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# Global Biogeochemical Cycles

## RESEARCH ARTICLE

10.1002/2017GB005799

### Key Points:

- Climate change increases phytoplankton C:N and C:P ratios, as a result of greater nutrient limitation in the future ocean
- Phytoplankton food quality, especially P content, is projected to decline substantially in the subtropics and Arctic Ocean over the 21st century
- Variable C:N:P phytoplankton stoichiometry results in increased ocean carbon export efficiency over the 21st century

### Supporting Information:

- Supporting Information S1

### Correspondence to:

L. Kwiatkowski,  
lester.kwiatkowski@lsce.ipsl.fr

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## The Impact of Variable Phytoplankton Stoichiometry on Projections of Primary Production, Food Quality, and Carbon Uptake in the Global Ocean

Lester Kwiatkowski<sup>1</sup> , Olivier Aumont<sup>2</sup>, Laurent Bopp<sup>1,3</sup> , and Philippe Ciais<sup>1</sup>

<sup>1</sup>Laboratoire des Sciences du Climat et de l'Environnement, IPSL, CEA/CNRS/UVSQ, Gif-sur-Yvette, France, <sup>2</sup>Laboratoire d'Océanographie et de Climatologie: Expérimentation et Approches Numériques, IPSL, CNRS/UPMC/IRD/MNH, Paris, France, <sup>3</sup>Laboratoire de Météorologie Dynamique (LMD/IPSL), CNRS/Ecole Normale Supérieure, Paris Cedex 05, France

**Abstract** Ocean biogeochemical models are integral components of Earth system models used to project the evolution of the ocean carbon sink, as well as potential changes in the physical and chemical environment of marine ecosystems. In such models the stoichiometry of phytoplankton C:N:P is typically fixed at the Redfield ratio. The observed stoichiometry of phytoplankton, however, has been shown to considerably vary from Redfield values due to plasticity in the expression of phytoplankton cell structures with different elemental compositions. The intrinsic structure of fixed C:N:P models therefore has the potential to bias projections of the marine response to climate change. We assess the importance of variable stoichiometry on 21st century projections of net primary production, food quality, and ocean carbon uptake using the recently developed Pelagic Interactions Scheme for Carbon and Ecosystem Studies Quota (PISCES-QUOTA) ocean biogeochemistry model. The model simulates variable phytoplankton C:N:P stoichiometry and was run under historical and business-as-usual scenario forcing from 1850 to 2100. PISCES-QUOTA projects similar 21st century global net primary production decline (7.7%) to current generation fixed stoichiometry models. Global phytoplankton N and P content or food quality is projected to decline by 1.2% and 6.4% over the 21st century, respectively. The largest reductions in food quality are in the oligotrophic subtropical gyres and Arctic Ocean where declines by the end of the century can exceed 20%. Using the change in the carbon export efficiency in PISCES-QUOTA, we estimate that fixed stoichiometry models may be underestimating 21st century cumulative ocean carbon uptake by 0.5–3.5% (2.0–15.1 PgC).

## 1. Introduction

Ocean biogeochemical models quantify the response and feedbacks between climate, ocean biogeochemistry, and marine ecosystems (Bacastow & Maier-Reimer, 1990; Reid et al., 2009). Ocean biogeochemical (OBGC) models are used to project carbon and ecosystem dynamics on decadal to centennial timescales and are coupled components of current generation Earth system model (ESM) simulations (Taylor et al., 2011). While the complexity of OBGC models embedded in ESMs is highly variable (Kwiatkowski et al., 2014), they typically simulate the lower tropic levels of marine ecosystems (e.g., phytoplankton and zooplankton) and the biogeochemical cycles of carbon and other major nutrients (e.g., nitrogen, phosphorus, iron, and silica). Almost all such models, however, assume fixed phytoplankton C:N:P stoichiometry. Here we explore the impact of the inclusion of variable phytoplankton stoichiometry on 21st century projections of net primary production (NPP), food quality (N and P content of phytoplankton biomass), and ocean carbon uptake using a new quota OBGC model.

### 1.1. Monod and Quota Models

The OBGC models coupled in ESMs are generally Monod formulations (Monod, 1942) with respect to carbon, nitrogen and phosphorus. In such models the stoichiometry of C:N:P is fixed at Redfield values and phytoplankton growth is limited by external nutrient concentrations typically via either threshold or multiplicative combinations of individual nutrient effects (Terry, 1980). The C:N:P stoichiometry of phytoplankton, however, has been shown to exhibit considerable spatiotemporal variability from the Redfield ratio in measurements and model studies (Ho et al., 2003; Karl et al., 2001; Martiny et al., 2013). Drivers of this stoichiometric variability include phytoplankton lineage, growth rate, nutrient, light and temperature conditions, and interactions between these affects (Moreno & Martiny, 2018). C:N:P variability is ultimately a consequence of plasticity in the expression of phytoplankton cell structures (e.g., chloroplasts and ribosomes) with

different elemental compositions (Rhee, 1978). Proteins and light harvesting pigments such as chlorophyll are relatively high in N (Finkel et al., 2016), while polyphosphates, membrane lipids, and nucleic acids are P rich. Given the substantial chlorophyll and protein content of light harvesting machinery, photosynthesis is considered a predominately N intensive process (Geider & La Roche, 2002), while the RNA content of ribosomes leads cellular biosynthesis to be considered a largely P intensive process (Moreno & Martiny, 2018; Sterner & Elser, 2002). Under P limitation phytoplankton typically express proteins to increase P uptake and access organically bound P (Martiny et al., 2006). They may also utilize inorganic P storage and decrease cellular P requirements by substituting nonphosphorus membrane lipids for phospholipids (Van Mooy et al., 2009). Similar processes occur under N limitation with upregulation of ammonia transport and the increased utilization of N sources such as nitrate and organically bound N (Herrero et al., 1985; Tolonen et al., 2006); however, evidence suggests that phytoplankton C:N is more constrained than C:P (Moore et al., 2013; Quigg et al., 2003).

