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1 **Biological or Microbial Carbon Pump? The role of phytoplankton stoichiometry in**

2 **ocean carbon sequestration**

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20 **Key words**:

21 Microbial Carbon Pump, Biological Carbon Pump, Plankton Stoichiometry,

22 Recalcitrant DOM, Marine Ecosystem Models

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Abstract

Once fixed by photosynthesis carbon becomes part of the marine food web. The fate of this carbon has two possible outcomes: it may be respired and released back to the ocean and potentially the atmosphere as CO_2 or retained in the ocean interior and/or marine sediments for extended time scales. The most important biologically mediated processes responsible for long term carbon storage in the ocean are the biological carbon pump (BCP) and the microbial carbon pump (MCP). While acting simultaneously in the ocean, the balance between these two mechanisms is thought to vary depending on the trophic state of the environment. Using previously published formulations, we propose a modelling framework to simulate variability in the MCP: BCP ratio as a function of external nutrients. Our results suggest that the role of the MCP might become more significant under future climate change conditions where increased stratification enhances the oligotrophic nature of the surface ocean. Based on these model results, we propose a conceptual framework in which the internal stoichiometry of phytoplankton, modulating both grazing pressure and DOM production (via phytoplankton exudation), plays a crucial role in regulating the MCP: BCP ratio.

Introduction

Assessing the capacity of the ocean to sequester atmospheric CO_2 is one of the key challenges in oceanography. Consequently, a large number of studies have been dedicated to the physical and biological mechanisms capable of transporting carbon from the surface ocean to its interior (Volk and Hofert, 1985; Sarmiento and Gruber, 2006 and references therein). Amongst the biological processes, the so-called Biological Carbon Pump (BCP) is the most widely recognized and extensively studied (Honjo *et al*., 2008 and 2014; Henson *et al*., 2012; Lutz *et al*., 2007; Passow and Carlson 2012). However, the more recently defined Microbial Carbon Pump (MCP, Jiao *et al*., 2010) provides an additional biological mechanism which may significantly contribute to the capacity of the ocean to store atmospheric CO_2.

Both the MCP and BCP facilitate the long term storage of carbon in the ocean, however, they are conceptually different. The BCP mainly describes the fixation of CO_2 into particulate organic carbon (POC) and its subsequent transfer to the deep ocean through gravitational sinking. Conversely, the MCP does not imply any physical transportation but is instead based upon a bacterially mediated chemical transformation of dissolved organic matter (DOM) from labile (i.e., rapidly degradable) to recalcitrant forms (i.e., slowly degradable). Current estimates suggest that the carbon stored over long time scales (i.e., millennia) through the MCP is ~0.4% of the annual oceanic primary production (Legendre *et al*., 2015). The amount of carbon exported by the BCP over 2000 m depth ranges from 0.6 to 1.3% of the annual primary production (Legendre *et al*., 2015).

While the MCP and BCP occur simultaneously in the ocean, the balance between the two is thought to vary both spatially and temporally depending on the trophic conditions of the environment (Jiao *et al*, 2010). BCP is thought to dominate in conditions where nutrient sufficiency favours large plankton groups (e.g. diatoms) resulting in large, fast-sinking detritus (marine snow and/or fecal pellets). Conversely, oligotrophic regions dominated by small phytoplankton species (Jardillier *et al*., 2013) will support the microbial loop and fuel the MCP (Legendre *et al*., 2015). Nutrient deficiency is expected to enhance the MCP by substantially altering ("unbalancing") phytoplankton stoichiometry and producing DOM with high C:N and C:P ratios. Additionally, stoichiometrically unbalanced phytoplankton is poor quality food for zooplankton (Urabe and Sterner 1996; Siuda and Dam, 2010; Loladze et al., 2000; Jones and Flynn 2005). This in turn decreases zooplankton assimilation efficiency resulting in the release of carbon-rich detritus resistant to bacterial degradation (Jiao *et al*., 2014; Mitra, 2006; Polimene *et al*., 2015). Both the geographical distribution and intensity of nutrient limitation in the global ocean is projected to increase as a consequence of climate change induced increases in

1 thermal stratification (Polovina *et al*., 2008); under this scenario a strengthening role for the MCP has

2 been hypothesized for the future oceans (Jiao *et al*., 2010).

