1

2

3

4

5

6 **Variable C:N:P stoichiometry of dissolved organic matter cycling in the**

7 **Community Earth System Model**

8

9

10

11

12

13

14 Robert T. Letscher*, J. Keith Moore, Yi-Cheng Teng, and François Primeau

15 Earth System Science, University of California, Irvine, CA USA.

16 *corresponding author: robert.letscher@uci.edu

17

18

18   **Abstract**

19   Dissolved organic matter (DOM) plays an important role in the ocean's biological carbon

20   pump by providing an advective/mixing pathway for ~20% of export production. DOM is

21   known to have a stoichiometry depleted in nitrogen (N) and phosphorus (P) compared to

22   the particulate organic matter pool, a fact that is often omitted from biogeochemical-

23   ocean general circulation models. However the variable C:N:P stoichiometry of DOM

24   becomes important when quantifying carbon export from the upper ocean and linking the

25   nutrient cycles of N and P with that of carbon. Here we utilize recent advances in DOM

26   observational data coverage and offline tracer-modeling techniques to objectively

27   constrain the variable production and remineralization rates of the DOM C/N/P pools in a

28   simple biogeochemical-ocean model of DOM cycling. The optimized DOM cycling

29   parameters are then incorporated within the Biogeochemical Elemental Cycling (BEC)

30   component of the Community Earth System Model and validated against the compilation

31   of marine DOM observations. The optimized BEC simulation including variable DOM

32   C:N:P cycling was found to better reproduce the observed DOM spatial gradients than

33   simulations that used the canonical Redfield ratio. Global annual average export of

34   dissolved organic C, N, and P below 100m was found to be 2.28 Pg C yr^{-1} (143 Tmol C

35   yr^{-1}), 16.4 Tmol N yr^{-1}, and 1 Tmol P yr^{-1}, respectively with an average export C:N:P

36   stoichiometry of 225:19:1 for the semilabile (degradable) DOM pool. DOC export

37   contributed ~25% of the combined organic C export to depths greater than 100m.

38

1. Introduction

Dissolved organic matter (DOM) is an important pool linking nutrient cycles of nitrogen (N) and phosphorus (P) to the ocean's carbon cycle. Following its net production in the surface ocean, DOM provides an advective pathway for removal of biologically fixed carbon (C) to the deep ocean, accounting for ~20% of the C exported within the ocean's biological pump (Hansell, 2013). Remineralization of DOM in the ocean's interior is carried out by microbial heterotrophs, respiring C while releasing inorganic N and P nutrients back to the water column. The concept of the Redfield ratio (Redfield, 1958; Redfield et al., 1963) has been a unifying paradigm in ocean biogeochemistry linking the stoichiometry of biological production and phytoplankton cellular material to that of the remineralization of detrital organic matter (OM) and inorganic nutrient ratios in the water column. At the global scale, production/decomposition of particulate OM (POM) in the ocean is thought to largely follow the canonical Redfield ratio of 106:16:1 for C:N:P, however some recent studies have suggested more variable C:N:P ratios (i.e., Martiny et al., 2013a; 2013b) and only recently has variable C:N:P stoichiometry been introduced into Earth System Models (e.g. Vichi et al., 2007; Dunne et al., 2013). Large deviations from the Redfield ratio have been documented for DOM (Aminot and Kérouel, 2004; Hopkinson and Vallino, 2005). Hopkinson and Vallino (2005) found DOM production and decomposition to follow a stoichiometry of 199:20:1, indicating the more efficient export of C within DOM per mol of N and P relative to sinking POM. This finding is significant in light of evidence that future perturbations to the ocean from global climate change may favor enhanced partitioning of production to DOM (Wohlers et al., 2009; Kim et al., 2011). Thus accounting for variable stoichiometry within the

61 DOM pool that deviates from the Redfield ratio requires a re-evaluation of the controls

62 on C export and their response to future perturbations due to climate change.

63   Here we aim to utilize recent advances in DOM data coverage to incorporate variable

64 production and decomposition stoichiometry within the DOM tracers of the

65 Biogeochemical Elemental Cycling (BEC) model in order to improve representation of

66 this important carbon export flux and associated nutrient cycles. The BEC tracks the

67 cycling of key biogeochemical tracers (e.g. C, N, P, Fe, etc.) and runs within the ocean

68 general circulation component of the Community Earth System Model (CESM) (Moore

69 et al., 2004). The current release of CESM v1.2.1 contains five DOM related tracers:

70 semilabile DOC, DON, and DOP pools as well as refractory DON and DOP pools

71 (Moore et al., submitted). Here we have added a sixth DOM tracer, refractory DOC. Our

72 approach is to optimize the BEC DOM parameters using available observations, by

73 applying a fast offline solver based on a direct-matrix inversion (DMI) of a linear model

74 of DOM cycling; an approach similar to previous applications for marine radiocarbon

75 (Khatiwala et al., 2005) and marine organic matter cycling (Kwon and Primeau, 2006;

76 Hansell et al., 2009). The 3D ocean circulation is obtained from the offline tracer-

77 transport model for the ocean component of the CESM (Bardin et al., 2014). The DMI

78 solver uses a parallel multifrontal sparse matrix inversion approach as implemented in the

79 MUMPS solver (Amestoy et al. 2001; 2006) to quickly obtain the equilibrium solutions

80 needed to objectively calibrate the biogeochemical parameters of the DOM cycling

81 model by minimizing the misfit between the model and observations. The DOM cycling

82 parameters from the equilibrium solution of the offline model are then incorporated

83 within the BEC and optimized with only minor additional tuning.

84   The remainder of this article is organized as follows. Section 2 describes: 1) the

85   current representation of DOM cycling in the BEC v1.2.1, 2) the global ocean dataset of

86   DOM observations utilized for the optimization, 3) structure of the offline DOM cycling

87   model and the DMI solver, and 4) the modified BEC model with improved DOM cycling

88   parameters with the metrics employed for optimization. Section 3 details the results of 1)

89   the offline DOM cycling model solution, 2) the reference CESM-BEC v1.2.1 simulation,

90   as well as 3) the BEC simulation with optimized DOM cycling, including a comparison

91   of DOM cycling metrics. Sections 3.4 and 3.5 describe a comparison of multiple DOM

92   cycling schema and an evaluation of direct uptake of DOP by phytoplankton in the BEC

93   model, respectively. We conclude with a discussion and summary of our results in

94   Section 4.

95

96   **2. Methods**

97   *2.1 DOM cycling in the Standard BEC v1.2.1*

98   Model simulations with the optimized DOM parameters are compared against a

99   reference simulation using the standard version of the CESM-BEC v1.2.1, which we refer

100   to as 'REF'. The BEC model runs within the ocean physics component of CESM1 (Gent

101   et al., 2011), which is the Parallel Ocean Program, v2 (Smith et al., 2010). Detailed

102   description and evaluation of the ocean general circulation model is given by

103   Danabasoglu et al. (2011). Additional documentation, model output, and model source

104   code are available online (www2.cesm.ucar.edu). The REF simulation has a nominal

105   horizontal resolution of 1º with 60 vertical levels ranging in thickness from 10m (in the

106   upper 150m) with increasing layer thickness increasing with depth below 150m. Results

107   are presented for the final twenty-year annual average from a 310-year simulation.

