Biological carbon pump revisited: Feedback mechanisms between climate and the Redfield ratio

Anne Willem Omta,[1] Jorn Bruggeman,[1] S. A. L. M. Kooijman,[1] and Henk A. Dijkstra[2]

[1]   Biological activity gives rise to a difference in carbon concentration between the ocean surface and the deep waters. This difference is determined by the carbon:nutrient ratio of the sinking organic material and it is crucial in determining the distribution of CO_2 between the atmosphere and the ocean. For this reason, it is interesting to determine whether the physical environment affects the carbon:nitrogen ratio of phytoplankton. Using a model with a novel representation of the effect of temperature on phytoplankton stoichiometry, we have investigated the influence of mixed-layer depth and water temperature on the elemental composition of an algal community. In the light-limited regime, the carbon:nutrient ratio turns out to decrease with increasing mixed-layer depth and temperature. Hence our model suggests the existence of a positive feedback between temperature and atmospheric CO_2 content through the stoichiometry of phytoplankton. This feedback may have contributed to the glacial/interglacial cycles in the atmospheric CO_2 concentration. **Citation:** Omta, A. W., J. Bruggeman, S. A. L. M. Kooijman, and H. A. Dijkstra (2006), Biological carbon pump revisited: Feedback mechanisms between climate and the Redfield ratio, *Geophys. Res. Lett.*, *33*, L14613, doi:10.1029/2006GL026213.

1.   Introduction

[2]   It has been almost 30 years since ice core measurements first revealed that the concentration of carbon dioxide in the atmosphere has been varying in step with glacial/interglacial cycles [*Berner et al.*, 1979]. However, there is yet no explanation for these glacial/interglacial CO_2 variations [*Kohfeld et al.*, 2005]. Several studies explain the variations by changes in oceanic primary productivity and subsequent sedimentation of organic carbon. One proposed mechanism [*Martin*, 1990] invokes enhanced iron fertilisation of the Southern Ocean resulting from increased dust deposition, a consequence of a drier and colder climate. Other proposed mechanisms include a decreased release of carbon dioxide from the Southern Ocean because of enhanced stratification [*François et al.*, 1997], shifts in dominant plankton types [*Archer and Maier-Reimer*, 1994], and changes in the ocean pH through shifts in $CaCO_3$ concentration of the ocean [*Archer et al.*, 2000].

[3]   [*Broecker*, 1982] brought forward the hypothesis that the excess CO_2 was stored in the deep ocean during the Ice Ages. He noticed that the growth, sinking and remineralisation of phytoplankton give rise to a difference in carbon concentration between the ocean surface and the deep waters. This difference can be explained by assuming a dynamic equilibrium between sinking of organic material and upward diffusion of inorganic carbon and nutrients. It was given the name 'soft-tissue carbon pump' by [*Volk and Hoffert*, 1985] and it is proportional to the difference in nutrient concentration between the deep and the surface ocean:

$$\Delta C = R\Delta N \qquad (1)$$

with ΔC the difference in inorganic carbon concentration between the deep and the surface ocean, R the carbon:nutrient (Redfield) ratio of the biota, and ΔN the difference in DIN concentration between the deep and the surface ocean. Based on this concept, Broecker argued that the biota control the partitioning of carbon between the atmosphere and the deep sea through their carbon:nutrient ratio. He then went on to calculate that the Redfield ratio should have been 30% higher during glacial times than during interglacials to explain the low glacial atmospheric carbon concentrations. However, Broecker did not provide any biological explanation for a variation of the Redfield ratio in step with the glacial/interglacial cycles.

[4]   In this paper, we will address novel biological mechanisms for such variations of the Redfield ratio. Using our PINC (Phytoplankton Internal Nitrogen and Carbon) model, we have studied the influence of water temperature and mixed-layer depth on phytoplankton carbon:nutrient ratios. These ratios turn out to be strongly dependent on variations in mixed-layer depth and to increase with decreasing temperature. This key mechanism may turn out to be important to understand CO_2 changes during glacial-interglacial transitions. The classical NPZD model [*Fasham et al.*, 1990] takes phytoplankton composition fixed, and hence cannot represent our proposed mechanism.