3   Although the MCP has been conceptually linked to nutrient supply and food quality for

4 zooplankton (Jiao *et al*., 2014), a coherent modelling framework to test the effect of nutrients on the

5 balance between MCP and BCP is still lacking. In this paper, we present a modelling framework able

6 to simulate the partition of carbon between the BCP and the MCP as a function of nutrient

7 concentrations. To achieve this, we combined the model of Polimene *et al.* (Polimene *et al.,* 2015)

8 describing the effect of phytoplankton stoichiometry on grazing (a process called Stoichiometric

9 Modulation of Predation, SMP, Mitra 2006) with a model describing the interaction between

10 heterotrophic bacteria and DOM, including the production of recalcitrant DOC (Polimene *et al*., 2006).

11 The two models (Polimene *et al.,* 2015 and 2006) were incorporated within the European Regional

12 Seas Ecosystem Model (ERSEM, Butenschon *et al*., 2016) and share the same currencies (C, N, P) and

13 underlying assumptions. Based on modelling results, we propose a conceptual framework in which the

14 stoichiometry of primary producers is the central factor regulating the magnitude of the MCP relative

15 to the BCP.

16

17 **The Model**

18   The combined model is composed of five biotic components (Fig. 1): one phytoplankton

19 functional type, three zooplankton functional types (microzooplankton, mesozooplankton and

20 heterotrophic nanoflagellates) and one heterotrophic bacteria functional type. The abiotic state

21 variables include nutrients (ammonium, nitrate, phosphate and silicate), DOM (labile, semi-labile, and

22 semi-refractory) and POM. The POM is further differentiated into three categories according to

23 size/sinking velocity: i) small detritus, derived from phytoplankton (through stress-enhanced mortality),

24 ii) medium size detritus, derived from microzooplankton (through mortality and not assimilated food)

25 and iii) large size detritus derived from mesozooplankton (through mortality and not assimilated food,

26 the latter implicitly accounting for faecal pellets). The formulation describing the predatory interaction

27 between phytoplankton (P in Fig 1) and microzooplankton (Z1 in Fig 1) through the SMP is described

28 in Polimene *et al*. (Polimene *et al*., 2015) and is summarised in SI. The SMP simulates a decrease in

29 ingestion and assimilation efficiency when microzooplankton graze on carbon-rich (i.e.,

30 stoichiometrically unbalanced) phytoplankton. The bacterial production of recalcitrant DOC described

31 through the cellular release of excess of carbon and the release of capsular material is detailed in

32 Polimene *et al*. (Polimene *et al*., 2006) and succinctly described in SI. All the equations describing the

dynamics of the other plankton functional types and abiotic state variables are fully described in Butenschon *et al.* (Butenschon *et al.*, 2016). We refer the reader to these papers for a complete review of model equations, assumptions and underlying philosophy. Model parameters were typically taken from published literature (e.g., Polimene *et al.*, 2006; Blackford *et al.*, 2004; Polimene *et al.*, 2015). The only parameters we tuned were the half saturation constant for food and the food threshold parameter for the functional type Z1. These two parameters were increased (to 40 and 10 mg C m^{-3}, respectively) with respect to the values used in Polimene *et al.* (Polimene *et al.*, 2015).