An alternative to fixed stoichiometry Monod models are so called quota models, in which, phytoplankton growth rate for a limiting nutrient ( $n$ ) is described not by external nutrient concentration but by the internal nutrient concentration or cell quota (Caperon, 1968; Droop, 1968). Quota models have been shown to successfully explain empirical datasets (e.g., Bi et al., 2012; Droop, 1968) and have been incorporated with Michaelis-Menten nutrient uptake descriptions and Liebig's law of the minimum in models of phytoplankton growth and stoichiometry (Klausmeier et al., 2004; Legović & Cruzado, 1997). These models predict that at low growth rates, cellular stoichiometry tracks nutrient supply, but at higher growth rates converges to species specific optimum values, in agreement with experimental data (Klausmeier et al., 2004). Although multiple quota formulations have been described (Baklouti et al., 2006; Flynn, 2001), the present study utilizes the following:

$$f^n = 1 - \frac{Q_0^n}{Q^n} \quad (1)$$

where  $f^n$  is the effect of a given nutrient on phytoplankton growth rate,  $Q^n$  is the internal ratio of nutrient  $n$  to carbon biomass, and  $Q_0^n$  is the subsistence or minimum quota of the respective nutrient. Quota-type OBG models therefore require the additional simulation of internal nutrient concentrations in each phytoplankton class, and consequently represent a substantial increase in the number of prognostic variables and computational cost. While fixed stoichiometry OBG models remain extremely powerful and computationally efficient, their inherent structure has the potential to bias projections of the marine ecosystem response to a changing climate. In particular, as such models assume stoichiometrically constant nutrient consumption and export ratios, they may overestimate the impact on primary production and consequently carbon export fluxes due to stratification driven reductions in photic zone nutrient concentrations (Behrenfeld et al., 2001, 2006; Kwiatkowski et al., 2017; Laufkötter et al., 2015; Teng et al., 2014). Such biases have the potential to further influence the simulation of ocean oxygen content which may be of particular interest in zones of increasing hypoxia (Anderson & Mitra, 2010; Flynn, 2001, 2010).

## 1.2. Phytoplankton Nutritional Quality

Ecological efficiencies and the transfer of energy through the marine food chain depend on phytoplankton attributes such as edibility and nutritional quality, which vary with taxonomic composition and stoichiometry (Dickman et al., 2008; Finkel et al., 2009; Rossoll et al., 2012). Phytoplankton carbon content typically exceeds zooplankton demand, while nitrogen and phosphorus are generally limiting. High phytoplankton C:N and C:P has associated costs for zooplankton with excess carbon stored, excreted, respired, or avoided through changes to foraging behavior (Malzahn et al., 2009; Plath & Boersma, 2001). Such processes typically reduce the efficiency of zooplankton herbivory (Urabe & Sterner, 1996; Urabe et al., 2002) and the transfer of energy to higher trophic levels (Malzahn et al., 2007, 2009). Throughout this study we therefore equate increases in simulated phytoplankton C:N and C:P with reductions in "food quality."

With climate change resulting in an increasingly stratified ocean, phytoplankton will be typically exposed to lower concentrations of bioavailable N and P, while light levels in the surface mixed layer will generally increase (Steinacher et al., 2010), both of which may affect phytoplankton stoichiometry. In addition, changes in ecological stressors (Bopp et al., 2013) are likely to disproportionately impact certain phytoplankton species, affecting taxonomic composition. The combined effect of these drivers will influence the mean

nutritional quality of phytoplankton. In contrast to Monod models that are only capable of addressing questions of changing phytoplankton functional types (PFTs), the quota model adopted herein facilitates projections of phytoplankton nutritional quality that are due to changes in both stoichiometry and the relative abundance of PFTs.

### 1.3. The PISCES-QUOTA Model

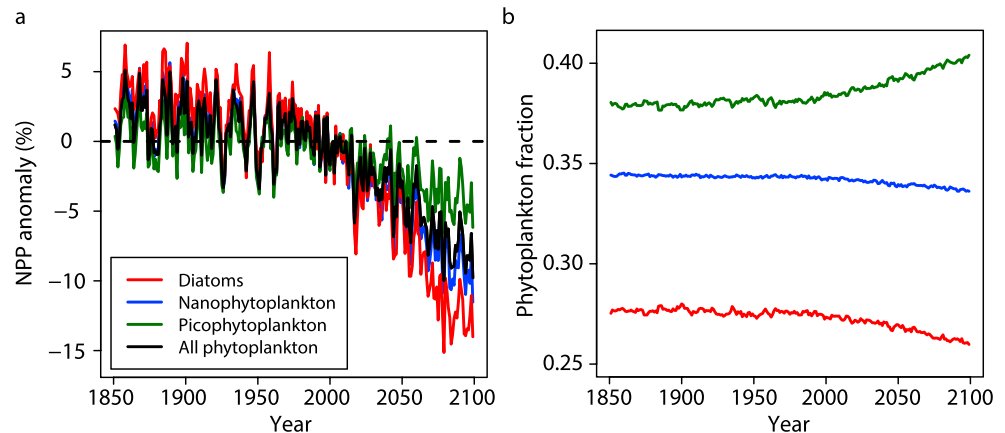
Using a recently developed quota version of the PISCES ocean biogeochemistry model (PISCES-QUOTA), we explore the implications of variable phytoplankton stoichiometry on global climate projections. We examine how anthropogenic climate change over the 21st century is projected to affect the C:N and C:P ratios of phytoplankton and the impact of such changes in stoichiometry on NPP and ocean carbon export. Changes in ocean carbon export efficiency are used to estimate the potential cumulative 21st century ocean carbon uptake bias between fixed and variable stoichiometry ocean biogeochemistry models. PISCES-QUOTA model output is also used to evaluate how nitrogen and phosphorus nutrient limitation in the global ocean is likely to change over the coming century.

