

1 "Projections of oceanic N₂O emissions in the 21st century using the IPSL Earth System
2 Model"

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24

25 0. Abstract

26

27 The ocean is a substantial source of nitrous oxide (N₂O) to the atmosphere, but little is
28 known on how this flux might change in the future. Here, we investigate the potential
29 evolution of marine N₂O emissions in the 21st century in response to anthropogenic
30 climate change using the global ocean biogeochemical model NEMO-PISCES. Assuming
31 nitrification as the dominant N₂O formation pathway, we implemented two different
32 parameterizations of N₂O production which differ primarily at low oxygen (O₂)
33 conditions. When forced with output from a climate model simulation run under the
34 business-as-usual high CO₂ concentration scenario (RCP8.5), our simulations suggest a
35 decrease of 4 to 12 % in N₂O emissions from 2005 to 2100, i.e., a reduction from 4.03 /
36 3.71 to 3.54 / 3.56 TgN yr⁻¹ depending on the parameterization. The emissions decrease
37 strongly in the western basins of the Pacific and Atlantic oceans, while they tend to
38 increase above the Oxygen Minimum Zones (OMZs), i.e., in the Eastern Tropical Pacific
39 and in the northern Indian Ocean. The reduction in N₂O emissions is caused on the one
40 hand by weakened nitrification as a consequence of reduced primary and export
41 production, and on the other hand by stronger vertical stratification, which reduces the
42 transport of N₂O from the ocean interior to the ocean surface. The higher emissions over
43 the OMZ are linked to an expansion of these zones under global warming, which leads to
44 increased N₂O production associated primarily with denitrification. While there are
45 many uncertainties in the relative contribution and changes in the N₂O production
46 pathways, the increasing storage seems unequivocal and determines largely the decrease in
47 N₂O emissions in the future. From the perspective of a global climate system, the
48 averaged feedback strength associated with the projected decrease in oceanic N₂O
49 emissions amounts to around -0.009 W m⁻²K⁻¹, which is comparable to the potential
50 increase from terrestrial N₂O sources. However, the assesment for a compensation
51 between the terrestrial and marine feedbacks calls for an improved representation of N₂O
52 production terms in fully coupled next generation of Earth System Models.

53

56 Nitrous oxide (N₂O) is a gaseous compound responsible for two key feedback
57 mechanisms within the Earth's climate. First, it acts as a long-lived and powerful
58 greenhouse gas (Prather et al., 2012) ranking third in anthropogenic radiative forcing
59 after carbon dioxide (CO₂) and methane (CH₄) (Myrhe et al., 2013). Secondly, the
60 ozone (O₃) layer depletion in the future might be driven mostly by N₂O after the drastic
61 reductions in CFCs emissions start to show their effect on stratospheric chlorine levels
62 (Ravishankara et al., 2009). The atmospheric concentration of N₂O is determined by the
63 natural balance between sources from land and ocean and the destruction of N₂O in the
64 atmosphere largely by photolysis (Crutzen, 1970; Johnston, 1971). The natural sources
65 from land and ocean amount to ~6.6 and 3.8 TgN yr⁻¹, respectively (Ciais et al., 2013).
66 Anthropogenic activities currently add an additional 6.7 TgN yr⁻¹ to the atmosphere,
67 which has caused atmospheric N₂O to increase by 18% since pre-industrial times (Ciais
68 et al., 2013), reaching 325 ppb in the year 2012 (NOAA ESRL Global Monitoring
69 Division, Boulder, Colorado, USA, <http://esrl.noaa.gov/gmd/>).

70 Using a compilation of 60,000 surface ocean observations of the partial pressure of N₂O
71 (pN₂O), Nevison et al. (2004) computed a global ocean source of 4 TgN yr⁻¹, with a
72 large range of uncertainty from 1.2 to 6.8 TgN yr⁻¹. Model derived estimates also differ
73 widely, i.e., between 1.7 and 8 TgN yr⁻¹ (Nevison et al., 2003; Suntharalingam et al.,
74 2000). These large uncertainties are a consequence of too few observations and of poorly
75 known N₂O formation mechanisms, reflecting a general lack of understanding of key
76 elements of the oceanic nitrogen cycle (Gruber and Galloway, 2008; Zehr and Ward,
77 2002), and of N₂O in particular (e.g., Zamora et al., 2012, Bange et al., 2009 or Freing
78 et al., 2012, among others). A limited number of interior ocean N₂O observations were
79 made available only recently (Bange et al., 2009), but they contain large temporal and
80 spatial gaps. Information on the rates of many important processes remains insufficient,
81 particularly in natural settings. There are only few studies from a limited number of
82 specific regions such as the Arabian Sea, Central and North Pacific, Black Sea, the
83 Bedford Basin and the Scheldt estuary, which can be used to derive and test model
84 parameterisations (Mantoura et al., 1993; Bange et al., 2000; Elkins et al., 1978; Farias et
85 al., 2007; Frame and Casciotti, 2010; Westley et al., 2006; Yoshida et al., 1989; Punshon

86 and Moore, 2004; De Wilde and De Bie, 2000).

87 N_2O is formed in the ocean interior through two major pathways and consumed only in
88 oxygen minimum zones through denitrification (Zamora et al., 2012). The first
89 production pathway is associated with nitrification (conversion of ammonia, NH_4^+ , into
90 nitrate, NO_3^-), and occurs when dissolved O_2 concentrations are above $20 \mu\text{mol L}^{-1}$. We
91 subsequently refer to this pathway as the high- O_2 pathway. The second production
92 pathway is associated with a series of processes when O_2 concentrations fall below ~ 5
93 $\mu\text{mol L}^{-1}$ and involve a combination of nitrification and denitrification (hereinafter
94 referred to as low- O_2 pathway) (Cohen and Gordon, 1978; Goreau et al., 1980; Elkins et
95 al., 1978). As nitrification is one of the processes involved in the aerobic remineralization
96 of organic matter, it occurs nearly everywhere in the global ocean with a global rate at
97 least one order of magnitude larger than the global rate of water column denitrification
98 (Gruber, 2008). A main reason is that denitrification in the water column is limited to
99 the OMZs, which occupy only a few percent of the total ocean volume (Bianchi et al.,
100 2012). This is also the only place in the water column where N_2O is being consumed.

101 The two production pathways have very different N_2O yields, i.e., fractions of nitrogen-
102 bearing products that are transformed to N_2O . For the high- O_2 pathway, the yield is
103 typically rather low, i.e., only about 1 in several hundred molecules of ammonium
104 escapes as N_2O (Cohen and Gordon, 1979). In contrast, in the low- O_2 pathway, and
105 particularly during denitrification, this fraction may go up to as high as 1:1, i.e., that all
106 nitrate is turned into N_2O (Tiedje, 1988). The relative contribution of the two pathways
107 to global N_2O production is not well established. Sarmiento and Gruber (2006)
108 suggested that the two may be of equal importance, but more recent estimates suggest
109 that the high- O_2 production pathway dominates global oceanic N_2O production (Freing
110 et al., 2012).

111 Two strategies have been pursued in the development of parameterizations for N_2O
112 production in global biogeochemical models. The first approach builds on the
113 importance of the nitrification pathway and its close association with the aerobic
114 remineralization of organic matter. As a result the production of N_2O and the
115 consumption of O_2 are closely tied to each other, leading to a strong correlation between
116 the concentration of N_2O and the apparent oxygen utilization (AOU). This has led to the
117 development of two sets of parameterizations, one based on concentrations, i.e., directly

118 as a function of AOU (Butler et al., 1989) and the other based on the rate of oxygen
119 utilization, i.e. OUR (Freing et al., 2009). Additional variables have been introduced to
120 allow for differences in the yield, i.e., the ratio of N₂O produced over oxygen consumed,
121 such as temperature (Butler et al., 1989) or depth (Freing et al., 2009). In the second
122 approach, the formation of N₂O is modeled more mechanistically, and tied to both
123 nitrification and denitrification by an O₂ dependent yield (Suntharalingam and
124 Sarmiento, 2000; Nevison et al., 2003; Jin and Gruber, 2003). Since most models do not
125 include nitrification explicitly, the formation rate is actually coupled directly to the
126 remineralization of organic matter. Regardless of the employed strategy, all
127 parameterizations depend to first order on the amount of organic matter that is being
128 remineralized in the ocean interior, which is governed by the export of organic carbon to
129 depth. The dependence of N₂O production on oxygen levels and on other parameters
130 such as temperature only acts at second order. This has important implications not only
131 for the modeling of the present-day distribution of N₂O in the ocean, but also for the
132 sensitivity of marine N₂O to future climate change.

133 Over this century, climate change will perturb marine N₂O formation in multiple ways.
134 Changes in productivity will drive changes in the export of organic matter to the ocean
135 interior (Steinacher et al., 2010; Bopp et al., 2013) and hence affect the level of marine
136 nitrification. Ocean warming might change the rate of N₂O production during
137 nitrification (Freing et al., 2012). Changes in carbonate chemistry (Bindoff et al., 2007)
138 might cause changes in the C:N ratio of the exported organic matter (Riebesell et al.,
139 2007), altering not only the rates of nitrification, but also the ocean interior oxygen levels
140 (Gehlen et al., 2011). Finally, the expected general loss of oxygen (Keeling et al., 2010;
141 Cocco et al., 2012; Bopp et al., 2013) could substantially affect N₂O production via both
142 nitrifier denitrification and classic denitrification.

143 Ocean biogeochemical models used for IPCC's 4th assessment report estimated a decrease
144 between 2% and 13% in primary production (PP) under the business-as-usual high CO₂
145 concentration scenario A2 (Steinacher et al., 2010). A more recent multi-model analysis
146 based on the models used in IPCC's 5th assessment report also suggest a large reduction of
147 PP down to 18% by 2100 for the RCP8.5 scenario (Bopp et al., 2013). In these
148 simulations, the export of organic matter is projected to decrease between 6% and 18%
149 in 2100 (Bopp et al., 2013), with a spatially distinct pattern: in general, productivity and

150 export are projected to decrease at mid- to low-latitudes in all basins, while productivity
151 and export are projected to increase in the high-latitudes and in the South Pacific
152 subtropical gyre (Bopp et al., 2013). A wider spectrum of responses was reported
153 regarding changes in the ocean oxygen content. While all models simulate decreased
154 oxygen concentrations in response to anthropogenic climate change (by about 2 to 4% in
155 2100), and particularly in the mid-latitude thermocline regions, no agreement exists with
156 regard to the hypoxic regions, i.e., those having oxygen levels below $60 \mu\text{mol L}^{-1}$ (Cocco
157 et al., 2012; Bopp et al., 2013). Some models project these regions to expand, while
158 others project a contraction. Even more divergence in the results exists for the suboxic
159 regions, i.e., those having O_2 concentrations below $5 \mu\text{mol L}^{-1}$ (Keeling et al., 2010;
160 Deutsch et al., 2011; Cocco et al., 2012; Bopp et al., 2013), although the trend for most
161 models is pointing towards an expansion. At the same time, practically none of the
162 models is able to correctly simulate the current distribution of oxygen in the OMZ (Bopp
163 et al., 2013). In summary, while it is clear that major changes in ocean biogeochemistry
164 are looming ahead (Gruber, 2011), with substantial impacts on the production and
165 emission of N_2O , our ability to project these changes with confidence is limited.