2.   PINC Model

[5]   We have based our PINC model (inspired by the earlier mixotroph model of [*Kooijman et al.*, 2002]) on the Dynamic Energy Budget (DEB) theory [*Kooijman*, 2000]. DEB theory is a modelling framework for individual organisms based on first principles. It deals with both energy and stoichiometry, and with populations as sets of interacting individuals. A cornerstone of the theory is the partitioning of total biomass into structural mass and one or several reserves. We apply this principle to distinguish three components with different elemental compositions within the phytoplankton: structural mass (consisting of carbon and

[1]Department of Theoretical Life Sciences, Faculty of Earth and Life Sciences, Vrije Universiteit, Amsterdam, Netherlands.
[2]Institute for Marine and Atmospheric Research Utrecht (IMAU), Department of Physics and Astronomy, Universiteit Utrecht, Utrecht, Netherlands.
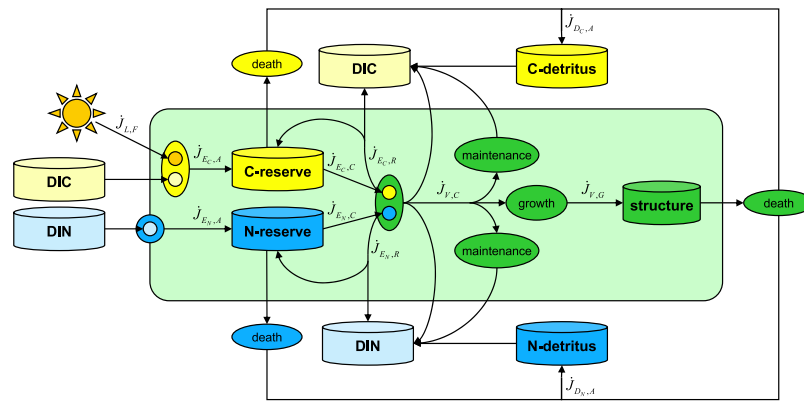
Figure 1. A schematic depiction of the PINC model organism; the organisms need DIC and light to form C-reserve; only DIN is needed to form N-reserve. The dead organic material is divided into N-detritus and C-detritus which remineralise into DIN and DIC respectively.

nitrogen in a fixed 10:1 ratio), an organic carbon reserve (consisting of carbon only), and a nitrogen reserve (consisting of nitrogen only). The relative amounts of reserves affect the C:N ratio of the organisms. Mortality is implemented as a death rate that is constant in time. This may be thought of as natural mortality in combination with a parameterisation of grazing by zooplankton. Mortality differs from maintenance in the sense that dead biomass becomes part of detritus, rather than being remineralised instantaneously. The detritus sinks into the deep sea; to close the carbon cycle, we impose a simple constant turnover of detritus. This might be interpreted as mineralisation of detritus by some constant background population of bacteria. The model organism is schematically depicted in Figure 1; a full description can be found in the auxiliary material.[1]

[6] Since most biological reactions are thermally activated, the rates of most biological processes have an Arrhenius-like temperature dependence. Therefore, we multiplied all the physiological rates with the same Arrhenius factor. This seems justified, because various physiological processes (i.e., reproduction, ingestion, growth, and aging) of organisms, for example of Daphnia Magna [*Kooijman et al.*, 1989], have been shown to have approximately the same activation energy. However, the temperature dependence of photosynthesis only exhibits Arrhenius behaviour at high light intensities whereas the rate of photosynthesis is almost insensitive to temperature at low light intensities (see e.g. [*Maxwell et al.*, 1994; *Allewalt et al.*, 2006]). This can be understood from the fact that photosynthesis consists of light and dark reaction steps [*Warburg*, 1925]. To obtain the desired temperature dependence of photosynthesis in the low-irradiance limit, we also multiplied the saturation light flux with the Arrhenius factor.

