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MODELLING THE RESPONSE OF THE MARINE MICRO ALGAE *EMILIANA HUXLEYI* TO AN ELEVATION OF pCO_2

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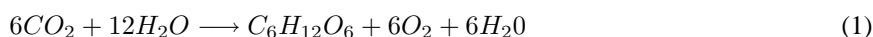
Abstract: Coccolithophorids are marine microalgae producing micro calcite plates. Under certain circumstances these microorganisms can form massive blooms which can be detected by satellites. These phytoplanktonic organisms play an important role in atmospheric CO₂ trapping through large scale precipitations of calcium carbonate in the oceans. However, recent experiments revealed that the associated fluxes that represent a sink of carbon may be slow down by an increase in atmospheric CO₂ concentration. In this paper we design models to account for the decrease in calcification and photosynthesis rates observed after an increase of pCO_2 in *Emiliana huxleyi* continuous photobioreactors. Since the involved mechanisms are still not completely clear, we developed several models, each of them based on a different hypothesis. These models are kept at a very general level, by maintaining the growth and calcification functions in a generic form, *i.e.* independent on the shape of these functions and on parameters values. The analysis is thus performed using these generic functions were the only hypothesis is an increase of these rates with respect to the regulating carbon species. As a result, each model responds differently to a pCO_2 elevation. Surprisingly, the only model whose behaviour is in agreement with the experimental results corresponds to a coupling of photosynthesis and calcification with carbonate as the regulating species, whereas bicarbonate is the substrate of these processes.

Keywords: coccolithophore, photosynthesis, calcification, model, pCO_2 .

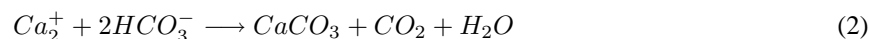
1 Introduction

Coccolithophorids are both autotrophic and calcifying phytoplanktonic species playing a major role in global biogeochemical cycling of elements. *Emiliana huxleyi* is an ubiquitous coccolithophorid (see Figure 1) that forms very spread and dense blooms detectable from space by satellites (see Figure 2), due to the highly scattering calcareous plates produced during growth.

Photosynthesis and calcification are biological processes which transform dissolved inorganic carbon (DIC) into respectively particulate organic and inorganic matter which, being denser than seawater, sink towards the oceanic floor. The export of particulate organic carbon (POC) from the surface oceanic layers, insured by the biological pump, constitutes a sink of carbon on a geological scale [5]:



The DIC precipitation into particulate inorganic carbon (PIC), and more specifically into calcium carbonate, also constitutes a sink of carbon, even if calcification produces CO_2 :



Being responsible for almost 70% of the biogenic carbonate precipitation in the oceans, these communities have been studied in the context of the predicted increase of CO_2 in the atmosphere resulting from the anthropogenic activity [7]. Based on the accumulation rate of CO_2 observed in the atmosphere from the beginning of the industrial era, current models roughly predict a doubling of the partial pressure of the atmospheric CO_2 (pCO_2) at the

end of the 21th century. Since the atmosphere tends to be in equilibrium with the superficial oceanic layers, the change in atmospheric CO_2 will have a direct effect on the CO_2 seawater concentration, and consequently on the carbonate system speciation. For example, [10] have calculated that, if the pCO_2 was doubled in the seawater, the concentration of carbonate should be reduced by 50 % approximately, and the pH by 0.35 units. The consequences are not only on the chemical properties but also on the biological processes. The reductions mentioned above, by diminishing the buffer capacity of sea water, will enhance the production of CO_2 via calcification. Under these conditions, the expected increase of pCO_2 for the next decades would exert a positive feedback on the production of CO_2 by the calcifying communities [6]. Nevertheless, recent studies have shown that cellular calcification could be depressed consequently to a rise of pCO_2 in seawater. For example, by increasing pCO_2 in phytoplankton cultures by the means of strong acid additions, [8, 11] induced a significant decrease of the calcification rate and of the calcification/photosynthesis ratio in *Gephyrocapsa oceanica*, and, with a less extend, in *Emiliana huxleyi*. Therefore, an increase in atmospheric pCO_2 can have antagonistic effects on the production of CO_2 by calcification, so that consequences on the long term are difficult to predict.