166 In this study, we explore the implications of these future changes in ocean physics and
167 biogeochemistry on the marine N_2O cycle, and make projections of the oceanic N_2O
168 emissions from year 2005 to 2100 under the high CO_2 concentration scenario RCP8.5.
169 We analyze how changes in biogeochemical and physical processes such as net primary
170 production (NPP), export production and vertical stratification in this century translate
171 into changes in oceanic N_2O emissions to the atmosphere. To this end, we use the
172 NEMO-PISCES ocean biogeochemical model, which we have augmented with two
173 different N_2O parameterizations, permitting us to evaluate changes in the marine N_2O
174 cycle at the process level, especially with regard to production pathways in high and low
175 oxygen regimes. We demonstrate that while future changes in the marine N_2O cycle will
176 be substantial, the net emissions of N_2O appear to change relatively little, i.e., they are
177 projected to decrease by about 10% in 2100.

178

179 2. Methodology

180

181 2.1 NEMO-PISCES Model

182

183 Future projections of the changes in the oceanic N₂O cycle were performed using the
184 PISCES ocean biogeochemical model (Aumont and Bopp, 2006) in offline mode with
185 physical forcings derived from the IPSL-CM5A-LR coupled model (Dufresne et al.,
186 2013). The horizontal resolution of NEMO ocean general circulation model is 2° x 2° cos
187 Ø (Ø being the latitude) with enhanced latitudinal resolution at the equator of 0.5°.
188 PISCES is a biogeochemical model with five nutrients (NO₃, NH₄, PO₄, Si and Fe), two
189 phytoplankton groups (diatoms and nanophytoplankton), two zooplankton groups
190 (micro and mesozooplankton), and two non-living compartments (particulate and
191 dissolved organic matter). Phytoplankton growth is limited by nutrient availability and
192 light. Constant Redfield C:N:P ratios of 122:16:1 are assumed (Takahashi et al., 1985),
193 while all other ratios, i.e., those associated with chlorophyll, iron, and silicon (Chl:C,
194 Fe:C and Si:C) vary dynamically.

195

196 2.2 N₂O parameterizations in PISCES

197

198 We implemented two different parameterizations of N₂O production in NEMO-PISCES.
199 The first one, adapted from Butler et al. (1989) follows the oxygen consumption
200 approach, with a temperature dependent modification of the N₂O yield (P.TEMP). The
201 second one is based on Jin and Gruber (2003) (P.OMZ), following the more mechanistic
202 approach, i.e., it considers the different processes occurring at differing oxygen
203 concentrations in a more explicit manner.

204 The P.TEMP parameterization assumes that the N₂O production is tied to nitrification
205 only with a yield that is at first order constant. This is implemented in the model by
206 tying the N₂O formation in a linear manner to O₂ consumption. A small temperature
207 dependence is added to the yield to reflect the potential impact of temperature on
208 metabolic rates. The production term of N₂O, i.e., $J^{P.TEMP}(N_2O)$, is then mathematically
209 formulated as:

$$210 \quad J^{P.TEMP}(N_2O) = (\gamma + \theta T) J(O_2)_{consumption} \quad (1)$$

211 where γ is a background yield (0.53×10^{-4} mol N₂O/mol O₂ consumed), θ is the
212 temperature dependency of γ (4.6×10^{-6} mol N₂O (mol O₂)⁻¹ K⁻¹), T is temperature (K),
213 and $J(O_2)_{consumption}$ is the sum of all biological O₂ consumption terms within the model.

214 The same ratio between constants γ and θ is used in the model as in the original
215 formulation from Butler et al. (1989). Although this parameterization is very simple, a
216 recent analysis of N₂O observations supports such an essentially constant yield, even in
217 the OMZ of the Eastern Tropical Pacific (Zamora et al., 2012).

218 The P.OMZ parameterization, formulated after Jin and Gruber (2003), assumes that the
219 overall yield consists of a constant background yield and an oxygen dependent yield. The
220 former is presumed to represent the N₂O production by nitrification, while the latter is
221 presumed to reflect the enhanced production of N₂O at low oxygen concentrations, in
222 part driven by denitrification, but possibly including nitrification as well. This
223 parameterization includes the consumption of N₂O in suboxic conditions. This gives:

$$224 \quad J^{P.OMZ}(N_2O) = (\alpha + \beta f(O_2))J(O_2)_{consumption} - k N_2O \quad (2)$$

225 where α is, as in Eq.(1), a background yield ($0.9 \cdot 10^{-4}$ mol N₂O/mol O₂ consumed), b is
226 a yield parameter that scales the oxygen dependent function ($6.2 \cdot 10^{-4}$), $f(O_2)$ is a unitless
227 oxygen-dependent step-like modulating function, as suggested by laboratory experiments
228 (Goreau et al., 1980) (Fig. S1, Supplementary Material), and k is the 1st order rate
229 constant of N₂O consumption close to anoxia (zero otherwise). For k , we have adopted a
230 value of 0.138 yr^{-1} following Bianchi et al. (2012) while we set the consumption regime
231 for O₂ concentrations below $5 \mu\text{mol L}^{-1}$. The constant α is in the same order of
232 magnitude as the one proposed by Jin and Gruber (2003), while b is two orders of
233 magnitude smaller. The use of the original value would result in a significant increase of
234 N₂O production associated with OMZs and, hence, in a departure from the assumption
235 of dominant nitrification.

236 The P.OMZ parameterization permits us the independent quantification of the N₂O
237 formation pathways associated with nitrification and those associated with low-oxygen
238 concentrations (nitrification/denitrification) and their evolution in time over the next
239 century. Specifically, we consider the source term $\alpha J(O_2)_{consumption}$ as that associated with
240 the nitrification pathway, while we associated the source term $b f(O_2) J(O_2)_{consumption}$ with
241 the low-oxygen processes (Fig. S2, Supplementary Material).

242 N₂O production is inhibited by light in the model, and therefore N₂O production in
243 P.TEMP and P.OMZ parameterizations only occurs below a fixed depth of 100m.

244 We employ a standard bulk approach for simulating the loss of N₂O to the atmosphere

245 via gas exchange. We use the formulation of Wanninkhof et al. (1992) for estimating the
246 gas transfer velocity, adjusting the Schmidt number for N₂O and using the solubility
247 constants of N₂O given by Weiss and Price (1980). We assume a constant atmospheric
248 N₂O concentration of 284 ppb in all simulations to explore future changes inherent to
249 ocean processes without feedbacks due to changes in the atmosphere.

250

251 2.3 Experimental design

252

253 NEMO-PISCES was first spun up during 3000 years using constant pre-industrial
254 dynamical forcings fields from IPSL-CM5A-LR (Dufresne et al., 2013) without
255 activating the N₂O parameterizations. This spin-up phase was followed by a 150-yr long
256 simulation, forced by the same dynamical fields now with N₂O production and N₂O sea-
257 to-air flux embedded. The N₂O concentration at all grid points was prescribed initially to
258 20 nmol L⁻¹, which is consistent with the MEMENTO database average value of 18
259 nmol L⁻¹ below 1500m (Bange et al., 2009). During the 150-yr spin-up, we diagnosed
260 the total N₂O production and N₂O sea-to-air flux and adjusted the α , β , γ and θ
261 parameters in order to achieve a total N₂O sea-to-air flux in the two parameterizations at
262 equilibrium close to 3.85 TgN yr⁻¹ (Ciais et al., 2013). In addition, the relative
263 contribution of the high-O₂ pathway in the P.OMZ parameterization was set to 75% of
264 the total N₂O production based on Suntharalingam et al. (2000), where a sensitivity
265 model analysis on the relative contribution of high- and low-O₂ production pathways
266 showed that a higher contribution of nitrification (75%) than denitrification (25%)
267 achieved the best model performance compared to the data product from Nevison et al.
268 (1995). P.TEMP can be considered as 100% nitrification, testing in this way the
269 hypothesis of nitrification as the dominant pathway of N₂O production on a global scale.
270 Nitrification could contribute with up to 93% of the total production based on
271 estimations considering N₂O production along with water mass transport (Freing et al.,
272 2012).

273 Projections in NEMO-PISCES of historical (from 1851 to 2005) and future (from 2005
274 to 2100) simulated periods were done using dynamical forcing fields from IPSL-CM5A-
275 LR. These dynamical forcings were applied in an offline mode, i.e. monthly means of
276 temperature, velocity, wind speed or radiative flux were used to force NEMO-PISCES.

277 Future simulations used the business-as-usual high CO₂ concentration scenario (RCP8.5)
278 until year 2100. Century scale model drifts for all the biogeochemical variables presented,
279 including N₂O sea-to-air flux, production and inventory, were removed using an
280 additional control simulation with IPSL-CM5A-LR pre-industrial dynamical forcing
281 fields from year 1851 to 2100. Despite the fact that primary production and the export
282 of organic matter to depth were stable in the control simulation, the air-sea N₂O
283 emissions drifted (an increase of 5 to 12% in 200 yr depending on the parameterization)
284 due to the short spin-up phase (150 yrs) and to the choice of the initial conditions for
285 N₂O concentrations.

286

287 3. Present-day oceanic N₂O

288

289 3.1 Contemporary N₂O fluxes

290

291 The model simulated air-sea N₂O emissions show large spatial contrasts, with flux
292 densities varying by one order of magnitude, but with relatively small differences between
293 the two parameterizations (Fig. 1a and 1b). This is largely caused by our assumption that
294 the dominant contribution (75%) to the total N₂O production in the P.OMZ
295 parameterization is the nitrification pathway, which is then not so different from the
296 P.TEMP parameterization, where it is 100%. As a result, the major part of N₂O is
297 produced in the subsurface via nitrification, contributing directly to imprint changes into
298 the sea-to-air N₂O flux without a significant meridional transport (Suntharalingam and
299 Sarmiento, 2000).

300 Elevated N₂O emission regions (> 50 mgN m⁻² yr⁻¹) are found in the Equatorial and
301 Eastern Tropical Pacific, in the northern Indian ocean, in the northwestern Pacific, in the
302 North Atlantic and in the Agulhas Current. In contrast, low fluxes (< 10 mgN m⁻² yr⁻¹)
303 are simulated in the Southern Ocean, Atlantic and Pacific subtropical gyres and southern
304 Indian Ocean. The large scale distribution of N₂O fluxes is coherent with Nevison et al.
305 (2004) (Fig. 1c). This comes as a natural consequence of the relatively high contribution
306 of nitrification and hence hotspots of N₂O emissions are associated with regions where
307 higher export of organic matter occurs in the model.

