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Quantitative modeling of microalgae based sequestration of atmospheric CO_2

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Marine microalgae have been identified as a considerable sink of atmospheric CO_2. Since macroscopic ecosystems cannot be studied experimentally with the required microscopic spatial resolution, a novel modeling method is being presented to quantify this sequestration process. The presented modeling studies indicate that the fixation of carbon by microalgae is species-specific and depends on competition effects among multiple species.

Introduction

When industrialization started, anthropogenic CO_2 releases considerably increased.[1] This causes increasing environmental concerns and therefore, studying the fate of this greenhouse gas has become a major effort.[2] Since algal photosynthesis is producing about half of the global primary carbon generation,[3–5] phytoplankton based CO_2 sequestration has a major impact on the climate.[6–14] In order to predict future environmental conditions, it is essential to understand the facts that govern phytoplankton-based CO_2 fixation.

Marine microalgae sequester CO_2 by the uptake of HCO_3^-, a nutrient, which is produced *via*:[11] $CO_{2(g)} \rightarrow CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$. Therefore, knowing $CO_{2(g)}$ and measuring HCO_3^- concentrations in marine ecosystem would enable quantitation of carbon sequestration by phytoplankton. However, microalgae cells (typical diameter 5–20 μm (ref. 15)) produce a concentration gradient within a microscopic vicinity due to their very localized nutrient uptake. Therefore, in order to quantify the sequestration process, an *in situ* measurement of HCO_3^- concentration with microscopic resolution would be required. But, such measurements are very challenging in particular since a macroscopic ecosystem contains a large number of microscopic cells.[16] On the other hand, modeling methods can accomplish a prediction of HCO_3^- concentrations with microscopic spatial resolution. In this work, an assessment of microalgae based CO_2 sequestration is being reported with the goal to quantitatively describe the conversion of atmospheric CO_2 into microalgal biomass. This quantitative model is based on describing all physical and chemical processes namely dissolution of atmospheric CO_2, HCO_3^- formation and transport within an aqueous ecosystem, microalgae species-specific HCO_3^- uptake, and HCO_3^- utilization for biomass production. Additionally, nutrient competition has been found to impact the CO_2 sequestration and therefore needs to be considered[17–20] as well.

Methods

In this study, the aforementioned steps describing the transformation of atmospheric CO_2 into microalgal biomass are linked by means of a novel 'concentration field'[21] approach. This space- and time-dependent concentration field describes the HCO_3^- concentration distribution within an ecosystem. The dissolution of CO_2 from the atmosphere into an aqueous ecosystem and its subsequent conversion into HCO_3^- are described by chemical kinetics in the cited, previous study. Additionally, a mass transport mechanism explains the distribution of HCO_3^- within an ecosystem. Two microalgae species, *i.e. Nannochloropsis oculata* and *Dunaliella salina*, have been considered here individually as well as in a competition situation. To properly describe the model, several species-specific and environment dependent parameters that explain the cells' nutrient uptake and utilization needed to be determined experimentally.[22–24] These parameters were determined in previous work[21] and were utilized in this study.

In order to quantify the amount of CO_2 sequestered by a culture of microalgae all aspects of a marine ecosystem need to be modelled. For this purpose, a macroscopic ecosystem is assumed to consist of microscopic, cuboid 'blocks' each of which represents a small volume surrounding a cell cluster. Each of these blocks was assumed to contain a single cell cluster of either *D. salina* or *N. oculata*, or for species mixtures two cell clusters for one of each, respectively. In the latter case, a competition between *N. oculata* and *D. salina* for the HCO_3^-

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supply establishes. From the overall HCO_3^- concentration, *i.e.* the sum contained in all blocks, a cell culture's carbon sequestration has been derived.