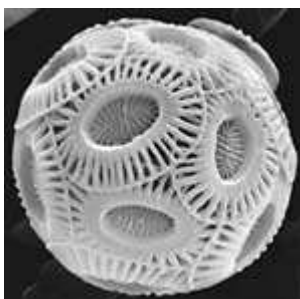


Figure 1: Microscopic view of *Emiliana huxleyi* ($\times 10000$).

The objective of this paper is to derive a set of models to explain the carbon fixation mechanisms and to reproduce chemostat experiments published in [9] where pCO_2 was doubled to simulate the future evolution of atmospheric CO_2 .



Figure 2: Bloom of *E.huxleyi* detected from satellite (south of Cornwall, UK)

2 Model design

2.1 Introduction

We have considered 2 classes of models, which suppose respectively that photosynthesis and calcification are either coupled (class CI) or uncoupled (class UI). There is a consensus to admit that HCO_3^- is the substrate of

calcification, and that reaction (2) produces a CO_2 which can then be used for photosynthesis together with the HCO_3^- and/or CO_2 directly uptaken by the cell. In the proposed series of models we investigated several possibilities for the regulation of these processes. Indeed, we assume that the regulation is not necessarily driven by the substrate availability, but that it can result from another species concentration, among HCO_3^- , CO_2 and CO_3^{2-} . Therefore, we examined the possibility that, for each class of models (CI or UI) these species can be regulating photosynthesis or calcification.

Name	Meaning	Unit
S_1	nitrogen	$mmol.L^{-1}$
D	dissolved inorganic carbon (CO_2, HCO_3^-, CO_3^{2-})	$mmol.L^{-1}$
N	particulate nitrogen	$mmol.L^{-1}$
Q	internal quota of nitrate per unit of biomass	/
X	biomass (organic carbon concentration)	$mmol.L^{-1}$
C	calcium carbonate	$mmol.L^{-1}$
S_2	Calcium	$mmol.L^{-1}$

Table 1: Meaning of the state variables whose evolution is described by each of the 12 proposed models.

The 12 models use the same state variables (Table 1), which makes their comparison possible. The algal biomass in the chemostat (X) is represented by the POC concentration together with the particulate nitrogen concentration (N). The concentration of nitrate (NO_3^-) in the chemostat (S_1) is explicitly taken into account since it is the limiting nutrient for growth. The cellular quota of nitrogen (Q), is thus expressed as the N/X ratio. The dissolved inorganic carbon and calcium (Ca^{2+}) concentrations are denoted D and S_2 respectively. Finally, C is the PIC concentration, i.e. the calcite contained in attached as well as free coccoliths. The concentrations in the chemostat renewal medium are denoted with the subscript in .

2.2 The carbonate system

The carbonate alkalinity (CA) represents the electric charges carried in the carbonate system:

$$CA = [HCO_3^-] + 2[CO_3^{2-}] \quad (3)$$

The total alkalinity (TA) is defined by [10]:

$$TA = CA + [B(OH)_4^-] + [OH^-] - [H^+] \quad (4)$$

Let us denote $\lambda = TA - 2S_2$. In a first approximation, the ions mainly contributing to λ depend on the salinity and remain constant. In the same way, we assume that $\lambda_0 = [B(OH)_4^-] + [OH^-] - [H^+]$ remains constant compared to CA. Finally we have $CA = \lambda - \lambda_0 + 2S_2$.