308 There are however several discrepancies between the model and the data product. At high

309 latitudes, the high N₂O emissions observed in the North Pacific are not well represented
310 in our model, with a significant shift towards the western part of the Pacific basin, similar
311 to other modeling studies (e.g., Goldstein et al., 2003; Jin and Gruber, 2003). The OMZ
312 in the North Pacific, located at approximately 600m deep, is underestimated in the
313 model due to the deficient representation of the Meridional Overturning Circulation
314 (MOC) in the North Pacific in global ocean biogeochemical models, which in turn
315 might suppress low oxygenated areas and therefore one potential N₂O source.
316 Discrepancies between model and observations also occur in the Southern Ocean, a
317 region whose role in global N₂O fluxes remains debated due to the lack of observations
318 and the occurrence of potential artifacts due to interpolation techniques reflected in data
319 products such as that from Nevison et al., 2004. (e.g., Suntharalingam and Sarmiento,
320 2000, and Nevison et al, 2003). The model also overestimates N₂O emissions in the
321 North Atlantic. The emphasis put on the nitrification pathway suggests that hotspots of
322 carbon export are at the origin of elevated concentrations of N₂O in the subsurface. N₂O
323 is quickly outgassed to the atmosphere, leading to such areas of high N₂O emissions in
324 the model.

325 Model-data discrepancies can be seen as a function of latitude in Figure 1d. The modeled
326 N₂O flux maxima peak at around 40°S, i.e., around 10° north to that estimated by
327 Nevison et al. (2004), although Southern Ocean data must be interpreted with caution.
328 In the northern hemisphere the stripe in the North Pacific is not captured by the model,
329 splitting the flux from the 45°N band into two peaks at 38°N and 55°N

330

331 3.2 Contemporary N₂O concentrations and the relationship to O₂

332

333 The model results at present day were evaluated against the MEMENTO database
334 (Bange et al., 2009), which contains about 25,000 measurements of co-located N₂O and
335 dissolved O₂ concentrations. Table 1 summarizes the standard deviation and correlation
336 coefficients for P.TEMP and P.OMZ compared to MEMENTO. The standard deviation
337 of the model output is very similar to MEMENTO, i.e., around 16 nmol L⁻¹ of N₂O.
338 However, the correlation coefficients between the sampled data points from
339 MEMENTO and P.TEMP / P.OMZ are 0.49 and 0.42 respectively. Largest
340 discrepancies are found mostly in the deep ocean and in the OMZs.

341 Figure 2 compares the global average vertical profile of the observed N₂O against the
342 results from the two parameterisations. The in-situ observations show three characteristic
343 layers: the upper 100m layer with low (~10 nmol L⁻¹) N₂O concentration due to gas
344 exchange keeping N₂O close to its saturation concentration, the mesopelagic layer,
345 between 100 and 1500m, where N₂O is enriched via nitrification and denitrification in
346 the OMZs, and the deep ocean beyond 1500m, with a relatively constant concentration
347 of 18 nmol L⁻¹ on average. Both parameterizations underestimate the N₂O concentration
348 in the upper 100 meters, where most of the N₂O is potentially outgassed to the
349 atmosphere. In the second layer, P.OMZ shows a fairly good agreement with the
350 observations in the 500 to 900m band, whereas P.TEMP is too low by ~10 nmol L⁻¹.
351 Below 1500m, both parameterizations simulate too high N₂O compared to the
352 observations. This may be caused by the lack or underestimation of a sink process in the
353 deep ocean, or by the too high concentrations used to initialize the model, which persist
354 due to the rather short spin-up time of only 150 yrs.

355 The analysis of the model simulated N₂O concentrations as a function of model
356 simulated O₂ shows the differences between the two parameterizations more clearly (Fig.
357 3a and 3b). Such a plot allows us to assess the model performance with regard to N₂O
358 (Jin and Gruber, 2003), without being subject to the strong potential biases introduced
359 by the model's deficiencies in simulating the distribution of O₂. This is particularly
360 critical in the OMZs, where all models exhibit strong biases (Cocco et al., 2012; Bopp et
361 al., 2013) (see also Fig. 3c). P.TEMP (Fig. 3a) slightly overestimates N₂O for dissolved
362 O₂ concentrations above 100 μmol L⁻¹, and does not fully reproduce either the high N₂O
363 values in the OMZs or the N₂O depletion when O₂ is almost completely consumed.
364 P.OMZ (Figure 3b) overestimates the N₂O concentration over the whole range of O₂,
365 with particularly high values of N₂O above 100 nmol L⁻¹ due to the exponential function
366 used in the OMZs. There, the observations suggest concentrations below 80 nmol L⁻¹ for
367 the same low O₂ values, consistent with the linear trend observed for higher O₂, which
368 seems to govern over most of the O₂ spectrum, as suggested by Zamora et al. (2012). The
369 discrepancy at low O₂ concentration may also stem from our choice of a too low N₂O
370 consumption rate under essentially anoxic conditions. Finally, it should be considered
371 that most of the MEMENTO data points are from OMZs and therefore N₂O
372 measurements could be biased towards higher values than the actual open ocean average,

373 where our model performs better.

374

375 4. Future oceanic N₂O

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377 4.1 N₂O sea-to-air flux

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379 The global oceanic N₂O emissions decrease relatively little over the next century (Fig. 4a)
380 between 4% and 12%. Namely, in P.TEMP, the emissions decrease by 0.15 TgN yr⁻¹
381 from 3.71 TgN yr⁻¹ in 1985-2005 to 3.56 TgN yr⁻¹ in 2080-2100 and in P.OMZ, the
382 decrease is slightly larger at 12%, i.e., amounting to 0.49 Tg N yr⁻¹ from 4.03 to 3.54
383 TgN yr⁻¹. Notable is also the presence of a negative trend in N₂O emissions over the 20th
384 century, most pronounced in the P.OMZ parameterization. Considering the change over
385 the 20th and 21st centuries together, the model projects a decrease between 7 and 15%.

386 These relatively small global decreases mask more substantial changes at the regional scale,
387 with a mosaic of regions experiencing a substantial increase and regions experiencing a
388 substantial decrease (Fig. 4b and 4c). In both parameterizations, the oceanic N₂O
389 emissions decrease in the northern and south western oceanic basins (e.g., the North
390 Atlantic and Arabian Sea), by up to 25 mgN m²yr⁻¹. In contrast, the fluxes are simulated
391 to increase in the Eastern Tropical Pacific and in the Bay of Bengal. For the Benguela
392 Upwelling System (BUS) and the North Atlantic a bi-modal pattern emerges in 2100. As
393 was the case for the present-day distribution of the N₂O fluxes, the overall similarity
394 between the two parameterizations is a consequence of the dominance of the nitrification
395 (high-O₂) pathway in both parameterizations.

396 Nevertheless there are two regions where more substantial differences between the two
397 parameterizations emerge: the region overlying the oceanic OMZ at the BUS and the
398 Southern Ocean. In particular, the P.TEMP parameterization projects a larger
399 enhancement of the flux than P.OMZ at the BUS, whereas the emissions in the Southern
400 Ocean are enhanced in the P.OMZ parameterization.

401

402 4.2 Drivers of changes in N₂O emissions

403

404 The changes in N₂O emissions may stem from a change in net N₂O production, a change

405 in the transport of N₂O from its location of production to the surface, or any
406 combination of the two, which includes also changes in N₂O storage. Next we determine
407 the contribution of these mechanisms to the overall decrease in N₂O emissions that our
408 model simulated for the 21st century.

409

410 4.2.1 Changes in N₂O production

411

412 In both parameterizations, global N₂O production is simulated to decrease over the 21st
413 century. The total N₂O production in P.OMZ decreases by 0.41 TgN yr⁻¹ in 2080-2100
414 compared to the mean value over 1985-2005 (Fig. 5a). The parameterization P.OMZ
415 allows to isolate the contributions of high- and low-O₂ and will be analysed in greater
416 detail in the following sections. N₂O production via the high-O₂ pathway in P.OMZ
417 decreases in the same order than total production, by 0.35 TgN yr⁻¹ in 2080-2100
418 compared to present. The N₂O production in the low-O₂ regions remains almost
419 constant across the experiment. In P.TEMP parameterization, the reduction in N₂O
420 production is much weaker than in P.OMZ due to the effect of the increasing
421 temperature. N₂O production decreases by 0.07 TgN yr⁻¹ in 2080-2100 compared to
422 present (Fig. 5b).

423 The vast majority of the changes in the N₂O production in the P.OMZ parameterization
424 is caused by the high-O₂ pathway with virtually no contribution from the low-O₂
425 pathway (Fig. 5a). As the N₂O production in P.OMZ parameterization is solely driven
426 by changes in the O₂ consumption (Eq. (2)), which in our model is directly linked to
427 export production, the dominance of this pathway implies that primary driver for the
428 future changes in N₂O production in our model is the decrease in export of organic
429 matter (CEX). It was simulated to decrease by 0.97 PgC yr⁻¹ in 2100, and the high degree
430 of correspondence in the temporal evolution of export and N₂O production in Fig. 5a
431 confirms this conclusion.

432 The close connection between N₂O production associated with the high-O₂ pathway and
433 changes in export production is also seen spatially (Fig. 5c), where the spatial pattern of
434 changes in export and changes in N₂O production are extremely highly correlated (shown
435 by stippling). Most of the small deviations are caused by lateral advection of organic
436 carbon, causing a spatial separation between changes in O₂ consumption and changes in

437 organic matter export.
438 As there is an almost ubiquitous decrease of export in all of the major oceanic basins
439 except at high latitudes, N₂O production decreases overall as well. Hotspots of reductions
440 exceeding -10 mgN m⁻²yr⁻¹ are found in the North Atlantic, the western Pacific and
441 Indian basins (Fig. 5c). The fewer places where export increases, are also the locations of
442 enhanced N₂O production. For example, a moderate increase of 3 mgN m⁻² yr⁻¹ is
443 projected in the Southern Ocean, South Atlantic and Eastern Tropical Pacific. The
444 general pattern of export changes, i.e., decreases in lower latitudes, increase in higher
445 latitudes, is consistent generally with other model projection patterns (Bopp et al., 2013),
446 although there exist very strong model-to-model differences at the more regional scale.
447 Although the global contribution of the changes in the low-O₂ N₂O production is small,
448 this is the result of regionally compensating trends. In the model's OMZs, i.e., in the
449 Eastern Tropical Pacific and in the Bay of Bengal, a significant increase in N₂O
450 production is simulated in these locations (Fig. 5d), with an increase of more than 15
451 mgN m⁻² yr⁻¹. This increase is primarily driven by the expansion of the OMZs in our
452 model (shown by stippling), while changes in export contribute less. In effect, NEMO-
453 PISCES projects a 20% increase in the hypoxic volume globally, from 10.2 to 12.3 x 10⁶
454 km³, and an increase in the suboxic volume from 1.1 to 1.6 x 10⁶ km³ in 2100 (Fig. 5e).
455 Elsewhere, the changes in the N₂O production through the low-O₂ pathway are
456 dominated by the changes in export, thus following the pattern of the changes seen in the
457 high-O₂ pathway. Overall these changes are negative, and happen to nearly completely
458 compensate the increase in production in the OMZs, resulting in the near constant
459 global N₂O production by the low-O₂ production pathway up to year 2100.