The model was run in an idealized box (Fig. 1) assumed to be homogenously mixed (i.e. zero-dimensional) under constant light and temperature. This assumption allowed us to focus explicitly on the effect of variation of nutrients on the BCP:MCP ratio. In particular, to investigate the impact of increasing nutrients on phytoplankton stoichiometry, grazing mortality, phytoplankton DOM release (through exudation), and BCP:MCP ratio, we explored a range of nutrient concentrations varying from 0.1 to 10 mmol m^{-3} of nitrate with phosphate at a fixed ratio of 1:16. The model was run with and without the effect of phytoplankton stoichiometry on grazing (SMP) to investigate the specific effect of this process on the simulated MCP: BCP ratio. In the simulations without SMP the standard ERSEM formulation describing grazing in microzooplankton was used (see SI and Butenschon *et al.*, 2016). All the fluxes presented in Fig. 2 were calculated after the system had reached a steady-state condition. BCP (mg C m^{-2} d^{-1}) was calculated through the flux of particulate organic carbon exported (via gravitational sinking) outside of the box represented in Fig. 1. MCP (mg C m^{-2} d^{-1}) was computed by summing the bacterial production of semi-labile and semi-refractory DOM (as described in Polimene *et al.*, 2006) within the box represented in Fig. 1. A sensitivity analysis on the effects of POM sinking velocities on the simulated MCP:BCP ratio is offered in the SI. Phytoplankton aggregation and sinking is not considered in our implementation. However, a sensitivity experiment investigating the effect of this process on the simulation of the MCP:BCP ratio is described in SI

It should be noted that the terms "semi-labile" and "semi-refractory" are used in Polimene *et al.* (Polimene *et al.*, 2006) to identify DOC degradable on a time scale of weeks and months, respectively. As such, our model only describes the production of what is commonly classified as semi-labile DOM (Hansell, 2013) and does not consider the refractory DOM with a turn over time spanning from years to millennia. Refractory DOM is the main pool responsible for long term carbon sequestration in the ocean and, to the best of our knowledge, it is not considered in currently published model formulations. However, despite the lack of truly refractory DOM, the model we present accounts for the bacterially-mediated transformation of labile to non-labile DOM which is the fundamental process underpinning the MCP (Jiao *et al.*, 2010). Here we consider the bacterially mediated production of non-

1 labile DOC described in Polimene *et al*. (Polimene *et al.,* 2006) as the first step leading to the

2 production of refractory DOM (Amon and Banner, 1996) and therefore a proxy of the MCP. Similarly,

3 we recognize that the simulation of carbon sequestration through the BCP (i.e. carbon export below the

4 permanent pycnocline or in the sediments) is not possible in our idealized system. For these reasons, it

5 is important to stress that the simulated fluxes here labelled as MCP and BCP are processes

6 underpinning biologically-mediated carbon sequestration but cannot be used for a quantitative

7 assessment of the carbon effectively sequestered through the two pumps. We argue that this

8 approximation is acceptable for the purely conceptual purpose of this paper.

9

Results

11   The simulated relationship between phytoplankton internal stoichiometry and the external

12 concentration of nitrate given as initial condition is displayed in Fig. 2A. When nitrate is low (<5 mmol

13 m^{-3} for the simulation with SMP enabled and lower than 3 mmol m^{-3} for the simulation with SMP

14 disabled), phytoplankton tend to be unbalanced, reaching C:N ratios higher than the Redfield value of

15 6.6. The divergence from a balanced condition (C:N≈Redfield ratio) is more pronounced with SMP

16 (C:N >9) than in the run without SMP (C:N ≈7). When nitrate concentration increases, the

17 phytoplankton C:N ratio decreases reaching a threshold value which in our model is assumed to be half

18 of the Redfield ratio (C:N≈3.5). Under high nutrient regimes (nitrate > 5 mmol m^{-3}) the difference

19 between the two simulation scenarios (with and without SMP) is negligible.

20   With SMP enabled, the ratio between the carbon exuded by phytoplankton and that transferred to

21 the higher trophic levels through grazing changes from a value of ca. 1 to a value higher than 20 (Fig.

