

GEOSCIENCES

Special Topic: Marine Carbon Sequestration and Climate Change

Modelling marine DOC degradation time scalesLuca Polimene^{1,*}, Richard B. Rivkin², Ya-Wei Luo³, Eun Young Kwon⁴, Marion Gehlen⁵, M. Angelica Peña⁶, Nannan Wang³, Yantao Liang⁷, Hermann Kaartokallio⁸ and Nianzhi Jiao³**INTRODUCTION**

Marine dissolved organic carbon (DOC) is formed of a large number of highly diverse molecules. Depending on the environmental conditions, a fraction of these molecules may become progressively resistant to bacterial degradation and accumulate in the ocean for extended time scales. This long-lived DOC (the so-called recalcitrant DOC, RDOC) is thought to play an

important role in the global carbon cycle by sequestering carbon into the ocean interior and potentially affecting the climate. Despite this, RDOC formation is underrepresented in climate models. Here we propose a model formulation describing DOC recalcitrance through two state variables: one representing the bulk DOC concentration and the other representing its degradability (κ) which varies depending on the balance

between the production of 'new' DOC (assumed to be easily degradable) and bacterial DOC utilization assumed to leave behind more recalcitrant DOC. We propose this formulation as a means to include RDOC dynamics into climate model simulations.

Assessing the capacity of the ocean to store atmospheric CO₂ is one of the major challenges for oceanographers. Several physical and biological

