

EarthArXiv

May 25, 2024

Dear EarthArXiv Editors,

We are submitting our manuscript, "Phytoplankton variable stoichiometry modifies key biogeochemical fluxes and the functioning of the biological pump" by Nicola A. Wiseman, J. Keith Moore, Adam C. Martiny, and Robert Letscher, for publication as a research article in *Science Advances*. We are therefore additionally submitting the manuscript to EarthArXiv as a non-peer reviewed preprint.

The **Redfield Ratio**, a key oceanographic paradigm for more than 50 years, suggests that the elemental ratios of phytoplankton stoichiometry are static, at fixed proportions of Carbon/Nitrogen/Phosphorus/Iron/Silicon. However, field observations over the last decade have shown that the elemental composition of phytoplankton is quite dynamic, with large-scale patterns linked to nutrient availability, whereby phytoplankton reduce their cellular quotas (relative to carbon, nutrient/C ratios) when ambient concentrations are low (Martiny et al., 2013; Wang et al., 2019; Wiseman et al., 2023). Our model is the first to include realistic ranges for cellular quotas (based on fieldwork) for each of the key growth-limiting nutrients in the oceans (N, P, Si, and Fe). We investigate the impacts of including dynamic elemental uptake ratios for phytoplankton on global biogeochemical cycles, including ocean carbon uptake and storage using a state-of-the-art earth system model, the Community Earth System Model (CESM).

Our results demonstrate that accounting for **dynamic plankton stoichiometry significantly modifies the marine nitrogen cycle fluxes and the magnitude and spatial patterns of carbon export from surface waters by the ocean biological pump**. The biological pump strongly impacts climate by modifying surface carbon concentrations and modifying air-sea CO₂ fluxes. Thus, Earth System Models (ESMs) must incorporate dynamic stoichiometry to avoid biasing future climate projections.

We do not have any conflicts of interest to report. All authors have approved the manuscript and agree with its submission to *Science Advances*. The model output is under School of Geographical Sciences, University of Bristol University Rd, Bristol, BS8 1SS +44 77690 67629 nicola.wiseman@bristol.ac.uk



curation at Dryad and will be made available as netCDF files for both simulations from the manuscript, as well as a github repository containing corresponding analysis scripts upon review.

Yours sincerely

Dr. Nicola A. Wiseman **Senior Research Associate**

Martiny, A. C. *et al.* Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter. *Nat. Geosci.* **6**, 279–283 (2013).

Wang, W.-L., Moore, J. K., Martiny, A. C. & Primeau, F. W. Convergent estimates of marine nitrogen fixation. *Nature* **566**, 205–211 (2019).

Wiseman, N. A., Moore, J. K., Twining, B. S., Hamilton, D. S. & Mahowald, N. M. Acclimation of phytoplankton Fe:C ratios dampens the biogeochemical response to varying atmospheric deposition of soluble iron. *Global Biogeochem. Cycles* (2023) doi:10.1029/2022gb007491

School of Geographical Sciences, University of Bristol University Rd, Bristol, BS8 1SS +44 77690 67629 nicola.wiseman@bristol.ac.uk

Title: Phytoplankton variable stoichiometry modifies key biogeochemical fluxes and the functioning of the ocean biological pump

Authors: Nicola A. Wiseman^{1,2}*†, J. Keith Moore¹, Adam C. Martiny¹, Robert Letscher³

Affiliations:

5

10

¹Department of Earth System Science, University of California Irvine; Irvine, 92697, California, USA

²Bristol Research Initiative for the Dynamic Global Environment (BRIDGE), School of Geographical Sciences, University of Bristol; Bristol, BS8 1SS, United Kingdom

³Earth Sciences and Ocean Process Analysis Laboratory, University of New Hampshire; Durham, 03824,New Hampshire, USA

*Corresponding author. Email: nicola.wiseman@bristol.ac.uk

†Present address: Bristol Research Initiative for the Dynamic Global Environment (BRIDGE), School of Geographical Sciences, University of Bristol, Bristol, United Kingdom

Abstract: Ocean biota absorb carbon at the surface and export some to the ocean interior via the biological pump, affecting surface carbon, air-sea CO₂ exchange, and climate. Marine phytoplankton growth is often limited by nutrients (nitrogen, phosphorus, iron, silicon). The efficiency of carbon export is therefore constrained by nutrient availability and the nutrient/carbon ratios in the biota (stoichiometry). Field observations suggest widespread variability in phytoplankton stoichiometry (C/N/P/Fe/Si). Incorporating variable stoichiometry in marine biogeochemical models alters the magnitude and spatial patterns of carbon export by the biological pump and key nitrogen cycle fluxes, while fixed-stoichiometry models underestimate ocean carbon uptake and overestimate atmospheric CO₂. Thus, Earth System Models need to include dynamic plankton stoichiometry to enable more accurate projections of the carbon cycle and climate.