3. Results and Discussion

[7] To investigate the effect of mixed-layer depth and of temperature on the stoichiometry of phytoplankton, we have modelled the population in a steady mixed layer (without a seasonal cycle) for six different values of the mixed-layer depth H_m: 0, 25, 50, 75, 100, and 150 m, and at each of the mixed-layer depths, for four different temperatures: 10°C, 15°C, 20°C, and 25°C, with the PINC parameter values listed in Table 1. The results were obtained after 25 simulation years. At this point in time, the DIC and DIN distributions have not yet reached equilibrium, because diffusion is very slow below the mixed layer, but the plankton concentration and stoichiometry are in equilibrium. The structural biomass concentrations are a few μM which compares well with plankton concentrations that are typically observed at the surface of the open ocean [*Falkowski et al.*, 2003].

[8] The plankton C:N ratio generally increases with decreasing mixed-layer depth [*Diehl et al.*, 2005] and with decreasing temperature (Figure 2), except in the range of very shallow mixed layers, where the reverse trends are seen. The relationship between mixed-layer depth and stoichiometry emerges, because the uptake of inorganic carbon into the carbohydrate reserve strongly depends on light availability. If the mixed layer is very thick, the plankton spends a large amount of time in relatively deep water, where there is little light and carbon uptake is slow. This leads to a low C:N ratio of the organic matter. Given a certain mixed-layer depth, the plankton receives the same amount of light at each temperature. Except in the range of very shallow mixed layers, the irradiance is so low that the photosynthesis rate is almost independent of temperature, while the rates of other processes such as nitrate assimilation and growth increase with increasing temperature. This means that the ratios of the carbon uptake to the nitrate uptake and to the carbon use for growth increase with decreasing temperature. Therefore the damming up of carbohydrate reserves is larger at lower temperatures and hence the C:N ratio of the organic matter decreases with increasing temperature.

[9] GCM simulations [*Shin et al.*, 2003; *Otto-Bliesner et al.*, 2003] suggest that during the Ice Ages, the mixed layer was generally thicker which, according to our model results, has the effect of lowering the carbon:nitrogen ratio of phytoplankton, but the SST were lower than today which should have the opposite effect. According to Broecker's calculation, the C:N ratio should have been 30% higher during glacial times to account for the lower atmospheric

---

[1]Auxiliary materials are available at ftp://ftp.agu.org/apend/2006gl026213.

Table 1. Model Organism Parameter Values; Values at 15°C for Temperature-Dependent Parameters

Parameter	Interpretation	Dimension	Value
$n_{N,V}$	N-content of structure	mole N/mole C	0.1
$\dot{j}_{EC,Am}$	max. C uptake	d^{-1}	2.5
K_C	sat. const. C uptake	μM C	500
$\dot{J}_{L,FK}$	sat. light flux	mole/(m^2 day)	25
$\dot{J}_{L,F}$	light flux	mole/(m^2 day)	$50*e^{\frac{z}{d}}$
d	extinction length	m	14
$\dot{j}_{EN,Am}$	max. N uptake	mole N/(mole C*d)	0.25
K_N	sat. const. N uptake	μM N	0.1
$y_{E_C,V}$	mole C reserve required per mole structure	−	1.5
$y_{E_N,V}$	mole N reserve required per mole structure	mole N/mole C	0.15
$\dot{k}_E$	reserve turnover	d^{-1}	4.0
$\dot{k}_M$	maintenance rate	d^{-1}	0.1
$\dot{h}_V$	death rate	d^{-1}	0.1
κ	fraction of excess reserve flux fed back into reserve	−	0.9
$\dot{h}_D$	detritus decay rate	d^{-1}	0.1
$T_{Arr} \left(= \frac{E_a}{k} \right)$	Arrhenius temperature	K	12500
w_S	sinking velocity detritus	m/day	10
$K(z < H_m)$	diffusion constant below mixed layer	m^2/day	1
$K(z > H_m)$	diffusion constant within mixed layer	m^2/day	10000