In order to compute the $[HCO_3^-]$ and $[CO_3^{2-}]$ concentrations, we use the dissociation constants of the carbon dioxide (K_1) and bicarbonate (K_2) (the proton concentration, $[H^+]$ is denoted h):

$$K_1 = \frac{h[HCO_3^-]}{[CO_2]} \text{ and } K_2 = \frac{h[CO_3^{2-}]}{[HCO_3^-]} \quad (5)$$

The total dissolved inorganic carbon (D) is defined as:

$$D = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \quad (6)$$

Note that, in the considered pH range, we have $[HCO_3^-] \gg [CO_3^{2-}] \gg [CO_2]$ (see for example [10]). It follows that, in a first approximation, bicarbonate is the main carbon species in the bicarbonate system:

$$[HCO_3^-] \simeq D \quad (7)$$

We deduced from equations (3) and (6), in the considered pH range:

$$[CO_3^{2-}] \simeq CA - D = \lambda - \lambda_0 + 2S_2 - D \quad (8)$$

2.3 The coupled models

In the CI class models, photosynthesis and calcification are coupled so that the carbon assimilation for the coccoliths (C) and for the biomass (X) can be represented as follows:

$$\frac{1-\alpha}{\alpha}S_2 + \frac{1}{\alpha}D \xrightarrow{\mu(\cdot)X} \frac{1-\alpha}{\alpha}C + X \quad (9)$$

where $\mu(\cdot)$ represents the specific algal growth rate. The coupling between photosynthesis and calcification induces the same expression $\mu(\cdot)X$ for the kinetics of these two processes. The constant α represents the proportion of the total up taken DIC which is allocated to photosynthesis.

Following the quota model viewpoint [3, 2, 4], we consider that growth and external NO_3 (S_1) uptake are uncoupled. The nitrogen mass transfer is thus given by:

$$S_1 \xrightarrow{\rho(\cdot)X} N \quad (10)$$

where N is the algal nitrogen and $\rho(\cdot)$ the external NO_3 uptake rate.

We can now straightforwardly (see *e.g.* [1]) derive from the mass transfer equations (9) and (10) the mass balance based model (d is the dilution rate):

$$\dot{S}_1 = d(S_{1in} - S_1) - \rho(S_1)X \quad (11)$$

$$\dot{Q} = \rho(S_1) - \mu(Q, Dp)Q \quad (12)$$

$$\dot{X} = -dX + \mu(Q, Dp)X \quad (13)$$

$$\dot{C} = -dC + \frac{1-\alpha}{\alpha}\mu(Q, Dp)X \quad (14)$$

$$\dot{D} = d(D_{in} - D) - \frac{1}{\alpha}\mu(Q, Dp)X - K_L a(\psi(S_2, D) - K_{HP}CO_2) \quad (15)$$

$$\dot{S}_2 = d(S_{2in} - S_2) - \frac{1-\alpha}{\alpha}\mu(Q, Dp)X \quad (16)$$

where $CO_2 = \psi(S_2, D)$ is derived from equations (5), (8) and (7).

Hypothesis 1 We assume that $\rho(S_1)$ is an increasing function of the NO_3 concentration (S_1), and that $\mu(Q, Dp)$ is an increasing function of both the internal nitrogen quota (Q) and the DIC species (Dp) selected for its role in the regulation of growth and calcification.

It must be emphasised, at this level, that the qualitative analysis to determine the qualitative response to a pCO_2 increase, remains valid for any functions $\rho(S_1)$ and $\mu(Q, Dp)$ with the considered qualitative properties.

The 3 models of the CI class, named CI- HCO_3^- , CI- CO_2 , CI- CO_3^{2-} differ only by the inorganic carbon component Dp controlling photosynthesis and calcification.

2.4 The uncoupled models

This class of models supposes that calcification and photosynthesis are uncoupled, so that incorporation of inorganic carbon follows two different metabolic pathways:



where $\mu(\cdot)$ and $\sigma(\cdot)$ are the rate of photosynthesis and calcification, respectively. The process of nitrogen uptake is still assumed to be independent from carbon assimilation and follows thus reaction 10.

