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Global Evaluation of Particulate Organic Carbon Flux Parameterizations and Implications for Atmospheric pCO$_2$

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Key points:
- Three parameterizations for particulate organic carbon (POC) export are compared to global data.
- POC fluxes estimated from the Martin curve and the ballast hypothesis capture observations equally well at all depths.
- Globally, data constrain Martin's b to a range from 0.70 to 0.98. This range could modify atmospheric pCO$_2$ by only tens of ppm.

33 **Abstract**

34 The shunt of photosynthetically derived particulate organic carbon (POC) from the

35 euphotic zone and remineralization at depth comprises the basic mechanism of the

36 "biological carbon pump." POC raining through the "twilight zone" (euphotic depth

37 to 1km) and "midnight zone" (1 km to 4 km) is remineralized back to inorganic form

38 through respiration by heterotrophs and bacteria. Accurately modeling POC flux is

39 critical for understanding the "biological pump" and its impacts on air-sea CO_2

40 exchange and, ultimately, long-term ocean carbon sequestration. Yet, the

41 parameterizations of POC flux commonly used in simulations have not been tested

42 quantitatively against global datasets using the same modeling framework. Here, we

43 use a single one-dimensional physical-biogeochemical modeling framework to assess

44 the skill of three common POC flux parameterizations in capturing POC flux

45 observations from moored sediment traps and thorium-234 depletion. The

46 exponential decay, Martin curve, and ballast model are compared to data from 11

47 biogeochemical provinces distributed across the globe. In each province, the model

48 captures satellite-based estimates of surface primary production within uncertainties.

49 Goodness-of-fit is measured by how well the simulation captures the observations,

50 quantified by bias and the root-mean-squared-error and displayed using "target

51 diagrams." Comparisons are presented separately for the twilight zone and midnight

52 zone. We find the parameterization based on the ballast hypothesis shows no

53 improvement over a globally or regionally parameterized Martin curve. For all

54 provinces taken together, Martin's *b* that best fits the data is [0.70, 0.98]; this finding

55 reduces by at least a factor of 3 previous estimates of potential impacts on

56 atmospheric pCO_2 of uncertainty in POC export to a more modest range [-16 ppm,

57 +12 ppm].

2

58

1. Introduction

The biologically-mediated removal of organic carbon from surface waters against a dissolved inorganic carbon (DIC) gradient and its subsequent remineralization at depth is termed the "biological pump" [*Broecker and Peng,* 1982; *De La Rocha,* 2006], which can be separated into a "carbonate pump" and a "soft-tissue pump" [*Volk and Hoffert,* 1985] as well as a "microbial pump" [*Jiao et al.,* 2010]. The percentage of net primary production (NPP) exported from the euphotic zone as particulate organic carbon (POC) is at least 5%, with some estimates higher than 40% [*Martin et al.,* 1987; *Buesseler,* 1998; *Schlitzer,* 2000*; Boyd and Trull,* 2007; *Buesseler and Boyd,* 2009; *Henson et al.,* 2011]. Much of this material is respired, primarily by bacteria and zooplankton, within the "twilight zone" (euphotic depth to 1000 m) [*Steinberg et al.,* 2008]; only ~3% of exported NPP reaches the 1000 m depth horizon [*De La Rocha and Passow,* 2007]. On timescales of days to weeks the flux of POC is controlled by sinking speed and degradation rate. If in steady state, POC flux should be balanced by the input of limiting nutrients to the euphotic zone [*Passow and Carlson,* 2012; *Giering et al.,* 2017].

POC flux to depth is the hallmark of the biological pump, and is critical to setting surface ocean pCO_2 [*Parekh et al.,* 2006; *Kwon et al.,* 2009; *Kwon et al.,* 2011; *DeVries et al.,* 2012]. The pCO_2 gradient across the air-sea interface determines the direction of carbon flux across the surface. By converting DIC to organic carbon, biological activity reduces surface ocean pCO_2 and promotes CO_2 uptake by the ocean. The downward POC flux then sequesters carbon at depth. Changes in the efficiency of the biological pump, measured as the ratio of exported POC to primary

3

83   production has the potential to alter ocean carbon storage and atmospheric CO_2

84   [*Marinov et al.,* 2008a, 2008b; *Kwon et al.*, 2009; *Henson et al.* 2011]. *Parekh et al.*

85   [2006] estimate the atmospheric pCO_2 would be 150-200 μatm greater than the

86   current value if not for the biological control on the vertical DIC gradient. *Kwon et*

87   *al.* [2011] separate the sensitivity of atmospheric CO_2 to changes in the carbonate

88   pump versus the soft-tissue pump. They find that for a globally-averaged respired

89   carbon increase of 10 μmol kg^{-1}, the carbonate pump increases atmospheric CO_2 by

90   about 3.4% while the soft-tissue pump decreases atmospheric CO_2 by 5.3%, thus there

91   is a net 2% reduction in atmospheric CO_2 when both pumps are accounted for.

92

93   Projections using earth system models show a sizeable uncertainty across various

94   models with respect to the biological pump's response to 21st century climate change

95   [*Bopp et al.,* 2013; *Laufkötter et al.,* 2015; *Hauck et al.,* 2015; *Krumhardt et al.* 2016].

96   Accurate estimation the sensitivity of the biological pump to future climate change is

97   critical to economic evaluations of the impacts of climate change on ecosystem

98   services [*Barange et al.,* 2017]. Parameterizations used in earth system models would

99   ideally capture both the mean POC attenuation and the variability found in available

100   observations, and do so in a mechanistically-realistic manner, in order to reliably

101   predict future change in the strength and efficiency of the biological pump.

102

103   Early parameterizations of POC flux relate export either at a reference depth [*Martin*

104   *et al.,* 1987] or the euphotic zone primary production [*Suess,* 1980; *Betzer et al.,*

105   1984; *Pace et al.,* 1987] to the vertical POC flux through an empirically-derived

106   relationship. Although these parameterizations lack mechanistic realism, the *Martin*

107   *et al.* [1987] power law parameterization, in some cases with adjustment to different

108   ocean regions [*Henson et al.* 2012; *Guidi et al.* 2015], has been used widely to predict

109   carbon flux >2000m [*François et al.,* 2002; *Honjo et al.,* 2008]. Alternative to a

110   power law parameterization, an exponential curve has been used to describe

111   attenuation through an empirical fit to observations [*Lutz et al.,* 2002; *Boyd and Trull,*

112   2007; *Marsay et al.,* 2015]. Parameterizations assuming first-order kinetics and a

113   constant sinking speed have been used in biogeochemical models [*Walsh et al.,* 1988;

114   *Banse,* 1990; *Dutkiewicz et al.,* 2005; *DeVries and Weber*, 2017], which implies an

115   exponential decay of POC. More mechanistic parameterizations, such as those based

116   on the "ballast hypothesis" [*Armstrong et al.,* 2002] assume minerals associated with

117   POC increase the POC flux at depth, have been proposed.

118

119   To directly compare the various choices available for POC parameterization, a global

120   dataset with consistent treatment and a consistent model framework is required. The

121   choice of seasonal normalization in datasets [*Lutz et al.,* 2002; *Lutz et al.,* 2007;

122   *Honjo et al.,* 2008] can impact statistical fits, and simulated POC fluxes are dependent

123   both on the POC flux parameterization, and also on the simulated surface ocean

124   productivity. In a previous model-data comparison, *Howard et al.* [2006] used a three-

125   dimensional ocean model in which surface NPP responds to the POC

126   parameterization. They find that the ballast model captures observations more

127   accurately than the Martin curve, and that the geochemical distribution in the deep

128   ocean is sensitive to the parameterization used. However, there has not yet been a

129   comparison across all three common parameterizations in which the modeling

130   framework is identical, including identical surface NPP and POC production to drive

131   the vertical fluxes estimated by each parameterization.