5

10

15

20

25

The biological pump plays a key role in the global carbon cycle, driving ocean uptake of atmospheric carbon dioxide (CO_2) (1). Phytoplankton take up CO_2 and nutrients, converting them to biomass via photosynthesis. Some of this fixed carbon is exported to the ocean interior, lowering surface concentrations, and modifying air-sea exchange. The efficiency of carbon export is dependent on the surface flux, the depth of remineralization, and the time for the carbon to be transported back to the surface via circulation (2-4). These processes are sensitive to climate change, but the direction and magnitude of the sensitivity is poorly understood. For example, increases in sea surface temperatures lead to increased stratification in the surface ocean, which can reduce nutrient supply and therefore reduce phytoplankton productivity, but warming also potentially increases the rates of metabolic processes including phytoplankton growth (5–8). There are many compounding interactions associated with such processes, tied to changes in temperature and nutrient availability, and the global impacts of these changes on the biological pump on longer timescales are poorly constrained. Ocean uptake of CO2 will strongly impact climate on multi-century timescales (4,7,8).

Phytoplankton growth is primarily limited by nutrient availability. The ratio of carbon to nutrients in exported organic matter was used in models to simplify biogeochemical cycles, where a fixed, extended Redfield ratio was used to link the cycling of carbon and key growthlimiting nutrients, including nitrogen, phosphorus, iron, and silicon (C/N/P/Fe/Si). However, it is now widely accepted that phytoplankton elemental ratios are not fixed, modulating the efficacy of the biological export of carbon with respect to limiting nutrients (9–13). Field measurements of particulate organic matter (POM) find elevated C/N and C/P ratios in the oligotrophic gyres where nutrients are low (14). C/P ratios can vary by more than a factor of two, with the lowest values observed in the Southern Ocean (significantly below Redfield C/P <80 mol/mol), while the highest values are found in the western North Atlantic, exceeding 200 mol/mol (14). C/N variability is much smaller, with low values of ~5 mol/mol in the Southern Ocean, and highest values in the Indian Ocean (>8 mol/mol) (14).

One study of variable C/N in a steady state ocean model found using a fixed C/N underestimated total dissolved inorganic carbon inventory and ocean pCO₂ uptake, while using a variable C/N parameterization in a prognostic climate scenario yielded greater anthropogenic CO₂ uptake (15). Another highlighted the spatial and temporal variability of phytoplankton C/N 30 ratios for a single phytoplankton class, and proposed that this variability may help buffer decreases in carbon exported due to increased oligotrophy by compensation increases in the C/N ratio (16). Another study with variable C/N/P/Fe/Si in the PISCES-QUOTA model found that fixed stoichiometry (Fe and Si still variable) underestimated total 21st century ocean carbon uptake by 0.5-3.5%, and that picophytoplankton stocks did not decline as much as other 35 phytoplankton, due to their greater stoichiometric flexibility, highlighting the importance of variable stoichiometry for predicting changes in marine biodiversity (17). An additional study with PISCES-QUOTA focused on changes within the biological community, particularly phytoplankton and zooplankton biomass to investigate trophic amplification (18). Other studies utilizing variable phytoplankton C/N/P ratios found that including dynamic ocean biology 40 reduces the sensitivity of biogeochemical cycling to changes in ocean physics (19,20). Kwon et al. showed that CMIP6 models that included flexible C/N/P/Fe ratios projected small increases in net primary productivity (NPP) compared to fixed ratio models which showed decreases (21). Another study focused on iron cycling in the Pacific found strong links between iron limitation and net primary productivity, and highlighted the uncertainty that Fe/C stoichiometry plays in this response (22).

While previous studies focused on aspects of C/N/P/Fe/Si stoichiometry or their impacts on trophic interactions, none have explicitly investigated the impacts of fully variable versus fully fixed stoichiometry on global marine biogeochemical fluxes, particularly the carbon and nitrogen cycles. We hypothesize that variable stoichiometry will increase productivity and export in many regions, as phytoplankton acclimate to low nutrient availability by reducing their cellular quotas. Using fixed nutrient/carbon ratios also means that more nutrients will be exported per unit carbon in areas with high nutrient supply, potentially decreasing lateral nutrient transport to adjacent regions. Thus, there are downstream effects and complex nutrient interactions, leading to uncertainty about the impacts of varying phytoplankton stoichiometry. Earth System Models (ESMs) are valuable tools for investigating these complex, interacting processes.

The Community Earth System Model (CESM) includes an ocean ecosystem with three explicit phytoplankton groups: diatoms, pico-nanophytoplankton (a fraction of which acts as an implicit calcifier group, referred to collectively as "small phytoplankton" hereafter), and diazotrophs, all with variable nutrient quotas for phosphorus, iron, and silicon (*23–25*). The model was recently updated to include greater variability in phytoplankton iron quotas, with an improved match to observations (*23*). Here, we integrated a variable nitrogen quota, allowing for dynamic computation of phytoplankton C/N/P/Fe/Si ratios, as phytoplankton acclimate to changing ambient nutrient concentrations. For each nutrient, the cellular quota (nutrient/carbon ratio) for new growth is a function of ambient nutrient concentrations, with progressive reduction in cellular quotas as nutrient concentrations decline (Materials and Methods, fig. S1).