The following equations gives the structure adopted for the UI class models whatever the considered regulating species for photosynthesis (Dp) and calcification (Dc):

$$\dot{S}_1 = d(S_{1in} - S_1) - \rho(S_1)X \quad (18)$$

$$\dot{Q} = \rho(S_1) - \mu(Q, Dp)Q \quad (19)$$

$$\dot{X} = -dX + \mu(Q, Dp)X \quad (20)$$

$$\dot{C} = -dC + \sigma(Dc)X \quad (21)$$

$$\dot{D} = d(D_{in} - D) - \mu(Q, Dp)X - \sigma(Dc)X - K_L a(\psi(S_2, D) - K_{HP}CO_2) \quad (22)$$

$$\dot{S}_2 = d(S_{2in} - S_2) - \sigma(Dc)X \quad (23)$$

	CI			UI									E X P
	HCO ₃ ⁻	CO ₂	CO ₃ ²⁻	HCO ₃ ⁻	HCO ₃ ⁻	HCO ₃ ⁻	CO ₂	CO ₂	CO ₂	CO ₃ ²⁻	CO ₃ ²⁻	CO ₃ ²⁻	
D*	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗
Dp*	↗	↗	↘	↗	↗	↗	↗	↗	↗	↘	↘	↘	n.m.
Dc*	↗	↗	↘	↗	↗	↘	↗	↗	↘	↗	↗	↘	n.m.
X*	↗	↗	↘	↗	↗	↗	↗	↗	↗	↘	↘	↘	↘
Q*	↘	↘	↗	↘	↘	↘	↘	↘	↘	↗	↗	↗	↗
S ₁ *	↘	↘	↗	↘	↘	↘	↘	↘	↘	↗	↗	↗	n.m.
C*	↗	↗	↘	↗	↗	↘	↗	↗	↘	↘	↘	↘	↘
S ₂ *	↘	↘	↗	↘	↘	↗	↘	↘	↗	↗	↗	↗	n.m.
$\frac{C}{X}$ *	→	→	→	↗	↗	↘	↗	↗	↘	↗	↗	↘	↗
pH*	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘	↘
TA	↘	↘	↗	↘	↘	↗	↘	↘	↗	↗	↗	↗	↗

Table 2: Qualitative variations of the state variables at steady-state after an elevation of pCO₂ for the 12 considered models, and for the experimental results of [9] (n.m.: not measured).

There are 9 possible combinations of Dp and Dc for this equation system, depending on the regulating carbon species for calcification and photosynthesis among CO_2 , HCO_3^- and CO_3^{2-} . For example, in the model denoted UI-HCO₃⁻-CO₂, $Dp = [HCO_3^-]$ and $Dc = [CO_2]$

3 Study of the qualitative response of the models set

In order to determine which regulation mechanism is the most appropriate, we assess the qualitative model consistency with respect to experimental observations. We thus study the qualitative behaviour for both classes of models (coupled or uncoupled) and for all the considered potential regulating species. This analysis has been performed in the framework of general (increasing) functions $\mu(\cdot)$, $\rho(\cdot)$ and $\sigma(\cdot)$. It is thus independent of the parameters values (except in some particular cases) and provide us with a diagnosis on the model adequacy. This analysis is performed at steady-state. It mainly consists in determining the evolution of the equilibrium of the model when the CO₂ partial pressure is increased. In other term, if x_i^* is a state variable of a given model at equilibrium, we study the sign of $\frac{\partial x_i^*}{\partial pCO_2}$.

For sake of place limitation we only present the result of this analysis. The qualitative behaviour for each state variable in response to increased pCO₂ is presented in Table 2, depending on the carbon compounds driving the process. These results are also compared to the experiments outcomes from [9].