22 2B) once phytoplankton stoichiometry is unbalanced (Fig. 2A). However, in the absence of SMP, this

23 ratio attains a value lower than 1, even under low nutrient regimes. The relationship between external

24 nutrient concentrations and the BCP:MCP ratio is displayed in Fig. 2C. When nutrient concentration is

25 low, the ratio between MCP:BCP increases, concomitantly with the internal C:N ratio and the ratio

26 between exudation and grazing mortality. Model simulations suggest that the MCP:BCP ratio may

27 increase up to 6 times if the external nutrients are decreased and the SMP is considered in the models.

28 The MCP:BCP ratio ranges from 0.6 to 0.9 if the model is run without the SMP.

29

Discussion

31   Following the seminal work of Jiao and colleagues (Jiao *et al.,* 2010), the potential role played by

32 the MCP in ocean carbon sequestration and its relative magnitude with respect to the BCP received

particular attention (Legendre *et al*., 2015; Jiao *et al*., 2014; Hansell, 2013). However, modelling studies synergistically describing both the MCP and the BCP are at present lacking. We have created a modelling framework capable of simulating the nutrient-mediated variability of the MCP to BCP ratio as hypothesized by Jiao *et al*. (Jiao *et al*., 2010). The relationships between external nutrients and the MCP:BCP ratio emerge from the interplay between phytoplankton stoichiometry, zooplankton grazing, phytoplankton exudation and bacterial activity (Fig. 3). In particular, our model suggests that the effect of phytoplankton stoichiometry on microzooplankton grazing is crucial for determining the variability of the MCP:BCP ratio. Without SMP, the MCP:BCP ratio is much more stable, always remaining below 1 regardless of the external nutrient concentration. The importance of the stoichiometric balance of primary producers on trophic dynamics has previously been stressed in laboratory, field and modelling studies (Elser *et al*., 2000; Loladze *et al*., 2000; Mitra, 2006; Polimene *et al.*, 2015). Here we propose that variable stoichiometry within phytoplankton regulates the relative magnitude of the main two biologically-mediated mechanisms of carbon sequestration acting in the ocean. When nutrients are abundant, phytoplankton cells are stoichiometrically balanced (i.e., C:N:P ≈Redfield ratio of 106:16:1) and are effectively controlled by microzooplankton which can rely on highly nutritious food. Microzooplankton is then grazed upon by mesozooplankton and this triggers the evolution of the herbivorous food chain. Under these conditions, carbon export is dominated by zooplankton derived detritus (Fig. 3 and Fig. S1). The MCP plays a relatively minor role in this context as well balanced (nutrient rich) phytoplankton produce a limited amount of DOC. When external nutrients are low, the increase of the cellular C:N:P ratios decrease the nutritional quality of phytoplankton which become less palatable for the grazers. Such a decrease in "food quality" of phytoplankton decreases the grazing pressure from microzooplankton and therefore weakens the link between primary producers and metazoans. Ungrazed, carbon-rich phytoplankton release excess carbon through exudation in order to re-equilibrate internal stoichiometry. This increased production of carbon-rich material stimulates bacterial activity, eventually enhancing the MCP.

It should be noted that the reduction of the grazing activity may lead to an increase of POM in the system due to the increase of phytoplankton derived detritus due to natural mortality. This behaviour is simulated by the model under intermediate level of nutrient (i.e. nitrate > 1 and < 5 mmol m^{-3}, Fig S1). Under these nutrient conditions, the simulated MCP:BCP ratio slightly decreases if higher sinking velocities for POC are assumed (see supporting information and Fig S3). However, the increase of MCP relative to BCP under very low nutrient conditions (i.e. nitrate < 1 mmol m^{-3}) is always simulated by the model, regardless of the sinking velocity of particles (see supplementary information, Fig S2). Phytoplankton sinking due to stress-induced aggregation can also increase the export of particles

through the BCP (Turner, 2015). For this reason, we performed an additional sensitivity experiment meant to investigate the effect of this process on the simulated MCP:BCP ratio (see supplementary information, Fig. S4). Model simulation indicated that although affecting the values of the simulated MCP:BCP ratio under low nutrient conditions (Fig. S4), the addition of phytoplankton sink does not change the general dynamics of the system.