Results

Prior inverse model studies have inferred the stoichiometry of exported organic matter from observed nutrient distributions, in conjunction with an inverse biogeochemical model and a data-constrained ocean circulation (Fig. 1) (26,27). Inverse model studies constrained by the observed nutrient distributions diagnose elevated export C/P ratios (> 140) and N/P ratios (> 20) in the subtropical gyres, and lower ratios of C/P (< 100) and N/P (< 16) in regions with elevated surface phosphate concentrations (> 0.3 μ M), in agreement with field observations of particulate organic matter stoichiometry (26,27).

30

35

40

5

10

15

20

The GO-POPCORNv2 dataset is a global database of in situ surface Particulate Organic Matter (POM) C/N/P stoichiometry, with sampling primarily in the subtropical gyres (*28*). The bulk POM *in situ* measurements would include contributions from heterotrophic bacteria and non-sinking detrital particles, which are not included in our model. There is considerable variability in the observations, but clear trends of increasing nutrient/carbon ratios as ambient nutrient concentration decline within the gyres (Fig. 2, figs. S2-S3) (*28*). CESM and the inverse models capture the observed trends in stoichiometry as a function of nutrient concentration (Fig. 2, Figs. S2-S3). CESM has previously been tuned to capture variations of phytoplankton cellular Fe/C (*23*). Limited observations make evaluating the Si/C ratios more difficult. The model captures the observed patterns of elevated Si/C in iron-limited regions with elevated surface dSi concentrations, and the low Si/C seen under low Si conditions both in situ and in laboratory studies (*29–31*). Thus, our simple approach, dynamically linking phytoplankton stoichiometry of exported organic matter.

45 We compare our variable C/N/P/Fe/Si model simulation (VarAll) with a fixed-ratio 45 model version (FixAll) to investigate how dynamic plankton stoichiometry influences marine

biogeochemistry, in terms of the magnitude and spatial patterns of net primary production, sinking carbon export at 100m depth, air-sea CO2 flux, nitrogen fixation, and water column denitrification. Both models are able to replicate observations of surface nutrients, with a better fit for the VarAll simulation. Compared to World Ocean Atlas 2018, the r_s for VarAll and surface NO₃, PO₄, and SiO₃ are 0.89, 0.90, and 0.60, respectively. For FixAll, these values are 0.86, 0.91, and 0.33 respectively (*32*). For dissolved iron, we compare primarily to data collected from the GEOTRACES project, supplemented with historical data compilations (*33–35*). The r_s for dissolved iron in the top 200m is 0.43 for the VarAll model and 0.35 for the FixAll model.

5

10

15

30

35

40

The models have similar net primary production (NPP), but the FixAll simulation significantly underestimates particulate organic carbon (POC) export and key nitrogen cycle fluxes (N fixation and water-column (WC) denitrification) compared to the fully variable simulation (Figs. 3A-B, 4). The VarAll model has a total integrated NPP of 64.6 PgC/yr, POC Export at 100m of 7.6 PgC/yr, N fixation of 225 TgN/yr, and WC Denitrification of 95 TgN/yr, which are close to or within the range of previous satellite and model-based estimates (NPP = 52-67 PgC/yr, POC Export = 5-10 PgC/yr, N Fixation = 126-223 TgN/yr, WC Denitrification = 56-73 TgN/yr) (*27*,36–39). With fixed stoichiometry, NPP, POC Export, N Fixation, and WC denitrification decrease by 12%, 8%, 20%, and 17%, respectively (FixAll global fluxes: 56.9 PgC/yr, 7.0 PgC/yr, 179 TgN/yr).

The global export ratio (e-ratio, sinking POC/NPP at 100m) distribution in the VarAll model (fig. S4) shows higher e-ratios in the high latitudes, >0.075 in the Southern Ocean and >0.10 in the sub-polar North Atlantic and North Pacific. When compared to the FixAll model, the VarAll model has up to 0.02 increase in e-ratio in the high latitude North Atlantic, compared to up to a 0.05 decrease in the Southern Ocean, both of which are primarily driven by changes in POC export. In the Indian Ocean, which has increases in NPP and POC export throughout the basin, the e-ratio ratio change shows a bimodal pattern, with the Arabian Sea and gyre regions showing increases in e-ratio, while in the Laccadive Sea region (just south of India) the e-ratio decreases.