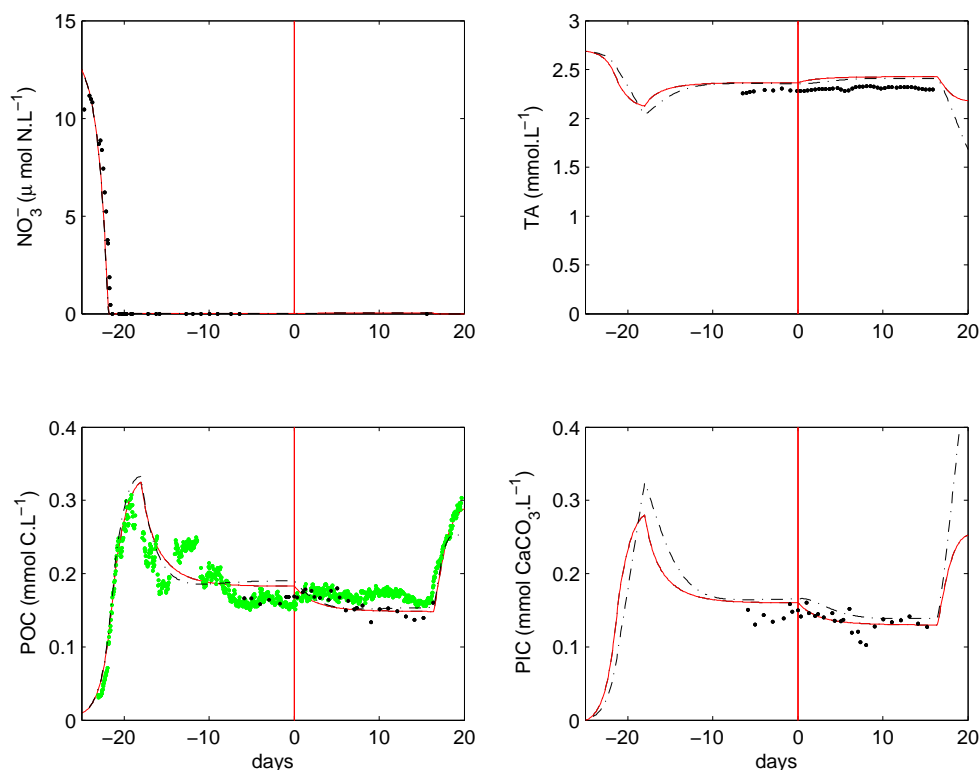


Figure 3: Comparison between model CI-CO_3^{2-} (-), $\text{UI-CO}_3^{2-} -\text{HCO}_3^-$ (...) and data for POC (X), PIC (C) Nitrate (S_1) and TA. Organic carbon is simultaneously estimated by biovolume (light grey points).

4 Numerical simulations

The parameters values and units are presented in Table 3. The computations were performed over 45 simulated days. The first 25 days were necessary to ensure that a steady-state had been reached for each variable. The partial pressure of carbon dioxide ($p\text{CO}_2$) was then instantly doubled ($340 \mu\text{atm}$ to $580 \mu\text{atm}$), with increase of bubbling (corresponding to a strong increase in $K_L a$) during 30 minutes. and the numerical behaviour of the system was observed for a further 20 days. In Figure 3 model simulations are compared to experimental data for models CI-CO_3^{2-} and $\text{UI-CO}_3^{2-} -\text{HCO}_3^-$.

5 Discussion

The first outcome of this study is that the models where HCO_3^- would straightforwardly drive photosynthesis and calcification (model CI-HCO_3^- or $\text{UI-HCO}_3^- -\text{HCO}_3^-$) predict increase of POC and PIC as well as calcification and photosynthesis rates; all these are contradicted by the experiments. In the same way, model $\text{UI-CO}_2 -\text{HCO}_3^-$ predicts a contradictory response. Indeed, all the models where only species CO_2 and/or HCO_3^- are involved have predictions that are opposite to experimental evidence. It is noteworthy that among these 6 models, the 2 CI models have exactly the same qualitative behaviour, and the same for the 4 UI models which behave identically. The difference between these 2 groups is their C/X predictions (constant for the CI models and increasing for the UI models). It follows thus that CO_3^{2-} is required in the regulation process to explain the experimental observations.