CO_2 concentrations. To obtain an estimate of the direction and of the order of magnitude of the difference in the algal stoichiometry between glacial and interglacial periods, we used data from the CCSM model [*Shin et al.*, 2003] to model our phytoplankton population with glacial SST and mixed-layer depths and with pre-industrial SST and mixed-layer depths. We divided the world ocean into six zonal boxes (50°S–40°–30°S–15°S–15°N–30°N–40°N–50°N) and we calculated the LGM and the pre-industrial C:N ratios in each of these boxes (see Table 2). With the standard PINC parameters, the LGM C:N ratios are between 2.4% (40°N–50°N) and 33% (15°N–30°N) higher than pre-industrial C:N ratios. If we weigh the contribution of each box with the ocean area within it, we obtain an average value of 12%. Hence, our model results indicate that the combined effect of the shallower mixed layers and lower SST is a significantly higher C:N ratio. Our predicted low-latitude pre-industrial C:N ratios are quite close to the stoichiometry of the organic material collected from sediment traps across the world ocean [*Schneider et al.*, 2003]. However, our prediction of an increase of the C:N ratio with latitude is not observed in the sediment traps.

[10] There have been a number of experimental studies about the effect of temperature on algal stoichiometry. These studies were reviewed recently by [*Woods et al.*, 2003]. In many cases, the C:N ratio turned out to increase with increasing temperature which seems to contradict our hypothesis of a decrease of the C:N ratio with increasing temperature in the low-irradiance range. However, these studies were usually performed under high light intensities. We retrieved one empirical study in which the effect of both light intensity and temperature on the stoichiometry of an alga, the red seaweed Gracilaria Tikvahiae, were investigated in a systematic way. The experimental results show a decrease of the C:N ratio with decreasing temperature at high light intensities, but an increase with decreasing temperature in the range of low light intensities [*Lapointe et al.*, 1984, Figure 2] which is consistent with our model predictions. However, this result was obtained for a macro-alga and thus it may not be entirely applicable to microscopic phytoplankton which provides the majority of primary productivity in the ocean. As far as we are aware,

such studies have not been performed with microphytoplankton. Therefore, we feel that an experimental test of our predictions regarding the relationship between irradiance and temperature on the one hand, and microphytoplankton stoichiometry on the other hand, is urgently required.

[11] A stronger biological carbon pump tends to generate increased anoxia at depth, while the observations do not support wide-spread anoxia during glacial times, because sedimentation of organic carbon on the seafloor does not seem to have been much higher during glacial times than today [*Kohfeld et al.*, 2005]. However, the glacial extent of anoxia may have been reduced by an acceleration in the ventilation of the thermocline. In fact, both observational evidence [*Slowey and Curry*, 1992; *Hall and Chan*, 2004] and simulation results [*Archer et al.*, 2000; *Liu et al.*, 2002] suggest an enhanced ventilation of the thermocline during glacial times.

[12] Recently, there has been progress in the development of models that describe variations in algal stoichiometry as a consequence of physiological acclimation and adaptation [*Geider et al.*, 1998; *Klausmeier et al.*, 2004], although often some arbitrary assumptions were made with respect to trade-offs. Nevertheless, physiological acclimation and adaptation do probably have an important influence on the stoichiometry of phytoplankton and hence we think that a
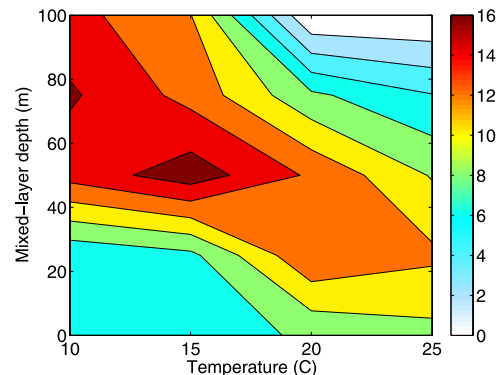

Figure 2. Carbon:nutrient ratio of detritus 30 m below the mixed layer as a function of H_m and temperature.