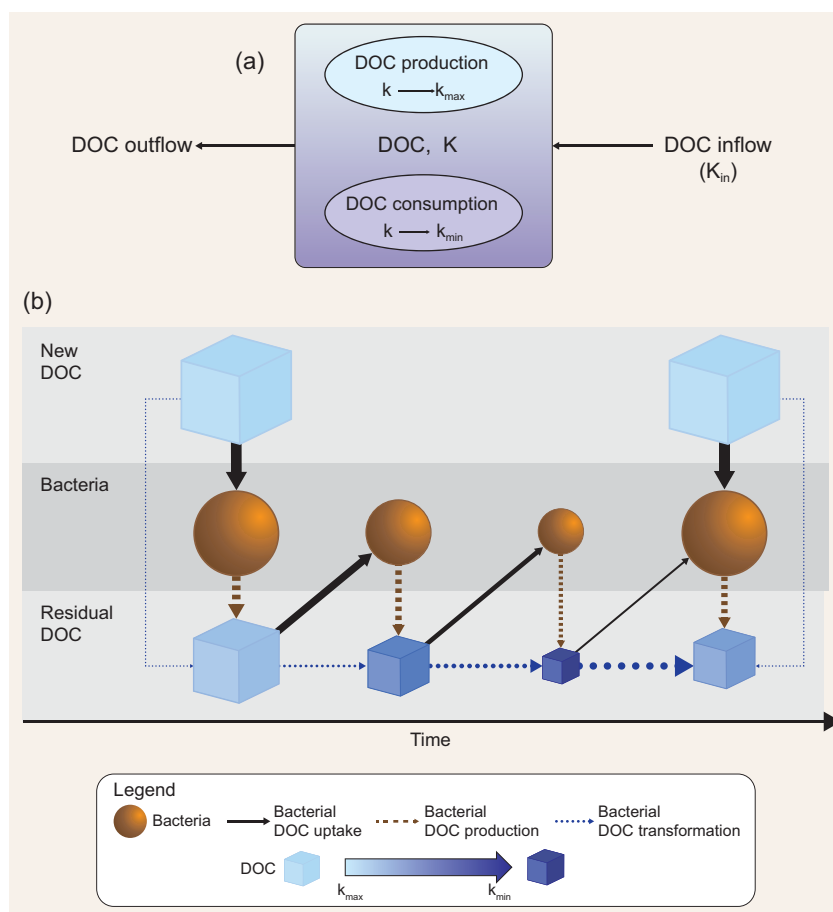


Figure 1. (a) Schematic representation of the model. DOC is the DOC concentration inside the box model; k is the DOC degradation function (see the main text for further explanation); DOC production is the DOC that is newly produced through primary production or other food web processes; DOC consumption is the DOC that is assimilated by bacteria. DOC production increases the value of k towards k_{max} while DOC consumption decreases the value of k towards k_{min} . The DOC transported inside the box (inflow) influences k depending on the degradation function associated with the incoming DOC (k_{in}) and on the magnitude of the flux (Equation 2.3, Table 1). Transported DOC can be expressed as an external forcing function if the model is used in a ‘standalone’ mode (e.g. the example reported in this paper) or through advective and/or diffusive fluxes from adjacent boxes if a 1D or 3D physical models are used. The export of DOC outside the box (outflow) does not affect k inside the box model. DOC has a concentration unit (e.g. mass per unit volume or area) while k is dimensionless. (b) Model functioning. Light-blue boxes indicate freshly produced, semi-labile DOC (i.e. with $k = k_{max}$). The degree of recalcitrance is represented by increasingly dark-blue colour. The interactions between bacteria and fresh DOC produce residual DOC with lower k . If the production of new DOC stops, DOC is biochemically altered and transformed and the value of k progressively decreases approaching k_{min} . If the production of fresh DOC starts again (or if fresh DOC is transported), k increases proportionally to the amount of the new DOC biologically produced and/or physically transported relative to the initial concentration of DOC (standing stock). Boxes and spheres represent pools (concentrations) while arrows indicate fluxes. Arrow widths represent the magnitude of the flux relative to the DOC pool.

mechanisms have been proposed to ‘pump’ CO_2 from the surface to the ocean interior, thus storing carbon for extended time frames [1,2]. Some of these mechanisms are driven by physical processes (i.e. the solubility pump) while others are the results of the

interactions between biology (primary production, particle formation, prey–predators interactions) and physics (gravitational sinking, mixing, convection). The latter processes have collectively been termed the ‘Biological Carbon Pump’. The recently

proposed Microbial Carbon Pump (MCP) provides an additional carbon sequestration mechanism primarily due to biological drivers [3]. Indeed, the main process underpinning the MCP is the bacterially mediated transformation of labile (i.e. rapidly degradable) dissolved organic carbon (DOC) into recalcitrant (i.e. slowly degradable) DOC (RDOC), which may accumulate into the ocean at time scales ranging from months to millennia, in this latter case sequestering atmospheric CO_2 into stable long-lived organic molecules [4]. The production of RDOC is not directly affected by physical processes (mixing, sinking or thermohaline circulation) and its production is depth-independent—that is, it is active through the entire water column [2]. However, abiotic forcing such as vertical mixing and photo-degradation may also affect the RDOC fate and its spatial distribution, thus influencing the strength and the efficiency of the MCP.

Being the latest recognized mechanism of ocean carbon sequestration, the MCP is also the least well investigated and represented in marine ecosystem models. Generally, DOC is modelled by using up to three state variables, with each of them characterized by a constant degradation time scale [5]. This approach is not consistent with the prevailing idea that the recalcitrance of DOC is an environmentally dependent property [3] emerging from the repeated transformation and selective use of the labile organic carbon substrates by bacteria [6]. Some models have explicitly described the bacterially mediated transformation of DOC into RDOC; however, these studies do not consider the long-lasting fractions of RDOC and are not able to simulate RDOC accumulation on time scales that are longer than seasonal [7].