132

133   In this study, we compare three common POC flux parameterizations using a single

134   one-dimensional numerical modeling framework in which NPP is not responsive to

135   the parameterization used; i.e. each parameterization is driven by the same surface

136   POC source. This model is applied in 11 *Longhurst* [2006] provinces for which

137   adequate POC flux data are available (Figure 1). We quantitatively evaluate, using a

138   suite of statistical tests, the exponential decay model, Martin curve, and the ballast

139   hypothesis against the recently released global POC flux dataset [*Mouw et al.,* 2016a]

140   that consists of POC flux observations from sediment traps supplemented with

141   thorium-234 depletion observations (2% of the data) spanning years 1976 to 2012.

142

143   **2. Methodology**

144   **2.1 Model Description**

145   The Massachusetts Institute of Technology general circulation model (MITgcm)

146   [*Marshall et al.,* 1997a, 1997b] is configured as a one-dimensional column with 77

147   vertical layers. Depths increase from a resolution of 10m in the surface to 650m in

148   the deepest layer. K-profile parameterization (KPP) simulates vertical mixing [*Large*

149   *et al.,* 1994]. The model uses a nutrient-restoring scheme with a relaxation time scale

150   of 30 days to approximate advection and diffusive processes that are not directly

151   simulated. Nutrients are restored towards the climatology appropriate for each

152   province in the euphotic zone when the simulated nutrient concentration falls below

153   the climatological value, while nutrients below the euphotic zone are constantly

154   restored towards climatology. Sediments are not included in the model, and thus

155   detritus slowly accumulates in the bottom grid cell; the bottom grid cell is ignored in

156   analyses.

157

158 The model is initialized with physical and biogeochemical observations and forced at

159 the surface with monthly climatological meteorological and radiative fields

160 appropriate for each province. Temperature, salinity, and nutrients are prescribed by

161 World Ocean Atlas 2013 [*Boyer et al., 2013*]. Alkalinity and DIC are prescribed

162 using GLobal Ocean Data Analysis Project (GLODAP) atlas [*Key et al., 2004*].

163 Photosynthetically active radiation (PAR) is prescribed using Sea-viewing WIde

164 Field-of-view Sensor (SeaWIFS) data [*Frouin et al., 2002*]. Surface dust deposition

165 is provided by *Mahowald et al.* [2005]. Surface wind stress is prescribed using

166 National Center for Environmental Prediction (NCEP) reanalysis 1 [*Kalnay et al.,*

167 *1996*].

168

169 The ecosystem model embedded in MITgcm is that of *Dutkiewicz et al.* [2005]. The

170 model includes two phytoplankton functional groups (diatoms and small

171 phytoplankton) and one zooplankton class. Phytoplankton growth can be light and

172 nutrient limited. Mortality rate and maximum growth rates of diatoms and small

173 phytoplankton are tuned for each province (supplementary Table S1) to best fit

174 satellite-based estimates of primary productivity (Table 1). The remineralization rate

175 (k) is set to 1/10 d^{-1} for POC and 1/150 d^{-1} for biogenic silica (opal). The dissolution

176 rate for particulate inorganic carbon (PIC) is 1/300 d^{-1}. The sinking speed (w) for

177 POC, PIC, and opal are fixed constants: POC and opal sink at a rate of 10 m d^{-1} while

178 PIC sinks at 15 m d^{-1}. These POC sinking speeds lie within the range of other

179 models, 2.5 m d^{-1} [*Yool et al., 2010*], 8 m d^{-1} [*Dutkiewicz et al., 2005*], 11-85 m d^{-1}

180 [*DeVries and Weber., 2017*]. The POC remineralization rate and sinking speed used

181 here imply a remineralization length scale ($\lambda = wk^{-1}$) of 100 m, similar to the *Lima*

182 *et al.* [2014] value of 130 m and within the range assumed by *Moore et al.* [2004].

183   This remineralization length scale is within the 50-200 m range that *Mouw et al.*

184   [2016b] found for most provinces, and the 69-265m range derived from the

185   optimization of *DeVries and Weber* [2016].

186

187   The model assumes 7% of phytoplankton are calcifiers, and therefore produce PIC.

188   Production of POC, PIC, and opal are due to mortality of phytoplankton and

189   zooplankton, as well zooplankton grazing on phytoplankton. The tendency of POC,

190   PIC, and opal production are shown below:

191
$$\frac{d[X^{prod}(z)]}{dt} = P_X^{prod}(z) + Z_X^{prod}(z) \quad (1)$$

192   where X=POC, PIC, or opal. $P_X^{prod}(z)$ represents production of X (mgX m^{-2} d^{-1}) at

193   depth (z, m) by phytoplankton (P) and $Z_X^{prod}(z)$ represents production of X (mgX m^{-2}

194   d^{-1}) at depth (z, m) by zooplankton (Z).

195

196   A 10-year simulation is run after a 10-year model spin up. The model uses a time

197   step of 200 seconds with an 8-day averaging period. This averaging period is chosen

198   to coincide with the time step of the vertically integrated production model (VGPM)

199   [*Behrenfeld and Falkowski,* 1997] which is used for comparison to modeled NPP.

200   VGPM satellite-based NPP estimates are obtained from

201   http://www.science.oregonstate.edu/ocean.productivity/ and the modeled NPP is

202   calculated as the integrated productivity in the euphotic zone.

203

204   **2.3 Exponential Decay Model**

205   The exponential decay model assumes that all the POC is labile with a constant

206   sinking speed, expressed in equation (2) [*Banse,* 1990].

207
$$F(z) = w_{poc}[POC(z)] \quad (2)$$

208   where $F(z)$ is the POC flux (mgC m^{-2} d^{-1}) at depth (z, m), w_{poc} is the sinking speed

209   of labile POC (m d^{-1}), and $[POC(z)]$ is the volume concentration of labile POC (mgC

210   m^{-3}) at depth. The tendency of POC to sink and remineralize is expressed in the

211   following form:

212
$$\frac{d[POC(z)]}{dt} = w_{poc}\frac{d[POC(z)]}{dz} - k_{poc}[POC(z)] \quad (3)$$

213   where the first term represents vertically sinking POC while the second term

214   represents a first-order remineralization scheme where POC is instantly remineralized

215   at each depth level (z) with k_{poc} being the remineralization rate. An expression for

216   the flux of labile POC is derived by applying equation (2) to a steady state version of

217   equation (3): $F(z) = F(z_o)EXP[(z - z_o)/\lambda]$, where $F(z_o)$ is the flux at reference

218   depth z_o and $\lambda = \frac{w_{poc}}{k_{poc}}$ is the remineralization length scale (e-folding length scale).

219   Table 2 provides definitions of all equation parameters.

220

221   The ecosystem model of *Dutkiewicz et al.* [2005] treats particulate organic matter as

222   exponentially decaying throughout the water column and assumes all POC is labile.

223   The full tendency of POC is defined in equation (4):

224
$$\frac{d[POC(z)]}{dt} = \frac{d[POC^{prod}(z)]}{dt} + w_{poc}\frac{d[POC(z)]}{dz} - f_T k_{poc}[POC(z)] \quad (4)$$

225   where the first term is the tendency of POC production (equation (1)) and the last two

226   terms represent sinking and remineralization (equation (3)). Temperature dependence

227   on remineralization rate is taken into account through an Arrhenius function: $f_T = A *$

228   $EXP[T_{AE}(T^{-1} - T_{ref}^{-1})]$, where A, T_{AE}, and T_{ref} are constants and T is the local

229   temperature (supplementary Table S2). POC flux at each level is calculated using

230   equation (2). This framework will be termed the "exponential decay model" for POC

231   flux.

