , these results could be explained because macrofauna promotes NH_4^+ -oxidizing
391 processes and the coupling between nitrification and denitrification ([Gilbert et al. 1995](#)). Thus,
392 sediment reworking processes of macrofauna promote nutrient recycling while preventing
393 eutrophication.

394 While there is, to some extent, experimental manipulative experiments that focus on the
395 effects of carbon mineralization rates of marine sediments on warming scenarios ([Finke and](#)
396 [Jorgensen 2008](#);[Robador et al. 2009](#);[Sanz-Lazaro et al. 2011b](#)), less information is available on
397 the mineralization rates of N and P. Marine sediments act as an important source of nutrients for
398 water column primary production ([Nixon 1981](#)). Global warming may lead to eutrophication of
399 the water column by increasing the nutrient release from sediments. For both nutrients, the
400 effluxes increased with temperature, but followed significantly different trends. PO_4^{3-} effluxes
401 increased linearly, highlighting that P mineralization is temperature dependent. On the other

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402 hand, NH_4^+ effluxes showed an exponentially increasing trend suggesting that N mineralization
403 is expected to be independent from temperature rises of up to 6°C. Since in most marine basins,
404 primary production in the water column is limited by N (Zehr and Kudela 2011), the predicted
405 increases in NH_4^+ effluxes may have important consequences for temperature rises above 6°C.
406 As an example, in the Baltic Sea, N demand of phytoplankton is $5.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ (Koop et al.
407 1990). Thus, in this case, phytoplankton demand of N would be surpassed above temperature
408 increments of 6°C or with no increments in temperature, under non- and organic enrichment
409 conditions, respectively. Under these scenarios, the excess NH_4^+ efflux could stimulate primary
410 production, which may lead to excessive proliferation of algae.

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411 Additionally it should be considered that the experiment was performed in darkness, as
412 the experiment was designed to simulate the generally low availability of light at the sediment
413 surface in relatively enclosed and shallow coastal areas exposed to eutrophication, such as in the
414 Danish coastal areas. Nevertheless, in other areas with more light availability autotrophic
415 processes are also important. This could lead to different results with regards to nutrient release
416 rates from the sediment.

417 In conclusion, in future scenarios of climate change, sediment PO_4^{3-} release is expected to
418 increase following the trends observed for OM mineralization rates in the sediment. The
419 magnitude of the release of PO_4^{3-} is influenced not only by local OM deposition rates but also by
420 sediment characteristics, particularly, the amount of reactive Fe in sediment. NH_4^+ release from
421 sediment is not expected to increase substantially with temperature increments of up to 6°C, in
422 organic polluted as well as in non-polluted sediments. However, more severe temperature rises
423 may be associated with an exponential increase in the release of NH_4^+ from sediments. As most
424 marine basins are N-limited, the excess release of NH_4^+ may set in motion a cascade of negative

425 effects leading to deteriorating environmental quality. These effects are expected to be more
426 detrimental in organic polluted areas as well as in coastal basins with no or restricted exchange
427 with ocean waters.

428

429

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588 Tables

589

590 Table 1: Depth-integrated (0–16 cm) pools of P and N (mean ± SE) in the sediment used in the
591 experiment (n=3, initial concentration) and the estimates on the amount of nutrient mineralized
592 during the experiment based on nutrient sediment-water column fluxes (n=6). Values inside
593 square brackets indicate the % of the nutrient mineralized out of the total added.

594

	Initial concentration (mmol m ⁻²)	Mineralized (mmol m ⁻²), by temperature		
		16°C	22°C	26°C
-OM				
P	8178 ± 548	2.65 ± 1.12	4.35 ± 1.71	5.64 ± 1.42
N	7662 ± 401	252 ± 57.5	141 ± 59.3	441 ± 138
+OM				
P	8205 ± 72.1	7.54 ± 1.33 [4.2]	13.54 ± 2.4 [7.6]	16.49 ± 2.24 [9.3]
N	9854 ± 292	641 ± 130 [17.9]	623 ± 121 [17.4]	721 ± 165 [20.1]

595 Notes: The 16°C treatment corresponds to the present mean sea surface temperature (SST) for summer
596 months in the Baltic Sea. The 22 and 26°C treatments were chosen as SST climate change scenarios in
597 60 and 100 years based on SST temperature rise observed in the last decades and expected raises (1°C
598 per decade in both cases). –OM and +OM correspond to non- and organic polluted treatments,
599 respectively. The organic matter addition to +OM cores corresponded to 26 mol POC m⁻², which is
600 comparable to the annual organic matter deposition in areas under the influence of mussel or fish farms.
601 The final cores were maintained at 16, 22, or 26°C in separate tanks containing filtered seawater.

602 Table 2: Depth-integrated (0–16 cm) pools of reactive Fe (III) and P bound to reactive Fe (mean
 603 \pm SE) for initial cores (n = 3) and final cores (n = 6). See notes at Table 1 for explanation about
 604 treatments.