108   A flow chart of organic matter cycling in the BEC is shown in Figure 1 and a list of

109   DOM parameter values from REF are given in Table 1. Primary production is carried out

110   amongst 3 phytoplankton groups, which take up available inorganic nutrients and have

111   losses to zooplankton grazing, sinking particulate organic matter (POM), and semilabile

112   DOM. Organic matter is produced with a C:N:P stoichiometry set to the slightly modified

113   Redfield ratio of Anderson and Sarmiento (1994), 117:16:1. Additional sources to

114   semilabile DOM include grazing losses when phytoplankton are grazed by zooplankton

115   as well as direct zooplankton losses. A variable fraction of DOM production is sent to the

116   refractory DOM (DOMr) pool, with different fractions going to the dissolved organic N

117   and P pools. Approximately fifteen percent of modeled primary production (PP) is sent to

118   the DOM pool via these sources, with the remainder of PP cycling as POM. It is

119   important to note that the BEC does not specifically track the total

120   production/decomposition of DOM, which is estimated to be 30-50% of net primary

121   production (NPP) (Carlson, 2002; and references therein). Rather, BEC semilabile and

122   refractory DOM tracers track the *accumulated* DOM pools that arise from the decoupling

123   of DOM production and consumption in time and space and are thus subject to advection

124   by the ocean circulation. These recalcitrant DOM fractions cycle on timescales of years

125   to centuries and represent a smaller portion of NPP, i.e. ~5-10% (Hansell, 2013). The

126   labile DOM pool, which cycles on timescales of minutes to days (Hansell, 2013) is not

127   explicitly modeled and is instead rapidly converted to inorganic carbon and nutrients at

128   each time step.

129   Microbial remineralization is the dominant sink for both POM and DOM pools and is

130   parameterized by assigned remineralization rates. POM is remineralized following a

131   prescribed remineralization vs. depth curve, with a length scale that increases with depth

132   (Moore et al., submitted). Semilabile DOM pools are assigned lifetimes

133   (1/remineralization rate) that depend on the light field with model grid cells where

134   photosynthetically active radiation (PAR) is >1% of surface irradiance being assigned a

135   euphotic zone lifetime. Semilabile DOM in model grid cells with PAR <1% is assigned a

136   mesopelagic zone lifetime. Remineralization is more rapid for semilabile DOM in the

137   euphotic zone, with lifetimes on the order of 5 months for DON + DOP and ~8 months

138   for DOC. Longer lifetimes for semilabile DOM are assigned in the mesopelagic zone

139   with the order of remineralization lifetimes following C > P > N. Remineralization of

140   refractory DOM follows a similar light dependence with a faster remineralization rate

141   given to DOMr in euphotic zone grid cells to parameterize a sink via UV oxidation

142   (Carlson, 2002). DOMr below the euphotic zone is remineralized over centennial

143   timescales.

144

145   *2.2 Database of DOM ocean observations*

146   We compiled publicly available and literature observations of DOM concentrations

147   into a single database for use in both the DMI-enabled linear DOM model as well as to

148   evaluate our BEC DOM optimization model runs. Briefly, the database contains over

149   34,000 observations of DOC, >18,000 observations of DON, and >2,000 observations of

150   DOP. Geographic coverage for the 5 ocean basins is moderately balanced for

151   observations of DOC and DON, however the Atlantic Ocean dominates available DOP

152 observations with DOP data completely lacking for the Indian, Southern, and Arctic

153 Oceans. Semilabile DOM is defined as the total observed DOM concentration less the

154 refractory concentration as determined from the asymptotic concentration of DOM depth

155 profiles. Refractory DOC concentrations vary by ocean basin in the range 37.7 µM

156 (South Pacific) to 45.0 µM (Arctic). Globally constant concentrations are used for

157 refractory DON (1.8 µM) and refractory DOP (0.03 µM). Full details of this DOM

158 database are given elsewhere (Letscher et al., submitted).

159

160 *2.3 Application of the DMI-enabled solver with a linear DOM cycling model*

161 *1st iteration – DOM source from BEC PP*

162 The linear DOM cycling model cycles DOM with one source/sink and uses an

163 idealized annual ocean circulation in offline mode from the CESM-POP2 ocean

164 circulation model (Bardin et al., 2014); nominal $1°\times1°$ horizontal resolution with 60

165 vertical levels, i.e. the same grid as the standard BEC v1.2.1. In this simple model of

166 DOM cycling, two tracers of DOM are simulated for each element, C, N, and P:

167 semilabile (SLDOM) and refractory (RDOM). The source for each DOM tracer is

168 parameterized as some variable fraction, *f*, of primary production and is formed within

169 the top model grid level with a thickness of 10m. The sink for each DOM fraction is

170 microbial remineralization parameterized with an assigned remineralization rate, κ, that

171 differs for the euphotic zone and deep ocean layers in the case of SLDOM. The

172 conservation equations for each DOM tracer are:

$$173 \quad \frac{\partial}{\partial t}\text{SLDOM} + \mathbf{T}\text{SLDOM} = f_1\text{PP} - \begin{cases} \kappa_1\text{SLDOM} & \text{if } z > -100\text{m} \\ \kappa_2\text{SLDOM} & \text{if } z < -100\text{m} \end{cases} \quad (1)$$

$$174 \quad \frac{\partial}{\partial t}\text{RDOM} + \mathbf{T}\text{RDOM} = f_2\text{PP} - \kappa_3\text{RDOM} \quad (2)$$

175

176 where $\mathbf{T}$ = advection-diffusion transport operator (a sparse matrix constructed using

177 output from the dynamical CESM-POP2 model as described in Bardin et al., 2014) and

178 PP = the annual average 3D primary production field from the coupled ocean-atmosphere

179 run of the CESM for the 1990s (Moore et al., 2013).