232

233   **2.4 Martin Curve**

234   Using data obtained from free-floating sediment traps, *Martin et al.* [1987] describe

235   POC flux attenuation using a normalized power function of the following form,

236   commonly referred to as the "Martin curve":

237 $$F(z) = F(100) \left(\frac{z}{100} \right)^{-b} \quad (5)$$

238   where $F(100)$ is the POC flux at 100m and b is the flux attenuation coefficient. The

239   Martin curve is equivalent to a decreasing remineralization rate with depth or an

240   increasing sinking speed with depth [*Lam et al.,* 2011]. *Villa-Alfageme et al.* [2016]

241   observed an increase in sinking speed with depth, possibly due to the gradual loss of

242   slow-sinking particles with depth. Small values of b imply a higher transfer

243   efficiency where more carbon remineralizes at deeper depths. Transfer efficiency is

244   defined as the fraction of exported organic matter that reaches a given depth below

245   the depth of export, with 100 m below the depth of export being where transfer

246   efficiency is typically estimated [*Buesseler and Boyd,* 2009]. Transfer efficiency and

247   b are inversely related: large values of b imply a small transfer efficiency with more

248   carbon remineralizing at shallower depths. *Martin et al.* [1987] calculated a global b

249   value of 0.858 using observations from nine locations in the Northeast Pacific.

250   Regional variations in the b parameter have been found to improve the statistical fits

251   at the scale of ocean provinces [*Henson et al.,* 2012; *Guidi et al.,* 2015] and across

252   ocean basins [*Berelson,* 2001; *Schlitzer,* 2002], implying regional variability in the

253   flux attenuation and transfer efficiency. *Marsay et al.* [2015] showed the b parameter,

254   and hence the flux attenuation, correlates with temperature. This pattern is plausibly

255 explained by a slowdown of microbial utilization of carbon as temperature decreases

256 [*Pomeroy and Diebel,* 1986; *Pomeroy et al.,* 1991]. Changes in *b*, when applied

257 globally in a biogeochemical model, have been shown to significantly impact

258 atmospheric CO_2 concentrations [*Kwon et al.,* 2009].

259

260 In this study, POC fluxes at depth based on the Martin curve are calculated offline

261 from surface production in MITgcm. In keeping with the original intent of the Martin

262 curve, we use equation (5) to calculate the flux at each depth level (z) using an export

263 depth of 100 m and export flux, $F(z_{100})$, from the exponential decay model runs.

264 Due to nutrient restoring below the euphotic zone, feedback of shallow

265 remineralization on surface production is negligible; thus, this approach is robust.

266 Runs with both the *Martin et al.* [1987] global *b* value of 0.858 as well as the *Guidi et*

267 *al.* [2015] and *Henson et al.* [2012] regional *b* values are performed for comparison.

268

269 **2.5 Ballast Hypothesis**

270 The ballast hypothesis proposed by *Armstrong et al.* [2002] asserts that "ballast"

271 minerals (PIC, opal, and dust), qualitatively associated with POC, increase the deep

272 ocean POC flux. Using observations from the equatorial Pacific, *Armstrong et al.*

273 [2002] observed that the ratio of organic carbon flux to total mass flux was nearly

274 constant below 1800 m and concluded ballast minerals are intimately related to the

275 POC flux. Mechanistically, the role of ballast minerals is not entirely clear. It has

276 been proposed that they act to increase the sinking speed and/or protect POC from

277 microbial respiration and zooplankton grazing. Thus, POC that is associated with

278 ballast minerals induces a higher transfer efficiency, delivering more POC to depth.

279 The ballast hypothesis asserts that sinking POC is a composed of "free" and ballast

280   mineral associated fractions (supplementary Figure S1). The free fraction has a

281   remineralization length scale as labile POC while POC qualitatively associated with

282   ballast minerals is partitioned between a "soft" and "hard" subclass, which represent

283   external and internal protection mechanisms, respectively [*Armstrong et al.,* 2002].

284   External protection constitutes physical removal from hydrolyzing enzymes by

285   adsorption of POC into mineral micropores and increasing sinking speed [*Mayer,*

286   1994]; POC associated with the soft fraction has the same remineralization profile as

287   its associated ballast mineral. Internal protection occurs when POC is encased in PIC

288   or opal, sheltering it from degradation until the mineral has dissolved [*Armstrong et*

289   *al.,* 2002; and references therein]. For this reason, the hard fraction has a very deep

290   remineralization length scale, representing refractory POC. However, *Iversen and*

291   *Robert* [2015] concluded that ballast minerals act only to increase sinking speed and

292   do not provide any protection to organic matter.

293

294   *Klaas and Archer* [2002] used a global dataset of sediment trap observations in the

295   midnight zone to distinguish three forms of ballast with the following carrying

296   capacities (grams of organic carbon per gram of ballast): PIC (0.094), opal (0.025),

297   and dust (0.035). Additionally, *Klaas and Archer* [2002] observed 80% of the POC

298   flux to the seafloor was associated with PIC, suggesting it is a more efficient ballast

299   mineral compared to opal and dust. There are three reasons why the carrying capacity

300   of PIC has been suggested to be greater than that of opal and lithogenic dust:

301   1. PIC sinks ~50% faster than opal for an equivalent particle radius [*Sarmiento*

302   *and Gruber,* 2006], since the density of PIC (2.71 g cm^{-3}) is ~30% greater than

303   the density of opal (2.1 g cm^{-3}) [*Klaas and Archer,* 2002].

304   2. Opal production and export is not as spatially uniform as PIC production and

305   export [*Sarmiento and Gruber,* 2006]. The ratio of opal flux to carbon flux

306   also varies regionally [*Ragueneau et al.,* 2000 Figure 5].

307   3. Lithogenic fluxes are generally too small to significantly impact the transfer

308   efficiency of organic carbon [*François et al.,* 2002].

309 However, some studies find evidence that does not support PIC having a higher

310 carrying capacity compared to opal or dust [*De La Rocha et al.,* 2008] or show

311 regional variability in the carrying capacity of each ballast mineral [*Wilson et al.,*

312 2012; *Pabortsava et al.,* 2017].

313

314 Published parameterizations for the ballast hypothesis have important differences:

315 *Moore et al.* [2004] and *Armstrong et al.* [2002] include PIC, opal, and lithogenic

316 material (dust) as ballast minerals while *Yool et al.* [2010] and *Dunne et al.* [2013]

317 omit ballasting from dust. The reader is referred to *Moore et al.* [2004] and *Lima et*

318 *al.* [2014] for a detailed description of the implementation of the ballast hypothesis in

319 a three-dimensional ocean model with dust.

320

321 For this study, the ecosystem model of *Dutkiewicz et al.* [2005] is augmented to

322 include ballasting from PIC, opal, and dust in a manner similar to that of *Moore et al.*

323 [2004] and *Lima et al*. [2014]. The implementation of the ballast hypothesis is based

324 on *Armstrong et al.* [2002] and assumes a portion of the POC production is associated

325 with PIC and opal production and surface dust deposition. Flux of POC is calculated

326 by multiplying the sinking speed by the concentration of POC associated with each

327 mineral (equation (6)):

328 $$F(z) = w_{poc}[POC(z)] + w_{pic}[POC_{PIC}(z)] + w_{opal}[POC_{opal}(z)]$$

329 $$+ w_{dust}[POC_{dust}(z)] \quad (6)$$

330 where w_X is the sinking speed of X=POC, PIC, opal, or dust, $[POC_Y(z)]$ is the

331 concentration of POC associated with Y=PIC, opal, or dust, and $[POC(z)]$ is the

332 concentration of free or labile POC. The tendency of POC associated with ballast

333 mineral Y is separated into a hard and soft subclass (equation (7)):

334 $$\frac{d[POC_Y(z)]}{dt} = \frac{d[POC_Y^{soft}(z)]}{dt} + \frac{d[POC_Y^{hard}(z)]}{dt} \quad (7)$$