460

461 4.2.2 Changes in storage of N₂O

462

463 A steady increase in the N₂O inventory is observed from present to 2100. The pool of
464 oceanic N₂O down to 1500m, i.e., potentially outgassed to the atmosphere, increases by
465 8.9 TgN from 1985-2005 to year 2100 in P.OMZ, whereas P.TEMP is less sensitive to
466 changes with an increase of 4.0 TgN on the time period considered (Fig. 6a). The
467 inventory in the upper 1500m in P.OMZ is 237.0 TgN at present, while in P.TEMP in
468 the same depth band is 179.8 TgN. This means that the projected changes in the

469 inventory represent an increase of about 4% and 2% in P.OMZ and P.TEMP
470 respectively.

471 This increase in storage of N₂O in the ocean interior shows an homogeneous pattern for
472 P.TEMP, with particular hotspots in the North Pacific, North Atlantic and the eastern
473 boundary currents in the Pacific (Fig. 6b). The spatial variability is more pronounced in
474 P.OMZ (Fig. 6c), related in part to the enhanced production associated with OMZs.
475 Most of the projected changes in storage are associated with shoaling of the mixed layer
476 depth (shown by stippling), suggesting that increase in N₂O inventories is caused by
477 increased ocean stratification. Enhanced ocean stratification, in turn, occurs in response
478 to increasing sea surface temperatures associated with global warming (Sarmiento et al.,
479 2004).

480

481 4.2.3 Effects of the combined mechanisms on N₂O emissions

482

483 The drivers of the future evolution of oceanic N₂O emissions emerge from the preceding
484 analysis. Firstly, a decrease in the high-O₂ production pathway driven by a reduced
485 organic matter remineralization reduces N₂O concentrations below the euphotic zone.
486 Secondly, the increased N₂O inventory at depth is caused by increased stratification and
487 therefore to a less efficient transport to the sea-to-air interface, leading to a smaller N₂O
488 flux.

489 The global changes in N₂O flux, N₂O production and N₂O storage for P.OMZ are
490 presented in Fig. 7. Changes in N₂O flux and N₂O production are mostly of the same
491 sign in almost all of the oceanic regions in line with the assumption of nitrification being
492 the dominant contribution to N₂O production. Changes in N₂O production in the
493 subsurface are translated into corresponding changes in N₂O flux. There is only one
494 oceanic region (Sub-Polar Pacific) where this correlation does not occur. N₂O inventory
495 increases in all of the oceanic regions. The increase in inventory is particularly
496 pronounced at low latitudes along the eastern boundary currents in the Equatorial and
497 Tropical Pacific, Indian Ocean and also in smaller quantities in the Atlantic Ocean.
498 Figure 7 shows how the decrease in N₂O production and increase in N₂O storage occurs
499 in all oceanic basins.

500

501 5. Caveats in estimating N₂O using ocean biogeochemical models

502

503 The state variables upon which representation of N₂O in models rely, i.e., oxygen and
504 export of carbon, are compared to the CMIP5 model ensemble to put our analysis in
505 context of the current state-of-the-art model capabilities. We focus here our analysis on
506 suboxic waters (O₂ < 5 μmol L⁻¹) and on export production. Whereas CMIP5 models
507 tend to have large volumes of O₂ concentrations in the suboxic regime, it is not the case
508 for our NEMO-PISCES simulation, which clearly underestimates the volume of low-
509 oxygen waters as compared to the oxygen corrected World Ocean Atlas 2005
510 (WOA2005*) (Bianchi et al., 2012). The fact that NEMO-PISCES forced by IPSL-
511 CM5A-LR is highly oxygenated is confirmed by Figure 8, where the histogram of the full
512 O₂ spectrum of WOA2005* and NEMO-PISCES is shown. The O₂ distribution in the
513 model shows a deficient representation of the OMZs, with higher concentrations than
514 those from observations. The rest of the O₂ spectrum is well represented in our model.

515 The O₂ distribution in the model (Fig. 9) shows a deficient representation of the OMZs,
516 with higher concentrations than those from observations in WOA2005* and the other
517 CMIP5 models. NEMO-PISCES is therefore biased towards the high O₂ production
518 pathway of N₂O due to the modeled O₂ fields.

519 When turning to the export of organic matter, NEMO-PISCES is close to the CMIP5
520 average value of 6.9 PgC yr⁻¹. The overall distribution of export is also very similar to the
521 CMIP5 model mean and both show smaller values than those from the data-based
522 estimate of 9.84 PgC yr⁻¹ from Dunne et al., 2007 (Fig. 9).

523 The uncertainties derived from present and future model projections can be estimated
524 using the spread in the CMIP5 model projection of export of organic matter and
525 assuming a linear response between nitrification (or export) and N₂O production in the
526 subsurface, which is assumed to be quickly outgassed to the atmosphere. In NEMO-
527 PISCES, a decrease in 13% in export leads to a maximum decrease in N₂O emissions of
528 12% in the P.OMZ scenario. Based on results by Bopp et al. (2013), changes in export of
529 carbon span -7% to -18% in the CMIP5 model ensemble at the end of the 21st century
530 and for RCP8.5. The spread would propagate to a similar range in projected N₂O
531 emissions across the CMIP5 model ensemble. Applying these values to present N₂O
532 emissions of 3.6 TgN yr⁻¹, uncertainties are then bracketed between -0.25 and -0.65 TgN

533 yr⁻¹.

534 Regarding the low-O₂ pathway, a similar approach is not that straight forward. Zamora et
535 al., (2012) found that a linear relationship between AOU and N₂O production might
536 occur even at the OMZ of the ETP. Zamora et al. (2012) acknowledged the fact that the
537 MEMENTO database includes N₂O advected from other regions and that mixing could
538 play a relevant role, smoothing the fit between N₂O and AOU from exponential to linear.
539 However, Zamora et al. (2012) quoting Frame and Casciotti (2010), suggested that
540 regions where an exponential relationship in N₂O production is present might be rare, that
541 other non-exponential N₂O production processes might occur and therefore the plot they
542 presented could describe the actual linear relationship between N₂O production and
543 oxygen consumption. Based on this hypothesis, we could refer again to the linear
544 relationship suggested in the high-O₂ and export scenario. However, in this case the
545 CMIP5 model projections of changes in the hypoxic and suboxic volumes differ
546 substantially. Most models project an expansion of the OMZs in the +2% to +16% range
547 in the suboxic volume (O₂ < 5 μmol L⁻¹). There are, however, models that project a slight
548 reduction of 2%. Spatial variability of projections add to the spread between CMIP5
549 models. These discrepancies suggest that uncertainties from this spread must be
550 interpreted with caution when estimating potential future N₂O emissions.

551 The use of O₂ consumption as a proxy for the actual N₂O production plays therefore a
552 pivotal role in the uncertainties in N₂O model estimations. Future model development
553 should aim at the implementation of mechanistic parameterizations of N₂O production
554 based on nitrification and denitrification rates. Further, in order to determine accurate
555 O₂ boundaries for both N₂O production and N₂O consumption at the core of OMZs
556 additional measurements and microbial experiments are needed. The contribution of the
557 high-O₂ pathway that was considered in this model analysis might be a conservative
558 estimate. Freing et al. (2012) suggested that the high-O₂ pathway could be responsible of
559 93% of the total N₂O production. Assuming that changes in the N₂O flux are mostly
560 driven by N₂O production via nitrification, that would suggest a larger reduction in the
561 marine N₂O emissions in the future. However, the mismatch between NEMO-PISCES
562 and the Nevison et al. (2004) spatial distribution of N₂O emissions in the western part of
563 the basins suggests that changes in the future might not be as big as those projected in the
564 model in such regions. Changes would be then distributed more homogeneously.

565 The model assumption neglecting N₂O production in the upper 100m avoids one
566 important source of uncertainty in estimating global oceanic N₂O fluxes. In case
567 nitrification occurs in the euphotic layer, our results would be facing a significant
568 uncertainty of at least ±25% in N₂O emissions according to Zamora and Oschlies (2014)
569 analysis using the UVic Earth System Climate Model. Finally, Zamora et al. (2012)
570 observed a higher than expected N₂O consumption at the core of the OMZ in the
571 Eastern Tropical Pacific, occurring at an upper threshold of 10 μmol L⁻¹. The
572 contribution of OMZs to total N₂O production remains an open question. N₂O
573 formation associated with OMZs might be counterbalanced by its own local
574 consumption, leading to the attenuation of the only increasing source of N₂O
575 attributable to the projected future expansion of OMZs (Steinacher et al., 2010; Bopp et
576 al., 2013).

577 The combined effect of climate change and ocean acidification has not been analyzed in
578 this study. N₂O production processes might be altered by the response of nitrification to
579 increasing levels of seawater pCO₂ (Huesemann et al., 2002; Beman et al. 2011). Beman
580 et al. (2011) reported a reduction in nitrification in response to decreasing pH. This
581 result suggests that N₂O production might decrease beyond what we have estimated only
582 due to climate change. Conversely, negative changes in the ballast effect could potentially
583 reinforce nitrification at shallow depth in response to less efficient POC export to depth
584 and shallow remineralization (Gehlen et al., 2011). Regarding N₂O formation via
585 denitrification, changes in seawater pH as a consequence of higher levels of CO₂ might
586 not be substantial enough to change the N₂O production efficiency, assuming a similar
587 response of marine denitrifiers as reported for denitrifying bacteria have in terrestrial
588 systems (Liu et al., 2010). Finally, the C:N ratio in export production (Riebesell et al.,
589 2007) might increase in response to ocean acidification, potentially leading to a greater
590 expansion of OMZs than simulated here (Oschlies et al., 2008; Tagliabue et al., 2011),
591 and therefore to enhanced N₂O production associated with the low-O₂ pathway.

592 Changes in atmospheric nitrogen deposition have not been considered in this study. It
593 has been suggested that due to anthropogenic activities the additional amount of reactive
594 nitrogen in the ocean could fuel primary productivity and N₂O production. Estimates are
595 however low, around 3-4% of the total oceanic emissions (Suntharalingam et al., 2012).