180

181 We tested the sensitivity of the linear DOM model results to multiple production

182 functions (CESM PP, DOM production flux from the BEC, satellite estimated PP),

183 however results suggest the differing source functions do not appreciably alter modeled

184 DOM distributions or parameter values.

185   Our initial construction of the linear DOM model allowed the sum of f_1+f_2 to vary

186 continuously between 0 and 0.5 and $\kappa_i \mid i=1\cdots3$ to vary logarithmically between 0.25 and

187 20 000 yr^{-1} by 24 discrete values. The direct-solver technique makes it possible to

188 objectively calibrate these parameters $f_i, \kappa_i \mid i=1\cdots3$ by using a numerical optimization

189 algorithm that rapidly tests each permutation of the discretized κ_i values, scaled by f_i, in

190 order to find the parameter set that minimizes the root mean square difference in the

191 misfit between the model-predicted and observed DOM concentration. A separate linear

192 DOM model (Equations 1-2) is solved for the DOC, DON, and DOP cases. The DMI

193 solver allows us to determine very efficiently the optimal lifetimes for the various DOM

194 pools. It is not practical to determine these using multiple forward simulations of the full

195 CESM-BEC, which would require years to decades of computer time.

196

197 *Optimized DOM parameter incorporation into the BEC model*

198 The optimized parameter values obtained from the DMI-enabled linear DOM model

199 were incorporated within the BEC to improve its representation of DOM cycling. The

200 BEC model has two tracers for each DOM pool, semilabile and refractory, with differing

201 lifetimes for the euphotic vs. mesopelagic zones. Thus the SLDOM lifetimes, κ_1 and κ_2,

202 from the DMI-enabled DOM model were applied to the BEC model semilabile tracers for

203 the euphotic zone and mesopelagic, respectively. The RDOM lifetime from the DMI-

204 enabled DOM model was applied throughout the full water column of the BEC model.

205 Further fine tuning of DOM lifetimes was carried out to provide the best DOM optimized

206 case, using the mean bias of the modeled concentrations versus the observations and the

207 log-transformed regression correlation coefficient between simulated and observed DOM

208 in the upper ocean, 0-500m, as comparison metrics. The BEC simulation containing the

209 set of improved DOM cycling parameters following the first iteration of the DMI-enabled

210 linear DOM model is termed 'DOM DEV'.

211

212 *2nd iteration of DMI-enabled linear DOM model – DOM source from BEC DOM*

213 *production flux*

214 Initial improvements to DOM cycling metrics within the BEC model were large upon

215 incorporation of the DMI-enabled linear DOM model parameter values, however because

216 of differences between the offline model and the full BEC model further improvements to

217   the DOM tracer lifetimes was possible. To achieve this the DMI-enabled linear DOM

218   model was modified such that the production for each tracer was held constant allowing

219   only the remineralization rate, κ_i, to be optimized from a choice of 48 discrete tracer

220   lifetimes spanning the range 0.7 to 20 000 yr^{-1}. Rather than using PP to get the production

221   flux of each DOM tracer, the semilabile and refractory DOM production fluxes

222   (SLDOMprod, RDOMprod) were extracted from the DOM DEV simulation and

223   prescribed in the modified DMI-enabled DOM model. The fraction of SLDOMprod and

224   RDOMprod to be applied each κ_i / $i=1\cdots4$ was diagnosed from the relative proportions

225   of each tracer residing in the euphotic or deep layers at the end of the DOM DEV

226   simulation of the BEC (see Fig. 2). At this step it was also desired to solve for the

227   remineralization rate associated for a secondary sink for DOMr due to photo-oxidation in

228   the surface layer. Thus equations 1 and 2 were modified to become equations 3 and 4 as

229   follows:

230

231    $$\frac{\partial}{\partial t}\text{SLDOM} + \mathbf{T}\text{SLDOM} = \text{SLDOMprod} - \begin{cases} \kappa_1 \text{SLDOM} & \text{if } z > -100\text{m} \\ \kappa_2 \text{SLDOM} & \text{if } z < -100\text{m} \end{cases} \qquad (3)$$

232    $$\frac{\partial}{\partial t}\text{RDOM} + \mathbf{T}\text{RDOM} = \text{RDOMprod} - \begin{cases} \kappa_4 \text{RDOM} & \text{if } z > -10\text{m} \\ \kappa_3 \text{RDOM} & \text{if } z < -10\text{m} \end{cases} \qquad (4)$$

233

234   The results obtained from the modified DMI-enabled linear DOM model were

235   incorporated into the final DOM OPT simulation of the BEC following minor tuning of

236   the κ parameter values.

237

3. Results

3.1 DOM parameter output from the DMI-enabled linear DOM model

1st iteration – DOM source from BEC PP

The objectively optimized DOM parameter values from the solutions to the DMI-enabled linear DOM model (DMI-DOM solver) are shown in Table 1. The fraction of the PP flux that accumulates as DOC, DON, and DOP is ~10%, with the percentage cycling as refractory DOM: DOCr = 0.6%, DONr = 0.4%, and DOPr = 0.15%. Optimized semilabile DOC exhibited the longest lifetimes with a lifetime of 34 years in the euphotic zone (EZ) and 2.9 years in the mesopelagic zone (MZ). Semilabile DON had an intermediate lifetime with respect to DOC and DOP, with an EZ lifetime of 8.7 years and MZ lifetime of 1.7 years. Semilabile DOP had the shortest lifetimes, with EZ lifetime = 5.8 years and MZ lifetime = 0.8 years. Optimization of the parameters for the refractory pools yielded lifetimes of 20,000 years, 9,000 years, and 5,000 years for DOCr, DONr, and DOPr, respectively.

2nd iteration of DMI-enabled linear DOM model – DOM source from BEC DOM production flux

Results from the modified DMI-enabled linear DOM model (MOD DMI-DOM solver), which used the BEC DOM production flux from the DOM DEV simulation are shown in Figure 2 and Table 1. Approximately 7% of primary production (PP) is routed to production of DOM, which is divided amongst semilabile (SLDOM) and refractory pools (RDOM). Remineralization lifetimes (κ_i^{-1}) differ for SLDOM depending on location in the water column with longer lifetimes for the euphotic zone (depths where

261 PAR > 1%) than for the mesopelagic zone. A similar faster rate of RDOM

262 remineralization is assigned in the surface layer (< 10m) to parameterize a sink due to

263 photo-oxidation. The parameter, %remin, represents the percentage of the DOM

264 production flux that is remineralized within each depth horizon on an annual basis with

265 the sum equal to 100% and is diagnosed from the DOM DEV simulation. The relative

266 magnitude of SLDOM remineralization that occurs within the EZ vs. the MZ was found

267 to be ~1.8:1 (Fig. 2). Only a small percentage of RDOM remineralization occurs in the

268 surface layer, i.e. 0.01-0.03% (Fig. 2). The optimal tracer lifetimes from the modified

269 DMI-DOM model were: 15 years for SLDOC in the EZ, 5 years for SLDOC in MZ,

270 15,000 years for RDOC, and 15 years for RDOC whilst in the surface layer (<10m).