## 2. Methods

PISCES-QUOTA has 39 prognostic compartments. Phytoplankton growth is controlled by five modeled limiting nutrients: nitrate and ammonium, phosphate, silicate, and iron. Five living compartments are represented: three phytoplankton size classes/groups corresponding to picophytoplankton, nanophytoplankton and diatoms, and two zooplankton size classes (microzooplankton and mesozooplankton). Phytoplankton stoichiometry is variable and is prognostically predicted by the model, while zooplankton are assumed to be strictly homeostatic (e.g., Meunier et al., 2014; Sterner & Elser, 2002; Woods & Wilson, 2013). As a consequence, the C:N:P:Fe ratios of zooplankton are maintained constant and are not allowed to vary.

Limitation of growth rate by nutrients as well as nutrient uptake and assimilation are modeled following the chain model of Pahlow and Oschlies (2009), in which the P quota limits N assimilation which in turn limits photosynthesis and phytoplankton growth. Phytoplankton nutrient uptake is computed based on optimal uptake kinetics to parameterize resource allocation between two competing functional pools (nutrient uptake sites and internal enzymes; Pahlow, 2005; Smith et al., 2009). Phytoplankton phosphorus to nitrogen ratios are modeled using a resource allocation formalism based on previous ecophysiological models (Daines et al., 2014; Klausmeier et al., 2004). The maximum and minimum N:P ratios are determined by the potential allocation between P-rich biosynthesis machinery, N-rich light harvesting apparatus, a nutrient uptake component, the carbon stores, and the remainder. This allocation depends on both cell size and the environmental conditions. As such, each phytoplankton group has different maximum and minimum N:P ratios with picophytoplankton typically having the highest N:P (Daines et al., 2014; Hillebrand et al., 2013). In PISCES-QUOTA the minimum P/C quota is 2, 2.2, and 2.4 mmol P (mol C)<sup>-1</sup> for picophytoplankton, nanophytoplankton, and diatoms, respectively. The minimum N/C quota is 0.055, 0.04, and 0.033 mol N (mol C)<sup>-1</sup> for picophytoplankton, nanophytoplankton, and diatoms, respectively, while the maximum N/C quota is 0.18 mol N (mol C)<sup>-1</sup> for all phytoplankton types. Although maximum P/C quotas are not explicitly specified in PISCES-QUOTA, they emerge from the maximum N/C quota and the N:P ratios set by the allocation of resources between different cellular components. These parameter values are informed by existing allometric relationships (Edwards et al., 2012; Litchman et al., 2007). Phytoplankton stoichiometry is not affected by ocean carbonation as has been tentatively observed in experiments (Riebesell et al., 2007) and simulated in OBG models (Oschlies et al., 2008; Tagliabue et al., 2011). As a consequence of variable phytoplankton stoichiometry, the response of zooplankton to the quality of their prey, also known as stoichiometric modulation of predation (SMP; Mitra & Flynn, 2005), is permitted in PISCES-QUOTA. When food quality declines as a result of the Fe:C ratio, the N:C ratio, or the P:C ratio of prey decreasing below optimal values, there is a corresponding decline in zooplankton gross growth efficiency. A complete description and evaluation of the model are provided in the supporting information.

PISCES-QUOTA was run off-line, forced with output from the Nucleus for European Modelling of the Ocean (NEMO) physical ocean model (Madec, 2015) on an ORCA tripolar grid with 2° horizontal resolution (ORCA2). The model was spun-up under preindustrial climate forcing for 650 years. Two PISCES-QUOTA model simulations of 250 years were conducted. The first simulation was forced by NEMO physical ocean output derived from historical (1851–2005) climate forcing and thereafter the high emission Representative



**Figure 1.** Global net primary production anomalies and phytoplankton community change. (a) Depth-integrated net primary production anomalies relative to 1990s values for diatoms (red), nanophytoplankton (blue), picophytoplankton (green), and all phytoplankton types (black). (b) The global fraction of each phytoplankton type.

Concentration Pathway 8.5 (RCP8.5) scenario (2006–2100; Riahi et al., 2011). The second simulation was a 250 year extension of the spin-up, run under preindustrial climate forcing and used to remove potential model drift.

