

Modelling marine DOC degradation time scales

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31 **Abstract**

32 Marine dissolved organic carbon (DOC) is formed of a large number of highly diverse
33 molecules. Depending on the environmental conditions, a fraction of these molecules may
34 become progressively resistant to bacterial degradation and accumulate in the ocean for
35 extended time scales. This long-lived DOC (the so-called recalcitrant DOC, RDOC) is
36 thought to play an important role in the global carbon cycle by sequestering carbon into the
37 ocean interior and potentially affecting the climate. Despite this, RDOC formation is
38 underrepresented in climate models. Here we propose a model formulation describing DOC
39 recalcitrance through two state variables: one representing the bulk DOC concentration and
40 the other representing its degradability (k) which varies depending on the balance between
41 the production of “new” DOC (assumed to be easily degradable) and bacterial DOC
42 utilization assumed to leave behind more recalcitrant DOC. We propose this formulation as a
43 means to include RDOC dynamics into climate model simulations.

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46 **Key words:** Recalcitrant Dissolved Organic Matter, Microbial Carbon Pump, numerical
47 models, ocean carbon sequestration

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61 **1. Introduction**

62 Assessing the capacity of the ocean to store atmospheric CO₂ is one of the major
63 challenges for oceanographers. Several physical and biological mechanisms have been
64 proposed to ‘pump’ CO₂ from the surface to the ocean interior thus storing carbon for
65 extended time frames [1, 2]. Some of these mechanisms are driven by physical processes (i.e.
66 the solubility pump) while others are the results of the interactions between biology (primary
67 production, particle formation, prey-predators interactions) and physics (gravitational
68 sinking, mixing, convection). The latter processes have collectively been termed ‘Biological
69 Carbon Pump’. The recently proposed Microbial Carbon Pump (MCP) provides an additional
70 carbon sequestration mechanism primarily due to biological drivers [3, 4]. Indeed, the main
71 process underpinning the MCP is the bacterially-mediated transformation of labile (i.e.
72 rapidly degradable) dissolved organic carbon (DOC) into recalcitrant (i.e. slowly degradable)
73 DOC (RDOC), which may accumulate into the ocean at time scales ranging from months to
74 millennia, in this latter case sequestering atmospheric CO₂ into stable long-lived organic
75 molecules [5]. The production of RDOC is not directly affected by physical processes
76 (mixing, sinking or thermohaline circulation) and its production is depth-independent i.e. it is
77 active through the entire water column [2]. However, abiotic forcing such as vertical mixing
78 and photo-degradation may also affect the RDOC fate and its spatial distribution, thus
79 influencing the strength and the efficiency of the MCP.

80 Being the latest recognised mechanism of ocean carbon sequestration, the MCP is also the
81 least-well investigated and represented in marine ecosystem models. Generally, DOC is
82 modelled by using up to three state variables, with each of them characterized by a constant
83 degradation time scale [6]. This approach is not consistent with the prevailing idea that the
84 recalcitrance of DOC is an environmental-dependent property [4, 7] emerging from the
85 repeated transformation and selective use of the labile organic carbon substrates by bacteria
86 [8]. Some models have explicitly described the bacterially-mediated transformation of DOC
87 into RDOC e.g. [9], however these studies do not consider the long lasting fractions of
88 RDOC and are not able to simulate RDOC accumulation on time scales that are longer than
89 seasonal [10].

90 One of the main challenges with modelling DOC accumulation beyond the seasonal time
91 scale is representing the turnover time of the various pools of RDOC which is formed of a
92 large number of highly diverse molecules with a continuum spectrum of degradation rates
93 [5]. Explicitly modelling such a wide diversity would end up in an unmanageable number of

94 state variables increasing the computational costs of the model and yielding a large number of
95 at best poorly constrained parameters. This is an important limiting factor especially when a
96 simulation is run within a global ocean or Earth-system model. In this paper, we propose a
97 conceptual framework capable of representing the continuum spectrum of DOC degradation
98 rates in a tractable way (Fig 1). The current formulation is meant to be generic and to be
99 implemented in numerical models with different levels of complexity, from ecosystem
100 models only accounting for implicit DOC remineralisation to process models explicitly
101 describing DOC-bacteria interactions.