One of the main challenges with modelling DOC accumulation beyond the seasonal time scale is representing the turnover time of the various pools of RDOC that is formed of a large number of highly diverse molecules with a continuum spectrum of degradation rates [4]. Explicitly modelling such a wide diversity would end up in an unmanageable number of state variables,

Table 1. Model equations.^a

	Model equations
1.DOC	$\frac{\partial \text{DOC}}{\partial t} = \frac{\partial \text{DOC}}{\partial t} \Big ^{Prod} - \frac{\partial \text{DOC}}{\partial t} \Big ^{Cons} + \frac{\partial \text{DOC}}{\partial t} \Big ^{Phys}$
1.1	$\frac{\partial \text{DOC}}{\partial t} \Big ^{Prod} = \text{Const}$
1.2	$\frac{\partial \text{DOC}}{\partial t} \Big ^{Cons} = L_k \cdot k \cdot \text{DOC}$
1.3	$\frac{\partial \text{DOC}}{\partial t} \Big ^{Phys} = \text{Const}$
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	$\frac{\partial k}{\partial t} \Big ^{Prod} = (k_{max} - k) \cdot \frac{\frac{\partial \text{DOC}}{\partial t} \Big ^{Prod}}{\text{DOC}^*}$
2.2	$\frac{\partial k}{\partial t} \Big ^{Cons} = (k - k_{min}) \cdot \frac{\frac{\partial \text{DOC}}{\partial t} \Big ^{Cons}}{\text{DOC}^*}$
2.3	$\frac{\partial k}{\partial t} \Big ^{Phys} = (k_{in} - k) \cdot \frac{\frac{\partial \text{DOC}}{\partial t} \Big ^{Phys}}{\text{DOC}^*}$ if $\frac{\partial \text{DOC}}{\partial t} \Big ^{Phys} > 0$
2.3.1	$\frac{\partial k}{\partial t} \Big ^{Phys} = 0$ if $\frac{\partial \text{DOC}}{\partial t} \Big ^{Phys} < 0$
	Time integration
3	$\text{DOC}^{t+1} = \text{DOC}^t + \frac{\partial \text{DOC}}{\partial t} \cdot \Delta t$
4	$k^{t+1} = k^t + \frac{\partial k}{\partial t} \cdot \Delta t$

^aThe equations presented in this table refer to the simplified example reported in this paper (Figs 2 and 3), which assumes constant production of DOC, implicit bacterial uptake and a constant transport of DOC. However, the proposed formulations describing DOC degradability (k) are also meant to be implemented in more complex models that have DOC production, consumption and physical transport represented by more complex equations. *DOC concentration in the box model (Fig. 1a) is assumed to be always >0 .

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

A NEW MODELLING FRAMEWORK OF DOC DEGRADATION SCALES

We propose to model transformations of the DOC pools (Fig. 1 and Table 1) using one state variable representing the bulk DOC concentration and a

degradation function $k(t)$. The use of a degradation function can have two different meanings. Depending on the model formulation, k can be (i) a function regulating the affinity of bacteria for a substrate, if bacteria biomass and DOC uptake are modelled explicitly [7], or (ii) a bulk rate constant representing DOC consumption in a model without explicit parameterization of the heterotrophic bacterial transformations of DOC [8]. In both cases, k describes the stability (i.e. resistance to degradation) of a one form of DOC (i.e. RDOC) with respect to another form of DOC (i.e. labile DOC) and ranges from a minimum (i.e. k_{min}) to a maximum (i.e. k_{max}) value. High k values imply high affinity by the bacteria for DOC or high consumption rate, while low k values indicate low affinity or low consumption rate. To give an example, a $k(t) = 0.01$ means that, at time t , RDOC is 100 times less susceptible to bacterial degradation (i.e. more stable) than labile DOC. While the degradation scale of labile DOC (assumed to

be 1 d^{-1}) is used as reference in our formulation (see the parameter L_k in Equation 1.2 in Table 1), we set the upper limit of the degradation function k_{max} to a lower value as our formulation is specifically designed to assess DOC degradation at time scales much longer than daily (i.e. from years to longer). Consequently, k_{max} has a value of 0.01, implying a DOC consumption rate of 100 days. It should be also stressed that, in this paper, we assume that bacteria dominate environmental DOC degradation and transformations; consequently, k represents only the biologically mediated DOC consumption and transformation. However, $\frac{\partial \text{DOC}}{\partial t} \Big|^{Conc}$ (Fig. 1, Equation 1.2) may also include abiotic processes in future model implementation. To explain model functioning and assumptions, we use a simple box model characterized by a concentration X of DOC with an associated degradation value equal to $k(t_0)$ (Fig. 1a).