335 POC in the soft subclass decays exponentially with a remineralization rate as its

336 associated ballast mineral while POC in the hard subclass decays exponentially with a

337 very long remineralization rate; POC in each subclass has the same sinking speed as

338 its associated ballast mineral. Each term in $\frac{d[POC_{PIC}(z)]}{dt}$ is defined in Table 3 and each

339 term in $\frac{d[POC_{opal}(z)]}{dt}$ is defined in Table 4. The source of dust in the model is from

340 surface deposition ($dust^{dep}$, mgDust m^{-2} d^{-1}). POC associated with dust solely

341 occurs in the surface grid cell ($\Delta z_{surf}, m$) and is separated into a hard and soft

342 subclass which decay exponentially. Each term in the tendency equation for POC

343 associated with dust $\left(\frac{d[POC_{dust}(z)]}{dt}\right)$ is defined in Table 5. The tendency of free POC

344 production is calculated by subtracting ballast associated POC from the total POC

345 production: $\frac{d\left[POC_{free}^{prod}(z)\right]}{dt} = \frac{d[POC^{prod}(z)]}{dt} - \left[\omega_{PIC}\left(\frac{d[PIC^{prod}(z)]}{dt}\right) + \right.$

346 $\omega_{opal}\left(\frac{d[opal^{prod}(z)]}{dt}\right) + \omega_{dust}\left(\frac{dust^{dep}}{\Delta z_{surf}}\right)\right]$, where $\frac{d[X^{prod}(z)]}{dt}$ is the production of

347 X=PIC or opal by phytoplankton and zooplankton (equation (1)) and ω_Y is the POC

348 carrying capacity for Y=PIC, opal, or dust. Each term in the tendency equation for

349 free POC $\left(\frac{d[POC(z)]}{dt}\right)$ is defined in Table 6.

350

2.6 Analysis

An 8-day climatology of POC flux within each province is created using the *Mouw et al.* [2016a] data compilation of *in situ* sediment trap and thorium-234 based measurements. PIC and opal fluxes are not analyzed due to insufficient spatial and temporal resolution in the field data. Dates are converted to day of year and aligned in time using the midpoint of the deployment. POC flux observations within each biogeochemical province as defined by *Longhurst* [2006] (provided by *VLIZ* [2009]) are aggregated and grouped by depth and day of year into 8-day segments. Observations are then aggregated to the model vertical grid in order to quantitatively compare to model output. In order to be considered in our comparison, observations must be available at depths greater than 1000 m and the model must capture the surface ocean production in a manner consistent with satellite retrievals. Coastal provinces are omitted.

Model performance is assessed by investigating the model-data misfit, defined as $\Delta(i) = \log[M(i)] - \log[O(i)]$ where $M(i)$ and $O(i)$ represent the ith model prediction and i[th] observed value respectively. Each observation is log base 10 transformed to alleviate skewedness from large values. The water column is partitioned into the twilight zone (100-1000m) and midnight zone (1000-4000m), with each analyzed separately. For consideration of variability, the full range of variability for the model and observations across each zone is compared. A set of six summary statistics are used as univariate measures of model performance [*Stow et al.*, 2009]:

374   1. Correlation: $r = \dfrac{\sum_{i=1}^{N}\{\log[M(i)] - \overline{\log[M(i)]}\}\,\{\log[O(i)] - \overline{\log[O(i)]}\}}{\left\{\sum_{i=1}^{N}[M(i) - \bar{M}]^2 \; \sum_{i=1}^{N}[O(i) - \bar{O}]^2\right\}^{\frac{1}{2}}}$

375   2. Root Mean Squared Difference: $RMSD = \left[\dfrac{1}{N}\sum_{i=1}^{N}\Delta(i)^2\right]^{\frac{1}{2}}$

376   3. Bias: $B = \overline{\log[\mathrm{M}(\imath)]} - \overline{\log[\mathrm{O}(\imath)]}$

377   4. Average Absolute Error: $AAE = \dfrac{\sum_{i=1}^{N}|\log[\mathrm{M}(i)] - \log[\mathrm{O}(i)]|}{N}$

378   5. Model Efficiency: $ME = 1 - \dfrac{\sum_{i=1}^{N}\{\log[\mathrm{M}(i)] - \log[\mathrm{O}(i)]\}^2}{\sum_{i=1}^{N}\{\log[\mathrm{O}(i)] - \overline{\log[\mathrm{O}(\imath)]}\}^2} = 1 - \left(\dfrac{RMSD}{s_O}\right)^2$

379   6. Reliability index: $RI = 10^{RMSD}$

380 The correlation (r) is a measure between -1 and 1 quantifying the degree to which the

381 simulation and observations linearly vary. The correlation only expresses how well

382 the simulation and observations vary together and does not account for systematic

383 biases; a correlation of 1 does not preclude a mean offset between the simulation and

384 observations. Additionally, this value is related to the coefficient of determination

385 (r^2), which expresses the variance explained by a linear regression.

386

387 Root mean squared difference (RMSD), bias (B), and average absolute error (AAE)

388 are all measures of the discrepancy between the simulated and observed mean.

389 Values near zero imply "good" model performance and large values imply "poor"

390 model performance using these metrics. The modeling efficiency (ME) can be used

391 as a transition value between good and poor model performance [*Nash and Sutcliffe,*

392 1970]. A skillful model by this metric has an ME value near one. Modeling

393 efficiency is related to RMSD: $ME = 1 - \left(\dfrac{RMSD}{s_O}\right)^2$, where s_O is the observed

394 variance. The reliability index (RI) quantifies the average factor by which the model

395 differs from observations. For example, an RI of 2 implies the model predictions

396 need to be multiplied by 2 in order to reconstruct the observations.

397

398   Model performance is visualized using normalized "target diagrams" [*Jolliff et al.,*

399   *2009*]. Target diagrams visualize bias and variability together (Figure 2a), giving

400   them an advantage over the commonly used "Taylor diagram" [*Taylor,* 2001], which

401   summarizes only the variability. Normalized target diagrams are based on the

402   following quadratic relationship:

403
$$\left(\frac{RMSD}{s_O}\right)^2 = \left(\frac{B}{s_O}\right)^2 + \left(\frac{uRMSD}{s_O}\right)^2 \quad (8)$$

404   where $uRMSD = \frac{1}{N}\sum_{i=1}^{N}[\Delta(i) - B]^2$ is the unbiased RMSD (or variance of the

405   model-data misfit), which measures the degree to which the model captures the

406   observed variance, bias (B) is a measure of how well the simulated mean captures the

407   observed mean, and s_O is the observed variance. Target diagrams provide a novel

408   way of visualizing B and uRMSD on a single plot: bias (B) on the y-axis and

409   unbiased RMSD (uRMSD) on the x-axis. The radial distance, $\left(\frac{RMSD}{s_O}\right)^2$, is related to

410   the modeling efficiency (ME): $\left(\frac{RMSD}{s_O}\right)^2 = 1 - ME$. ME is negative when the radial

411   distance is greater than one and modeling efficiency is positive when the radial

412   distance is less than one. Therefore, ME is visualized by plotting a circle with a

413   radius of one on a normalized target diagram; skillful models are within the circle.

414   Under- or over-estimation of the variability is quantified by multiplying uRMSD by

415   the sign of the observed variance (s_O) subtracted from the modeled variance (s_M).