Actually, this result can be explained much more simply by a simple argue based on the growth rate. We base this reasoning on the assumption that the growth rate (or photosynthesis rate) is an increasing function of both the internal quota and a controlling inorganic carbon compound. The experimentally observed biomass decrease induced by the shift of $p\text{CO}_2$ leads to an increase in the internal quota (particulate nitrogen stays constant). Now

	Values	Units
d	0 to 0.5	d^{-1}
S_{1in}	12.5	$\mu mol N.L^{-1}$
D_{in}	2.29	$mmol C.L^{-1}$
K_{La}	1.75	d^{-1}
ρ_m	100.19	$\mu mol N.mmol C^{-1}.d^{-1}$
k_{S_1}	0.038	$\mu mol N.L^{-1}$
K_1	$1.392.10^{-6}$	$mmol.L^{-1}$
K_2	$1.189.10^{-9}$	$mmol.L^{-1}$
K_H	36.7	$mmol CO_2.L^{-1}.\mu atm$
λ	-17.3110^3	$mmol.L^{-1}$
λ_0	86.0	$mmol.L^{-1}$

 Table 3: Estimates of the model parameters for model UI- CO_3^{2-} - HCO_3^-

	HCO_3^-	CO_3^{2-}	CO_2	Units
k_Q	34.4	28.2	61.03	$\mu mol N.mmol C^{-1}$
$\bar{\mu}$	2.22	1.61	5.62	d^{-1}
σ_m	0.83	0.83	0.8	d^{-1}
k_{Dc}	1.65	0.12	0.015	$\mu mol C.L^{-1}$
k_{Dp}	1.65	0.16	0.015	$\mu mol C.L^{-1}$

Table 4: Parameters used to fit the model to the data

if we keep in mind that, under chemostat steady state, the growth rate is constant (and equals d), this implies that the increase in internal quota must be compensated by a decrease of the controlling variable in order to maintain a constant growth rate. The only variable to decrease in response to the shift in the bicarbonate system is CO_3^{2-} , explaining thus why only this model can provide an adequation with the experiments.

At this point, note that if pH is considered as a possible controlling factor, it can also induce the same conclusion. However pH has rarely a direct effect and often impacts the physico chemical equilibria. This is the reason why pH was not investigated explicitly in our model, but we considered the variables that may more directly affect the processes.

Among the considered model, only the models where CO_3^{2-} regulates photosynthesis are compatible with the experimental decrease of POC and PIC. The 4 remaining models only differ by their predictions of the ratio PIC over POC. In fact models UI- CO_3^{2-} - HCO_3^- and UI- CO_3^{2-} - CO_2 have the same behaviour (C/X increases). These quantities are not affected by the pCO_2 change for model UI- CO_3^{2-} while they are of opposite trend for model UI- CO_3^{2-} - CO_3^{2-} (C/X decreases). However, due to the noise in the data, the slight experimental increase of the PIC over POC ratio is not significant and cannot be used to select one of the 4 models. Note however that if another experiment could measure a significant increase of this ratio, the most appropriate model would be UI- CO_3^{2-} - HCO_3^- or UI- CO_3^{2-} - CO_2 , where photosynthesis is regulated by CO_3^{2-} and calcification by HCO_3^- (or by CO_2).

6 Conclusion

In this study we have investigated the coupled effect of a nitrogen limitation and of a pCO_2 increase. Based on several possible regulation mechanisms we have proposed 12 models. These models are generic since they only rely on qualitative hypotheses (except for quantitative simulations where some functions were chosen). The only possible set of models that can explain both a decrease of calcification and of photosynthesis are models where photosynthesis is regulated by CO_3^{2-} (or pH). This seems to contradict the classical hypotheses, even if they were stated on the basis of nitrogen unlimited cultures. These unexpected results may also question the experimental