Table 2. Last Glacial Maximum and Pre-Industrial Values of Average H_m (in m), Average Sea Surface Temperature (in °C), and R for Different Zones on the Globe, Obtained From the CCSM

	50–40°S	40–30°S	30–15°S	15°S–15°N	15–30°N	30–40°N	40–50°N
H_m (LGM)	115	75	69	50	75	72	70
H_m (pre-ind.)	105	70	64	52	65	70	60
SST (LGM)	4	14	21	24	21.5	13	4
SST (pre-ind.)	7	16.5	23	26	23	17	8
R (LGM)	12.2	11.1	8.9	10.4	10.9	11.7	12.6
R (pre-ind.)	11.8	10.3	8.2	8.9	8.2	10.1	12.3

combination of this approach with ours would be a next step to understand the role of variations in plankton stoichiometry in glacial cycles.

References

Allewalt, J. P., M. M. Bateson, N. P. Revsbech, K. Slack, and D. M. Ward (2006), Effect of temperature and light on growth of and photosynthesis by synechococcus isolates typical of those predominating in the octopus spring microbial mat community of yellowstone national park, *Appl. Environ. Microbiol.*, *72*, 544–550.

Archer, D. E., and E. Maier-Reimer (1994), Effect of deep-sea sedimentary calcite preservation on atmospheric CO_2 concentration, *Nature*, *367*, 260–264.

Archer, D., A. Winguth, D. Lea, and N. Mahowald (2000), What caused the glacial/interglacial atmospheric pCO_2 cycles?, *Rev. Geophys.*, *38*, 159–189.

Berner, W., B. Stouffer, and H. Oeschger (1979), Past atmospheric composition and climate, gas parameters measured on ice cores, *Nature*, *275*, 53–55.

Broecker, W. S. (1982), Ocean geochemistry during glacial time, *Geochim. Cosmochim. Acta*, *46*, 1689–1705.

Diehl, S., S. Berger, and R. Wörhl (2005), Flexible algal nutrient stoichiometry mediates environmental influences on phytoplankton and its abiotic resources, *Ecology*, *6*, 2931–2945.

Falkowski, P. G., E. A. Laws, R. T. Barber, and J. W. Murray (2003), Phytoplankton and their role in primary, new, and export production, in *Ocean Biogeochemistry*, edited by M. J. R. Fasham, Springer, New York.

Fasham, M. J. R., H. W. Ducklow, and S. M. McKelvie (1990), A nitrogen-based model of plankton dynamics in the oceanic mixed layer, *J. Mar. Res.*, *48*, 591–639.

François, R., M. A. Altabet, E.-F. Yu, D. M. Sigman, M. P. Bacon, M. Frank, G. Bohrmann, G. Bareille, and L. D. Labeyrie (1997), Contribution of southern ocean surface-water stratification to low atmospheric CO_2 concentrations during the last glacial period, *Nature*, *389*, 929–936.

Geider, R. J., H. L. MacIntyre, and T. M. Kana (1998), A dynamic regulatory model of phytoplankton acclimation to light, nutrients, and temperature, *Limnol. Oceanogr.*, *43*, 679–694.

Hall, J. M., and L. H. Chan (2004), Ba/Ca in benthic foraminifera: Thermocline and middepth circulation in the North Atlantic during the last glaciation, *Paleoceanography*, *19*, PA4018, doi:10.1029/2004PA001028.

Klausmeier, C. A., E. Litchman, T. Daufresne, and S. A. Levin (2004), Optimal nitrogen-to-phosphorus stoichiometry of phytoplankton, *Nature*, *429*, 171–174.