416   Equation (9) shows the relationship used to construct target diagrams presented in this

417   manuscript, which is equivalent to equation (8):

418
$$(1 - ME) = B^{*2} + uRMSD^{*2} \quad (9)$$

419 where $B^* = \frac{B}{s_O}$ and $uRMSD^* = \frac{uRMSD}{s_O} sign(s_M - s_O)$. Normalized target diagrams

420 allow the display of multiple models on a single plot. They also visualize how well

421 each model captures the observed mean and variance along with the modeling

422 efficiency (ME). Target diagrams have previously been used to assess satellite

423 derived NPP estimates [*Friedrichs et al.,* 2009; *Saba et al.,* 2010; *Saba et al.,* 2011;

424 *Lee et al.,* 2015], surface chlorophyll [*Hofmann,* 2008; *Lazzari et al.,* 2012], and

425 physical variables such as temperature and salinity [*Hofmann,* 2008; *Pairaud et al.,*

426 2011].

427

428 The final component of our analysis is to determine the range of Martin's *b* that is

429 globally consistent with POC flux observations; and then to use this range to constrain

430 previous estimates of the potential sensitivity of atmospheric pCO_2 to uncertainty in

431 the biological pump [*Kwon et al.* 2009]. The normalized bias (B^*), the vertical axis in

432 normalized target diagrams, is our metric for best fit. As discussed in detail in section

433 3, the three parameterizations are better able to capture the observed mean POC flux

434 rather than POC flux variability, motivating the choice of B^* as a metric. For this

435 analysis, the model is run for each province with a range of *b* values from 0.40 to 1.40

436 (with increments of 0.01), the range of *b* from *Kwon et al.* [2009]. B^* is calculated

437 using observations only in the midnight zone, and in both the midnight and twilight

438 zones. A particular value of *b* "accurately" captures the observed mean if the B^* for

439 that model is within the range [-1,1] (supplementary Figure S2). The best-fit global *b*

440 range is taken as the interquartile range of all province-specific *b* values.

441 Atmospheric pCO_2 as a function of *b* is taken from the global 3-D biogeochemical

442 modeling study of *Kwon et al.* [2009]. In their most realistic model formulation

443 ("nutrient restoring", Supplementary Text T1), biological productivity changed in

18

444 response to export change and a constant rain ratio (PIC/POC) of 0.08 was used. For

445 our analysis, their results are digitized and interpolated with a cubic spline [*Kwon et*

446 *al.,* 2009, their Figure 3c]. The change in atmospheric pCO_2 (referenced to pCO_2

447 with b=0.858) is then inferred from this curve for the range of b values that we find to

448 best fit POC flux observations.

449

450 **3. Results**

451 Four biogeochemical provinces out of eleven are selected to be presented in the main

452 text since they span a range of latitudes (Figure 1). Simulated POC fluxes for each

453 parameterization in the selected provinces are shown alongside observations in Figure

454 3; all provinces are presented in supplementary Figures S3-S16, and considered in the

455 discussion and conclusions. Two provinces, Eastern Pacific subarctic gyres (PSAE)

456 and North Atlantic drift (NADR), were selected for focus because of their expected

457 collocation with the study regions for the Exports Processes in the Ocean from

458 RemoTe Sensing (EXPORTS) field campaign that is presently being planned [*Siegel*

459 *et al.,* 2016]. These sites also cover a range of ecosystem states. The simulated mean

460 annual primary production in each province captures the climatological range of mean

461 annual primary production, calculated using VGPM (Table 1). Although the model

462 does not fully capture the observed seasonality across some provinces (supplementary

463 Figure S17), it does capture the annual primary production, indicating the model is a

464 useful tool to study mean annual export, as done here.

465

466 3.1 **Twilight Zone**

467 For each province, the Martin curve, exponential model, and ballast hypothesis have

468 similar reliability indexes in the twilight zone (Figure 4), illustrating that these

469 parameterizations capture observations equally well within the twilight zone. This

470 corroborates *Buesseler and Boyd* [2009], who show that the Martin curve and

471 exponential model capture observations at shallow depths. The exponential decay

472 model has a tendency to underestimate the flux deep in the twilight zone in some

473 provinces such as the Pacific Equatorial Divergence (PEQD) (Figure 3). The

474 exponential model assumes a constant sinking speed and remineralization rate (i.e.

475 constant remineralization length scale) throughout the water column, which often

476 results in fluxes that decrease too quickly with depth [*Armstrong et al.,* 2002; *Lutz et*

477 *al.,* 2002]. The amount of variability in the modeled flux varies between provinces,

478 much due to variability in primary production.

479

480 The interquartile ranges for the three parameterizations overlap for each of the

481 univariate statistics (Figure 5), quantitatively supporting that these parameterizations

482 are equally good at capturing observations in the twilight zone. However, the

483 parameterizations tend to underestimate the observed variability in the twilight zone,

484 evident through negative uRMSD* values (Figure 6). Depending on the location, the

485 models either show a slight positive or negative bias (Figure 5, Figure 6). Overall, all

486 the models perform well in the twilight zone and are more skillful than simply setting

487 the POC flux to be the observed average (Figure 6).

488

489 3.2 **Midnight Zone**

490 The Martin curve and ballast hypothesis each capture observations well in the

491 midnight zone, while the exponential model underestimates the observed flux at these

492 depths (Figure 3; Figure 4). The exponential model underestimates the flux at depth

493 since a constant remineralization length scale does not allow for slowdown of

20

494   remineralization with depth or increasing sinking speed with depth. The global

495   Martin curve slightly underestimates the observed flux in some provinces, such as

496   PEQD (Figure 3), resulting from either too low POC fluxes out of the euphotic zone

497   or the use of a *b* parameter that is too large.

498

499   In the midnight zone, the interquartile range for summary statistics overlap for both

500   the Martin curve and ballast hypothesis (Figure 5); however, not for the exponential

501   model. Each summary statistic suggests the exponential model performs poorly in the

502   midnight zone compared to the Martin curve and ballast hypothesis:

503   1. Correlation interquartile range nearly symmetric about zero.

504   2. Large RMSD, AAE compared to Martin curve and ballast hypothesis.

505   3. Large negative bias compared to Martin curve and ballast hypothesis.

506   4. Large negative ME, suggesting poor model performance.

507   The exponential model for the midnight zone generally lies far from the origin in the

508   fourth quadrant in the target diagram (Figure 6), consistent with its underestimate of

509   the observed mean and overestimate of variability. However, if only one depth level

510   is resolved in the midnight zone then the normalized target diagram suggests the

511   exponential model reasonably captures the variability while underestimating the mean

512   (e.g. PSAE). For all provinces, the Martin curve and ballast hypothesis both have a

513   radial distance near unity on the normalized target diagram (Figure 6), suggesting

514   these models are equally skillful.

515

516   3.3 **Regional Attenuation Parameter**

517   Regional Martin curves, using attenuation parameters from *Henson et al.* [2012] and

518   *Guidi et al.* [2015], qualitatively agree with each other and with the global *b* estimates

21

519   (Figure 7, Figure 8). Regional *b* parameters can lead to an improved fit in the

520   midnight zone in specific provinces. For example, the *Guidi et al.* [2015] regional *b*

521   parameter reduces the bias in PEQD relative to the *Martin et al.* [1987] global *b* value

522   (Figure 2). This is further supported by the reliability index (RI) in the midnight zone

523   decreasing from 2.24 using *Martin et al.* [1987] global *b* value to 1.97 using the *Guidi*

524   *et al.* [2015] regional *b* parameter (Figure 8). However, when all 11 provinces are

525   considered, the interquartile range for each summary statistic overlaps (Figure 5),

526   which suggests on a global scale regional *b* values produce no statistically significant

527   improvement over the *Martin et al.* [1987] global *b* value.

528

529   4. **Discussion**

530   We use a consistent modeling framework to compare estimates of vertical POC flux

531   from three common parameterizations to a globally distributed dataset. We find that

532   the Martin curve and the ballast hypothesis capture observations equally well at all

533   depths. The exponential model is as skillful as the Martin curve and the ballast

534   hypothesis in the twilight zone (100-1000m), but not as skillful in the midnight zone

535   (1000-4000m).