271 DON tracer lifetimes were: 15 years for EZ SLDON, 5 years for MZ SLDON, 8,000

272 years for RDON, and 15 years for RDON at the surface. DOP tracer lifetimes were: 62

273 years for SLDOP in the EZ, 4.5 years for MZ SLDOP, 6,000 years for RDOP, and 15

274 years for photo-oxidation removal.

275

276 *3.2 Modeled DOM in the Standard CESM-BEC v1.2.1 (REF Simulation)*

277   A set of metrics were used to assess the performance and improvements to DOM

278 cycling for the CESM-BEC simulations including the global integrals of DOM

279 production, export, and C:N:P stoichiometry (Table 2) as well as the mean bias and

280 correlation coefficient (r) of the simulated DOM concentrations against the observational

281 dataset in the upper 500m (Table 3). Results and comparison of DOM cycling metrics

282 from the REF simulation are presented in Tables 2 and 3.

283   *DOC* – Total DOC production in the euphotic zone (upper 100m) for the REF

284   simulation is 10.5 Pg C yr^{-1} (Table 2). About 85% of this DOC production is

285   remineralized within the euphotic zone, yielding DOC export from the euphotic zone of

286   ~1.7 Pg C yr^{-1}. Modeled semilabile DOC concentrations from the REF simulation are

287   shown for the surface (Fig. 3A) with observations overlain by the colored dots. The

288   spatial extent of regions with elevated (>30 µM) semilabile DOC concentrations (i.e. the

289   subtropical gyres) is too large in the REF simulation compared to observations. Large

290   overestimates of simulated DOC are found in the Southern Ocean. Modeled semilabile

291   DOC concentrations for the REF simulation at 200m are shown in Figure 3B. Model

292   underestimates (up to ~75%) are observed in the oxygen deficient zones in the eastern

293   basins of the equatorial regions. Note that CESM v1.2.1 lacks a DOCr tracer so that

294   simulated DOC is for the semilabile pool only (here we have subtracted the observed

295   deep ocean DOC concentration for each basin from the DOC observations).

296   *DON* – Total euphotic zone DON production is 120 Tmol N yr^{-1} with >100m export

297   of 25.0 Tmol N yr^{-1} (Table 2). Modeled total DON concentrations (semilabile +

298   refractory) at the surface are similarly overestimated in the REF simulation (Table 3) by

299   up to 100% within the subtropical gyres of the Pacific and the eastern South Atlantic

300   Oceans (Fig 4A). Model-observation misfit is better at 200m (Fig. 4B), however biases of

301   15-25% remain (Table 3) in a number of regions (e.g. central equatorial Pacific, South

302   Indian Oceans).

303   *DOP* – Total euphotic zone DOP production is 7.43 Tmol P yr^{-1} with export out of

304   the euphotic zone valued at 1.30 Tmol P yr^{-1} (Table 2). Modeled DOP distributions are

305   shown in Figure 5A (surface), and 5B (200m), with observations mostly limited to the

306   Atlantic Ocean. The region of elevated simulated DOP (>0.25 µM) in the eastern South

307   Atlantic surface waters is located further to the east than is observed (Fig. 5A), possibly

308   owing to the snapshot nature of the observations (collected in Jan-Feb) compared to the

309   annually averaged simulation. Modeled DOP in the subsurface agrees reasonably well

310   with the Atlantic observations, except for a ~70% model overestimate in the South

311   Atlantic subtropical gyre (Fig. 5B).

312

313   *3.3 Modeled DOM in the DOM OPT simulation*

314   Results and comparison of DOM cycling metrics from the DOM OPT simulation

315   against the observational dataset and REF simulation are presented in Tables 2 and 3. For

316   a comparison of the set of DOM cycling parameter values between the REF and DOM

317   OPT simulations, see Table 1.

318   *DOC* – Total DOC production in the euphotic zone (upper 100m) for the DOM OPT

319   simulation is 4.16 Pg C yr^{-1} (Table 2). About 45% of this DOC is remineralized within

320   the euphotic zone, yielding DOC export from the EZ of 2.28 Pg C yr^{-1}, which is ~20%

321   larger than the result from a separate DOC data assimilative modeling study (Table 2;

322   Hansell et al., 2009). Combined with the particulate organic carbon export from 100m in

323   the DOM OPT simulation of 7.01 Pg C yr^{-1}, DOC contributes ~25% to the total 9.29 Pg

324   C yr^{-1} of export production in the CESM-BEC. Modeled total DOC concentrations

325   (semilabile + refractory) from the DOM OPT simulation are shown for the surface (Fig.

326   3C) and at 200m (Fig. 3D). There is generally good agreement between the simulated

327   fields and observations (colored dots) with the mean bias being <20% for the upper ocean

328   (0-500m; Table 3). Slightly larger model overestimations (up to ~30%) exist at the

329   surface for certain low-latitude ocean basins (e.g. tropical Atlantic, Indian Ocean).

330   *DON* – Total euphotic zone DON production is 30.7 Tmol N yr^{-1} with >100m export

331   of 16.4 Tmol N yr^{-1} (Table 2). Modeled total DON concentrations are improved over the

332   REF simulation at 200m (Fig. 4D), however overestimations of DON at the surface

333   remain in DOM OPT (Fig. 4C). Simulated surface DON overestimation is largest in the

334   low to mid latitudes, reaching ~30%. Opposite the pattern obtained for the low latitudes,

335   high latitude simulated DON is underestimated at the surface in the Southern Ocean (Fig.

336   4C) by up to ~35%. However, overall DON mean biases are small in the DOM OPT

337   simulation, i.e. <10% (Table 3).

338   *DOP* – Total euphotic zone DOP production is 2.94 Tmol P yr^{-1} with export out of

339   the euphotic zone of ~1 Tmol P yr^{-1} (Table 2). Modeled DOP distributions are shown in

340   Figure 5C (surface), and 5D (200m). The DOM OPT simulation captures the low

341   observed DOP concentrations in the North Atlantic, largely due to enhanced

342   phytoplankton direct uptake of DOP (see section 3.5). The region of elevated simulated

343   DOP (>0.25 µM) in the eastern South Atlantic surface waters continues to be located

344   further to the east than is observed (Fig. 5C) in the DOM OPT simulation as was also the

345   case in the REF simulation. Modeled DOP in the subsurface agrees reasonably well with

346   the Atlantic observations, reducing the large overestimates in the REF simulation (Fig.

347   5D, B). Overall mean DOP biases are similarly <10% for both the total and semilabile

348   pools (Table 3).