Kohfeld, K. E., C. le Quéré, S. P. Harrison, and R. F. Anderson (2005), Role of marine biology in glacial-interglacial CO_2 cycles, *Science*, *308*, 74–78.

Kooijman, S. A. L. M. (2000), *Dynamic Energy and Mass Budgets in Biological Systems*, Cambridge Univ. Press, New York.

Kooijman, S. A. L. M., N. van der Hoeven, and D. C. van der Werf (1989), Population consequences of a physiological model for individuals, *Functional Ecol.*, *3*, 325–336.

Kooijman, S. A. L. M., H. A. Dijkstra, and B. W. Kooi (2002), Light–induced mass turnover in a mono–species community of mixotrophs, *J. Theor. Biol.*, *214*, 233–254.

Lapointe, B. E., C. J. Dawes, and K. R. Tenore (1984), Interactions between light and temperature on the physiological ecology of gracilaria tikvahiae (gigartinales, rhodophyta) 2. Nitrate uptake and levels of pigments and chemical constituents, *Mar. Biol.*, *80*, 171–178.

Liu, Z., S. Shin, B. Otto-Bliesner, J. E. Kutzbach, E. C. Brady, and D. Lee (2002), Tropical cooling at the last glacial maximum and extratropical ocean ventilation, *Geophys. Res. Lett.*, *29*(10), 1409, doi:10.1029/2001GL013938.

Martin, J. (1990), Glacial-interglacial CO_2 change: The iron hypothesis, *Paleoceanography*, *5*, 1–13.

Maxwell, D. P., S. Falk, C. G. Trick, and N. P. A. Huner (1994), Growth at low temperature mimics high-light acclimation in chlorella vulgaris, *Plant Physiol.*, *105*, 535–543.

Otto-Bliesner, B. L., E. C. Brady, S. Shin, Z. Liu, and C. Shields (2003), Modeling El Niño and its tropical teleconnections during the last glacial-interglacial cycle, *Geophys. Res. Lett.*, *30*(23), 2198, doi:10.1029/2003GL018553.

Schneider, B., R. Schlitzer, G. Fischer, and E. M. Nöthig (2003), Depth-dependent elemental compositions of particulate organic matter (POM) in the ocean, *Global Biogeochem. Cycles*, *17*(2), 1032, doi:10.1029/2002GB001871.

Shin, S. I., Z. Liu, B. Otto-Bliesner, E. C. Brady, J. E. Kutzbach, and S. P. Harrison (2003), A simulation of the last glacial maximum using the NCAR-CCSM, *Clim. Dyn.*, *20*, 127–151.

Slowey, N. C., and W. B. Curry (1992), Enhanced ventilation of the North-Atlantic subtropical gyre thermocline during the last glaciation, *Nature*, *358*, 665–668.

Volk, T., and M. I. Hoffert (1985), Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO_2, in *The Carbon Cycle and Atmospheric CO_2: Natural Variations Archean to Present*, edited by E. T. Sundquist and W. S. Broecker, pp. 99–110, AGU, Washington D. C.

Warburg, O. (1925), Versuche über kohlensäureassimilation, *Naturwissenschaften*, *49/50*, 985–993.

Woods, H. A., W. Makino, J. B. Hotner, S. Hobbie, J. F. Harrison, K. Acharya, and J. J. Elser (2003), Temperature and the chemical composition of poikilothermic organisms, *Functional Ecol.*, *17*, 237–245.

———————————

J. Bruggeman, S. A. L. M. Kooijman, and A. W. Omta, Department of Theoretical Life Sciences, Faculty of Earth and Life Sciences, Vrije Universiteit, De Boelelaan 1087, NL-1081 HV Amsterdam, Netherlands. (anne.willem. omta@falw.vu.nl)

H. A. Dijkstra, Institute for Marine and Atmospheric Research Utrecht (IMAU), Department of Physics and Astronomy, Universiteit Utrecht, Princetonplein 5, NL-3582 CC Utrecht, Netherlands.