596 Longer simulation periods could reveal additional effects on N₂O transport beyond

597 changes in upwelling or meridional transport of N₂O in the subsurface (Suntharalingam
598 and Sarmiento, 2000) that have been observed in this transient simulation. Long-term
599 responses might include eventual ventilation of the N₂O reservoir in the Southern Ocean,
600 highlighting the role of upwelling regions as an important source of N₂O when longer
601 time periods are considered in model projections. Additional studies using other ocean
602 biogeochemical models might also yield alternative values using the same
603 parameterizations. N₂O production is particularly sensitive to the distribution and
604 magnitude of export of organic matter and O₂ fields defined in models.

605

606 6. Contribution of future N₂O to climate feedbacks

607

608 Changes in the oceanic emissions of N₂O to the atmosphere will have an impact on
609 atmospheric radiative forcing, with potential feedbacks on the climate system. Based on
610 the estimated 4 to 12% decrease in N₂O sea-to-air flux over the 21st century under
611 RCP8.5, we estimated the feedback factor for these changes as defined by Xu-Ri et al.
612 (2012). Considering the reference value of the pre-industrial atmospheric N₂O
613 concentration of 280 ppb in equilibrium, and its associated global N₂O emissions of 11.8
614 TgN yr⁻¹, we quantify the resulting changes in N₂O concentration per degree for the two
615 projected emissions in 2100 using P.TEMP and P.OMZ. The model projects changes in
616 N₂O emissions of -0.16 and -0.48 TgN yr⁻¹ respectively, whereas surface temperature is
617 assumed to increase globally by 3°C on average according to the physical forcing used in
618 our simulations. These results yield -0.05 and -0.16 TgN yr⁻¹ K⁻¹, or alternatively -1.25
619 and -3.80 ppb K⁻¹ for P.TEMP and P.OMZ respectively. Using Joos et al. (2001) we
620 calculate the feedback factor in equilibrium for projected changes in emissions to be -
621 0.005 and -0.014 W m⁻²K⁻¹ in P.TEMP and P.OMZ.

622 Stocker et al. (2013) projected changes in terrestrial N₂O emissions in 2100 using
623 transient model simulations leading to feedback strengths between +0.001 and +0.015 W
624 m⁻²K⁻¹. Feedback strengths associated with the projected decrease of oceanic N₂O
625 emissions are of the same order of magnitude as those attributable to changes in the
626 terrestrial sources of N₂O, yet opposite in sign, suggesting a compensation of changes in
627 radiative forcing due to future increasing terrestrial N₂O emissions. At this stage,
628 potential compensation between land and ocean emissions is to be taken with caution, as

629 it relies of a single model run with constant atmospheric N₂O.

630

631 7. Conclusions

632

633 Our simulations suggest that anthropogenic climate change could lead to a global
634 decrease in oceanic N₂O emissions during the 21st century. This maximum projected
635 decrease of 12% in marine N₂O emissions for the business-as-usual high CO₂ emissions
636 scenario would compensate for the estimated increase in N₂O fluxes from the terrestrial
637 biosphere in response to anthropogenic climate change (Stocker et al. 2013), so that the
638 climate-N₂O feedback may be more or less neutral over the coming decades.

639 The main mechanisms contributing to the reduction of marine N₂O emissions are a
640 decrease in N₂O production in high oxygenated waters as well as an increase in ocean
641 vertical stratification that acts to decrease the transport of N₂O from the sub-surface to
642 the surface ocean. Despite the decrease in both N₂O production and N₂O emissions,
643 simulations suggest that the global marine N₂O inventory may increase from 2005 to
644 2100. This increase is explained by the reduced transport of N₂O from the production
645 zones to the air-sea interface.

646 Differences between the two parameterizations used here are more related to
647 biogeochemistry rather than changes in ocean circulation. Despite sharing the high-O₂
648 N₂O production pathway, leading to a decrease in N₂O emissions in both cases, the role
649 of warming in P.TEMP or higher N₂O yields at low-O₂ concentrations in P.OMZ
650 translate into notable differences in the evolution of the two production pathways.
651 However, the dominant effect of changes in stratification in both parameterizations
652 drives ultimately the homogeneous response of the parameterizations considered in
653 model projections in the next century.

654 The N₂O production pathways demand however a better understanding in order to
655 enable an improved representation of processes in models. At a first order, the efficiencies
656 of the production processes in response to higher temperatures or increased seawater
657 pCO₂ are required. Second order effects such as changes in the O₂ boundaries at which
658 nitrification and denitrification occur must be also taken into account. In the absence of
659 process-based parameterizations, N₂O production parameterizations will still rely on
660 export of organic carbon and oxygen levels. Both need to be improved in global

661 biogeochemical models.
662 The same combination of mechanisms (i.e., change in export production and ocean
663 stratification) have been identified as drivers of changes in oceanic N₂O emissions during
664 the Younger Dryas by Goldstein et al. (2003). The N₂O flux decreased, while the N₂O
665 reservoir was fueled by longer residence times of N₂O caused by increased stratification.
666 Other studies point towards changes in the N₂O production at the OMZs as the main
667 reason for variations in N₂O observed in the past (Suthhof et al., 2001). Whether these
668 mechanisms are plausible drivers of changes beyond year 2100 remains an open question
669 that needs to be addressed with longer simulations.
670

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672

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680 7. References

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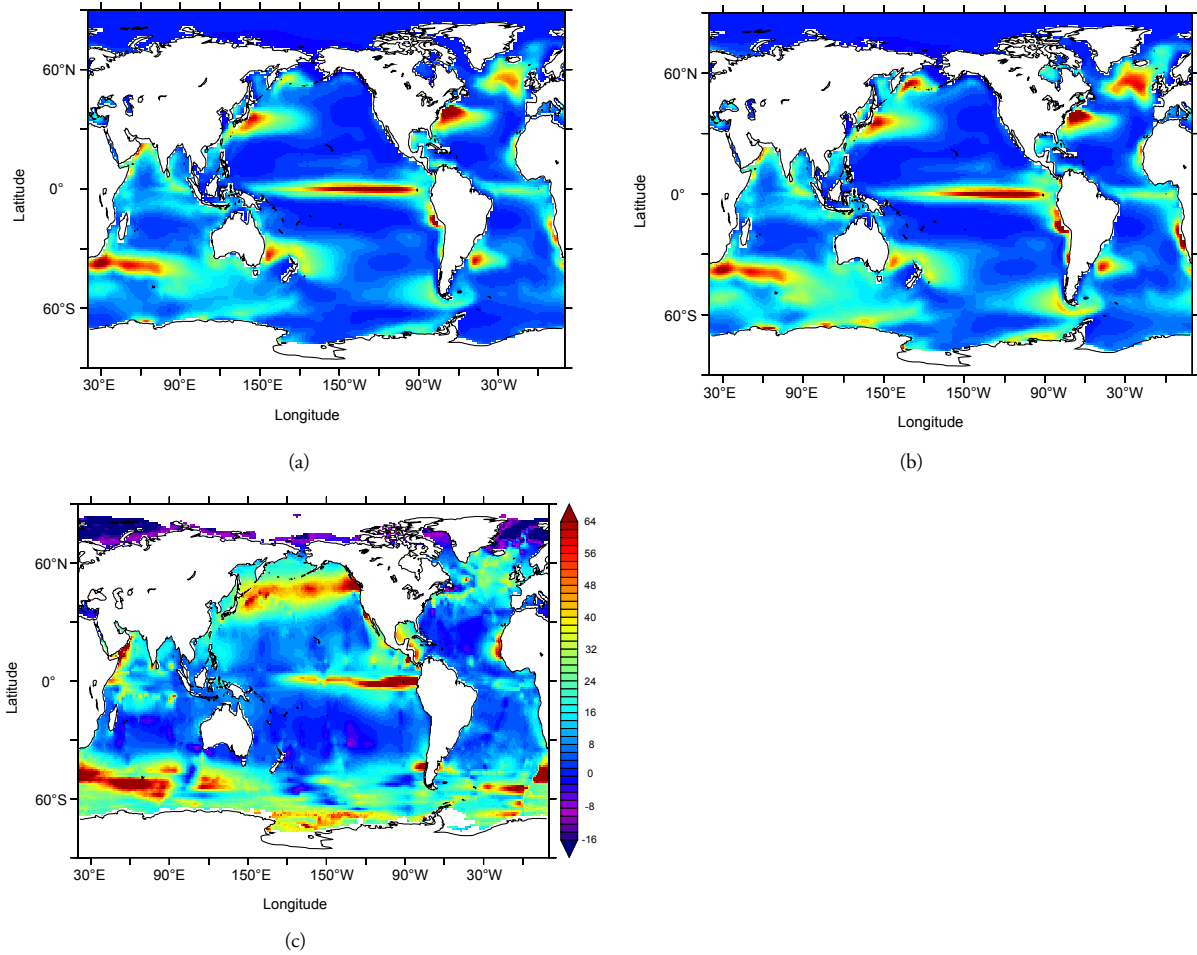
878 Table 1: Standard deviation and correlation coefficients between P.TEMP and P.OMZ
 879 parameterizations with respect to MEMENTO database observations (Bange et al., 2009).
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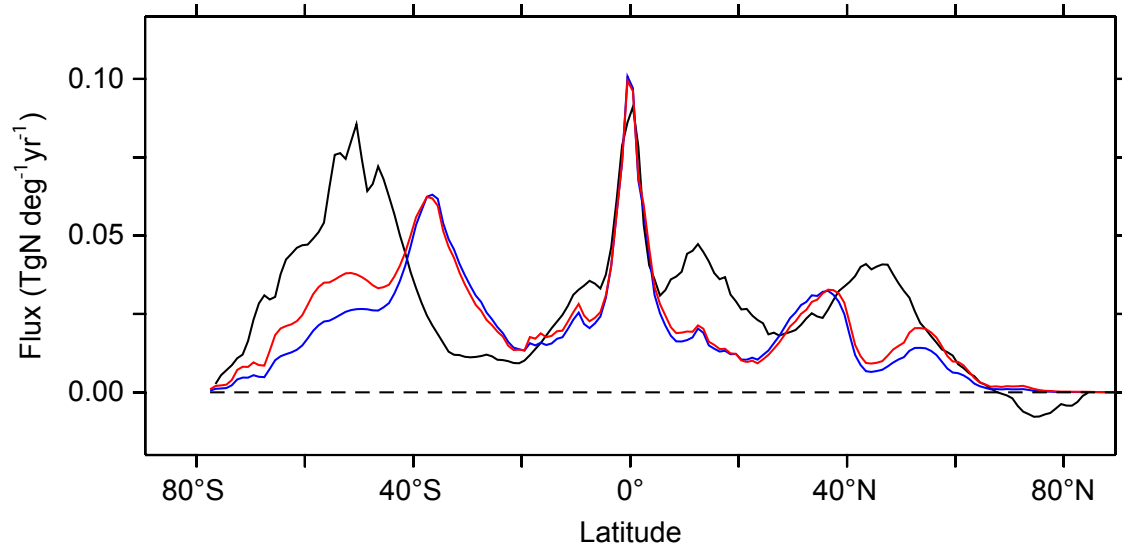
	P.TEMP	P.OMZ	OBS
Standard deviation (in nmol N ₂ O L ⁻¹)	12	18	16
Correlation coefficient with obs.	0.49	0.42	-

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883 Fig.1: N₂O sea-to-air flux (in mgN m⁻² yr⁻¹) from (a) P.TEMP parameterzation averaged
884 for the 1985 to 2005 time period in the historical simulation, (b) P.OMZ
885 parameterization over the same time period, (c) data product of Nevison et al. (2004) and
886 (d) latitudinal N₂O sea-to-air flux (in TgN deg⁻¹yr⁻¹) from Nevison et al. (2004) (black),
887 P.TEMP (blue) and P.OMZ (red).