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103 **2. A new modelling framework of DOC degradation scales**

104 We propose to model transformations of the DOC pools (Fig 1 and Table 1) using one
105 state variable representing the bulk DOC concentration and a degradation function $k(t)$. The
106 use of a degradation function can have two different meanings. Depending on the model
107 formulation k can be i) a function regulating the affinity of bacteria for a substrate, if bacteria
108 biomass and DOC uptake are modelled explicitly e.g. [9, 11] or ii) a bulk rate constant
109 representing DOC consumption in a model without explicit parameterization of the
110 heterotrophic bacterial transformations of DOC [12]. In both cases, k describes the stability
111 (i.e. resistance to degradation) of a one form of DOC (i.e. RDOC) with respect to another
112 form of DOC (i.e. labile DOC) and ranges from a minimum (i.e. k_{min}) to a maximum (i.e.
113 k_{max}) value. High k values imply high affinity by the bacteria for DOC or high consumption
114 rate, while low k values indicate low affinity or low consumption rate. To give an example, a
115 $k(t) = 0.01$ means that at time t , RDOC is 100 times less susceptible to bacterial degradation
116 (i.e. more stable) than labile DOC. While the degradation scale of labile DOC (assumed to be
117 1 d^{-1}) is used as reference in our formulation (see the parameter L_k in eq. 1.2 in Table 1) we
118 set the upper limit of the degradation function k_{max} to a lower value as our formulation is
119 specifically designed to assess DOC degradation at time scales much longer than daily (i.e.
120 from years to longer). Consequently, k_{max} has a value of 0.01 implying a DOC consumption
121 rate of 100 days. It should be also stressed that, in this paper, we assume that bacteria
122 dominate environmental DOC degradation and transformations, consequently k represents
123 only the biologically-mediated DOC consumption and transformation. However, $\left. \frac{\partial \text{DOC}}{\partial t} \right|^{Conc}$
124 ~~Cons~~ (Fig 1, eq 1.2) may also include abiotic processes in future model implementation. To

125 explain model functioning and assumptions, we use a simple box model characterised by a
126 concentration X of DOC with an associated degradation value equal to $k(t_0)$ (Fig 1a).

127 This model can be either considered as a standalone box model or as a spatial unit (i.e. a
128 subunit of a larger model grid) of a three-dimensional domain. In this latter case, k will be
129 dependent on space (x) and time (t) [i.e. $k = k(t, x)$]. DOC produced inside the box through
130 primary production has associated degradation that is equal to k_{max} . This is consistent with
131 previous findings suggesting that most of the DOC that is freshly produced by phytoplankton
132 is degraded by bacteria within tens of days [13]. As first approximation, here we do not
133 consider other food web processes (e.g. grazing) which are also known to produce DOC [14].

134 H, however, the term $\frac{\partial DOC}{\partial t} \Big|^{Prod}$ (Fig 1 and Eq 1.1) may also include other DOC
135 sources in future model implementation. The value of k inside the box model is affected by
136 the newly produced DOC proportionally to the increase in DOC and the difference between k
137 and k_{max} (eq. 2.1 in Table 1). Bacterial activity alters the DOC molecular structure and
138 composition by removing specific components (i.e. chemical reactive groups or compounds
139 or parts of them) and leaving behind biochemically altered material which becomes
140 progressively more recalcitrant [8]. The residual DOC fraction resulting from the DOC-
141 bacteria interactions also includes compounds derived from bacterial metabolism which are
142 resistant to further degradation difficult to degrade [8]. Here, we thus assume that every
143 time DOC is assimilated/consumed the remaining organic fraction becomes less biologically
144 available (i.e. more degraded) and its degradation time scales increases with k approaching
145 k_{min} . The decrease of k mimics the increased degradation state of DOC following bacteria
146 utilization [8] and is dependent on the decrease in DOC concentration inside the box and on
147 the difference between k and k_{min} (Fig 1 and Table 1).

148 Ocean circulation and vertical turbulent mixing strongly affects DOC distributions. For
149 example, DOC can be laterally transported or mixed within the water column [15].
150 Consequently, k is also affected by physical transportation of DOC. The DOC inflow into the
151 box model implies a change of the local k (i.e. inside the box) value dependent on the
152 degradability associated to the incoming DOC (k_{in}) and proportional to the magnitude of the
153 DOC flux into the box (Fig 1; eq. 2.3 in Table 1). If $k_{in} < k$, k will decrease, if $k_{in} > k$, k
154 will increase. DOC outflow does not affect the value of k associated to the remaining DOC.
155 It should be noted that here our models we does not describe explicitly represent the effect of
156 environmental factors, such as (including temperature and nutrients,) or grazer- and viral-

157 mediate mortality on phytoplankton and bacterial processes metabolisms. These effects,
158 which potentially impacting on both DOC production and consumption [14], are routinely
159 described in plankton models, and are therefore meant to be accounted for by the modelling
160 framework in which the proposed formulation is implemented.