This model can be either considered as a standalone box model or as a spatial unit (i.e. a subunit of a larger model grid) of a 3D domain. In this latter case, k will be dependent on space (x) and time (t) [i.e. $k = k(t, x)$]. DOC produced inside the box through primary production has associated degradation that is equal to k_{max} . This is consistent with previous findings suggesting that most of the DOC that is freshly produced by phytoplankton is degraded by bacteria within tens of days [9]. As a first approximation, here we do not consider other food web processes (e.g. grazing), which are also known to produce DOC [10]. However, the term $\frac{\partial \text{DOC}}{\partial t} \Big|^{Prod}$ (Equation 1.1) may also include other DOC sources in future model implementation. The value of k inside the box model is affected by the newly produced DOC proportionally to the increase in DOC and the difference between k and k_{max} (Equation 2.1 in Table 1). Bacterial activity alters the DOC molecular structure and composition by removing specific components (i.e. chemical reactive groups or compounds or parts of them) and leaving behind biochemically altered material that becomes progressively more recalcitrant [6]. The residual DOC fraction resulting from the DOC–bacteria

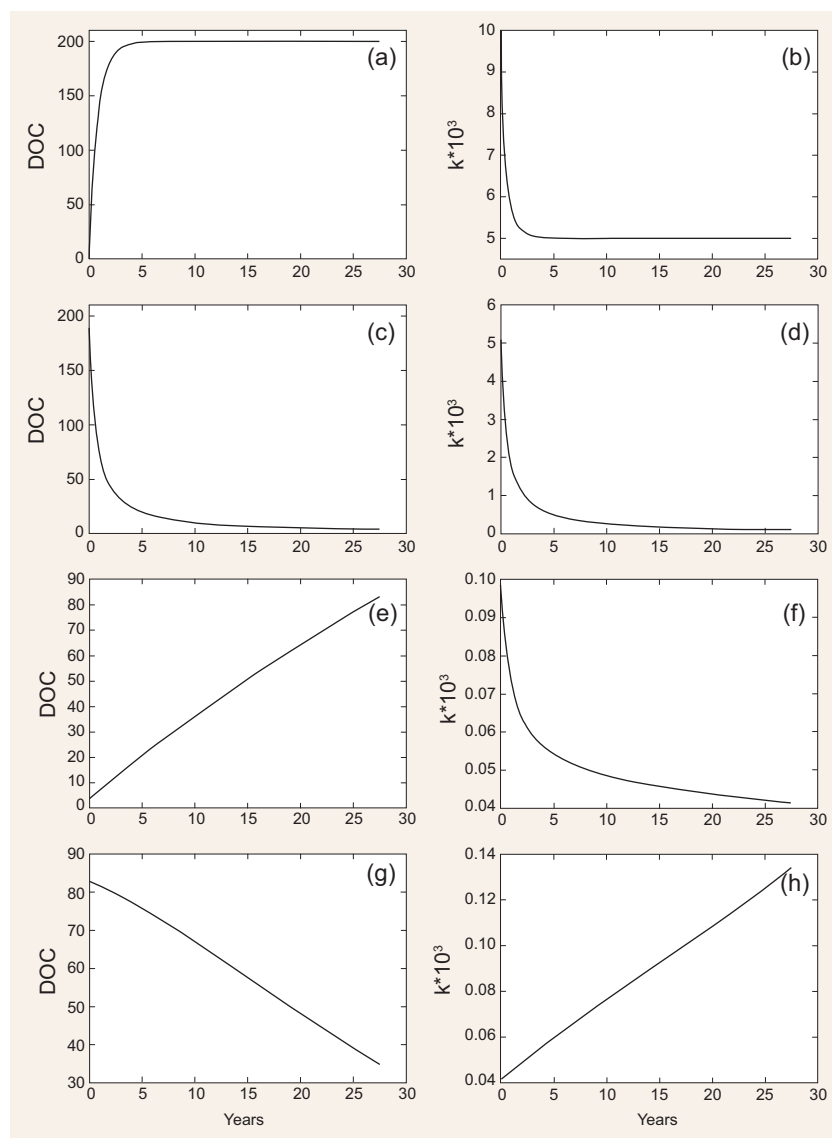


Figure 2. Model simulations. (a) and (b) Starting from low initial concentration (1 mg C m^{-3}) and a constant production rate of new DOC ($1 \text{ mg C m}^{-3} \text{ d}^{-1}$), the DOC concentration increases until reaching a steady state (i.e. consumption = production). Starting from a k value of $K_{\max}$, the modelled value of k exponentially decreases as a result of DOC utilization by bacteria (Equation 2.2 in Table 1) until a steady state is reached. (c) and (d) If DOC production stops, the DOC pool decreases with a decrease in k . (e) and (f) If allochthonous DOC with a k_{in} that is similar to the local value of k is mixed with the DOC inside the box model, the (combined) DOC accumulates, while k continues to decrease due to bacterial DOC consumption (Equation 2.2 in Table 1). (g) and (h) When there is a slow production ($0.001 \text{ mg C m}^{-3} \text{ d}^{-1}$) of fresh DOC (i.e. with $k = K_{\max}$) or fresh allochthonous DOC is transported inside the box (Fig. 1a) at the same rate (i.e. $0.001 \text{ mg C m}^{-3} \text{ d}^{-1}$), k increases and DOC is consumed.