349

350   *3.4. Comparison of multiple DOM cycling schemes in the CESM-BEC*

351   We have also tested other hypotheses for DOM cycling formulations such as non-

352   variable C:N:P cycling stoichiometry (i.e. DOM cycling occurs at the Redfield ratio) as

353   well as more rapid turnover of DOM in the EZ compared to the MZ (the DOM OPT

354   simulation contains more rapid turnover of DOM in the MZ, following the work of

355   Carlson et al., 2004; Letscher et al., 2013a). To test these hypotheses, we performed two

356   additional BEC simulations termed REDFIELD and EZRAPID using a coarser resolution

357   version of the BEC model with a nominal 3º horizontal resolution. The optimized cycling

358   parameter values obtained for DOC from the DOM OPT simulation were assigned to the

359   DON and DOP pools for the REDFIELD simulation to allow all DOM (C/N/P) to cycle

360   at the same rate and in the same proportions. The ability for phytoplankton to directly

361   utilize DOP is also turned off in the REDFIELD simulation. The optimized EZ and MZ

362   lifetimes for each DOM tracer from the DOM OPT simulation were reversed for the

363   EZRAPID simulation such that the shorter lifetime (more rapid remineralization rate)

364   was assigned to SLDOM in the EZ.

365   Results from 310-year simulations of these are compared against ~3º simulations of

366   REF and DOM OPT in Table 4. Results are similar for DOC when comparing the DOM

367   OPT and REDFIELD simulations, which is to be expected as the REDFIELD simulation

368   used the same DOC cycling parameters as the DOM OPT simulation. Faster turnover of

369   DOC in the EZ (EZRAPID simulations) had a detrimental effect on DOC mean biases,

370   resulting in large overestimations in the upper 500m (Table 4) when compared with faster

371   turnover in the MZ (DOM OPT). Large positive mean biases were also found for DON

372   within the REDFIELD and EZRAPID simulations when compared to the DOM OPT

373 (Table 4). Similar positive biases were found for DOP within the REDFIELD and

374 especially for the EZRAPID simulations, i.e. up to ~135% (Table 4).

375

376 *3.5 Direct DOP Uptake by Phytoplankton*

377   The longer lifetimes for semilabile DOP in the DOP OPT simulation (on the order of

378 years) allow for significant horizontal advection of DOP from the more productive gyre

379 margins (e.g. the NW African upwelling region) towards the Sargasso Sea, providing an

380 additional phosphorus source to the western North Atlantic. Each phytoplankton group

381 within the BEC model can directly utilize DOP to satisfy their phosphorus requirements

382 when phosphate concentrations are low (Moore et al., submitted). Literature reports of

383 this phenomenon are numerous (e.g. Bjorkman and Karl, 2003; Casey et al., 2009; Lomas

384 et al., 2010; Orchard et al., 2010) whereby phytoplankton make use of extracellular

385 alkaline phosphatases to cleave phosphate groups from DOP moieties such as phosphate

386 mono- and di-esters (Dyhrman and Ruttenberg, 2006; Sato et al., 2013) for subsequent

387 uptake of the liberated phosphorus. Sohm & Capone (2006) provide half-saturation

388 constants for DOP uptake by *Trichodesmium* spp. (a diazotroph) and bulk phytoplankton

389 (dominated by nano- and pico- phytoplankton) from the subtropical North Atlantic, and

390 suggested *Trichodesmium* species obtained much of their required phosphorus from DOP

391 in this region. Based partly on this study, the diazotrophs have been given a lower half-

392 saturation constant for DOP uptake than the other phytoplankton (Moore et al.,

393 submitted). Diatoms also exhibit alkaline phosphatase activity albeit at lower rates than

394 other plankton groups (Dyhrman & Ruttenberg, 2006; Nicholson et al., 2006), and were

395 thus assigned a greater half-saturation for DOP uptake than the other phytoplankton

396 groups in the BEC (consistent with their reduced efficiency in taking up dissolved

397 inorganic phosphorus in the model).

398   The fraction of total phosphorus uptake that is sustained by DOP uptake for each

399 phytoplankton group in the DOM OPT simulation is shown in Figure 6. DOP uptake is

400 largest by diazotrophs (Fig. 6B), with generally ~20% of P uptake from DOP in the

401 subtropical gyres, increasing to ~30-50% in the subtropical North Atlantic, western side

402 of the subtropical South Atlantic, and the eastern Mediterranean Sea. DOP uptake

403 represents a small fraction (<5%) of P uptake by the small phytoplankton and diatoms

404 (Fig. 6A and 6C) over much of the ocean, increasing to ~10% in the subtropical ocean

405 gyres.

406

407 **4. Discussion and Summary**

408   This study utilized a rapid solver of a simple linear biogeochemical cycling ocean

409 model, constrained by our compilation of marine DOM observations, to efficiently

410 optimize DOM biogeochemistry in the larger complexity CESM-BEC model. This

411 approach allows for a quicker and more quantitatively robust method for optimizing

412 biogeochemical ocean model parameters over the traditional 'hand'-tuning approach.

413 Model parameters determined with the modified DMI-enabled linear DOM model carried

414 over well when implemented in the full CESM-BEC (see Fig. 2). The DOM OPT

415 simulation contains reduced mean biases, improved correlation coefficients, and is more

416 consistent with the DOM observational constraints when compared to the REF simulation

417 (Fig. 3, 4, 5; Table 2, 3).

418   Our results demonstrate that allowing for non-Redfield stoichiometry in the DOM

419   pools significantly improves the match to observed DOM distributions. The order of

420   lability follows P > N > C, diagnosed from the calculated effective tracer lifetimes in

421   DOM OPT which include the net result of the sum of tracer sinks (~3.2 vs. 6.3 vs. 6.8

422   years for semilabile P, N, C; ~4300 vs. 6360 vs. 13,900 years for refractory P, N, and C).

423   The exact values of the DOM lifetimes determined in our study are dependent on the

424   underlying ocean circulation model used, however Hansell et al. (2012) determined

425   similar values for refractory DOC (16 000 yr) and combined semilabile and semi-

426   refractory DOC (~7 yr; estimated from their Fig. 5) while using a distinct ocean

427   circulation model than the one employed in the current study. In addition, the DOM

428   lifetimes from the DOM OPT simulation are in general agreement with available

429   estimates from the literature. Semilabile DOC lifetime has been estimated at ~1-13 years

430   in the mesopelagic of the Sargasso Sea (Hansell and Carlson, 2001), and ~7-22 years in

431   the mesopelagic of the North Pacific subtropical gyre (Abell et al., 2000). Semilabile

432   DON lifetimes have been estimated at ~3-12 years (Letscher et al., 2013a) or ~11-20

433   years (Abell et al., 2000) for marine DON and ~4-14 years for terrigenous derived DON

434   in the Arctic Ocean (Letscher et al., 2013b).

435   Our DOM OPT simulation estimated export C:N:P ratio of 225:19:1 for the

436   semilabile DOM is in excellent agreement with the estimate of 199:20:1 by Hopkinson

437   and Vallino (2005) and strongly supports the idea that DOC is exported efficiently

438   relative to DOP compared with the canonical Redfield ratio. The calculated export

439   efficiencies, that is the fraction of euphotic zone DOM production that is exported below

440   100m, are 55%, 53%, and 17.5% for DOC, DON, and DOP, respectively.