161 An example of how DOC and its associated degradation characteristics are dynamically
162 modelled as function of DOC production and consumption is given in Fig 2. Under specific
163 assumptions (see figure caption), the model can accumulate relatively labile DOC (i.e. $k \sim 10^{-3}$;
164 Fig 2 A-B), generate a small amount of long lasting DOC ($k \sim 10^{-4}$, Fig 2 C-D), accumulate
165 DOC increasingly resistant to degradation ($k \sim 10^{-5}$, Fig 2 E-F) and degrade RDOC when
166 fresh, labile DOC is produced or added to the system (Fig 2 G-H). This latter feature,
167 mimicking the so-called ‘priming effect’ [16, 17], is further explored in the simulations
168 reported in Fig 3. The rate of input of labile DOC (through production or transport) regulates
169 both the rate of consumption of recalcitrant DOC initially present and its degradability. The
170 consumption and degradability of recalcitrant DOC increase with the production of fresh
171 DOC. More specifically, the model predicts that the time required degrading half of the initial
172 stock of DOC decreases from ~ 50 to ~ 5 years if the productions of fresh DOC increases from
173 $1 \cdot 10^{-5}$ to $5 \cdot 10^{-2}$ $\text{mg C m}^{-3} \text{ d}^{-1}$. It needs to be stressed that this relationship and the patterns
174 displayed in Fig 2 are, at this stage of development, purely conceptual examples as a
175 quantitative validation against experimental data is still to be performed. Despite this,
176 however, and although performed in an highly simplified theoretical frame, model
177 simulations reproduce key aspects related to the MCP such as; i) the coupling between DOC
178 production and consumption observed in highly productive areas such as estuaries [18]; ii)
179 the decrease in DOC degradability when primary production is reduced or absent, as for
180 example in the deep-ocean [5]; and iii) the increase in DOC degradability following the
181 addition of freshly produced DOC [16].

182 183 **3. Towards modelling the MCP**

184 The general absence of RDOC and its dynamics in (most of) marine ecosystem models
185 may reflect the assumptions that the contribution of marine biota to global carbon
186 sequestration is mainly through the biological carbon pump [19] and that the majority of
187 RDOC reacts at time scales exceeding those investigated with current ecosystem and climate
188 models. However, although RDOC production rates and accumulation are poorly constrained,
189 the MCP is a ubiquitous process in the ocean [20] and its responses to climate change could

190 influence global biogeochemical cycles on decadal to geologic timescales [2,3,4]. For
 191 example, the projected increase in sea water temperature, thermal stratification, mid-latitude
 192 oligotrophication, ocean acidification, and increase in riverine discharge of both DOM and
 193 nutrients are all factors expected to change the MCP-mediated RDOC production [3, 4].
 194 However, the amplitude and the direction (positive or negative) of the feedback are highly
 195 uncertain at this stage of understanding. For this reason, we are proposing a simple model
 196 that can be used to investigate these potentially important processes with a hypothesis-testing
 197 approach. The formulation we propose (Table 1) is computationally ‘light’ and can be applied
 198 to represent slowly degradable DOC in models with different complexity, including large
 199 scale models which do not explicitly include bacteria. Next step in the development of ~~in our~~
 200 model will be to implement the ~~our~~ formulation into a simple 3-dimensional ocean
 201 biogeochemistry model to assess if the simulated variability of k is consistent, at global
 202 scales, with known properties of the ~~global~~ DOC pool ~~at a global scale~~ (e.g.- k should be
 203 smaller ~~lower~~ in the deep layers where RDOC is dominant [5]). Furthermore, by comparing
 204 DOC simulation with existing large dataset [14], it will be possible to evaluate if the
 205 proposed k_{min} and k_{max} values (Table 2) provide the best fit with observed DOC.

206 Concomitantly, with large scale simulations, process oriented experiments should be
 207 executed to evaluate if the bacterially-mediated ‘~~transformation~~’ of the DOC pool simulated
 208 by the model (through the variability of k , Fig 2) is quantitatively realistic. Mechanisms

209 regulating DOC production from primary production are quite well investigated and
 210 constrained, and a set of established models are present in literature [14]. As a consequence,

211 DOC production $\left(\frac{\partial DOC}{\partial t}\right)^{Prod}$ (~~Prod~~, in model equation, Table 1) can be represented in

212 different ways; from simple empirical relationships [15] to more mechanistic,

213 physiologically-based formulations ~~e.g.~~ [21]. In contrast to the relatively well-known

214 processes leading to the production of DOC by the marine food web, the bacterial-mediated
 215 biochemical transformation of DOC and the controlling factors that leads to the formation of

216 RDOC is still largely unknown. For example, although some studies suggest that RDOC

217 formation through the MCP can be enhanced by low inorganic nutrient concentrations [4,

218 22], quantitative relationships between inorganic nutrient availability to bacteria and the

219 production of RDOC still needs to be established. This limited observations makes the

220 modelled relationship between DOC consumption $\left(\frac{\partial DOC}{\partial t}\right)^{Cons}$ (~~Cons~~ in Table 1) and DOC

221 degradability (represented by k) highly uncertain and is thus a challenge to incorporate into
222 models.