### 3. Results

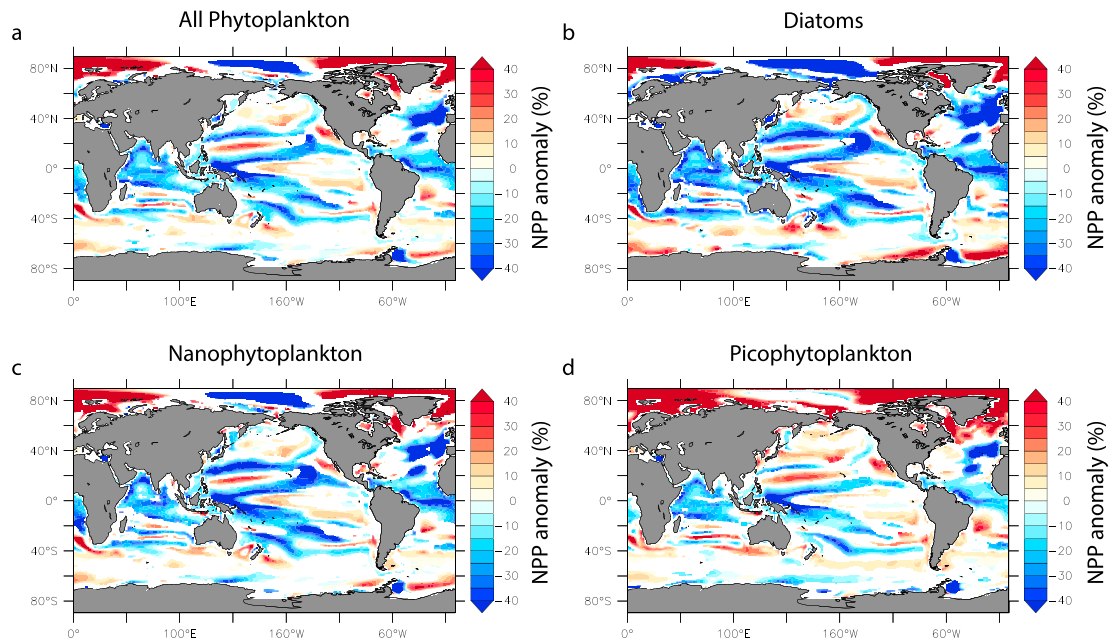
#### 3.1. Net Primary Production

Under RCP8.5 climate forcing, PISCES-QUOTA projects global primary production declines of 7.7% in the 2090s relative to the 1990s (Figure 1a). Diatoms exhibit the greatest relative NPP declines (12.4%), with nanophytoplankton declines similar to the phytoplankton mean (9.2%) and picophytoplankton declines the lowest (4.0%; Figure 1a). As a consequence of the differing PFT declines, PISCES-QUOTA projects a shift in phytoplankton community composition toward smaller phytoplankton size classes (Figure 1b). The community fraction of diatoms, the largest PFT, declines by 1.3% over the 21st century, while the fraction of nanophytoplankton declines by 0.6% and the fraction of picophytoplankton, the smallest PFT, increases by 1.9% (Figure 1b).

The sign and magnitude of projected NPP anomalies are spatially variable. Declines typically occur in the low and middle latitudes, where they can exceed 40% (Figure 2). These reductions are somewhat offset by patchy NPP increases in regions such as the Arctic Ocean where increases can exceed 40%. Low to middle latitude NPP generally declines with isolated increases in regions of the Pacific. Declines are most extensive for NPP of diatoms and nanophytoplankton, with picophytoplankton typically exhibiting more limited reductions. In contrast, in the Arctic, picophytoplankton experience the largest relative increases with less extensive increases in diatom and nanophytoplankton NPP. There are limited consistent changes in NPP in the Southern Ocean with all PFTs showing small regions of increase and decrease (Figure 2). At the ocean basin scale, projected NPP anomalies are highly correlated across phytoplankton types ( $r = 0.63\text{--}0.86$  (correlation coefficient),  $P < 0.0001$ ). As discussed below, this is suggestive of a common suite of drivers affecting all phytoplankton similarly.

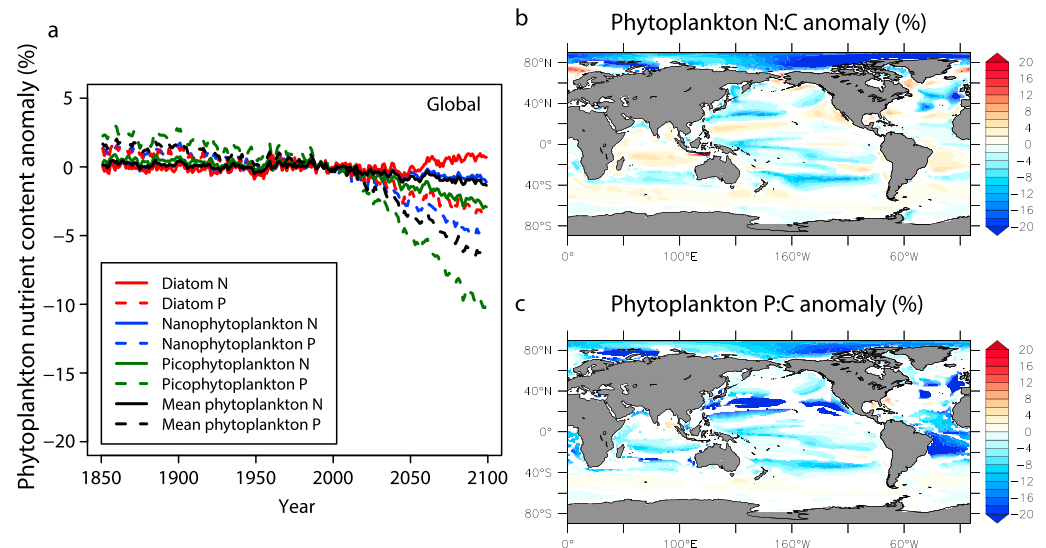
#### 3.2. Phytoplankton Quotas and Food Quality

PISCES-QUOTA projects that the N and P nutrient content of phytoplankton biomass will generally decline over the 21st century (Figure 3). This implies an increase in the C:N and C:P available to higher trophic levels. At the global scale, the decline in mean phytoplankton N content is limited (–1.1% in the 2090s relative to mean 1990s values; Figure 3). This decline is predominantly due to a reduction in picophytoplankton N content (–2.6%), with a smaller reduction in nanophytoplankton (–0.8%) and diatoms showing a slight increase in N content (0.8%; Figure 3). The global relative decline in mean phytoplankton P content (–6.4%) is larger than that of N and consistently negative across PFTs (picophytoplankton, –9.8%; nanophytoplankton, –4.8%; diatoms, –3.2%).