441   We found that best agreement with observed DOM distributions required a more

442   rapid degradation of semilabile DOM in the mesopelagic than in the euphotic zone. This

443   result is consistent with some incubation studies of DOM degradation (Carlson et al.,

444   2004; Letscher et al., 2013a). Possible hypotheses for this depth dependence on DOM

445   lifetimes in the real ocean are numerous, including differences in DOM

446   composition/quality (Skoog and Benner, 1997; Aluwihare et al., 2005; Goldberg et al.,

447   2011), microbial community structure (Giovannoni et al., 1996; Delong et al., 2006;

448   Treusch et al., 2009; Carlson et al., 2004; 2009; Morris et al., 2012), availability of

449   inorganic nutrients for heterotrophic utilization (Cotner et al., 1997; Rivkin and

450   Anderson, 1997; Caron et al., 2000), abundance of bacterial grazers (Caron et al., 2000),

451   and the presence or specific affinity of microbial cell membrane nutrient transporters

452   (Azam and Malfatti, 2007; Morris et al., 2010). However the relative importance of each

453   of these mechanisms are not well constrained, nor are any considered in the BEC model

454   formulation, and thus require further investigation.

455   Direct uptake of DOP by phytoplankton seemed necessary in our simulations to

456   capture the observed very low surface DOP concentrations in the Sargasso Sea. Yet there

457   are large uncertainties in the preference and uptake efficiencies for dissolved inorganic

458   phosphorus versus dissolved organic phosphorus by different phytoplankton groups.

459   Future field and lab studies are needed to reduce these uncertainties and to better quantify

460   the role of DOP in determining spatial patterns of nitrogen fixation. There is also a great

461   need for additional DOP measurements in every basin except the North Atlantic, along

462   with improved quality control and the development of a DOP standard reference material.

463

474

475   Figure 1. Schematic of organic matter cycling in the CESM-BEC. Primary production is

476   carried out by three phytoplankton functional types: small phytoplankton (which also

477   contains a subgroup of calcifying phytoplankton), diatoms, and diazotrophs. Sources to

478   DOM include direct losses from phytoplankton/zooplankton and from zooplankton

479   grazing of phytoplankton. The major sink for DOM is microbial remineralization,

480   parameterized with an assigned lifetime which differs between the euphotic zone and the

481   mesopelagic ocean. A small fraction of phytoplankton production is converted to

482   refractory DOM in the upper ocean with an additional source to DOMr from degradation

483   of sinking POM in the mesopelagic. DOMr is also lost via UV photo-oxidation in the

484   surface layer (<10m). The products of organic matter remineralization are dissolved

485   inorganic carbon, nitrate, ammonium, and phosphate.

486

487   Figure 2. Configuration of the DOM remineralization scheme and parameter values from

488   the modified DMI-enabled DOM model (Solver) and the DOM OPT simulation of the

489   CESM-BEC. Note the only minor changes to tracer lifetimes, κ_i^{-1}, between the modified

490   DMI-DOM model and the DOM OPT simulation. The value, %remin, represents the

491   percentage of the DOM production flux that is remineralized within each depth horizon

492   on an annual basis and is common to both models.

493

494   Figure 3. Plots of simulated semilabile [DOC] µM (colored contours) with observations

495   (colored dots) for the REF simulation at (A) the surface (EZ) and (B) 200m (MZ). Total

496   [DOC] µM (semilabile + refractory) for the DOM OPT simulation is shown for (C) the

497   surface (EZ) and (D) 200m (MZ). Note the difference in color scales between plots (A)

498   and (C); (B) and (D) as the REF simulation lacks a DOCr tracer.

499

500   Figure 4. Plots of simulated total [DON] µM (colored contours) with observations

501   (colored dots) for the REF simulation at (A) the surface (EZ), (B) 200m (MZ), and for the

502   DOM OPT simulation at (C) the surface (EZ), (D) 200m (MZ).

503

504   Figure 5. Plots of simulated total [DOP] µM (colored contours) with observations

505   (colored dots) for the REF simulation at (A) the surface (EZ), (B) 200m (MZ), and for the

506   DOM OPT simulation at (C) the surface (EZ), (D) 200m (MZ).

507

508   Figure 6. Fraction of total P uptake from DOP integrated over the euphotic zone (upper

509   100m) for (A) small phytoplankton, (B) diazotrophs, and (C) diatoms in the DOM OPT

510   simulation.

511

512   Table 1. Optimized DOM parameters from the DMI-enabled linear DOM model (DMI-

513   DOM solver) and the modified DMI model (MOD DMI-DOM solver) as well as the REF

514   and DOM OPT simulations of the CESM-BEC. Euphotic zone = 0-100m for the DMI-

515   DOM models and depths where PAR > 1% for REF and DOM OPT. The 'flux to DOM'

516   represents the fraction of primary production (PP) that accumulates as DOM while the

517   'fraction of DOM flux' represents the portion of the DOM production flux that

518   accumulates as semilabile (SL) or refractory (R) DOM. Parameters f_i | $i=1\cdots2$, κ_i |

519    $i=1\cdots4$ are defined in Equations 1-4. Surf = surface layer (<10m), reminR =

520   remineralization rate, sp = small phytoplankton, diat = diatoms, diaz = diazotrophs, k =

521   half saturation constant for DOP uptake, yr = year, and NA = not applicable.

522

523   Table 2. DOM production, export, and stoichiometry metrics for the REF and DOM OPT

524   simulations against observational constraints. Tmol = teramoles, 1 x 10^{12} mol; Pg =

525   petagrams, 1 x 10^{15} g.

526

527   Table 3. DOM mean bias and correlation coefficient in relation to the DOM observations

528   within the upper ocean (0-500m depth) for the REF and DOM OPT 1° simulations.

529   Observations of semilabile DOM are calculated as the total observed DOM concentration

530   less the asymptotic concentration below 1000m in each ocean basin.

531

Table 4. DOM mean bias and correlation coefficient in relation to the DOM observations

within the upper ocean (0-500m depth) for the REF, DOM OPT, REDFIELD, and

EZRAPID ~3º simulations. Observations of semilabile DOM are calculated as the total

observed DOM concentration less the asymptotic concentration below 1000m in each

ocean basin.

537

References

Abell, J., Emerson, S., and Renaud, P.: Distributions of TOP, TON, and TOC in the
    North Pacific subtropical gyre: Implications for nutrient supply in the surface ocean
    and remineralization in the upper thermocline, J. of Marine Research, 58, 203-222,
    2000.