536

537   Vertical attenuation of POC flux is ultimately controlled by particle sinking speed and

538   remineralization rate, each of which can change as the particle descends through the

539   water column. Potential processes influencing sinking speed and remineralization

540   rate include: mineral ballasting [*Armstrong et al.,* 2002; *François et al.,* 2002],

541   temperature [*Laws et al.,* 2000; *Marsay et al.,* 2015; *DeVries and Weber,* 2017],

542   oxygen concentration [*Devol and Hartnett,* 2001; *Van Mooy et al.,* 2002; *Keil et al.,*

543   2016; *Sanders et al.,* 2016; *DeVries and Weber,* 2017], and particle aggregation [*Burd*

22

544   *and Jackson,* 2009]. Some of these processes have been explicitly parameterized into

545   the "stochastic, Lagrangian aggregate model of sinking particles (SLAMS)", which

546   was able to reproduce sediment trap observed POC fluxes and some of its regional

547   variation [*Jokulsdottir and Archer,* 2016]. The relative and global importance of

548   these processes is unclear [*Burd et al.,* 2016] and their influence on sinking speed is

549   still an active area of research. For example, *Mari et al.,* [2017] show transparent

550   exopolymer particles (TEP) accumulates in the surface microlayer and needs to be

551   ballasted to overcome its low density in order to promote aggregation, which brings

552   into question the classic view that TEP increases POC flux by promoting aggregation

553   through its role as a "biological glue." Attenuation of POC flux is also effected by

554   surface processes that modify the character and lability of the POC that is exported.

555   For example, episodic events [*Lebrato et al.,* 2012; *Smith et al,* 2014], community

556   structure [*Guidi et al.,* 2009; *Guidi et al.,* 2016], and zooplankton processes [*Giering*

557   *et al.,* 2014; *Cavan et al.,* 2015; *Cavan et al.,* 2017; *Steinberg and Landry,* 2017] are

558   all likely important.

559

560   That we find that this implementation of the ballast hypothesis captures observations

561   in the twilight zone and midnight zone no better than the global and regional Martin

562   curves does not invalidate the ballast hypothesis. It simply indicates that the

563   interaction of ballast minerals with POC, as parameterized using standard approaches,

564   is not necessary to model POC flux in a manner that is statistically consistent with

565   observations from water column. A major issue here is, of course, the limited

566   coverage of these data in space and time [*Mouw et al*. 2016a,b; *Siegel et al.* 2016;

567   *Burd et al*. 2016]. The ballast hypothesis is based on a long-known correlation

568   between the flux of POC and the flux of ballast minerals [*Deuser et al.,* 1981] which

23

569   has been used to suggest ballast minerals are responsible for the flux of POC at depth,

570   either by increasing the sinking speed or protecting organic matter from oxidation

571   [*Armstrong et al.,* 2002; *François et al.,* 2002; *Klaas and Archer,* 2002]. The organic

572   matter content of sinking particles in the midnight zone is observed to be

573   approximately 5% by weight [*Armstrong et al.,* 2002]. An alternative view of this

574   correlation is that sinking POC scavenges neutrally-buoyant minerals [*Passow,* 2004],

575   which has been corroborated with a laboratory study [*Passow and De La Rocha,*

576   2006]. Additionally, *Passow and De la Rocha,* [2006] observed the POC to dry

577   weight percent concentration to be 2-3%, which is similar to the 5% observed by

578   *Armstrong et al.* [2002] in deep sediment traps, suggesting this may be the carrying

579   capacity of suspended minerals for POC. Many studies support the claim that ballast

580   minerals increase the sinking speed of aggregates [*De La Rocha and Passow,* 2007;

581   *Ploug et al.,* 2008; *Iversen and Ploug,* 2010]. However, the literature provides both

582   supporting [*Arnarson and Keil,* 2005; *Engel et al.,* 2009; *Le Moigne et al.,* 2013] and

583   opposing [*Ingalls et al.,* 2006; *Ploug et al.,* 2008; *Iversen and Robert,* 2015]

584   mechanistic evidence with respect to the degree to which ballast minerals protect

585   organic matter from oxidation.

586

587   4.1 **Modeling Recommendations**

588   Each parameterization investigated in this study may be useful in modeling studies,

589   but should be selected with consideration of the time and depth scales of interest. All

590   three parameterizations capture mean observations within the twilight zone and

591   therefore would be suitable for studies investigating the surface ocean on annual to

592   decadal time scales, i.e. where accurately capturing the deep ocean is not crucial.

593   However, for studies of the carbon cycle on centennial to millennial time scales,

594   including assessments of long-term ocean carbon sequestration, carbon supply to the

595   deep ocean should be important. In this case, the Martin curve and the ballast

596   hypothesis capture observations at depth equally well on the mean and therefore

597   would both be suitable.

598

599   We find that the empirical Martin curve has a predictive power comparable to the

600   mechanistic ballast hypothesis, despite the fact that it lacks a mechanistic foundation.

601   Though regional variability in the *b* parameter may improve the realism of the Martin

602   curve [*Henson et al.* 2012; *Guidi et al.,* 2015], it is still not mechanistic. The

603   exponential decay model's first-order kinetics are mechanistic to a degree, but this

604   approach excludes suggested mechanisms such as increasing sinking speed and

605   remineralization length scale with depth [*Villa-Alfageme et al.*, 2016]. The ballast

606   hypothesis is more mechanistic by allowing for refractory POC and allowing ballast

607   associated POC to sink faster with a longer remineralization length scale. However,

608   sinking speed and remineralization length scale of POC and ballast minerals still do

609   not increase with depth. Even though the ballast hypothesis is more mechanistic than

610   the exponential model and the Martin curve, it does not explain the observed

611   variability in POC flux at depth, which highlights a need for more complete

612   quantification of export mechanisms (see section 4). If simplicity is desired, our

613   recommendation would be to use the Martin curve in ecosystem models, but this

614   evaluation indicates that the ballast hypothesis would be an equally good choice.

615

616   In order to improve simulations of the biological pump, the relative significance of

617   mechanisms driving POC flux attenuation need to be better understood. The primary

618   limitation on this understanding is the lack of observational data with sufficient

25

619   spatio-temporal resolution to resolve ecosystem processes in the surface ocean that

620   generate POC and at the same time the processes driving remineralization at depth

621   [*Buessler and Boyd*, 2009; *Siegel et al.* 2016; *Burd et al.* 2016]. Drivers of temporal

622   variability in these mechanisms need also to be elucidated. To better constrain a

623   model on seasonal timescales, having sediment trap data with higher temporal

624   resolution and more sampling depths would be of great utility.

625

626   4.2 **Impacts on Atmospheric pCO$_2$**

627   The biological pump plays an important role regulating atmospheric pCO$_2$ [*Parekh et*

628   *al.,* 2006; *Kwon et al.,* 2009] and may help explain the drawdown of atmospheric

629   pCO$_2$ during glacial periods [*Sigman and Boyle,* 2000; *Buchanan et al.,* 2016] by

630   sequestering carbon in the deep ocean [*Yu et al.,* 2016]. Carbon raining to the

631   "midnight zone" (>1000 m) can be considered sequestered because it will be out of

632   contact with the atmosphere for at least 100 years [*Primeau,* 2005; *Ciais et al.,* 2013].

633   Using earth system model experiments, *Buchanan et al.,* [2016] find that the

634   biological pump explains about 58% of the increase in atmospheric pCO$_2$ from the

635   last glacial maximum to pre-industrial times. The current uncertainty with respect to

636   the biological carbon pump's role in setting atmospheric pCO$_2$ has significant

637   implications for our understanding of global climate regulation on time frames

638   ranging from centennial to millennial.