An "artificial ecosystem" of 128 μm × 128 μm × 32 μm (volume = 0.5 nL) has been modelled with a spatial resolution of 1 μm along each direction; this will be referred to as "grid". Initially, the concentration field covering this artificial ecosystem has been assumed to be void of HCO_3^-. Then, the $CO_{2(g)}$-concentration in the atmosphere above the artificial ecosystem was set to a user selected level and "switched on". This has been done, in separate simulations, for 300 ppm, 350 ppm, 400 ppm, 450 ppm and 500 ppm. These concentration ranges were chosen to simulate pre-industrial, present and potential future atmospheric $CO_{2(g)}$ concentration. For each atmospheric $CO_{2(g)}$ scenario, the top 1 μm layer of the simulated culture represented the air–water interface where $CO_{2(g)}$ partitions into the aqueous phase where it forms HCO_3^-. In this first step, this portion of the modeling was performed without cells being present in order to create, *via* diffusion, a realistic concentration field across the entire simulated area. In a second step, the cells' HCO_3^- uptake was "switched on" which modified the concentration field around them and initiated the production of additional cells. This turn-on defined $t = 0$. In a first simulation experiment, a fixed number (10^9) of either *D. salina* or *N. oculata* cells had been "inoculated" at a certain grid position of the artificial ecosystem. In case of species-competing mixtures, clusters of 10^9 cells of each species were inoculated at two different locations. For single-species cultures, cell clusters of either *D. salina* or *N. oculata* were inoculated at grid point $x, y, z = 56, 64, 16$ and $x, y, z = 72, 64, 16$, respectively. For mixed-species cultures, one cluster of each species had been inoculated at the stated grid points. It has been assumed that cell clusters (and nutrients) are not being moved by advection.

The sequestration process causes local concentration depletions around the cells which are then continuously replenished *via* diffusion of HCO_3^- newly generated at the air–water interface. Thus, there is a continuous fixation of atmospheric CO_2 into phytoplankton biomass. In order to simulate a real-world ecosystem, all the simulations were performed at the following physical and chemical conditions: temperature 20 °C, atmospheric pressure 1.0 atm, pH 8.2 and salinity 35.0 g kg^{-1} of seawater.

Results and discussion

The difference in HCO_3^- concentrations between the initial concentration field created in absence of cells and the subsequent one containing an increasing number of cells were utilized to quantify the sequestration process over time. Considering the volume of the artificial ecosystem, concentration differences between absence and presence of cells could be translated into absolute quantities in nanograms of HCO_3^- the cells had been sequestered. This had been done for several environmental conditions.

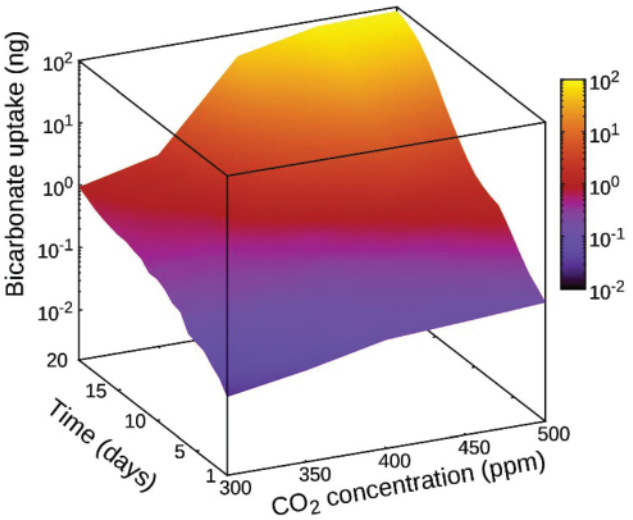

Fig. 1 Quantification of HCO_3^- sequestered (in ng; log-scale) over time at different levels of atmospheric CO_2 by *D. salina* species within the artificial ecosystem.

Fig. 1 and 2 depict the quantity of HCO_3^- sequestered by *D. salina* and *N. oculata* cultures, respectively. The species-specific HCO_3^- consumption (in ng) within the artificial ecosystem were shown over the course of 20 days at different atmospheric CO_2 concentration (300–500 ppm). As is shown in Fig. 1 and Fig. 2, the uptake behaviour depends on the growth time and more importantly on the atmospheric CO_2 concentration. The flatness of these surfaces indicates that, *D. salina* has a stronger dependency on the atmospheric CO_2 concentration than *N. oculata* and has quantitatively higher HCO_3^- uptake capacity (~1 order of magnitude) at said environmental conditions. In fact, the difference in the nutrient uptake behaviour is not unexpected as in a previous study,[21] the