Aluwihare, L. I., Repeta, D. J., Pantoja, S., and Johnson, C. G.: Two chemically distinct
    pools of organic nitrogen accumulate in the ocean, Science, 308(5724), 1007-1010,
    2005.

Amestoy, P. R., Duff, I. S., Koster, J., and L'Excellent, J.-Y.: A fully asynchronous
    multifrontal solver using distributed dynamic scheduling, SIAM Journal of Matrix
    Analysis and Applications, 23(1), 15-41, 2001.

Amestoy, P. R., Guermouche, A., L'Excellent, J.-Y., and Pralet, S.: Hybrid scheduling for
    the parallel solution of linear systems. Parallel Computing, 32 (2), 136-156, 2006.

Aminot, A., and Kérouel, R.: Dissolved organic carbon, nitrogen and phosphorus in the
    NE Atlantic and the NW Mediterranean with particular reference to non-refractory
    fractions and degradation, Deep Sea Research Part I, 51(12), 1975-1999, 2004.

Anderson, L. A., and Sarmiento, J. L.: Redfield ratios of remineralization determined by
    nutrient data analysis, Global Biogeochemical Cycles, 8, 65-80, 1994.

Azam, F., & Malfatti, F.: Microbial structuring of marine ecosystems, Nature Reviews
    Microbiology, 5(10), 782-791, 2007.

Bardin, A., Primeau, F., and Lindsay, K.: An offline implicit solver for simulating
    prebomb radiocarbon, Ocean Modelling, 73, 45-58, 2014.

Bjorkman, K. M., and Karl, D. M.: Bioavailability of dissolved organic phosphorus in the

569   euphotic zone at Station ALOHA, North Pacific Subtropical Gyre, Limnology and
570   Oceanography, 48(3), 1049-1057, 2003.

572   Carlson, C. A.: Production and removal processes, in: Biogeochemistry of marine
573   dissolved organic matter, Hansell, D. A. and Carlson, C. A., eds., Academic Press,
574   San Diego, 91-151, 2002.

576   Carlson, C. A., Giovannoni, S. J., Hansell, D. A., Goldberg, S. J., Parsons, R., and
577   Vergin, K.: Interactions between DOC, microbial processes, and community structure
578   in the mesopelagic zone of the northwestern Sargasso Sea, Limnology and
579   Oceanography, 49, 1073-1083, 2004.

581   Carlson, C. A., Morris, R., Parsons, R., Treusch, A. H., Giovannoni, S. J., and Vergin, K.
582   (2008), Seasonal dynamics of SAR11 populations in the euphotic and mesopelagic
583   zones of the northwestern Sargasso Sea, The ISME journal, 3(3), 283-295, 2009.

585   Caron, D. A., Lim, E. L., Sanders, R. W., Dennett, M. R., and Berninger, U. G.:
586   Responses of bacterioplankton and phytoplankton to organic carbon and inorganic
587   nutrient additions in contrasting oceanic ecosystems, Aquatic Microbial Ecology,
588   22(2), 175-184, 2000.

590   Casey, J. R., Lomas, M. W., Michelou, V. K., Dyhrman, S. T., Orchard, E. D.,
591   Ammerman, J. W., and Sylvan, J. B.: Phytoplankton taxon-specific orthophosphate
592   (Pi) and ATP utilization in the western subtropical North Atlantic, Aquatic Microbial
593   Ecology, 58(1), 31, 2009.

595   Cotner, J. B., Ammerman, J. W., Peele, E. R., and Bentzen, E.: Phosphorus-limited
596   bacterioplankton growth in the Sargasso Sea, Aquatic Microbial Ecology, 13(2), 141-
597   149, 1997.

599   Danabasoglu, G., Bates, S. C., Briegleb, B. P., Jayne, S. R., Jochum, M., Large, W. G., ...
600   and Yeager, S. G.: The CCSM4 ocean component, Journal of Climate, 25(5), 1361-
601   1389, 2011.

603   DeLong, E. F., Preston, C. M., Mincer, T., Rich, V., Hallam, S. J., Frigaard, N. U., ... and
604   Karl, D. M.: Community genomics among stratified microbial assemblages in the
605   ocean's interior, Science, 311(5760), 496-503, 2006.

607   Dunne, J. P., John, J. G., Shevliakova, E., Stouffer, R. J., et al.: GFDL's ESM2 global
608   coupled climate-carbon Earth System Models Part II: Carbon system formulation and
609   baseline simulation characteristics, Journal of Climate, 26(7), 2247-2267, 2013.

611   Dyhrman, S. T., and Ruttenberg, K. C.: Presence and regulation of alkaline phosphatase
612   activity in eukaryotic phytoplankton from the coastal ocean: Implications for
613   dissolved organic phosphorus remineralization, Limnology and Oceanography, 51(3),
614   1381-1390, 2006.

615

616 Gent, P. R., Danabasoglu, G., Donner, L. J., Holland, M. M., Hunke, E. C., Jayne, S. R.,
617   ... and Zhang, M.: The community climate system model version 4, Journal of
618   Climate, 24(19), 4973-4991, 2011.
619

620 Giovannoni, S. J., Rappé, M. S., Vergin, K. L., and Adair, N. L.: 16S rRNA genes reveal
621   stratified open ocean bacterioplankton populations related to the green non-sulfur
622   bacteria, Proceedings of the National Academy of Sciences, 93(15), 7979-7984, 1996.
623

624 Goldberg, S. J., Carlson, C. A., Brzezinski, M., Nelson, N. B., and Siegel, D. A.:
625   Systematic removal of neutral sugars within dissolved organic matter across ocean
626   basins, Geophysical Research Letters, 38(17), 2011.
627

628 Hansell, D. A.: Recalcitrant dissolved organic carbon fractions, Annual Review of
629   Marine Science, 5, 421-445, 2013.
630

631 Hansell, D. A., and Carlson, C. A.: Biogeochemistry of total organic carbon and nitrogen
632   in the Sargasso Sea: control by convective overturn, Deep Sea Research Part II, 48(8),
633   1649-1667, 2001.
634

635 Hansell, D. A., Carlson, C. A., Repeta, D. J., and Schlitzer, R.: Dissolved organic matter
636   in the ocean: A controversy stimulates new insights, Oceanography, 22(4), 202-211,
637   2009.
638

639 Hansell, D. A., Carlson, C. A., and Schlitzer, R.: Net removal of major marine dissolved
640   organic carbon fractions in the subsurface ocean, Global Biogeochemical Cycles,
641   26(1), 2012.
642

643 Hopkinson, C. S., and Vallino, J. J.: Efficient export of carbon to the deep ocean through
644   dissolved organic matter, Nature, 433(7022), 142-145, 2005.
645