605

	Initial concentration (mol m ⁻²)	Final concentration (mmol m ⁻²), by temperature		
		16°C	22°C	26°C
-OM				
Reactive Fe (III)	2.5 \pm 0.1	2.0 \pm 0.3	1.8 \pm 0.1	2.3 \pm 0.5
P bound to Fe	2.5 \pm 0.1	2.1 \pm 0.2	2.5 \pm 0.2	2.6 \pm 0.3
+OM				
Reactive Fe (III)	2.3 \pm 0.2	1.9 \pm 0.2	2.5 \pm 0.3	2.3 \pm 0.5
P bound to Fe	2.1 \pm 0.2	2.4 \pm 0.2	2.6 \pm 0.3	2.0 \pm 0.2

606

607

608 Table 3: Coefficients (means at 26°C) of the regression model for PO_4^{3-} and NH_4^+ sediment-
 609 water column flux (i.e. efflux) rates along temperature for non-organic polluted (-OM) and
 610 organic polluted (+OM) treatments. Regression model for PO_4^{3-} corresponds to a first order
 611 polynomial regression, while for NH_4^+ correspond to an exponential regression (Table A1).
 612 Significant effects ($p < 0.05$) are indicated in bold.

613

	PO_4^{3-} efflux rate	NH_4^+ efflux rate
	Coefficient (SE)	Coefficient (SE)
Intercept	0.207 (0.047)	13.58 (3.26)
OM	0.420 (0.076)	12.45 (5.27)
Temperature	0.016 (0.008)	0.946 (0.524)
OM x Temperature	0.028 (0.012)	0.108 (0.803)

614

615

616 Table 4: Initial C:N:P ratio of the organic matter in the sediment estimated from particulate
617 organic carbon, total nitrogen and total phosphorus and overall C:N:P ratio estimated from
618 nutrient and total CO₂ flux over the experimental period. C and total CO₂ flux data was reported
619 in Sanz-Lázaro *et al.* (2011b). See notes at table 1 for explanation of treatments.

	Initial ratio in the sediment	Overall ratio of the effluxes, by temperature		
		16°C	22°C	26°C
-OM				
C:N	12.7	13.3	25.3	15.1
C:P	11.6	849	656	988
N:P	0.9	63.8	25.9	65.3
+OM				
C:N	11.6	21.6	25.0	26.8
C:P	13.5	1866	1157	1174
N:P	1.2	86.5	46.3	43.7

620

621

622 Figure legends

623

624 Figure 1: Pools (mean \pm SE) of reactive Fe(III) versus depth for initial cores (n=3) and final
625 cores (n=6) in the different temperature treatments.

626

627 Figure 2: PO_4^{3-} and NH_4^+ efflux rates (n=6, mean \pm SE) during the experiment at the three
628 temperature scenarios under non- (-OM) and organic enrichment (+OM) conditions. Dotted lines
629 are the line of reference corresponding to 0.

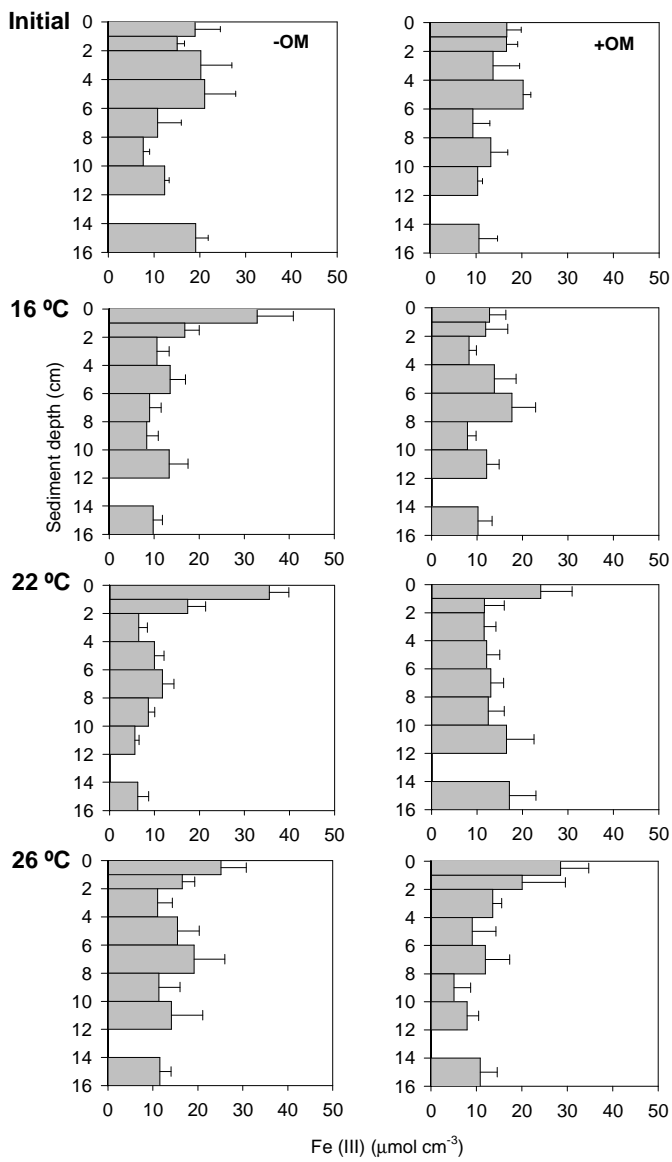
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631 Figure 3: Nutrient sediment-water column flux rates (n=6, mean \pm SE) versus temperature under
632 non- (-OM) and organic polluted (+OM) conditions. Lines indicate significant ($p < 0.05$)
633 regressions for -OM and +OM treatments. Type of regression was chosen according to the
634 AICc (corrected Akaike Information Criterion) (Table A1). R^2 refers to the whole regression
635 model for each nutrient which includes the factor OM.