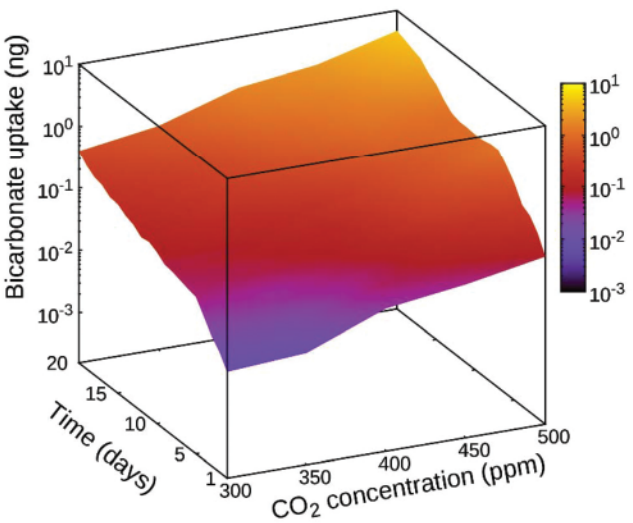

Fig. 2 Quantification of HCO_3^- sequestered (in ng; log-scale) over time at different levels of atmospheric CO_2 by *N. oculata* species within the artificial ecosystem.

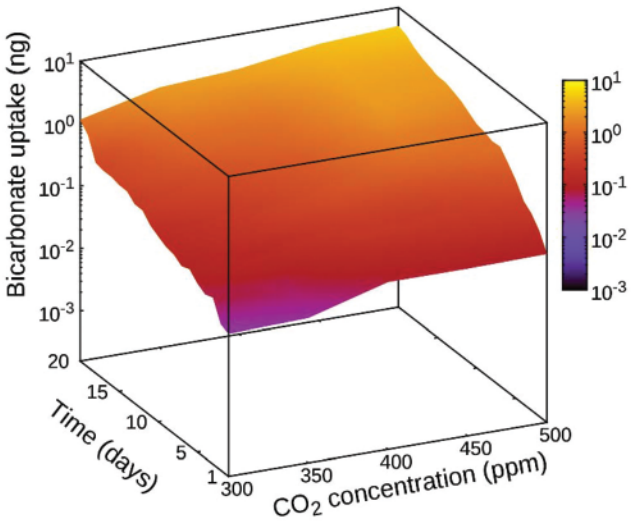

Fig. 3 Quantification of the combined HCO_3^- sequestration (in ng; log-scale) by *D. salina* and *N. oculata* over time at different levels of atmospheric CO_2.

maximum bicarbonate uptake rate for species *D. salina* were determined to be significantly higher than that of *N. oculata* (Fig. 1 in ref. 21).

Fig. 3 shows the combined sequestration of both species in binary cultures. In such a competition situation, in which the species mutually modify their environment, the HCO_3^- uptake by both species combined were found to be similar to the uptake behaviour of *N. oculata* (Fig. 2). It is also evident that *D. salina*'s sequestration performance is more impacted by the competition. This competition effect modifies the species-dependent bicarbonate uptake characteristics, more dominantly for *D. salina*.[21] In a competing situation, the sequestration performance of species can apparently invert. This means that competition needs to be factored in when assessing phytoplankton-based CO_2-sequestration. This is also a strong indication that multi-species sequestration models need to be species-specific.

Conclusions

The CO_2 concentration in the atmosphere is continuously rising which is considered a source of global warming. Since marine microalgae counterbalance this greenhouse gas through photosynthesis-based carbon fixation, it is crucial to understand mechanisms that control this sequestration. This study quantitatively investigates microalgae-based CO_2 sequestration by means of a novel modeling technique. This modeling approach is based on describing CO_2 dissolution out of the atmosphere into bodies of water where it forms HCO_3^-. This HCO_3^- is transported to phytoplankton cells which utilize it as a nutrient for biomass production. It was found that this utilization is highly species-specific. Furthermore, real-world ecosystems contain multiple species which compete for this common nutrient source. Therefore, studying phytoplankton-based CO_2 sequestration should consider the species composition in an ecosystem. For example, when cultured by itself, *D. salina* sequesters more HCO_3^- out of an environment than *N. oculata*. However, when both species compete for HCO_3^-, competition effects invert the sequestration capabilities of both species. Moreover, the overall quantities of fixed carbon drops considerably a fact that will require further studies. It has also been found that an increasing CO_2 concentration in the atmosphere results in a higher quantity of resulting biomass. This is indication that phytoplankton does counterbalance to a certain extent increased releases of this greenhouse gas.

Conflicts of interest

There are no conflicts to declare.

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