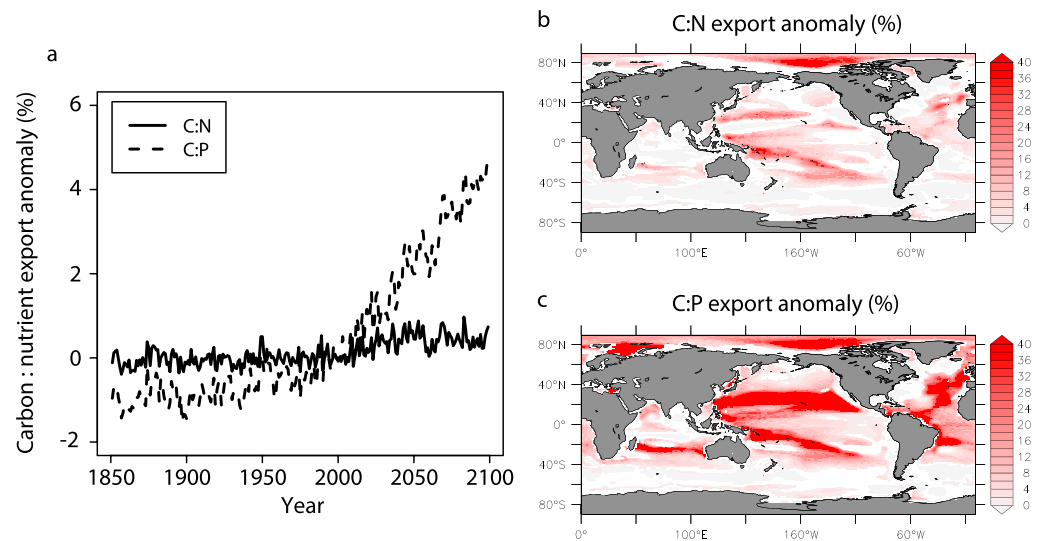


**Figure 2.** The spatial pattern of 21st century net primary production anomalies. Depth-integrated net primary production anomalies in the 2090s relative to the 1990s aggregated across (a) all phytoplankton types, and shown individually for (b) diatoms, (c) nanophytoplankton, and (d) picophytoplankton. Nonsignificant ( $p < 0.05$ ) values are displayed white.

The largest projected declines in aggregated phytoplankton N and P content are in the subtropics and Arctic Ocean where 21st century reductions can exceed 20% (Figure 3). N content declines are generally a consequence of stoichiometry changes in all three PFTs, while P content declines are principally due to picophytoplankton and nanophytoplankton with minimal influence of changes in diatoms (Figure S3). PISCES-QUOTA projects limited robust changes in phytoplankton N and P content in the Southern Ocean (Figure 3). Almost all (>95%) of the total 21st century declines in mean phytoplankton N and P content are due to changes in phytoplankton stoichiometry with a limited proportion of declines (<5%) due to shifts in phytoplankton community composition.



**Figure 3.** The change in phytoplankton nutrient content. (a) The global mean N and P phytoplankton nutrient content anomalies per unit C relative to mean 1990s values. (b) The N:C and (c) P:C anomalies in the 2090s relative to 1990s mean values for aggregated phytoplankton types. Nonsignificant ( $p < 0.05$ ) values are displayed white.



**Figure 4.** Change in carbon export efficiency. (a) The global carbon to nutrient export ratios at 100 m relative to mean 1990s values and (b) the spatial distribution of C:N export anomalies and (c) C:P export anomalies in the 2090s relative to mean 1990s values. Nonsignificant ( $p < 0.05$ ) values are displayed white.

### 3.3. Ocean Carbon Export

The PISCES-QUOTA model projects that total carbon export at 100 m will decline by 14.1% throughout the 21st century. Despite this, PISCES-QUOTA carbon export efficiency or the carbon export per unit of exported N and P, is projected to increase over the 21st century (Figure 4). The C:N ratio of exported particulate matter at 100 m increases by 0.4% at the global scale, while the C:P ratio increases by 4.3% (Figure 4). Changes in carbon export efficiencies are considerably higher in the Arctic and subtropical gyres where the C:N ratio commonly increases by  $>15\%$  and the C:P ratio by  $>30\%$ . In the Southern Ocean, however, carbon export efficiency remains largely unchanged (Figure 4).