interactions also includes compounds derived from bacterial metabolism that are resistant to fast degradation [6]. Here, we thus assume that, every time DOC is assimilated/consumed, the remaining organic fraction becomes less

biologically available (i.e. more degraded) and its degradation time scales increase with k approaching $k_{\min}$. The decrease in k mimics the increased degradation state of DOC following bacteria utilization [6] and is dependent

on the decrease in DOC concentration inside the box and on the difference between k and $k_{\min}$ (Fig. 1 and Table 1).

Ocean circulation and vertical turbulent mixing strongly affect DOC distributions. For example, DOC can be laterally transported or mixed within the water column [11]. Consequently, k is also affected by physical transportation of DOC. The DOC inflow into the box model implies a change in the local k (i.e. inside the box) value dependent on the degradability associated with the incoming DOC (k_{in}) and proportional to the magnitude of the DOC flux into the box (Fig. 1; Equation 2.3 in Table 1). If $k_{in} < k$, k will decrease; if $k_{in} > k$, k will increase. DOC outflow does not affect the value of k associated with the remaining DOC. It should be noted that our model does not explicitly represent the effect of environmental factors, such as temperature and nutrients, or grazer- and viral-mediate mortality on phytoplankton and bacterial processes. These effects, which potentially impact both DOC production and consumption [10], are routinely described in plankton models, and are therefore meant to be accounted for by the modelling framework in which the proposed formulation is implemented.

An example of how DOC and its associated degradation characteristics are dynamically modelled as a function of DOC production and consumption is given in Fig. 2. Under specific assumptions (see figure caption), the model can accumulate relatively labile DOC (i.e. $k \sim 10^{-3}$; Fig. 2a and b), generate a small amount of long-lasting DOC ($k \sim 10^{-4}$, Fig. 2c and d), accumulate DOC increasingly resistant to degradation ($k \sim 10^{-5}$, Fig. 2e and f) and degrade RDOC when fresh, labile DOC is produced or added to the system (Fig. 2g and h). This latter feature, mimicking the so-called 'priming effect' [12], is further explored in the simulations reported in Fig. 3. The rate of input of labile DOC (through production or transport) regulates both the rate of consumption of recalcitrant DOC initially present and its degradability. The consumption and degradability of recalcitrant DOC increase with the