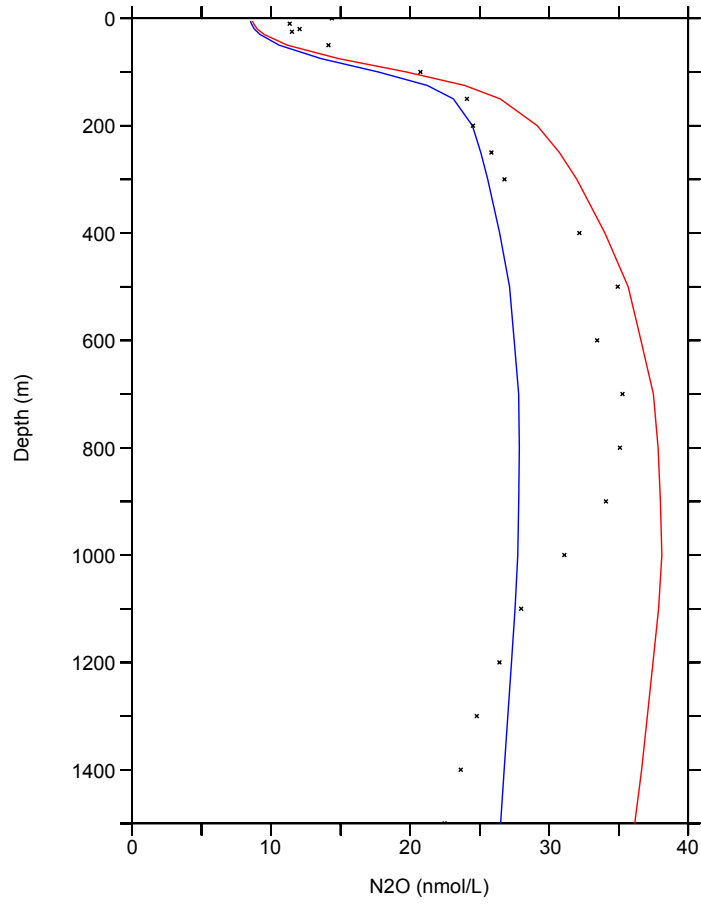




(d)

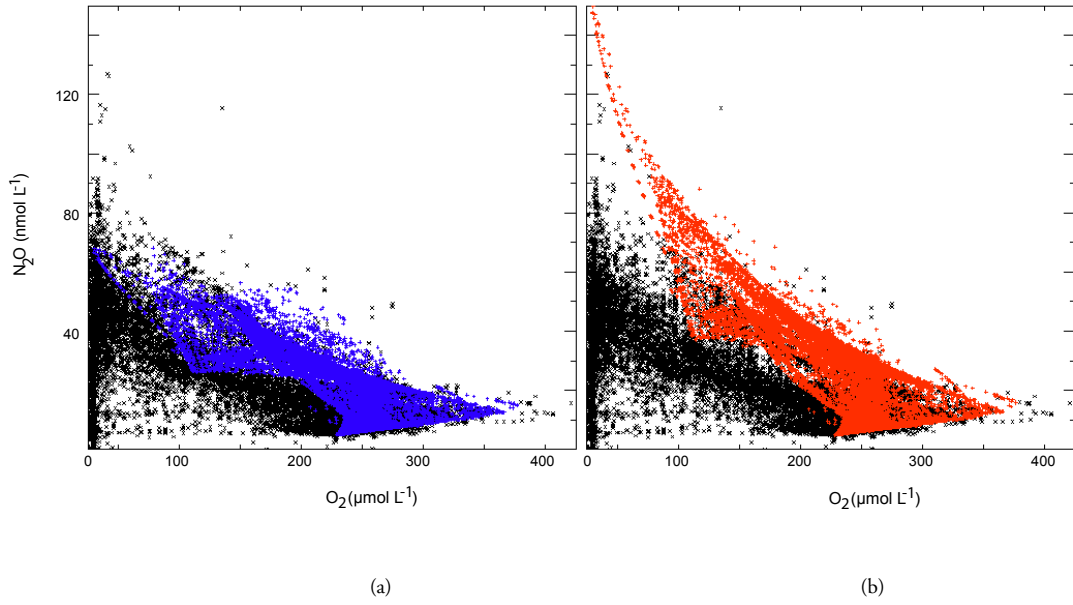
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893 Fig.2: Global average depth profile of N₂O concentration (in nmol L⁻¹) from the
894 MEMENTO database (dots) (Bange et al., 2009), P.TEMP (blue) and P.OMZ (red).
895 Model parameterizations are averaged over the 1985 to 2005 time period from the
896 historical simulation.

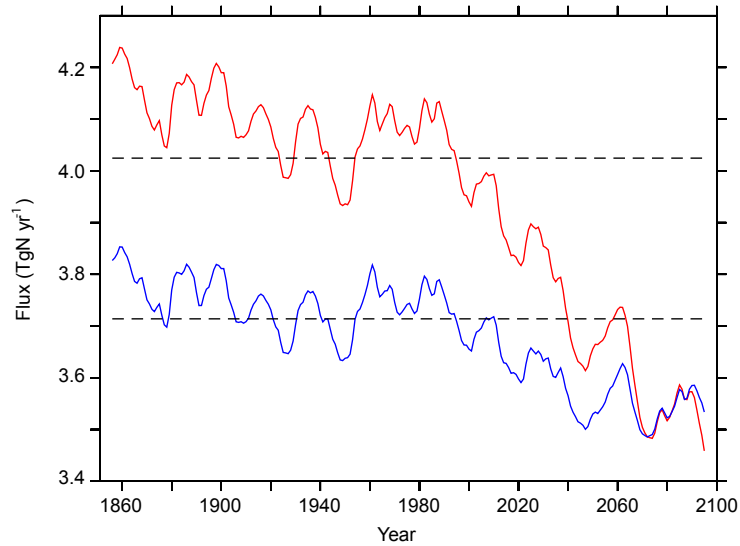


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899 Fig.3: Relationship between O_2 concentration (in $\mu\text{mol L}^{-1}$) and N_2O concentration (in
900 nmol L^{-1}) in the MEMENTO database (black) (Bange et al., 2009), compared to model
901 (a) P.TEMP (blue) and (b) P.OMZ (red) parameterizations averaged over the 1985 to
902 2005 time period from the historical simulation.

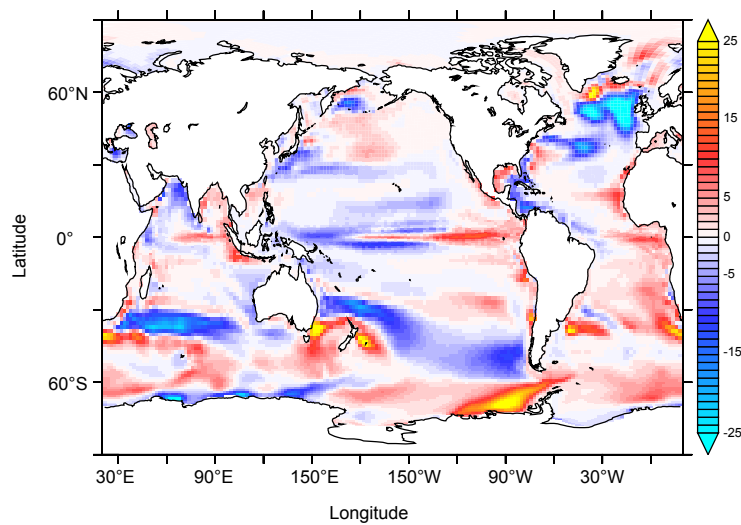


907 Fig 4: (a) N₂O sea-to-air flux (in TgN yr⁻¹) from 1851 to 2100 in P.TEMP (blue) and
 908 P.OMZ (red) using the historical and future RCP8.5 simulations. Dashed lines indicate
 909 the mean value over the 1985 to 2005 time period. Change in N₂O sea-to-air flux (mgN
 910 m⁻²yr⁻¹) from the averaged 2080-2100 to 1985-2005 time periods in future RCP8.5 and
 911 historical simulations in (b) P.TEMP and (c) P.OMZ parameterizations.



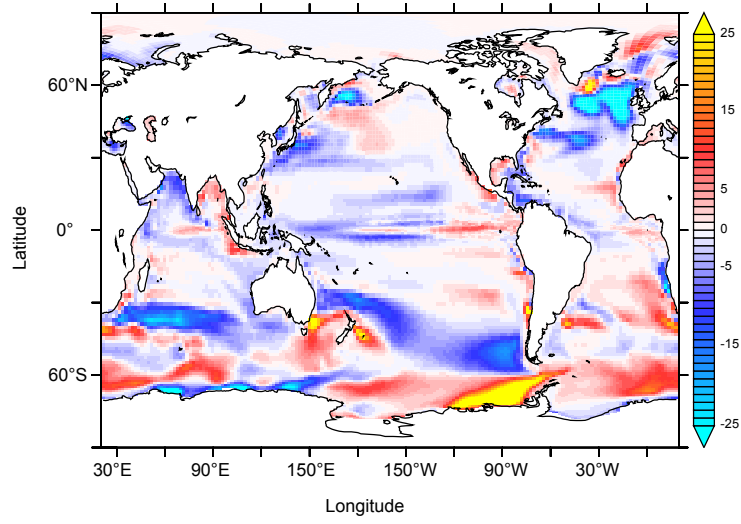
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(a)