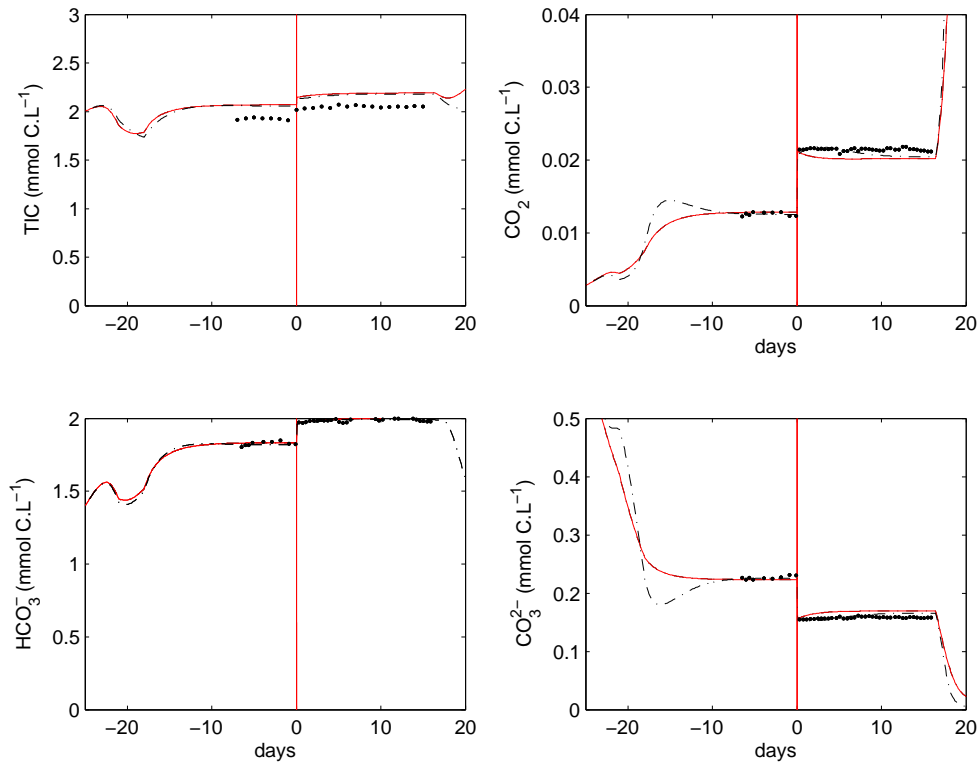


Figure 4: Comparison between model CI- CO_3^{2-} (-), UI- CO_3^{2-} - HCO_3^- (...) and data for the DIC species.

protocols where computation of dissolved inorganic carbon is made using classical methods (see *e.g.* [10]) under the hypotheses of equilibrium with atmospheric CO_2 which is not a valid approximation for chemostat cultures with high biomass concentration.

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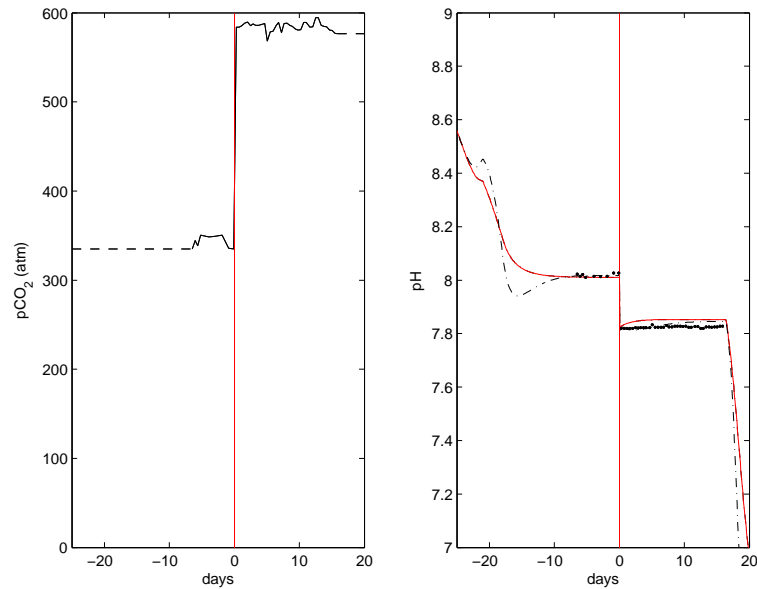


Figure 5: $p\text{CO}_2$ evolution and comparison between model CI-CO_3^{2-} (—), $\text{UI-CO}_3^{2-} - \text{HCO}_3^-$ (---) and data for pH.

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