While the proposed framework is conceptually plausible and readily usable for theoretical exercises, further model developments are required to simulate the dynamics underpinning the variability of the MCP: BCP ratio in a quantitative way. Detailed information of concentration and distribution of recalcitrant DOM are present in the literature (Hansell, 2013), however, much less is known about mechanisms and processes governing its production. Although some works have indicated that bacteria are capable of producing recalcitrant material over relatively short time scales (Tranvik, 1993; Ogawa *et al*., 2001; Osterholz *et al*., 2015), additional laboratory experiments investigating DOM processing by natural bacterial assemblages are required to identify the processes through which bacteria produce recalcitrant DOM and the environmental factors affecting them. In particular, the role played by the stoichiometry of the substrate in modulating bacteria growth efficiency and recalcitrant DOM production needs to be investigated. This needs to be coupled with laboratory experiments investigating zooplankton feeding behaviour as a function of phytoplankton stoichiometry so that the proposed conceptual framework may be validated. Experimental investigations designed to study all these processes in isolation are the foundations of a robust model development. Such experiments would provide physiological details required for the development of model formulations able to simulate emergent behaviours resulting from the interactions between phytoplankton, zooplankton and bacteria. When the individual model formulations are in place they will need to be merged and validated against observations. Mesocosm experiments provide a suitable framework to test the capability of models to simulate ecosystem interactions starting from single processes. The model thus validated can then be used to interpret environmental data and aid investigation of how climate change conditions may affect the capability of oceans to store anthropogenic carbon.

Even if we are still far from a reliable model capable of quantitatively describing the variability of the MCP:BCP ratio in the global ocean, we have demonstrated that existing process models represent a suitable platform to aid the design of future studies. Interestingly, the two models used were developed independently and for different purposes. This implies that the relationships shown in Fig 2

are emergent properties. This confirms that the addition of more detailed physiology in ecosystem models (e.g., the stoichiometric modulation of grazing) improve their capacity to simulate emergent behaviours (Allen and Polimene, 2011). Our results underline the importance of three elements essential to simulating the variability of carbon fluxes in response to environmental forcing. The first is a fully resolved microbial loop, the second is the variable stoichiometry within plankton functional types and organic matter and the third is a better representation of zooplankton behaviour and physiology. None of the dynamics shown could have been simulated without variable stoichiometry and SMP present in the model.

Funding

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Figure Captions

Fig. 1. Box model used in this study. P=generic phytoplankton. Z1= microzooplankton; Z2=heterotrophic nanoflagellates; Z3=mesozooplankton (producing large detritus); B=heterotrophic bacteria; DOM= labile dissolved organic matter; RDOM=recalcitrant dissolved organic matter; POM=particulate organic matter. Dotted arrows indicate density dependent mortality closure (i.e. cannibalism). A simple remineralization closure re-injecting inorganic nutrients from exported detritus at a rate of 0.05 d^{-1} is applied at the lower boundary of the water column. All living functional types were initialised with 20 mg C m^{-3} with N and P assumed to follow Redfield stoichiometry. DOM was initialised with 80 mg C m^{-2} and 1 and 0.1 mmol m^{-3} of nitrogen and phosphorus, respectively. The initial conditions for RDOM and detritus were assumed to be zero. Blue arrows indicate the main pathways leading to the BCP while red arrows indicate the main pathways leading to the MCP.