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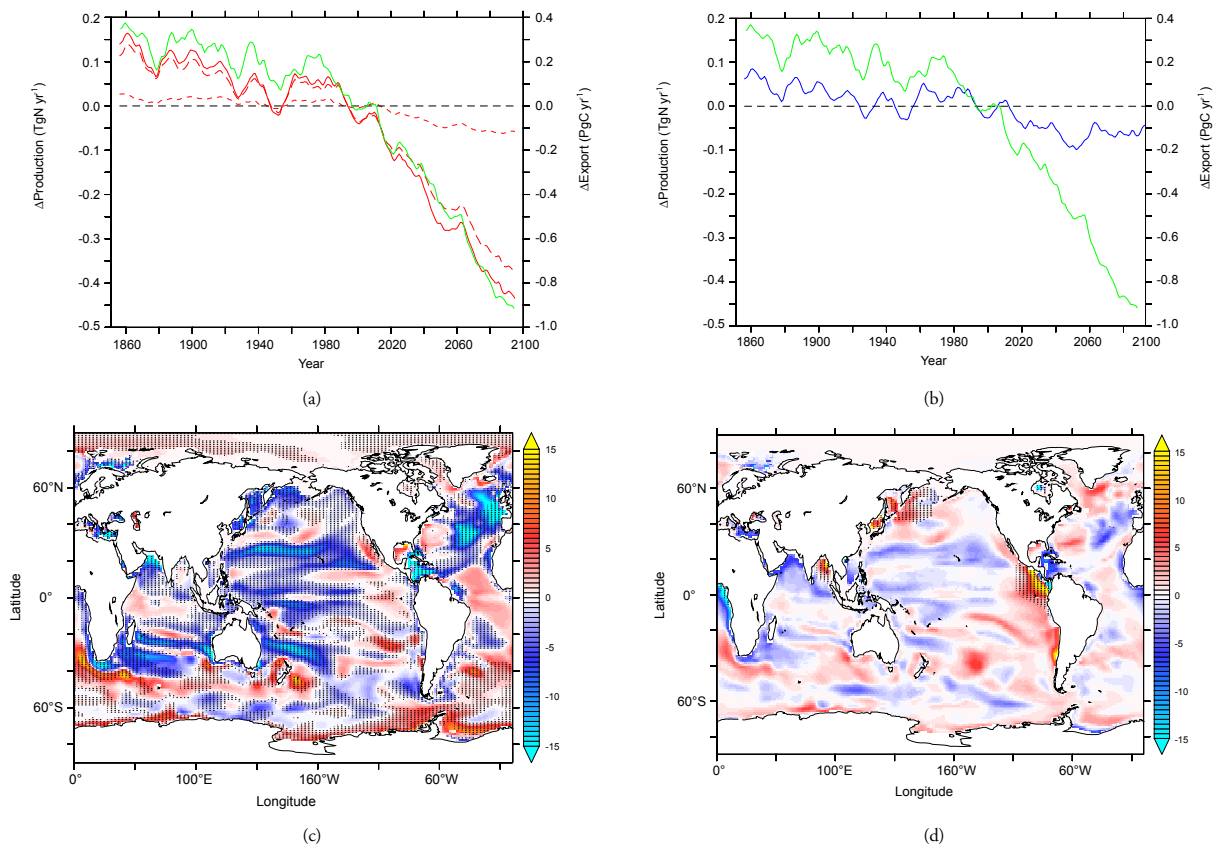
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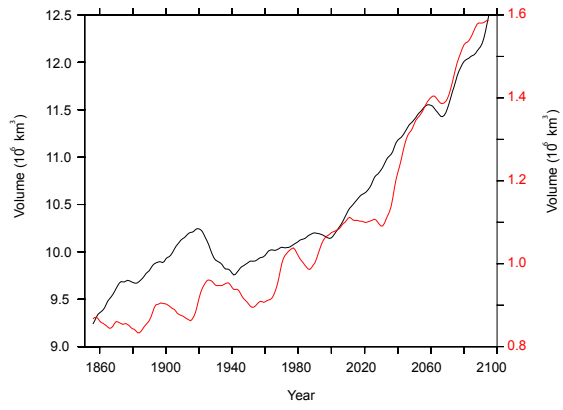


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(c)

920 Fig 5: (a) Anomalies in export of organic matter at 100m (green), low-O₂ production
 921 pathway (short dashed red), high-O₂ production pathway (long dashed red) and total
 922 P.OMZ production (red) from 1851 to 2100 using the historical and future RCP8.5
 923 simulations. (b) Anomalies in export of organic matter at 100m (green) and P.TEMP
 924 production (blue) over the same time period. (c) Change in high-O₂ production pathway
 925 of N₂O (in mgN m⁻² yr⁻¹) in the upper 1500m between 2080-2100 to 1985-2005
 926 averaged time periods. Hatched areas indicate regions where change in export of organic
 927 matter at 100m deep have the same sign as in changes in high-O₂ production pathway. (d)
 928 Change in low-O₂ production pathway of N₂O (in mgN m⁻² yr⁻¹) in the upper 1500m
 929 between 2080-2100 to 1985-2005 averaged time periods. Hatched areas indicate regions
 930 where oxygen minimum zones (O₂ < 5 μmol L⁻¹) expand. (e) Volume (in 10⁶ km³) of
 931 hypoxic (black, O₂ < 60 μmol L⁻¹) and suboxic (red, O₂ < 5 μmol L⁻¹) areas in the 1851
 932 to 2100 period in NEMO-PISCES historical and future RCP8.5 simulations.
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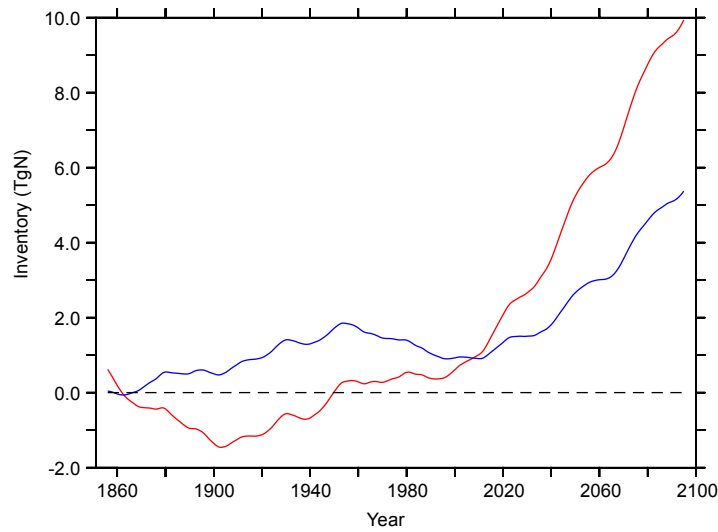




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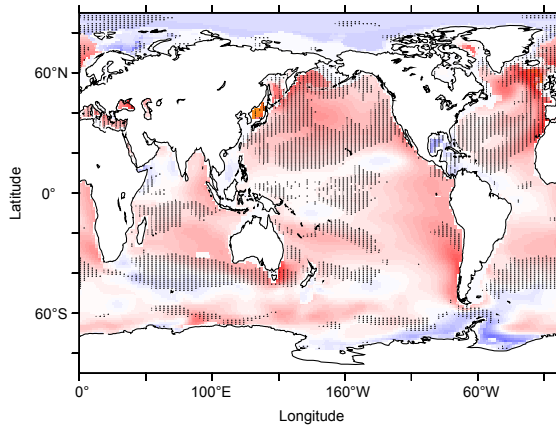
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936 Fig 6: (a) Anomalies in N₂O inventory (in TgN) from 1851 to 2100 in P.TEMP (blue)
 937 and P.OMZ (red) using the historical and future RCP8.5 simulations in the upper
 938 1500m. Change in vertically integrated N₂O concentration (in mgN m⁻²) in the upper
 939 1500m using NEMO-PISCES model mean from the averaged 2080-2100 to 1985-2005
 940 time periods in future RCP8.5 and historical scenarios respectively in (b) P.TEMP and (c)
 941 P.OMZ. Hatched areas indicate regions where the annual mean mixed layer depth is
 942 reduced by more than 5m in 2080-2100 compared to 1985-2005.

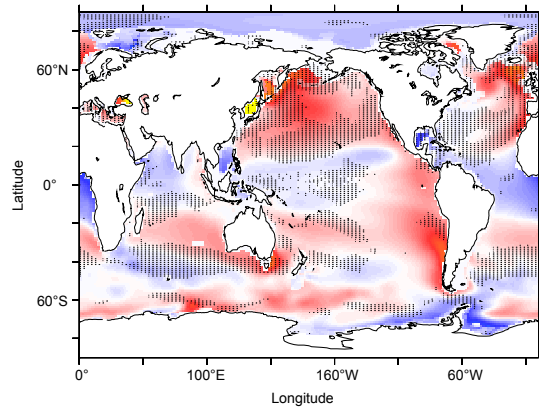


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(a)