The lower POC export in the FixAll model is driven by lower surface nutrient concentrations, but is further enhanced by a community dominated by small phytoplankton in the more oligotrophic regions (fig. S5). When phytoplankton nutrient uptake ratios are fixed, growth-limiting nutrients are exported more efficiently, further increasing nutrient stress in surface waters, favoring smaller phytoplankton and leading to decreases in NPP and POC export. Further, with variable stoichiometry, small phytoplankton may out-compete diatoms within the HNLC regions, resulting in increased small phytoplankton biomass and reduced diatom biomass. This leads to the decrease in Southern Ocean POC export without significant changes in NPP. Additionally, diatoms require silicon and are highly sensitive to silicon availability, which causes them to have significant reductions in biomass in low Si areas (such as the oligotrophic gyres) in the FixAll case. (fig. S5B). The regions where diatoms have higher biomass in the FixAll case are upwelling regions where Si is returned to the surface and rapidly utilized (such as the Southern Ocean and sub-polar North Pacific). When diatoms can vary their Si uptake reducing their quotas, their distribution expands to occupy low-Si regions. This suggests that diatom Si/C acclimation is critical for explaining the global distribution of diatoms, preventing Si-limitation of growth over much of the lower latitudes.

 Nitrogen fixation and water column denitrification increase under variable stoichiometry
 (Fig. 4). Nitrogen fixation increases globally, up nearly 300%, but particularly in the Atlantic and Indian Ocean gyres where diazotrophs can reduce their quotas and maintain higher growth rates

(Fig. 4). With fixed ratios, surface phosphate declines in the North Atlantic and Indian basins and surface dissolved iron declines in the Pacific, increasing P and Fe stress for diazotrophs. Nitrogen fixation rates in the North Atlantic are particularly dependent on phosphate (40). WC denitrification decreases 17% with fixed stoichiometry, with little change in the spatial pattern, due to decreases in diatom production and export over the Bay of Bengal and in the eastern equatorial Pacific. The volume of low oxygen (<30 mmol/m³) waters decreases 23% with fixed stoichiometry.

Both models were run for 300 years with dynamic, single-box, atmospheric CO₂, initiated at 284ppm. Averaged over the final 20 years, the FixAll scenario had 303ppm atmospheric CO₂ concentration, while the VarAll scenario had 299ppm atmospheric CO₂, indicating modestly more efficient CO₂ uptake in the VarAll case over the simulation. The spatial pattern of the carbon export strongly impacts the sequestration time and ultimate climate impacts (3), in addition to the absolute magnitude of the flux.

Discussion

The phytoplankton stoichiometry model captures large-scale observed elemental stoichiometries. It is built on the frugal phytoplankton concept, whereby phytoplankton acclimate to increasing nutrient stress by decreasing the cellular quota of the nutrient (41). Applying this concept to all the growth-limiting nutrients, with prescribed minimum and maximum nutrient:carbon ratios, allows for dynamic phytoplankton stoichiometry tied to available nutrients, that captures the observed global patterns. The acclimation to low nutrient conditions (reducing quotas) strongly impacts marine biogeochemical cycles, increasing the strength and modifying the spatial patterns of carbon export by the biological pump.

The coupling of biogeochemical cycles is strongly influenced by variable phytoplankton stoichiometry. Although it is possible to reproduce surface nutrient and net primary productivity distributions with both models, the VarAll model utilizes additional observational constraints of POM and individual phytoplankton cell stoichiometric variability, not captured by the FixAll model. This highlights the importance of using multiple observational constraints to better capture complex interactions between the biogeochemical cycles.

The phytoplankton nutrient quotas are higher than the elemental ratios in the exported organic matter diagnosed with inverse models. This suggests substantial ecosystem processing of 30 organic matter produced by phytoplankton prior to export. In our model this is achieved by assuming zooplankton mortality is exported with a modified Redfield ratio, thus, both zooplankton and phytoplankton stoichiometry influences the elemental export ratios. Further research is needed on the stoichiometry of the biota and the processes contributing to ecosystemlevel processing of phytoplankton biomass. 35

While adding additional tracers to represent explicit nutrient pools for variable stoichiometry does add computational cost to an already computational expensive simulation, we hope that this work highlights some of the potential biases that may be occurring within Earth System models by using simplified or limited variable stoichiometry. Fixed ratio models will overestimate the declines in NPP and export with increasing stratification, with biases in the spatial patterns of carbon export. The fixed ratio models may also introduce significant biases in the ocean CO₂ inventory, with the ocean taking up less CO₂. Integrated nitrogen fixation and water column denitrification are also significantly lower in the FixAll model, which could lead to biases in bioavailable nitrogen, the primary limiting nutrient over much of the global ocean, also impacting the carbon cycle. Additionally, phytoplankton nutrient content is important for

5

10

20

15

25

40

simulating changes in biomass for upper trophic levels, which is of interest for communities focused on the climate change impacts of marine ecosystems, but also for fisheries projections, which may have significant socioeconomic implications. These results stress the need for Earth System Models to capture the complexities of the cycling of nitrogen, phosphorus, iron, and silicon in the oceans, as they all influence and modify the strength and spatial patterns of the biological pump and marine ecosystem dynamics.