223 The understanding of the mechanisms underpinning RDOC formation and accumulation
224 was so far limited by the difficulty in characterizing and quantitatively measuring RDOC (i.e.
225 on a chemical structure basis). Although we are still far from a complete chemical
226 characterization of RDOC, in recent years, state-of-the-art mass spectrometry techniques,
227 have allowed the identification of specific combinations of elements (in terms of C:H and C:O
228 ratios) and molecular masses which characterize RDOC [23, 24]. Such ‘chemical fingerprint’
229 allows RDOC to be recognised in bacterial cultures and is observed to be produced
230 ubiquitously by bacteria in remarkably short time frames (months, e.g. [25]). Controlled, *ad*
231 *hoc* performed experiments exploiting these techniques and specifically addressing microbial
232 RDOC production starting from labile substrates (under different environmental condition
233 e.g. temperature and nutrient concentration) are required to iteratively calibrate, validate and
234 refine our model. In addition to traditional, laboratory-based experiments, in the next future,
235 model development will also benefit from newly designed studies performed with large
236 volume facilities [26] which may strategically combine the advantage of a controlled system
237 with the realism of the dynamics observed within them. Only after a rigorous,
238 experimentally-based validation our model can be used for reliable (quantitative) prediction
239 of MCP dynamics. ~~In the meantime, however, a~~ Although the model is at an early stage of
240 development, we ~~would like to~~ propose ~~that it is~~ a means to include RDOC dynamics into
241 climate model simulations. Such simulations will represent a powerful hypothesis-testing tool
242 to complement experimental and field studies in the investigation of the role played by the
243 MCP in ocean carbon sequestration in past, present and future oceans.

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Table 1. Model equations*

Model Equations	
1.DOC	$\frac{\partial DOC}{\partial t} = \frac{\partial DOC}{\partial t} \Big ^{Prod} - \frac{\partial DOC}{\partial t} \Big ^{Cons} + \frac{\partial DOC}{\partial t} \Big ^{Phys}$
1.1	$\frac{\partial DOC}{\partial t} \Big ^{Prod} = Const$
1.2	$\frac{\partial DOC}{\partial t} \Big ^{Cons} = L_k \cdot k \cdot DOC$
1.3	$\frac{\partial DOC}{\partial t} \Big ^{Phys} = Const$
2. k	$\frac{\partial k}{\partial t} = \frac{\partial k}{\partial t} \Big ^{Prod} - \frac{\partial k}{\partial t} \Big ^{Cons} + \frac{\partial k}{\partial t} \Big ^{Phys}$
2.1	$\frac{\partial k}{\partial t} \Big ^{Prod} = (k_{max} - k) \cdot \frac{\frac{\partial DOC}{\partial t} \Big ^{Prod}}{DOC^{\wedge}}$
2.2	$\frac{\partial k}{\partial t} \Big ^{Cons} = (k - k_{min}) \cdot \frac{\frac{\partial DOC}{\partial t} \Big ^{Cons}}{DOC^{\wedge}}$
2.3	$\frac{\partial k}{\partial t} \Big ^{Phys} = (k_{in} - k) \cdot \frac{\frac{\partial DOC}{\partial t} \Big ^{Phys}}{DOC^{\wedge}} \quad \text{if } \frac{\partial DOC}{\partial t} \Big ^{Phys} > 0$
2.3.1	$\frac{\partial k}{\partial t} \Big ^{Phys} = 0 \quad \text{if } \frac{\partial DOC}{\partial t} \Big ^{Phys} < 0$

Time integration	
3	$DOC^{t+1} = DOC^t + \frac{\partial DOC}{\partial t} \cdot \Delta t$
4	$k^{t+1} = k^t + \frac{\partial k}{\partial t} \cdot \Delta t$

340 *The equations presented in this table refer to the simplified example reported in this paper
 341 (Figs 2-3) which assumes constant production of DOC, implicit bacterial uptake and a
 342 constant transport of DOC. However, the proposed formulations describing DOC
 343 degradability (k), is also meant to be implemented in more complex models which have DOC
 344 production, consumption and physical transport represented by more complex equations.
 345 ^DOC concentration in the Box Model (Fig 1a) is assumed to be always >0
 346