639

640   Applying B* as a metric to limit Martin's *b* to a range consistent with the

641   observations in each province (section 2.6) reveals that Martin's global *b* (=0.858)

642   value is contained within the range of reasonable estimates for each province (Figure

643   9A). When data in the twilight zone and midnight zone are considered, and all

644   provinces *b* values collected, the interquartile range of *b* values is 0.68 – 1.13 (Figure

645   9C) while the range is 0.70 – 0.98 when only considering observations solely in the

646   midnight zone (Figure 9D). The midnight zone contains 25-75% of observations in

647   each province (>33% mean, Figure 9B) indicating sufficient data are available for the

648   latter comparison.

649

650   Thus, the best-fit global range for *b* is 0.68 – 1.13 across both the twilight and

651   midnight zone, and 0.70 – 0.98 for only the midnight zone. These ranges are

652   substantially less than 0.4 to 1.4 used in the model of *Kwon et al.* [2009] to estimate

653   potential impacts on atmospheric pCO_2. In their most realistic model configuration,

654   this range of *b* leads to a range of equilibrium atmospheric pCO_2 of almost 100 ppm [-

655   46ppm, +52ppm]. Since only the carbon that reaches the midnight zone is

656   sequestered on the long-term, our data-constrained range of *b* that is most applicable

657   to the control of atmospheric pCO_2 is 0.70 – 0.98. This constrained range leads to

658   change in atmospheric pCO_2 from -16 ppm to +12 ppm in the *Kwon et al.* [2009]

659   model (supplementary Table S3). This indicates that uncertainty in the biological

660   pump, as globally constrained by the available POC flux data, has the potential to

661   vary modern atmospheric pCO_2 by approximately 1/3 the range suggested by *Kwon et*

662   *al.* [2009], i.e. only a few tens of ppm [-16 ppm, +12 ppm].

663

664   **5. Conclusions**

665   The *Mouw et al.* [2016a] dataset is a comprehensive collection of POC flux

666   measurements that allows a regional assessment of the skill of the Martin curve,

667   exponential decay model, and ballast hypothesis parameterizations. When these three

668   parameterizations are compared to observations throughout the water column in 11

669   biogeochemical provinces we find:

670   1. Twilight zone observations are captured equally well by the all three

671   parameterizations.

672   2. Midnight zone observations are captured equally well by the Martin curve and

673   ballast hypothesis.

674   All three parameterizations would be equally good choices for modeling studies

675   addressing the upper ocean, but only the ballast hypothesis or Martin curve should be

676   selected if export to depths below 1000m is of interest.

677

678   Parameterizations using the global b value of *Martin et al.* [1987] were compared

679   with province specific b values of *Guidi et al.* [2015] and *Henson et al.* [2012].

680   Province-specific b values can reduce the bias in the midnight zone POC fluxes in

681   some regions relative to Martin's global b value (Figure 2). However, when all

682   provinces are considered, the interquartile range for each summery statistic overlaps

683   (Figure 5), indicating no global benefit of province-specific b values. Province-

684   specific b values may still be suitable for studies with a regional focus. For all

685   provinces taken together, the range of Martin's b that best fits data from the midnight

686   zone where long-term carbon sequestration occurs is [0.70, 0.98]. Based on previous

687   global biogeochemical modeling [*Kwon et al.,* 2009], this limited range of b has the

688   capacity to change atmospheric pCO_2 by only a few tens of ppm [-16 ppm, +12 ppm].

689

690   The paucity of high-resolution observations makes it impossible to discern the relative

691   importance of various export mechanisms, many of which are discussed in Section 4.

692   At a given depth level, the *Mouw et al.* [2016a] dataset shows variability spanning an

693   order of magnitude (Figure 3) that cannot yet be mechanistically explained, and thus

694   cannot yet be accurately modeled. The role of ecosystem structure on export, the

695   biotic and abiotic transformation of particles to different class sizes, and variability

696   through space and time are key areas of research [*Burd et al.,* 2016; *Mouw et al.,*

697   2016b]. There is also a great need for seasonally resolved observations at a variety of

698   locations for more complete elucidation and quantification of export mechanisms

699   [*Siegel et al.* 2016].

700

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1092 **Tables**

1093

1094 **Table 1**. Annual primary production.

Province [short name]	VGPM[†,‡] [g m^{-2}]	Simulation[†] [g m^{-2}]
NPSW	96 ± 53	137 ± 1
PSAW	148 ± 55	113 ± 113
SPSG	108 ± 29	71 ± 34
NADR*	251 ± 88	249 ± 100
NASW	113 ± 23	134 ± 2
NPPF	202 ± 61	230 ± 140
PNEC	128 ± 37	118 ± 58
PEQD*	155 ± 53	114 ± 58
ANTA	51 ± 31	39 ± 49
SANT*	100 ± 59	83 ± 88
PSAE*	148 ± 45	108 ± 99

1095 * indicates province is presented in the main text.

1096 † Uncertainty is one standard deviation.

1097 ‡ VGPM is satellite-observed net primary production.

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1099   **Table 2**. Definition of equation parameters.

Parameter	Units	Definition
$F(z)$	mgC m^{-2} d^{-1}	POC flux
$[POC(z)]$	mgC m^{-3}	Volume concentration of labile POC
$[POC_Y(z)]$	mgC m^{-3}	Volume concentration of POC associated with Y
$[POC_Y^{hard}(z)]$	mgC m^{-3}	Volume concentration of POC associated with Y in the hard subclass
$[POC_Y^{soft}(z)]$	mgC m^{-3}	Volume concentration of POC associated with Y in the soft subclass
$[X^{prod}(z)]$	mgC m^{-3}	Volume concentration of production of X
$P_X^{prod}(z)$	mgC m^{-3} d^{-1}	Production of X at depth z by phytoplankton
$Z_X^{prod}(z)$	mgC m^{-3} d^{-1}	Production of X at depth z by zooplankton
w_X	m d^{-1}	Sinking speed of X
w_{dust}	m d^{-1}	Sinking speed of dust
$k_X = \dfrac{w_X}{\lambda_X}$	d^{-1}	Remineralization rate of X
$k_Y^{hard} = \dfrac{w_Y}{\lambda_{hard}}$	d^{-1}	Remineralization rate of hard subclass for Y
λ_X	m	Remineralization length scale of X
λ_{hard}	m	Remineralization length scale of hard subclass
ω_Y	gC gY^{-1}	POC carrying capacity of Y
f_Y^{hard}	dimensionless	Fraction of Y routed to hard subclass
$dust^{dep}$	mgDust m^{-2} d^{-1}	Surface dust deposition
Δz_{surf}	m	Depth of surface grid cell
b	dimensionless	Flux attenuation parameter

1100   X = POC, PIC, or opal
1101   Y = PIC, opal, or dust
1102

1103 **Table 3:** Tendency equation for POC associated with PIC at depth z $\left(\frac{d[POC_{PIC}(z)]}{dt}\right)$.

1104 The summation of the parameter column produces the full tendency equation.

1105

Parameter	Definition
$\omega_{PIC} f_{PIC}^{hard} \left(\dfrac{d[PIC^{prod}(z)]}{dt}\right)$	Tendency of hard POC associated with PIC
$\omega_{PIC}(1 - f_{PIC}^{hard}) \left(\dfrac{d[PIC^{prod}(z)]}{dt}\right)$	Tendency of soft POC associated with PIC
$w_{PIC} \left(\dfrac{d[POC_{PIC}^{hard}(z)]}{dz}\right)$	Sinking of hard POC associated with PIC
$w_{PIC} \left(\dfrac{d[POC_{PIC}^{soft}(z)]}{dz}\right)$	Sinking of soft POC associated with PIC
$-k_{PIC}^{hard}[POC_{PIC}^{hard}(z)]$	Remineralization of hard POC associated with PIC
$-k_{PIC}[POC_{PIC}^{soft}(z)]$	Remineralization of soft POC associated with PIC

1106
1107

1108 **Table 4:** Tendency equation for POC associated with opal at depth z $\left(\frac{d[POC_{opal}(z)]}{dt}\right)$.