Fig. 2. Simulated relationships between external nutrient concentration (nitrate) and (A) phytoplankton C:N ratio (mol mol^{-1}), (B) phytoplankton exudation (release of DOC) to grazing mortality ratio (adim), and (C) MCP:BCP ratio (adim). In panel C, the grey line line marks the point where MCP and BCP are equal. For nitrate concentrations higher than 5 mmol m^{-3} the simulated ratios remained constant. The model was run with and without the Stoichiometric Modulation of Predation (SMP)

Fig. 3. Conceptual model linking phytoplankton stoichiometry to the biological and microbial carbon pumps. P=phytoplankton; μZ=microzooplankton; mZ=mesozooplankton; B=bacteria; POM=particulate organic matter; DOM=dissolved organic matter; RDOM=recalcitrant DOM. The thickness of the arrows indicates the relative importance of each process in panel A and B. When C:N:P in phytoplankton is highly unbalanced (C:N >9, see Fig. 2), phytoplankton is less efficiently grazed by microzooplankton. This reduces the amount of mesozooplankton and large detritus in the system and the POC pool is dominated by phytoplankton derived detritus. At the same time, phytoplankton release excess of carbon (via exudation) which stimulate the bacterial production of recalcitrant DOM, enhancing the microbial carbon pump (Panel A)When cellular stoichiometry