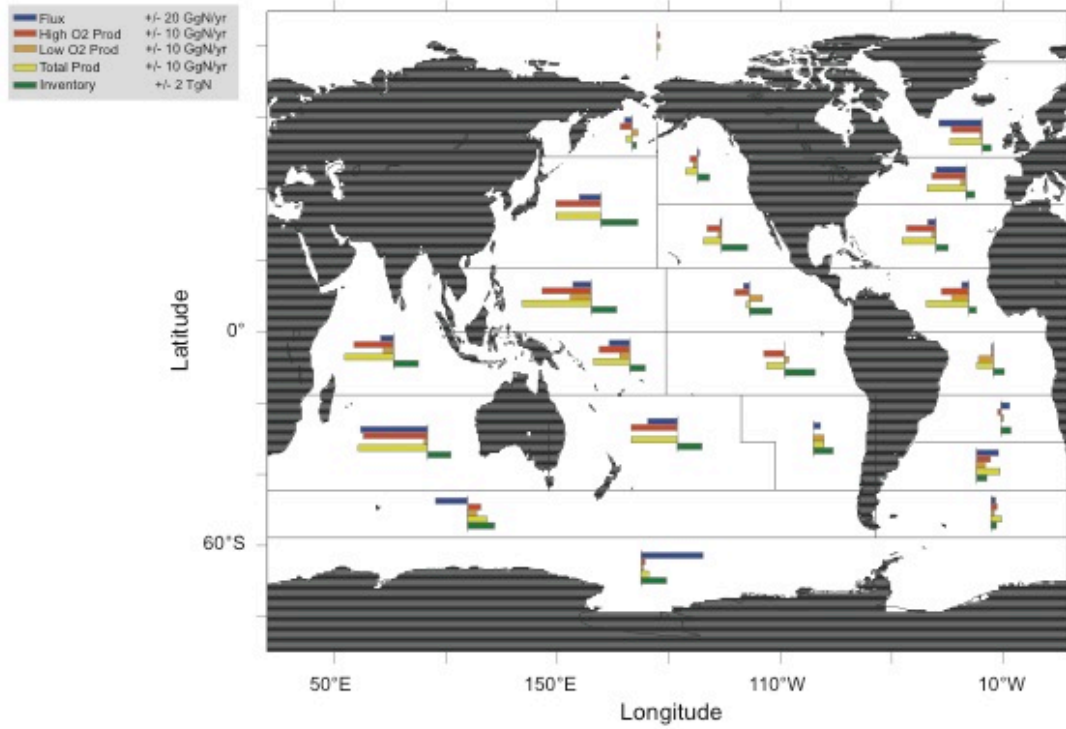
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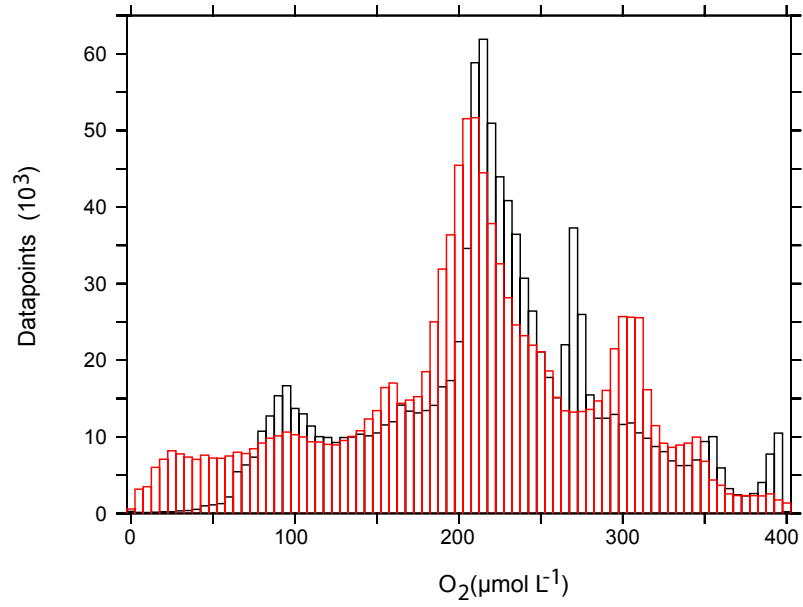
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948 Fig. 7: Change in the whole water column in N₂O sea-to-air flux (blue), high-O₂
 949 production pathway (red), low-O₂ production pathway (orange), total N₂O production
 950 (yellow) and N₂O inventory (green) for P.OMZ from the averaged 2080-2100 to present
 951 1985-2005 averaged time period in the NEMO-PISCES historical and future RCP8.5
 952 simulations (based on Mikaloff-Fletcher et al. (2006) oceanic regions).



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955 Figure 8: Distribution of O₂ concentration in NEMO-PISCES 1985 to 2005 averaged
956 time period (black) compared to the oxygen-corrected World Ocean Atlas (red) from
957 Bianchi et al. (2012). Interval widths are O₂ concentrations at steps of 5 μmol L⁻¹.

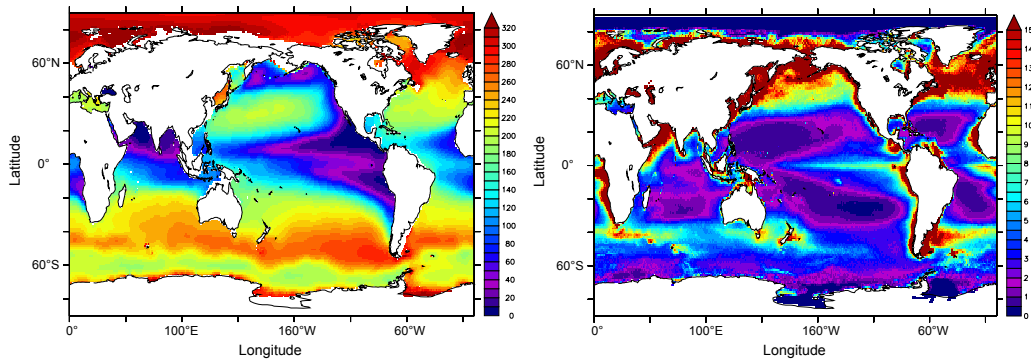


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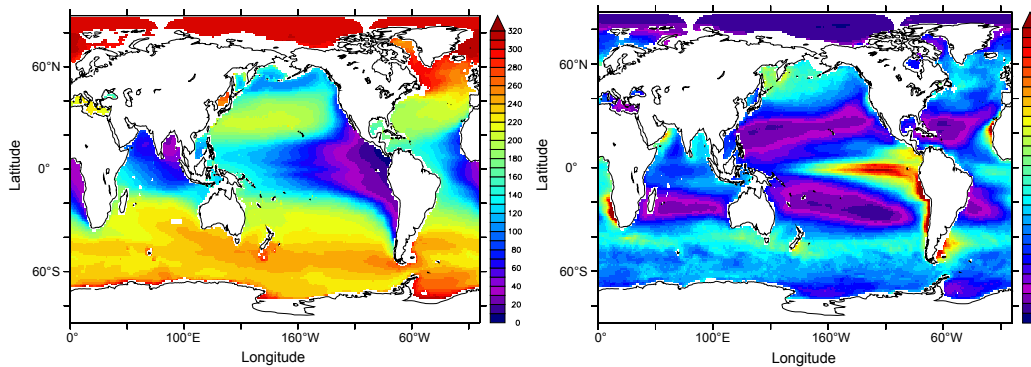
960 Figure 9: Averaged O₂ concentration between 200-600m depth (in $\mu\text{mol L}^{-1}$) (left) and
961 export of carbon (in $\text{mmolC m}^{-2} \text{d}^{-1}$) (right) in (a) WOA2005* and Dunne et al. (2007),
962 (b) CMIP5 model mean historical simulations over the 1985-2005 time period and (c)
963 NEMO-PISCES for the present 1985-2005 time period.

964 a. WOA2005* and Dunne et al., 2007



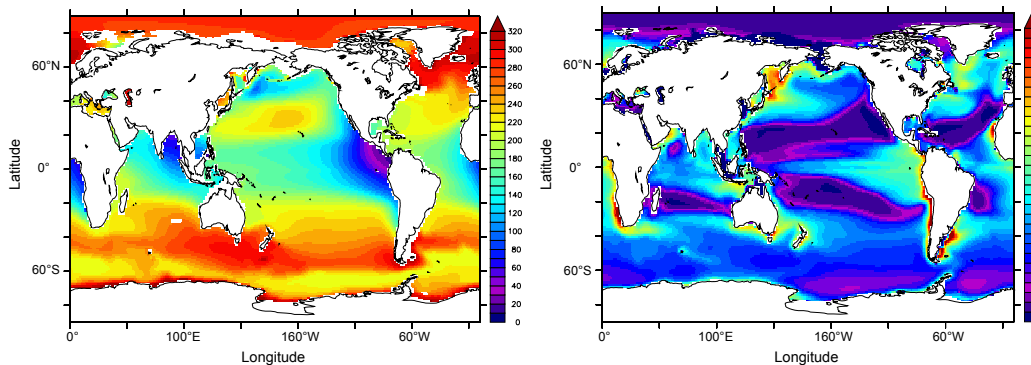
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966 b. CMIP5 model mean



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968 c. NEMO-PISCES



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970 SUPPLEMENTARY MATERIAL

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972 The O_2 modulation function $f(O_2)$ in P.OMZ is defined as,

$$f(O_2) = \left\{ \begin{array}{ll} \frac{O_2}{O_2^{*1}} & O_2 < O_2^{*1} \\ 1 & O_2^{*1} < O_2 < O_2^{*2} \\ 0.7 \cdot \exp - 0.5(O_2 - O_2^{*2})/O_2^{*2} + \\ 0.3 \cdot \exp - 0.05(O_2 - O_2^{*2})/O_2^{*2} & O_2 \geq O_2^{*2} \end{array} \right\}$$

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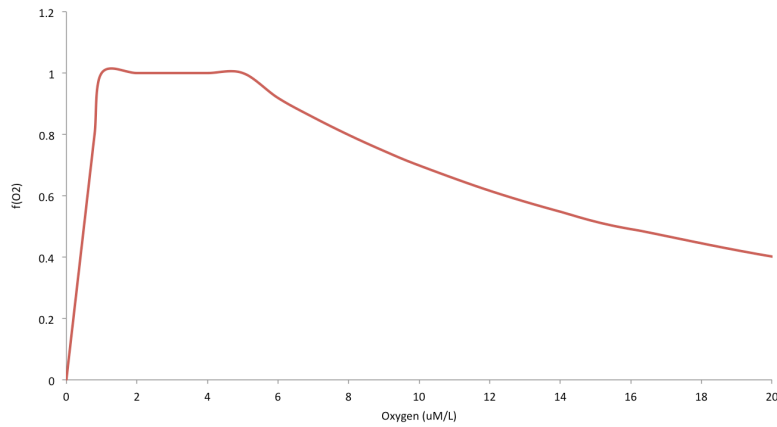
974 where O_2^{*1} is $1 \mu\text{mol L}^{-1}$ and O_2^{*2} is $5 \mu\text{mol L}^{-1}$. The shape of the function is shown in Fig.

975 S1.

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977 Fig. S1: Oxygen modulating function $f(O_2)$ in the low- O_2 production pathway term

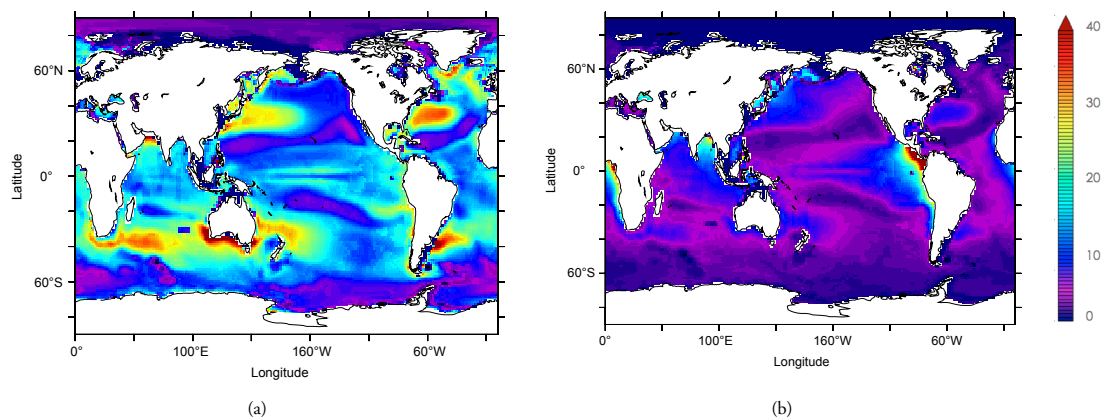
978 included in P.OMZ from Goreau et al. (1980).



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981 Fig. S2: Vertically integrated (a) high-O₂ and (b) low-O₂ production pathways (in gN m⁻²
982 yr⁻¹) in P.OMZ for the averaged 1985 to 2005 historical simulation.
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