References and Notes

- 1. Volk, T. & Hoffert, M. I. Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric CO2 changes. in *The Carbon Cycle and Atmospheric CO2 : Natural Variations Archean to Present* **32**, 99–110 (1985). doi:10.1029/GM032p0099
- 2. Liu, Y., Moore, J. K., Primeau, F. & Wang, W. L. Reduced CO2 uptake and growing nutrient sequestration from slowing overturning circulation. *Nat. Clim. Chang.* **13**, 83–90 (2022). doi:10.1038/s41558-022-01555-7
- 3. DeVries, T., Primeau, F. & Deutsch, C. The sequestration efficiency of the biological pump. *Geophys. Res. Lett.* **39**, L13601 (2012). doi:<u>10.1029/2012GL051963</u>
- 4. Kwon, E., Primeau, F. & Sarmiento, J. The impact of remineralization depth on the air–sea carbon balance. *Nat. Geosci.* **2**, 630–635 (2009). doi:10.1038/ngeo612
- 5. Moore, J. K. *et al.* Sustained climate warming drives declining marine biological productivity. *Science (1979)* **359**, 1139–1143 (2018). doi:10.1126/science.aao6379
 - 6. Passow, U. & Carlson, C. A. The biological pump in a high CO2 world. *Mar. Ecol. Prog. Ser.* **470**, 249–271 (2012). doi:10.3354/meps09985
 - Sarmento, H., Montoya, J. M., Vázquez-Domínguez, E., Vaqué, D. & Gasol, J. M. Warming effects on marine microbial food web processes: how far can we go when it comes to predictions? *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 365, 2137–2149 (2010). doi:10.1098/rstb.2010.0045
 - 8. Henson, S. A., Laufkötter, C., Leung, S., Giering, S. L., Palevsky, H. I., & Cavan, E. L. Uncertain response of ocean biological carbon export in a changing world. *Nat. Geosci.*, **15**, 248-254 (2022).
 - 9. Bruland, K. W., Donat, J. R. & Hutchins, D. A. Interactive influences of bioactive trace metals on biological production in oceanic waters. *Limnol. Oceanogr.* **36**, 1555–1577 (1991).
 - 10. Redfield, A. C., Ketchum, B. C. & Richards, F. A. The influence of organisms on the composition of sea water. in *The Sea* **2**, 26–77 (1963).
- 11. Martiny, A. C. *et al*. Strong latitudinal patterns in the elemental ratios of marine plankton and organic matter. *Nat. Geosci.* **6**, 279–283 (2013).
 - 12. Weber, T. S. & Deutsch, C. Ocean nutrient ratios governed by plankton biogeography. *Nature* **467**, 550–554 (2010).
 - 13. Twining, B. S., Baines, S. B. & Fisher Nicholas S and Landry, M. R. Cellular iron contents of plankton during the Southern Ocean Iron Experiment (SOFeX). *Deep Sea Res. Part I* **51**, 1827–1850 (2004).

10

5

20

15

25

30

- 14. Tanioka, T. *et al*. Global patterns and predictors of C:N:P in marine ecosystems. *Commun Earth Environ* **3**, (2022).
- Schneider, B., Engel, A. & Schlitzer, R. Effects of depth-and CO2-dependent C: N ratios of particulate organic matter (POM) on the marine carbon cycle. *Global Biogeochem. Cycles* 18, GB2018 (2004). doi:10.1029/2003GB002184.
- 16. Kwiatkowski, L., Aumont, O., Bopp, L. & Ciais, P. The Impact of Variable Phytoplankton Stoichiometry on Projections of Primary Production, Food Quality, and Carbon Uptake in the Global Ocean. *Global Biogeochem. Cycles* **32**, 516–528 (2018).
- 17. Ayata, S. D., Lévy, M., Aumont, O., Sciandra, A., Sainte-Marie, J., Tagliabue, A., & Bernard, O. Phytoplankton growth formulation in marine ecosystem models: should we take into account photo-acclimation and variable stoichiometry in oligotrophic areas? *Journal of Marine Systems* **125**, 29-40 (2013).
- 18. Kwiatkowski, L., Aumont O, Bopp L. Consistent trophic amplification of marine biomass declines under climate change. *Glob Change Biol.* **25**, 218-229 (2019).
- 19. Buchanan, P. J., Matear, R. J., Chase, Z., Phipps, S. J. & Bindoff, N. L. Dynamic Biological Functioning Important for Simulating and Stabilizing Ocean Biogeochemistry. *Global Biogeochem. Cycles* **32**, 565–593 (2018).
 - 20. Tanioka, T. & Matsumoto, K. Buffering of ocean export production by flexible elemental stoichiometry of particulate organic matter. *Global Biogeochem. Cycles* **31**, 1528–1542 (2017).
 - 21. Kwon, E. Y. *et al.* Nutrient uptake plasticity in phytoplankton sustains future ocean net primary production. *Sci Adv* **8**, eadd2475 (2022). doi:10.1126/sciadv.add2475.
 - 22. Tagliabue, A. *et al*. An iron cycle cascade governs the response of equatorial Pacific ecosystems to climate change. *Glob. Chang. Biol.* **26**, 6168-6179 (2020).
- 23. Wiseman, N. A., Moore, J. K., Twining, B. S., Hamilton, D. S. & Mahowald, N. M. Acclimation of phytoplankton Fe:C ratios dampens the biogeochemical response to varying atmospheric deposition of soluble iron. *Global Biogeochem. Cycles* **37**, e2022GB007491 (2023).
 - 24. Moore, J. K., Doney, S. C. & Lindsay, K. Upper ocean ecosystem dynamics and iron cycling in a global three-dimensional model. *Global Biogeochem. Cycles* **18**, (2004).
 - 25. Long, M. C., Moore, J. K., Lindsay, K., Levy, M., Doney, S. C., Luo, J. Y., et al. Simulations with the Marine Biogeochemistry Library (MARBL). *Journal of Advances in Modeling Earth Systems*, **13**, e2021MS002647 (2021).
 - 26. Teng, Y.-C., Primeau, F. W., Moore J Keith and Lomas, M. W. & Martiny, A. C. Globalscale variations of the ratios of carbon to phosphorus in exported marine organic matter. *Nat. Geosci.* **7**, 895-898 (2014).
 - 27. Wang, W.-L., Moore, J. K., Martiny, A. C. & Primeau, F. W. Convergent estimates of marine nitrogen fixation. *Nature* **566**, 205–211 (2019).
 - 28. Tanioka, T. *et al.* Global Ocean Particulate Organic Phosphorus, Carbon, Oxygen for Respiration, and Nitrogen (GO-POPCORN). *Sci Data* **9**, 688 (2022).