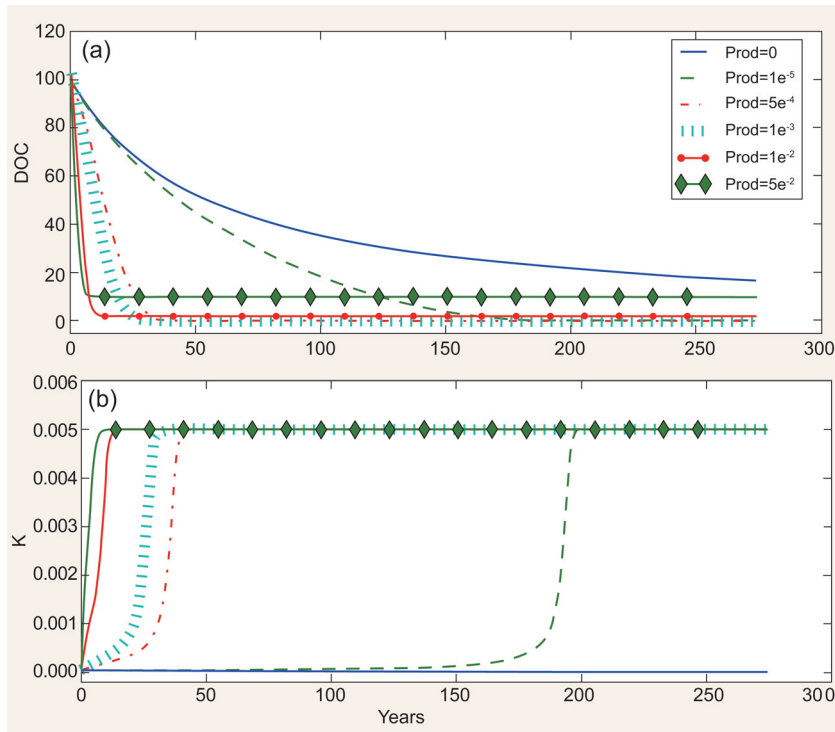


Figure 3. Effect of fresh DOC on recalcitrant DOC consumption. (a) Consumption of ‘old’ DOC (i.e. DOC with initial $k = 5 \cdot 10^{-5}$) at different production rates [prod ($\text{mg C m}^{-3} \text{ d}^{-1}$)] of ‘new’ DOC (i.e. DOC with $K = k_{\text{max}}$). (b) k dynamics at different production rates of ‘new’ DOC.

Table 2. Model parameters.

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

^aThese parameters may assume slightly different meanings depending on the model used; see the main text for further explanations. k_{max} and k_{min} were estimated considering the orders of magnitude of the life times of semi-labile and refractory DOC, respectively [4]). DOC[^]: the value of this parameter refers to the example reported in Fig. 2e and f.

production of fresh DOC. More specifically, the model predicts that the time required for degrading half of the initial stock of DOC decreases from ~50 to ~5 years if the production of fresh DOC increases from $1 \cdot 10^{-5}$ to $5 \cdot 10^{-2} \text{ mg C m}^{-3} \text{ d}^{-1}$. It needs to be stressed that this relationship and the patterns displayed in Fig. 2 are, at this stage of development, purely conceptual examples, as a quantitative validation

against experimental data is still to be performed. Despite this, however, and although performed in a highly simplified theoretical frame, model simulations reproduce key aspects related to the MCP, such as (i) the coupling between DOC production and consumption observed in highly productive areas such as estuaries [13]; (ii) the decrease in DOC degradability when primary production is reduced or absent, as for example in

the deep ocean [4]; and (iii) the increase in DOC degradability following the addition of freshly produced DOC [12].