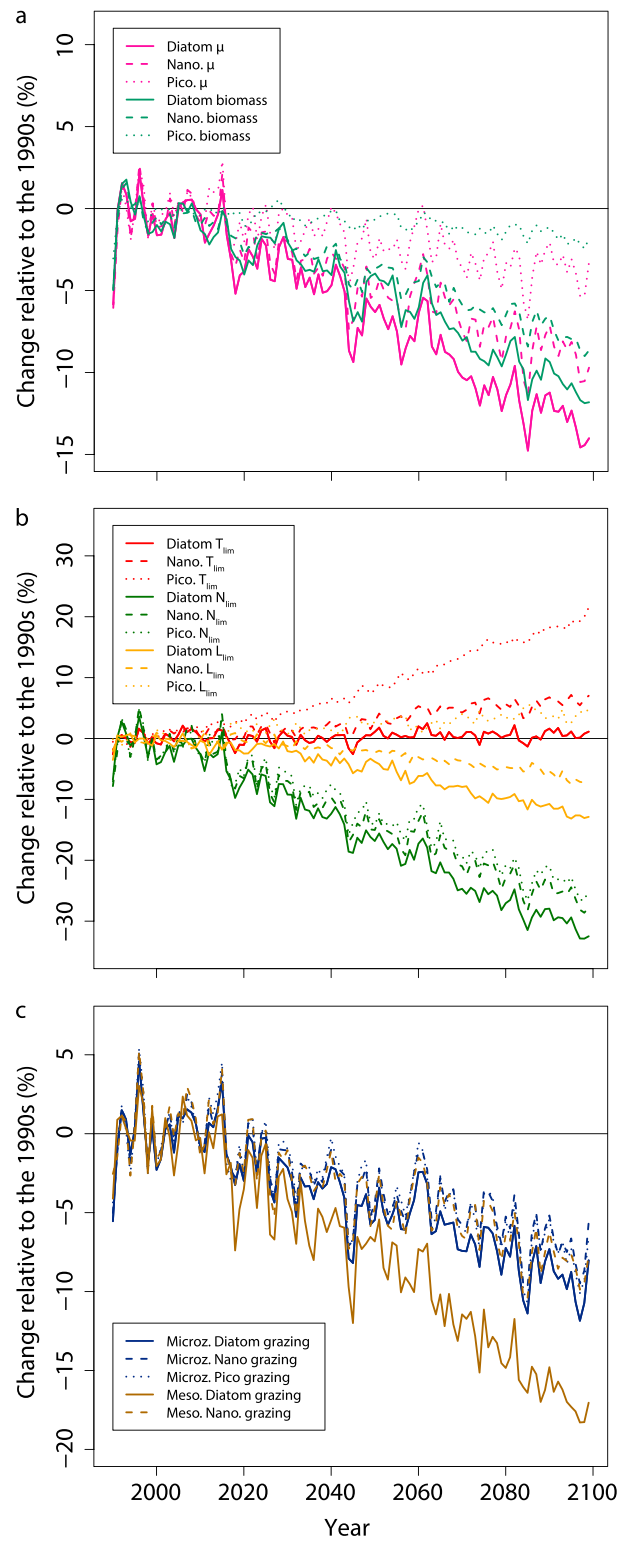
## 4. Discussion

### 4.1. The Drivers of NPP Change

The PISCES-QUOTA projected global NPP decline over the 21st century (7.7%) is comparable with current generation fixed stoichiometry models, which generally project declines of 0–20% (Bopp et al., 2013). It is also highly similar to recent estimates based on observationally constraining the relationship between the inter-annual variability and long-term sensitivity of NPP ( $6 \pm 3\%$ ; Kwiatkowski et al., 2017).

NPP is the product of phytoplankton growth rate ( $\mu$ ) and phytoplankton biomass ( $P$ ). In PISCES-QUOTA,  $\mu$  is determined by the multiplicative combination of light, temperature, and nutrient limitation terms, while  $P$  is influenced by both  $\mu$  and additional phytoplankton loss terms such as mortality, sinking, and zooplankton grazing. The principal driver of  $\mu$  declines over the 21st century is increasing nutrient limitation. This is offset by reductions in temperature limitation and moderated somewhat by changes in light limitation (Figure 5). Diatom growth rates show the largest declines, due to the greatest impact of increasing nutrient and light limitation, combined with the least benefit from reductions in temperature limitation. In contrast, picophytoplankton growth rates decline the least, as increasing nutrient limitation has less impact and is largely offset by reductions in temperature and light limitation.

The mechanisms driving projected NPP changes in PISCES-QUOTA could be broadly characterized as “bottom-up” with NPP reductions driven by decreases in phytoplankton growth rates. However, across phytoplankton types the relative decline in  $P$  over the 21st century is less than that of  $\mu$  and therefore,  $P$  declines are lower than those of NPP. This is explained by a reduction in “top-down” microzooplankton and mesozooplankton grazing rates which reduces the loss of phytoplankton biomass to mortality (Figure 5). Therefore, although NPP declines are due to bottom-up processes, the magnitude of such declines is moderated to some extent by top-down grazing. In a subset of fixed stoichiometry Coupled Model Intercomparison



**Figure 5.** The drivers of net primary production reductions in PISCES-QUOTA RCP8.5 simulations. (a) The depth-integrated global change in growth rates ( $\mu$ ) and biomass ( $P$ ) of each phytoplankton type, (b) the affect of temperature, light and nutrient limitation ( $T_{lim}$ ,  $L_{lim}$ , and  $N_{lim}$ ) on growth rates of each phytoplankton type, and (c) the phytoplankton mortality due to specific grazing rates of microzooplankton and mesozooplankton. All values are depth integrated and expressed as anomalies relative to mean 1990s values. Growth and grazing rates are biomass weighted so that changes in these terms approximately account for global biomass anomalies.



Project Phase 5 (CMIP5) models, declines in tropical surface ocean NPP have been shown to be due to diverse changes in both bottom-up and top-down processes (Laufkötter et al., 2015). Similar to PISCES-QUOTA, NPP declines in some models were driven by reductions in  $\mu$ , while in others declines were the result of increases in zooplankton grazing.

The shift in phytoplankton community structure toward an increased proportion of the smaller picophytoplankton class is a consequence of both differing cell quotas and the biophysical constraints imposed by cell size in changing environmental conditions. Smaller phytoplankton have a larger surface area per unit volume, and can therefore support more transporters per unit volume and a thinner diffusion boundary layer. In an increasingly stratified ocean with greater nutrient limitation in the low latitudes, small-celled phytoplankton are at a competitive advantage and their proportion of the phytoplankton community increases (Li, 2002). The PISCES-QUOTA projections are consistent with the majority of fixed stoichiometry ocean biogeochemistry models which generally project reductions in diatom community fraction over the 21st century (Bopp et al., 2005; Cabré et al., 2014; Marinov et al., 2010). They are also consistent with the phytoplankton fossil record over the Cenozoic, which shows shifts toward smaller phytoplankton cell sizes during periods of increased ocean stratification (Finkel et al., 2005).