5

10

20

15

25

30

35

- 29. Takeda, S. Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. *Nature* **393**, 774–777 (1998).
- 30. Mosseri, J., Quéguiner, B., Armand, L. & Cornet-Barthaux, V. Impact of iron on silicon utilization by diatoms in the Southern Ocean: A case study of Si/N cycle decoupling in a naturally iron-enriched area. *Deep Sea Res. Part 2 Top. Stud. Oceanogr.* **55**, 801–819 (2008).
- Christina, L., Hutchins, D. A., Brzezinski, M. A. & Zhang, Y. Effects of iron and zinc deficiency on elemental composition and silica production by diatoms. *Mar. Ecol. Prog. Ser.* **195**, 71–79 (2000).
- 32. Garcia, H. *et al*. World Ocean Atlas 2018. Vol. 4: Dissolved Inorganic Nutrients (phosphate, nitrate and nitrate + nitrite, silicate). *NOAA Atlas NESDIS 84*, 35pp (2019).
- 33. Moore, J. K. & Braucher, O. Sedimentary and mineral dust sources of dissolved iron to the world ocean. *Biogeosciences* **5**, 631–656 (2008).
- 34. GEOTRACES Intermediate Data Product Group. The GEOTRACES Intermediate Data Product 2021 (IDP2021). Preprint at (2021). NERC EDS British Oceanographic Data Centre NOC. doi:10.5285/cf2d9ba9-d51d-3b7c-e053-8486abc0f5fd
- 35. Tagliabue, A. *et al*. A global compilation of dissolved iron measurements: focus on distributions and processes in the Southern Ocean. *Biogeosciences* **9**, 2333–2349 (2012).
- 36. Behrenfeld, M. J., E. Boss, D. A. Siegel, and D. M. Shea. Carbon-based ocean productivity and phytoplankton physiology from space, *Global Biogeochem. Cycles* **19**, GB1006 (2005).
- 37. Westberry, T., Behrenfeld, M. J., et al. Carbon-based primary productivity modeling with vertically resolved photoacclimation. *Global Biogeochem. Cycles* **22**, GB2024 (2008).
 - Silsbe, G. M., M. J. Behrenfeld, K. H. Halsey, A. J. Milligan, and T. K. Westberry. The CAFE model: A net production model for global ocean phytoplankton, *Global Biogeochem*. *Cycles* **30**, 1756–1777 (2016).
- 39. DeVries, T. & Weber, T. The export and fate of organic matter in the ocean: New constraints from combining satellite and oceanographic tracer observations. *Global Biogeochem. Cycles* **31**, 535–555 (2017).
 - 40. Letscher, R. T. & Moore, J. K. Preferential remineralization of dissolved organic phosphorus and non-Redfield DOM dynamics in the global ocean: Impacts on marine productivity, nitrogen fixation, and carbon export. *Global Biogeochem. Cycles* **29**, 325–340 (2015).
 - 41. Galbraith, E. D. & Martiny, A. C. A simple nutrient-dependence mechanism for predicting the stoichiometry of marine ecosystems. *Proc. Natl. Acad. Sci. U. S. A.* **112**, 8199–8204 (2015).