1109 The summation of the parameter column produces the full tendency equation.

1110

Parameter	Definition
$\omega_{opal} f_{opal}^{hard} \left(\dfrac{d[opal^{prod}(z)]}{dt}\right)$	Tendency of hard POC associated with opal
$\omega_{opal}(1 - f_{opal}^{hard}) \left(\dfrac{d[opal^{prod}(z)]}{dt}\right)$	Tendency of soft POC associated with opal
$w_{opal} \left(\dfrac{d[POC_{opal}^{hard}(z)]}{dz}\right)$	Sinking of hard POC associated with opal
$w_{opal} \left(\dfrac{d[POC_{opal}^{soft}(z)]}{dz}\right)$	Sinking of soft POC associated with opal
$-k_{opal}^{hard}[POC_{opal}^{hard}(z)]$	Remineralization of hard POC associated with opal
$-f_T k_{opal}[POC_{opal}^{soft}(z)]$	Remineralization of soft POC associated with opal

1111 f_T is the temperature-dependency function [supplementary Table S3]

1112

1113 **Table 5:** Tendency equation for POC associated with dust at depth z $\left(\frac{d[POC_{dust}(z)]}{dt}\right)$.

1114 The summation of the parameter column produces the full tendency equation.

1115

Parameter	Definition
$\omega_{dust} f_{dust}^{hard} \left(\frac{dust^{dep}}{\Delta z_{surf}}\right)$	Tendency of hard POC associated with dust
$\omega_{dust}(1 - f_{dust}^{hard}) \left(\frac{dust^{dep}}{\Delta z_{surf}}\right)$	Tendency of soft POC associated with dust
$w_{dust} \left(\frac{d[POC_{dust}^{hard}(z)]}{dz}\right)$	Sinking of hard POC associated with dust
$w_{dust} \left(\frac{d[POC_{dust}^{soft}(z)]}{dz}\right)$	Sinking of soft POC associated with dust
$-k_{dust}^{hard}[POC_{dust}^{hard}(z)]$	Remineralization of hard POC associated with dust
$-k_{dust}[POC_{dust}^{soft}(z)]$	Remineralization of soft POC associated with dust

1116
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1118   **Table 6:** Tendency equation for labile POC at depth z $\left(\frac{d[POC(z)]}{dt}\right)$ used in the ballast

1119   model. The summation of the parameter column produces the full tendency equation.

1120

Parameter	Definition
$\left(\dfrac{d[POC^{prod}(z)]}{dt}\right)$	Tendency of POC production by phytoplankton and zooplankton
$-\omega_{PIC}\left(\dfrac{d[PIC^{prod}(z)]}{dt}\right)$	Tendency of POC associated with PIC production
$-\omega_{opal}\left(\dfrac{d[opal^{prod}(z)]}{dt}\right)$	Tendency of POC associated with opal production
$-\omega_{dust}\left(\dfrac{dust^{dep}}{\Delta z_{surf}}\right)$	Tendency of POC associated with dust deposition
$w_{poc}\left(\dfrac{d[POC(z)]}{dz}\right)$	Sinking of labile POC
$-f_T k_{poc}[POC(z)]$	Remineralization of labile POC

1121 f_T is the temperature-dependency function [supplementary Table S3]

1122

1123
1124   **Figure 1**. Simulated provinces presented in the paper are shown in dark gray. Light
1125   gray provinces are presented in supplementary. Red dots are locations of flux
1126   observations from sediment traps and thorium-234 depletion.
1127
1128   **Figure 2**. Target diagrams displaying average model skill at each region (SANT,
1129   PEQD, PSAE, NADR) for the *Martin et al.* [1987] global *b* value (Martin), *Henson et*
1130   *al.* [2012] regional *b* values (Henson), and *Guidi et al.* [2015] regional *b* values
1131   (Guidi) in the twilight zone (red) and midnight zone (blue). The black circle is the
1132   normalized standard deviation of the observed POC flux. Symbols within the circle
1133   indicate that the parameterization captures the observed POC flux more accurately
1134   than using the mean of the observed data (modeling efficiency > 0) at each region.
1135
1136   **Figure 3**. Simulated POC flux (black) with standard deviation (gray) compared with
1137   observed POC flux (blue) for the Martin curve (column 1), exponential model
1138   (column 2), and ballast model (column 3) at four provinces (SANT, PEQD, PSAE,
1139   NADR). Depth is relative to the surface. Twilight zone extends from 100m – 1000m
1140   and midnight zone is >1000m.
1141
1142   **Figure 4**. Cross plot of simulated POC flux versus observed POC flux for the Martin
1143   curve, exponential model, and ballast model at four provinces (SANT, PEQD, PSAE,
1144   NADR). Colors represent depth below surface: the upper twilight zone (100-500m),
1145   lower twilight zone (500-1000m), upper midnight zone (1000-2500m), and lower
1146   midnight zone (2500-4000m). The reliability index (RI) for each zone is indicated at
1147   top left in each panel.
1148
1149   **Figure 5**. Box and whisker plots of summary statistics in the twilight zone (red) and
1150   midnight zone (blue) for each parameterization (Exponential, Ballast, *Martin et al.*
1151   [1987] global *b* value, *Henson et al.* [2012] regional *b* values, and *Guidi et al.* [2015]
1152   regional *b* values). These box and whisker plots account for all simulated provinces
1153   (11 total).
1154
1155   **Figure 6**. Target diagrams displaying average model skill at each region (SANT,
1156   PEQD, PSAE, NADR) for the exponential model, Martin curve, and ballast model in
1157   the twilight zone (red) and midnight zone (blue). The black circle is the normalized
1158   standard deviation of the observed POC flux. Symbols within the circle indicate that
1159   the parameterization captures the observed POC flux more accurately than using the
1160   mean of the observed data (Modeling Efficiency (ME) > 0) at each region.
1161
1162   **Figure 7**. Simulated POC flux (black) with standard deviation (gray) compared with
1163   observed POC flux (blue) using the global *b* value of *Martin et al.* [1987] (column 1),
1164   regional *b* value of *Henson et al.* [2012] (column 2), and regional *b* values of *Guidi et*
1165   *al.* [2015] (column 3) at four provinces (SANT, PEQD, PSAE, NADR). Depth is
1166   relative to the surface. Twilight zone extends from 100m – 1000m and midnight zone
1167   is >1000m.
1168
1169   **Figure 8**. Cross plot of simulated POC flux versus observed POC flux using the
1170   global *b* value of *Martin et al.* [1987], *Henson et al.* [2012] regional b values, and
1171   *Guidi et al.* [2015] regional *b* values at four provinces (SANT, PEQD, PSAE,
1172   NADR). Colors represent depth below surface: the upper twilight zone (100-500m),

1173   lower twilight zone (500-1000m), upper midnight zone (1000-2500m), and lower
1174   midnight zone (2500-4000m). The reliability index (RI) for each zone is indicated at
1175   top left in each panel.
1176
1177   **Figure 9.** A: Range of *b* values for each province. Light gray bar uses data in the
1178   twilight and midnight zone while dark bars only use data in the midnight zone. B:
1179   percentage of observations in the midnight zone for each province. C: Histogram of
1180   normalized occurrence of *b* values fit to observations in the twilight and midnight
1181   zone D: Histogram of normalized occurrence of *b* values fit to observations in the
1182   twilight and midnight zone. Red line is at *Martin et al.* [1987] global *b* value of 0.858.
1183   Dotted lines are the 25th percentile and 75th percentile. Solid black line is the median.
1184 ΔpCO_2 is relative to pCO_2 with b=0.858 [*Kwon et al.,* 2009].