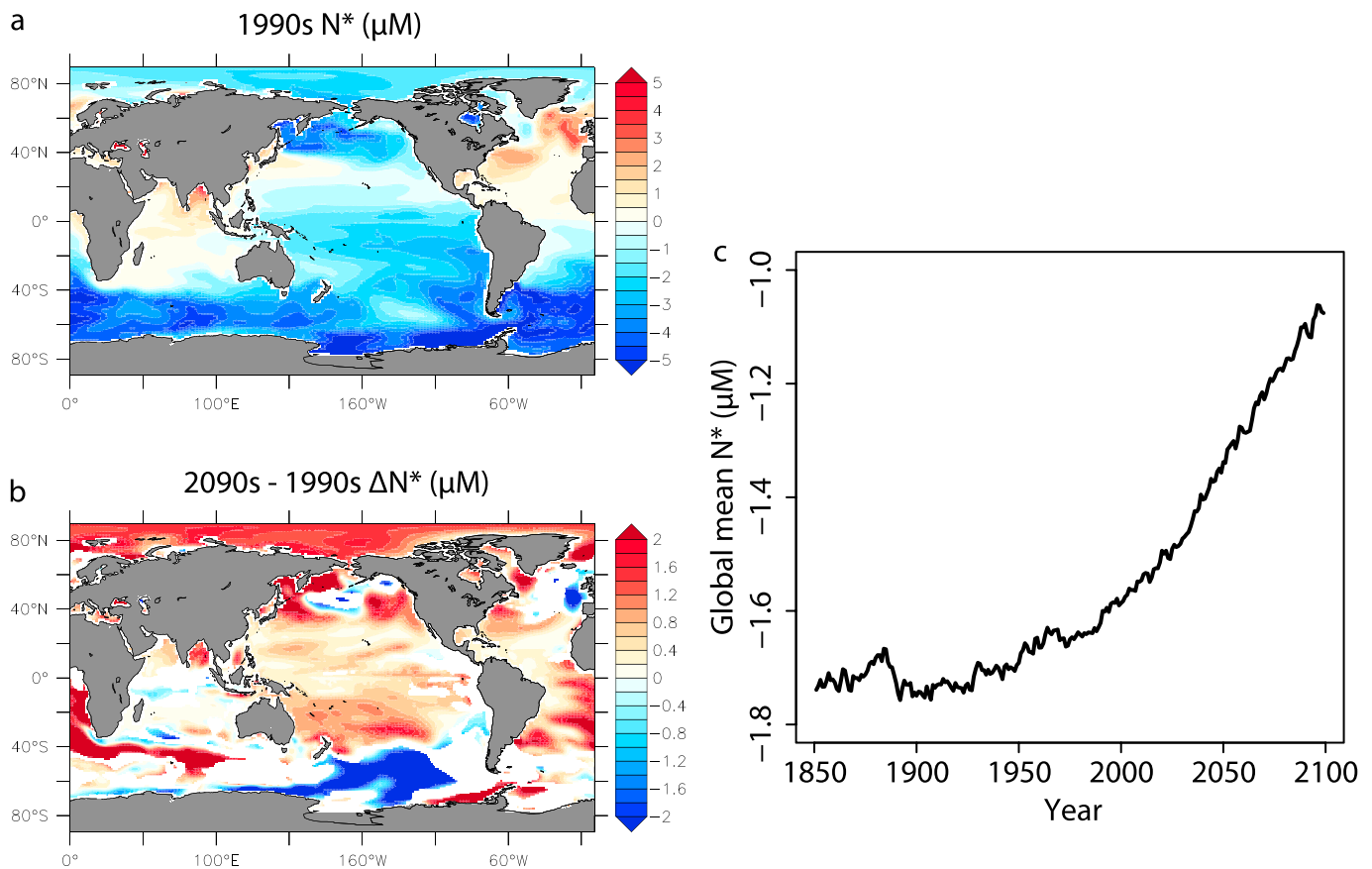
#### 4.2. Declining Phytoplankton Food Quality

The PISCES-QUOTA projections of declining food quality are predominantly due to changing phytoplankton stoichiometry with a limited contribution due to changing phytoplankton community composition. As the ocean increasingly stratifies under warming, less nutrient rich deep water is mixed into the photic zone. PISCES-QUOTA projects that with the exception of a few limited regions, P concentrations in the upper ocean will decline throughout the 21st century (Figure S8). Similar declines are projected for N with the exception of low latitude regions where nitrogen fixation occurs, where N concentrations are projected to increase (Figures S8 and S9). It is these declines in nutrient concentrations in the photic zone that drive the general 21st century shift in phytoplankton stoichiometry toward lower N and especially P content of biomass (Figure 3).

##### 4.2.1. Shifting N to P Limitation

Throughout the 21st century, PISCES-QUOTA projects a global transition from N to P limitation in the upper ocean.  $N^*$  values, or the excess of N relative to the Redfield ratio equivalence of P ( $[\text{NO}_3^-] - 16[\text{PO}_4^{3-}]$ ; Deutsch & Weber, 2012), increase almost globally in the upper ocean (Figure 6). This is due to temperature-driven increases in nitrogen fixation in the first half of the 21st century consuming P while enhancing N concentrations. In the second half of the 21st century, global mean N fixation declines due to increasing P limitation, however, the regions of low-latitude N fixation expand poleward driving a continued increase in global  $N^*$  values (Figures 6 and S9). Similar increases and expansion of N fixation have been previously observed in mixed layer ecosystem models under 21st century climate forcing (Boyd & Doney, 2002). This shift from N to P limitation is the principal driver of greater relative declines in P content than N content across all PFTs. It is worth noting that PISCES-QUOTA models N fixation in the same manner as the standard PISCES model (Aumont et al., 2015). This parameterization, which is highly idealized, is predominantly based on studies of *Trichodesmium* (e.g., Mills et al., 2004; Zehr, 2011) and assumes that N fixation is limited to warm waters ( $>20^\circ\text{C}$ ), with high light levels, low nitrogen, and adequate iron and phosphorus. Recent observations of diverse N fixing communities across ocean basins (e.g., Gradoville et al., 2017) are challenging the paradigm that N fixation is solely due to cyanobacteria in warm, oligotrophic, surface waters. However, we currently lack the extent of observations and experimental data required to describe these alternative N fixers in OBGC models such as PISCES-QUOTA.