636

637 Figure 1

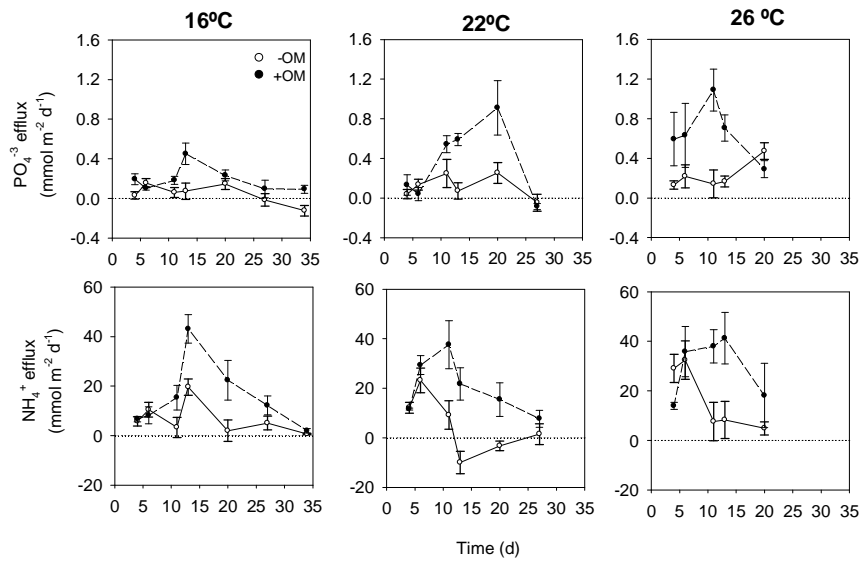
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640 Figure 2

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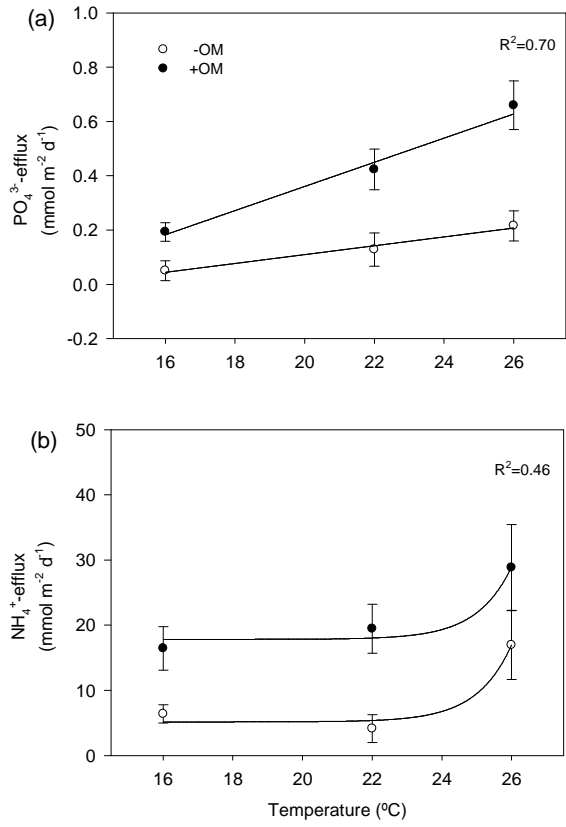
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645 Figure 3

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649 Appendix

650

651 Table A1: AICc (corrected Akaike Information Criterion) of the different regression models for

652 PO_4^{3-} and NH_4^+ efflux rates.

653

	AICc	
	PO_4^{3-} efflux rates	NH_4^+ efflux rates
$y_i = \beta_0 + \beta_1 x_i$	-31.940	247.60
$y_i = \beta_0 + \beta_1 e^{x_i}$	-23.032	243.04
$y_i = \beta_0 + \beta_1 x_i + \beta_2 x_i^2$	-26.321	248.63
$y_i = \beta_0 + \beta_1 \frac{1}{x_i}$	-30.336	248.95

654

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656