is close to the Redfield ratio (balanced), phytoplankton is effectively grazed by microzooplankton which, in turn, is preyed by mesozooplankton. Detrital carbon is mainly channelled into the POC pool which is dominated by large (fast sinking) particles (e.g. faecal pellets). In this context, carbon sequestration is mainly due to the biological carbon pump (Panel B)).
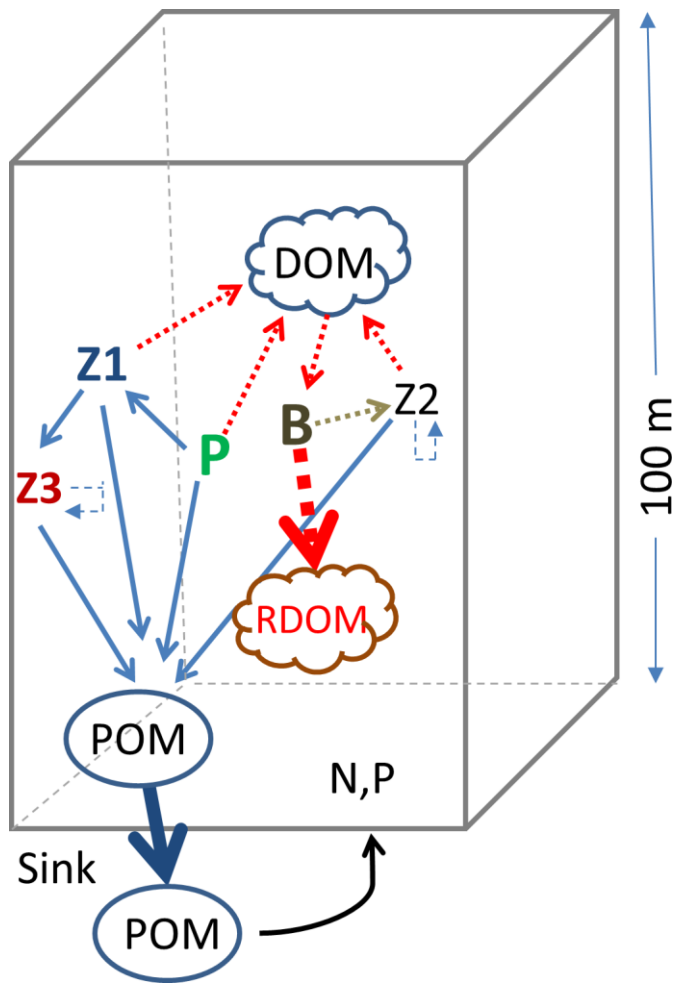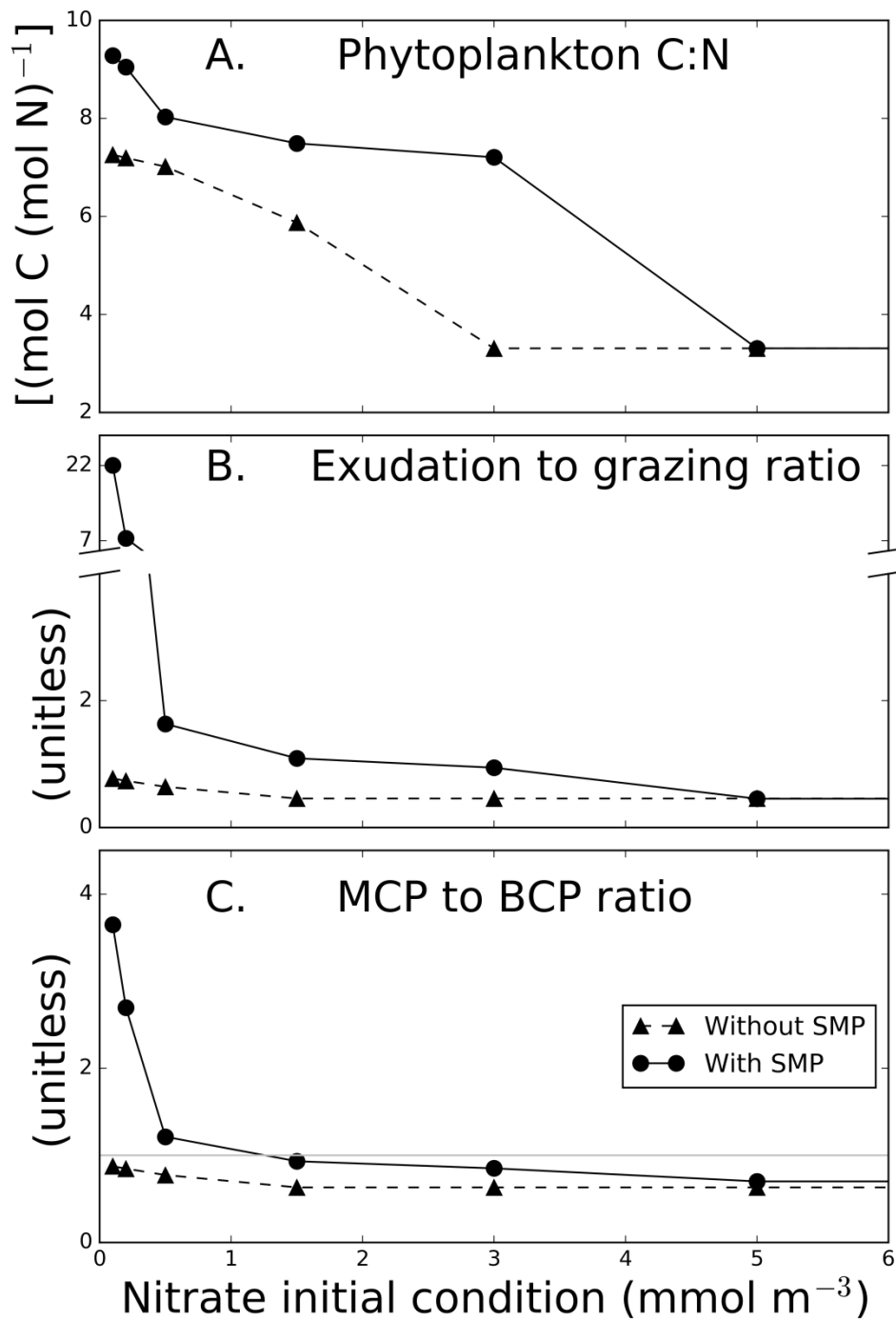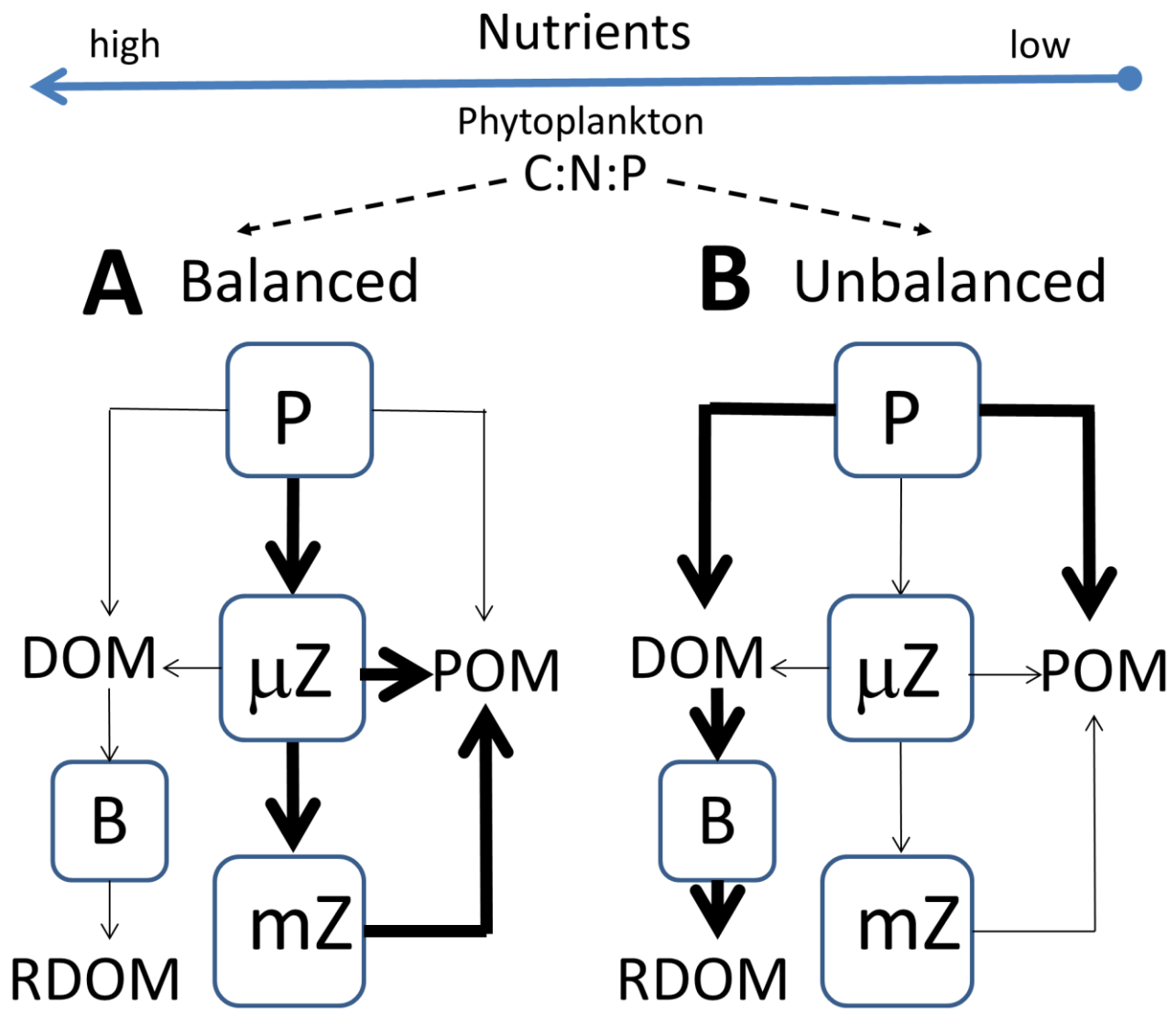
Fig. 1

A.   Phytoplankton C:N

B.   Exudation to grazing ratio

C.   MCP to BCP ratio

Without SMP
With SMP

Nitrate initial condition (mmol m^{-3})

1
2   **Fig. 2**