646 Khatiwala, S., Visbeck, M., and Cane, M. A.: Accelerated simulation of passive tracers in
647   ocean circulation models, Ocean Modelling, 9, 51-69, 2005.
648

649 Kim, J. M., Lee, K., Shin, K., Yang, E. J., Engel, A., Karl, D. M., and Kim, H. C.: Shifts
650   in biogenic carbon flow from particulate to dissolved forms under high carbon
651   dioxide and warm ocean conditions, Geophysical Research Letters, 38(8), 2011.
652

653 Kwon, E. Y., and Primeau, F.: Optimization and sensitivity study of a biogeochemistry
654   model using an implicit solver and in situ phosphate data, Global Biogeochemical
655   Cycles 20(4), 2006.
656

657 Letscher, R. T., and Moore, J. K.: Preferential remineralization of dissolved organic
658   phosphorus and non-Redfield DOM dynamics in the global ocean, submitted to
659   Global Biogeochemical Cycles, 2014.
660

661 Letscher, R. T., Hansell, D. A., Carlson, C. A., Lumpkin, R., and Knapp, A. N.:
662   Dissolved organic nitrogen in the global surface ocean: Distribution and fate, Global
663   Biogeochemical Cycles, 27, 141-153, 2013a.

665 Letscher, R. T., Hansell, D. A., Kadko, D., and Bates, N. R.: Dissolved organic nitrogen
666   dynamics in the Arctic Ocean, Marine Chemistry, 148, 1-9, 2013b.

668 Lomas, M. W., Burke, A. L., Lomas, D. A., Bell, D. W., Shen, C., Dyhrman, S. T., and
669   Ammerman, J. W.: Sargasso Sea phosphorus biogeochemistry: an important role for
670   dissolved organic phosphorus (DOP), Biogeosciences, 7(2), 695-710, 2010.

672 Martiny, A. C., Pham, C. T. A., Primeau, F. W., Vrugt, J. A., Moore, J. K., Levin, S. A.,
673   and Lomas, M. W.: Strong latitudinal patterns in the elemental ratios of marine
674   plankton and organic matter, Nature Geoscience, 6, 279–283, 2013a.

676 Martiny, A. C., Vrugt, J. A., Primeau, F. W., and Lomas, M. W.: Regional variation in
677   the particulate organic carbon to nitrogen ratio in the surface ocean, Global
678   Biogeochemical Cycles, 27, 723– 731, 2013b.

680 Moore, J. K., Doney, S. C., and Lindsay, K.: Upper ocean ecosystem dynamics and iron
681   cycling in a global three-dimensional model, Global Biogeochemical Cycles, 18(4),
682   2004.

684 Moore, J. K., Lindsay, K., Doney, S. C., Long, M. C., and Misumi, K.: Ecosystem
685   Dynamics and biogeochemical cycling in the Community Earth System Model
686   [CESM1(BGC)]: Comparison of the 1990s with the 2090s under the RCP4.5 and
687   RCP8.5 Scenarios, Journal of Climate, 26(23), 9291-9312, 2013.

689 Moore, J. K., Lindsay, K., Letscher, R. T., and Mayorga, E.: Improving ocean
690   biogeochemistry simulation in the Community Earth System Model, submitted to
691   Geoscientific Model Development, 2014.

693 Morris, R. M., Frazar, C. D., and Carlson, C. A.: Basin-scale patterns in the abundance of
694   SAR11 subclades, marine Actinobacteria (OM1), members of the Roseobacter clade
695   and OCS116 in the South Atlantic, Environmental Microbiology, 14(5), 1133-1144,
696   2012.

698 Morris, R. M., Nunn, B. L., Frazar, C., Goodlett, D. R., Ting, Y. S., & Rocap, G.:
699   Comparative metaproteomics reveals ocean-scale shifts in microbial nutrient
700   utilization and energy transduction, The ISME journal, 4(5), 673-685, 2010.

702 Nicholson, D., Dyhrman, S., Chavez, F., and Paytan, A.: Alkaline phosphatase activity in
703   the phytoplankton communities of Monterey Bay and San Francisco Bay, Limnol.
704   Oceanogr, 51(2), 874-883, 2006.

706 Orchard, E. D., Ammerman, J. W., Lomas, M. W., and Dyhrman, S. T.: Dissolved

707   inorganic and organic phosphorus uptake in Trichodesmium and the microbial
708   community: The importance of phosphorus ester in the Sargasso Sea, Limnology and
709   oceanography, 55(3), 1390-1399, 2010.
710
711 Redfield, A. C., Ketchum, B. H., and Richards, F. A.: The influence of organisms on the
712   composition of seawater, in The sea: ideas and observations on progress in the study
713   of the seas, 2, 1963.
714
715 Redfield, A. C.: The biological control of chemical factors in the environment, American
716   Scientist, 46, 205-221, 1958.
717
718 Rivkin, R. B., and Anderson, M. R.: Inorganic nutrient limitation of oceanic
719   bacterioplankton, Limnology and Oceanography, 730-740, 1997.
720
721 Sato, M., Sakuraba, R., and Hashihama, F.: Phosphate monoesterase and diesterase
722   activities in the North and South Pacific Ocean, Biogeosciences, 10(11), 2013.
723
724 Skoog, A., and Benner, R.: Aldoses in various size fractions of marine organic matter:
725   Implications for carbon cycling, Limnology and Oceanography, 42(8), 1803-1813,
726   1997.
727
728 Smith, R. D., Jones, P. W., Briegleb, B., Bryan, F., Danabasoglu, G., Dennis, J., ... and
729   Yeager, S.: The parallel ocean program (POP) reference manual: ocean component of
730   the community climate system model (CCSM), Los Alamos National Laboratory,
731   LAUR-10-01853, 2010.
732
733 Sohm, J. A., and Capone, D. G.: Phosphorus dynamics of the tropical and subtropical
734   north Atlantic: Trichodesmium spp. versus bulk plankton, Marine Ecology Progress
735   Series, 317, 21, 2006.
736
737 Treusch, A. H., Vergin, K. L., Finlay, L. A., Donatz, M. G., Burton, R. M., Carlson, C.
738   A., and Giovannoni, S. J.: Seasonality and vertical structure of microbial communities
739   in an ocean gyre, The ISME journal, 3(10), 1148-1163, 2009.
740
741 Vichi, M., Pinardi, N., and Masina, S.: A generalized model of pelagic biogeochemistry
742   for the global ocean ecosystem, Part I: Theory, J. Marine Systems, 64, 89-109, 2007.
743
744 Wohlers, J., Engel, A., Zöllner, E., Breithaupt, P., Jürgens, K., Hoppe, H. G., ... and
745   Riebesell, U.: Changes in biogenic carbon flow in response to sea surface warming,
746   Proceedings of the National Academy of Sciences, 106(17), 7067-7072, 2009.
747