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348 **Table 2.** Model Parameters

Parameter	Symbol	Value
Degradation rate of labile DOC	$L_k (d^{-1})$	1
Max degradation rate relative to L_k *	$k_{max} (adim)$	$1 \cdot 10^{-2}$
Min degradation rate relative to L_k *	$k_{min} (adim)$	$1 \cdot 10^{-7}$
k associated to the incoming DOC^	$k_{in} (adim)$	$1 \cdot 10^{-5}$
Model time step	Δt (sec)	900

349 *These parameters may assume slightly different meanings depending on the model used, see
 350 the main text for further explanations. k_{max} and k_{min} were ~~as~~ estimated considering the
 351 orders of magnitude of the life times of semi-labile and refractory DOC, respectively
 352 [5](Hansell 2013) while k_{min} was estimated considering the average age of deep ocean
 353 DOC (4000-6000 years, Hansell et al., 2012). ^The value of this parameter refers to the
 354 example reported in Fig2 (E-F)

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368 **Figure captions**

369 | **Fig 1 Aa.** *Schematic representation of the model.* DOC is the DOC concentration inside the
370 box model; k is the DOC degradation function (see the main text for further explanation).
371 *DOC production* is the DOC that is newly produced through primary production or other
372 food web processes; *DOC consumption* is the DOC that is assimilated by bacteria. DOC
373 production increases the value of k towards k_{max} while DOC consumption decreases the
374 value of k towards k_{min} . The DOC transported inside the box (inflow) influences k **and the**
375 **effect** depending on the degradation function associated to the incoming DOC (k_{in}) and on
376 the magnitude of the flux (Eq 2.3, Table 1). Transported DOC can be expressed as an
377 external forcing function if the model is used in a ‘stand-alone’ mode (e.g. the example
378 reported in this paper) or through advective and/or diffusive fluxes from adjacent boxes if a
379 1- or 3-dimensional physical models are used. The export of DOC outside the box (outflow)
380 does not affect k inside the box model. DOC has concentration unit (e.g. mass per unit
381 volume or area) while k is dimensionless. **B. Fig 1b.** *Model functioning.* Light blue boxes
382 indicate freshly produced, semi-labile DOC (i.e. with $k = k_{max}$). The degree of recalcitrance
383 is represented by increasingly dark blue colour. The interaction between bacteria and fresh
384 DOC produces residual DOC with lower k . If the production of new DOC stops, DOC is
385 biochemically altered and transformed and the value of k progressively decreases
386 approaching k_{min} . If the production of fresh DOC starts again (or if fresh DOC is
387 transported) k increases proportionally to the amount of the new DOC biologically produced
388 and/or physically transported relative to the initial concentration of DOC (standing stock).
389 **Boxes and spheres represent pools (concentrations) while arrows indicate fluxes. Arrows**
390 **width represents the magnitude of the flux relative to the DOC pool**

391

392 **Fig 2.** Model simulations. A-B= Starting from low initial concentration (1 mg C m^{-3}) and a
393 constant production rate of new DOC ($1 \text{ mg C m}^{-3} \text{ d}^{-1}$), the DOC concentration increases until

394 reaching a steady state (i.e. consumption = production). Starting from a k value of k_{max} , the
395 modelled value of k exponentially decreases as a result of DOC utilization by bacteria (eq.
396 2.2 in Table 1) until a steady state is reached. C-D= if DOC production stops, the DOC pool
397 decreases with a decrease of k . E-F= if allochthonous DOC with a k_{in} that is similar to the
398 local value of k is mixed with the DOC inside the box model, the (combined) DOC
399 accumulates, while k continues to decrease due to bacterial DOC consumption (eq. 2.2 in
400 Table 1). G &H= When there is a slow production ($0.001 \text{ mg C m}^{-3} \text{ d}^{-1}$) of fresh DOC (i.e.
401 with $k = k_{max}$) or fresh allochthonous DOC is transported inside the box (Fig 1a) at the
402 same rate (i.e. $0.001 \text{ mg C m}^{-3} \text{ d}^{-1}$), k increases and DOC is consumed

403

404 **Fig 3.** Effect of fresh DOC on recalcitrant DOC consumption. A= Consumption of ‘old’
405 DOC (i.e. DOC with initial $k = 5 \cdot 10^{-5}$) at different production rates [Prod ($\text{mg C m}^{-3} \text{ d}^{-1}$)]
406 of ‘new’ DOC (i.e. DOC with $k=k_{max}$). B= k dynamics at different production rates of ‘new’
407 DOC.