Acknowledgments: We thank the Martiny group for collecting and analyzing POM data as part of the GO-SHIP and AMT programs. The GEOTRACES 2021 Intermediate Data Product (IDP2021) represents an international collaboration and is endorsed by the Scientific Committee on Oceanic Research (SCOR). The many researchers and funding agencies responsible for the collection of data and quality control are thanked for their contributions to the IDP2021.

Funding: This work was supported by the DOE BER Earth System Modeling Program (DE-SC0016539 to J.K.M).

Author contributions:

10

15

5

20

30

25

35

Conceptua	lization: JKM, ACM
Methodolo	ogy: NAW, JKM, ACM
Investigati	on: NAW, JKM
Visualizat	ion: NAW, JKM
Funding A	cquisition: JKM, ACM
Project Ac	lministration: JKM
Supervisio	n: JKM, ACM
Writing –	original draft: NAW, JKM
Writing –	review & editing: NAW, JKM, ACM, RL
Competin	g interests: Authors declare that they have no competing interests.
Data and as NetCDI MATLAB wiseman/C https://esc	materials availability: The simulations used in this manuscript are available F files via Dryad at the following [link available upon manuscript submission]. code for visualization can be found on github: <u>https://github.com/nicola- CESM-BECStoich</u> . Instructions for downloading CESM can be found at omp.github.io/CESM/versions/cesm2.2/html/downloading_cesm.html.
Supplementary N	Materials
Materials and Me	thods

Figs. S1 to S5

Table S1

20

5

10



Fig. 1.Stoichiometry of the sinking particulate flux at 100m. Here we show the CESM Fe/C ratio (**A**), the C/N ratio (**B**), the C/P ratio (**D**), and the N/P ratio (**F**) of the sinking particulate flux at 100m. Also shown are inverse model estimates of the C/P ratio (26) (**C**) and the N/P ratio (27) (**E**).



Fig. 2. The N/P ratio of particulate organic matter in the surface ocean (*28*) is plotted against surface phosphate concentration from the World Ocean Atlas 2018 (*32*). Also shown is the N/P ratio of surface biomass (phytoplankton and zooplankton) and the sinking particulate export from CESM, and the exported N/P from an inverse model (*27*), where model N/P ratios are plotted against simulated surface phosphate concentration.



Fig 3. Differences in key biological pump fluxes between the variable stoichiometry model and the fixed stoichiometry model. The differences between annual (**A**) net primary production, (**B**) sinking particulate organic carbon export, and C) e-ratio comparing the VarAll -FixAll simulations. Net primary production (**A**) and POC export (**B**) changes are shown as percent change, while e-ratio (**C**) change is shown as absolute change in value. Note: color scales are not at even intervals, but adjust to highlight large range of observed changes.



Fig 4. Differences in nitrogen fixation between the variable stoichiometry model and the fixed stoichiometry model. Differences in annual nitrogen fixation comparing the VarAll and FixAll simulations. Red indicates increased nitrogen fixation when phytoplankton can vary their resource acquisition. Note: color scales are not at even intervals, but adjusted to highlight large range of observed changes.



Supplementary Materials for

5 Phytoplankton variable stoichiometry modifies key biogeochemical fluxes and the functioning of the ocean biological pump

Nicola A. Wiseman, J. Keith Moore, Adam C. Martiny, Robert Letscher

Corresponding author: nicola.wiseman@bristol.ac.uk

The PDF file includes:

Materials and Methods Figs. S1 to S5 Table S1

Materials and Methods

We used a modified version of CESM v1.2, which includes biogeochemical modifications that were introduced in CESM v2, including an explicit ligand, iron model²¹⁻²³. The model includes three explicit phytoplankton groups (pico-nanophytoplankton, diatoms, and diazotrophs), one implicit group (coccolithophores, which are a variable fraction of the small phytoplankton group), and one zooplankton group (23-25). The model was initiated at preindustrial CO₂ levels (284ppm) for 300 years using COREv2 interannual forcing, and we analyzed the output averaged over the last 20 years. Atmospheric CO_2 was allowed to respond to air-sea CO_2 fluxes. This version of the model includes new equations and parameterization for phytoplankton nutrient quotas. - (- 1)

10

$$gQn = \begin{cases} gQn_{max} & \text{where } DIN \ge NOpt \\ max \left(gQn_{max} \times \frac{DIN}{NOpt}, gQn_{min} \right) & \text{where } DIN < NOpt \end{cases}$$
(Eq. 1)

There are some modifications to the P/C formulation for new growth (gQp) in order to maintain appropriate N/P values as N/C ratios acclimate (Eq. 2). After calculating the initial gQp under the phosphorus conditions, the scaling with N availability only occurs where DIN < NOpt, using the previously calculated gQp. Phytoplankton are also allowed to assimilate both phosphate and dissolved organic phosphorus, so we define P_{tot} as the sum of these. Phytoplankton Fe/C ratios follow the same formula as N/C (Eq. 3).