TOWARDS MODELLING THE MCP

The general absence of RDOC and its dynamics in (most) marine ecosystem models may reflect the assumptions that the contribution of marine biota to global carbon sequestration is mainly through the biological carbon pump and that the majority of RDOC reacts at time scales (millennia) exceeding those investigated with current ecosystem and climate models. However, since the MCP is a ubiquitous process in the ocean, even small alterations in its functioning due to climate change could impact on global biogeochemical cycles on much smaller timescales [2,3]. For example, the projected increase in sea-water temperature, thermal stratification, mid-latitude oligotrophication, ocean acidification and increase in riverine discharge of both dissolved organic matter and nutrients are all factors expected to change the MCP-mediated RDOC production [3]. However, the amplitude and the direction (positive or negative) of the feedback are highly uncertain at this stage of understanding. For this reason, we are proposing a simple model that can be used to investigate these potentially important processes with a hypothesis-testing approach. The formulation we propose (Table 1) is computationally ‘light’ and can be applied to represent slowly degradable DOC in models with different complexity, including large-scale models that do not explicitly include bacteria. The next step in the development of our model will be to implement the formulation into a simple 3D ocean biogeochemistry model to assess whether the simulated variability of k is consistent, at global scales, with known properties of the DOC pool (e.g. k should be smaller in the deep layers where RDOC is dominant [4]). Furthermore, by comparing DOC simulation with existing large datasets [10], it will be possible to evaluate whether the

proposed k_{min} and k_{max} values (Table 2) provide the best fit with observed DOC.

Concomitantly with large-scale simulations, process-oriented experiments should be executed to evaluate whether the bacterially mediated transformation of the DOC pool simulated by the model (through the variability of k , Fig. 2) is quantitatively realistic. Mechanisms regulating DOC production from primary production are well investigated and constrained, and a set of established models is present in the literature [10]. As a consequence, DOC production ($\frac{\partial DOC}{\partial t}|_{Prod}$, in model equation, Table 1) can be represented in different ways, from simple empirical relationships [11] to more mechanistic, physiologically-based formulations [7]. In contrast to the relatively well-known processes leading to the production of DOC by the marine food web, the bacterially mediated biochemical transformation of DOC and the controlling factors that lead to the formation of RDOC are still largely unknown. For example, although some studies suggest that RDOC formation through the MCP can be enhanced by low inorganic nutrient concentrations [3], quantitative relationships between inorganic nutrient availability to bacteria and the production of RDOC still need to be established. This limited observation makes the modelled relationship between DOC consumption ($\frac{\partial DOC}{\partial t}|_{Cons}$ in Table 1) and DOC degradability (represented by k) highly uncertain and thus a challenge to incorporate into models.

The understanding of the mechanisms underpinning RDOC formation and accumulation has so far been limited by the difficulty in characterizing and quantitatively measuring RDOC (i.e. on a chemical structure basis). Although we are still far from a complete chemical characterization of RDOC, in recent years, state-of-the-art mass spectrometry techniques have allowed the identification of specific combinations of elements (in terms of C:H and C:O ratios) and molecular masses that characterize RDOC [15]. Such a 'chemical fingerprint' allows RDOC to be recognized in bacterial cultures and is

observed to be produced ubiquitously by bacteria in remarkably short time frames (e.g. months [16]). Controlled, *ad hoc* performed experiments exploiting these techniques and specifically addressing microbial RDOC production starting from labile substrates (under different environmental conditions, e.g. temperature and nutrient concentrations) are required to iteratively calibrate, validate and refine our model. In addition to traditional, laboratory-based experiments, in the near future, model development will also benefit from newly designed studies performed with large-volume facilities [17] that may strategically combine the advantage of a controlled system with the realism of the dynamics observed within them. Only after a rigorous, experimentally based validation can our model be used for reliable (quantitative) prediction of MCP dynamics. Although the model is at an early stage of development, we propose that it is a means to include RDOC dynamics into climate model simulations. Such simulations will represent a powerful hypothesis-testing tool to complement experimental and field studies in the investigation of the role played by the MCP in ocean carbon sequestration in past, present and future oceans.

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