1.
$$gQp = \begin{cases} gQp_{max} & \text{where } P_{tot} \ge POpt \\ max \left(\frac{gQp_{max} \times P_{tot}}{POpt}, gQp_{min} \right) & \text{where } P_{tot} < POpt \end{cases}$$
(Eq. 2)
2.
$$gQp = max \left(\frac{gQp \times DIN}{NOpt}, gQp_{min} * 0.5 \right) & \text{where } DIN < NOpt \\ gQfe = \begin{cases} gQfe_{max} & \text{where } dFe > FeOpt \\ max \left(gQfe_{max} \times \frac{dFe}{FeOpt}, gQfe_{min} \right) & \text{where } dFe < FeOpt \end{cases}$$
(Eq. 3)

There are also modifications to the Si/C formulation in order to allow for diatoms to increase the Si/C uptake ratio when dFe is low (Eq. 4). 11

$$gQsi = \begin{cases} gQsi_{max} & \text{where } dFe = 0 \\ min \left(0.133 \times \frac{FeOpt}{dFe}, gQsi_{max} \right) & \text{where } 0 < dFe < FeOpt & \text{where } Si(OH)_4 \ge SiOpt \\ 0.133 & \text{where } dFe > FeOpt & (Eq. 4) \\ max \left(0.133 \times \frac{Si(OH)_4}{SiOpt}, gQsi_{min} \right) & \text{where } Si(OH)_4 < SiOpt \end{cases}$$

Observations of particulate organic matter (POM) are from the GO-POPCORNv2 database (28). Phytoplankton cellular iron to carbon ratios were previously compiled from multiple sources (23). The parameters determined for each cellular nutrient ratio are provided (table S1). Initial parameter values for C/N/P variable quotas (XOpt, gQx_{min}, gQx_{max}) were approximated from comparison to GO-POPCORNv2 POM and nutrient data, where POM

20

15

5

nutrient:carbon ratios where plotted against respective nutrient, to approximate nutrient concentration at which the quotas begin to decrease (XOpt), the maximum quota (gQx_{max}), and minimum quota (gQx_{min}). These parameters were then iteratively tuned until a best-case was reached (in terms of simulating global nutrient patterns and surface chlorophyll). The fixed ratio model (FixAll) held the same values for each phytoplankton group. For C/N/P, these values were set to Redfield values (106/16/1). For Fe:C and Si:N, a middle range value was chosen (7.0 µmol/mol and 0.5 mol/mol, respectively).



Fig. S1.

Phytoplankton nutrient to carbon (X:C) ratio for new growth as a function of dissolved ambient nutrient concentration [X]. XOpt determines the dissolved ambient nutrient concentration at which phytoplankton X:C reaches it maximum value (gQx_max). X:C decreases linearly with decreasing dissolved nutrient concentration between the prescribed, group-specific maximum (gQx_max) and minimum (gQx_min) quotas. X here applies for nitrogen, phosphorus, iron, and silica.



Fig. S2.

The C/P ratio of particulate organic matter in the surface ocean (*28*) is plotted against surface phosphate concentration from the World Ocean Atlas 2018 (*32*). Also shown is the CESM C/P ratio for surface biomass (phytoplankton and zooplankton) and the sinking particulate flux, and an inverse model estimate of the exported C/P ratio (*26*), where both are plotted against simulated surface phosphate concentration.



Fig. S3.

The C/N ratio of particulate organic matter in the surface ocean (*28*) is plotted against surface nitrate concentration from the World Ocean Atlas 2018 (*30*). Also shown is the CESM C/N ratio for surface biomass (phytoplankton and zooplankton) and the sinking particulate flux as a function of simulated surface nitrate concentration.



Fig. S4.

Global patterns of e-ratio in the VarAll simulation. Lighter colors indicate a higher e-ratio, which is defined as the sinking carbon flux at 100m / the net primary production.



Fig. S5.

Changes in phytoplankton biomass by type for A) small phytoplankton, B) diatoms, and C) diazotrophs. Red indicates increased biomass when phytoplankton can vary their resource acquisition.

	Small Phytoplankton	Diatoms	Diazotrophs
NOpt, gQn_min, gQn_max	0.6, 0.111, 0.15	0.6 0.111, 0.15	0.6, 0.125, 0.167
POpt, gQp_min ¹ , gQp_max	0.6, 0.0067, 0.00943396	0.6, 0.00769231, 0.00943396	0.6, 0.0033, 0.0083
FeOpt, gQfe_min, gQfe_max	2.0e-3, 2.5e-6, 100.0e-6	2.0e-3, 2.5e-6, 100.0e-6	2.0e-3, 4.0e-6, 140.0e-6
SiOpt, gQsi_min, gQsi_max	N/A	10.0, 0.041668, 0.83335	N/A
gQn, gQp, gQfe, gQsi	0.150943, 0.00943396, 7.0e-6, 0.0754717		

¹P/C minimum quotas can be reduced to a smaller value due to the N/P scaling

Table S1.

Model parameters for phytoplankton nutrient quotas.