The larger relative declines in phytoplankton P content than N content also reflects the greater cellular P:C than N:C plasticity (Geider & La Roche, 2002). While the greater N and P declines of picophytoplankton relative to nanophytoplankton, and in turn diatoms, is a consequence of these parameterized plasticities, and in particular the generally high optimum N:P of picophytoplankton and low optimum N:P of diatoms (Arrigo et al., 1999; Baer et al., 2017; Bertilsson et al., 2003; Martiny et al., 2013). Picophytoplankton in particular have generally higher N content and lower P content than other phytoplankton types, and therefore, community shifts can contribute to the aggregate change in phytoplankton food quality. The influence of community shifts on mean phytoplankton food quality over the 21st century in PISCES-QUOTA projections is minimal, however, with only 0.06 of the 1.1% decline in phytoplankton N content and 0.1 of the 6.4% decline in



**Figure 6.**  $N^*$  values in the upper ocean. (a) The mean 1990s  $N^*$  ( $[\text{NO}_3^-] - 16[\text{PO}_4^{3-}]$ ) in the top 100 m of the water column, (b)  $N^*$  anomalies in the 2090s relative to the 1990s, and (c) the global mean  $N^*$  from 1850 to 2100. Nonsignificant ( $p < 0.05$ ) anomalies are displayed white.

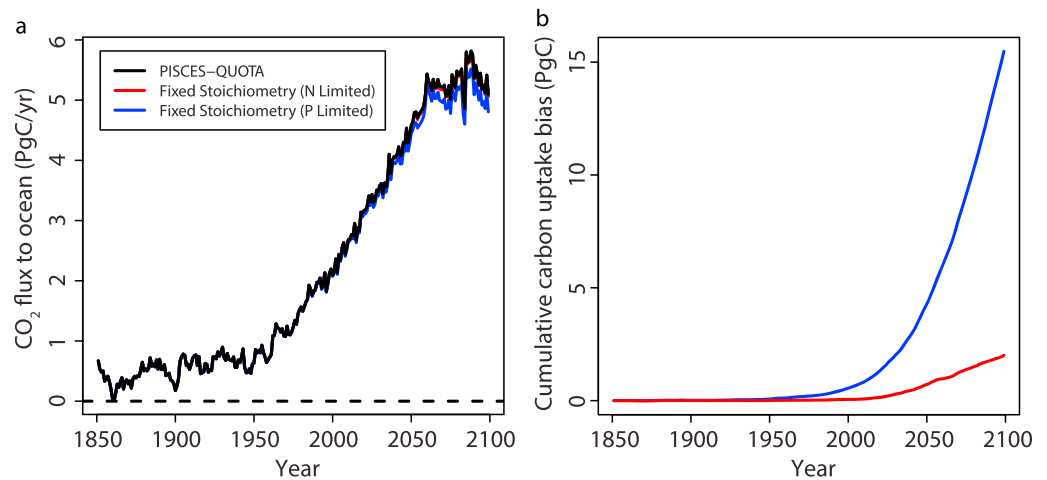
phytoplankton P content due to changing community composition. As such, almost all of the total 21st century declines in phytoplankton food quality are due to changes in phytoplankton stoichiometry.

The response of zooplankton to reduced prey quality, or stoichiometric modulation of predation (SMP), is highly diverse (Mitra & Flynn, 2005). Zooplankton ingestion rates can both increase and decrease in response to diminished prey quality (Mitra et al., 2007). Although yet to be demonstrated in the open ocean, experimental evidence (Malzahn et al., 2007, 2009; Urabe & Sterner, 1996) suggests that projections of declining phytoplankton food quality are likely to reduce the efficiency of energy transfer to higher trophic levels. These impacts are likely to be largest in the subtropical gyres and Arctic Ocean, where phytoplankton P and N declines are most extensive.

### 4.3. Implications for Ocean Carbon Uptake

Using PISCES-QUOTA to estimate the potential for fixed stoichiometry models to overestimate declines in ocean carbon uptake throughout the 21st century is not straightforward. A direct calculation of the additional ocean carbon uptake in PISCES-QUOTA is not possible due to the absence of a comparative fixed stoichiometry model. Nonetheless, a first-order upper estimate of the additional ocean carbon uptake can be calculated based on the change in the ratio of C:N:P in exported particulate matter.

PISCES-QUOTA global ocean carbon export at 100 m declines by 14.1% over the 21st century under RCP8.5. This is within the wide range of the current generation fixed stoichiometry CMIP5 models which project carbon export declines of 7 to 18% under RCP8.5 (Bopp et al., 2013). However, the C:N and C:P ratio of exported particulate matter increases 0.4% and 4.3% respectively, over the 21st century. These increases in carbon export efficiency, largely driven by the subtropical gyres and Arctic where phytoplankton stoichiometry changes are most extensive, would not be possible in a fixed stoichiometry model. It follows, therefore,



**Figure 7.** Estimated ocean carbon uptake biases under fixed stoichiometry. (a) The PISCES-QUOTA CO<sub>2</sub> flux from the atmosphere to the ocean (black). The colored lines show the estimated atmosphere to ocean CO<sub>2</sub> flux in fixed stoichiometry models under the assumption that global carbon export is entirely N limited (red) or P limited (blue). (b) The cumulative underestimation of ocean carbon uptake by comparative fixed stoichiometry models under the assumption that export is N limited (red) or P limited (blue).

that in a comparable fixed stoichiometry model, this additional exported carbon would remain in the surface ocean and limit the net flux of atmosphere-ocean CO<sub>2</sub>. PISCES-QUOTA projects that global ocean carbon uptake will increase by 3.3 PgC/year over the 21st century from 2.0 PgC/year in the 1990s to 5.3 PgC/year in the 2090s (Figure 7). Therefore, by the end of the 21st century a comparable fixed stoichiometry model would underestimate the increase in annual ocean carbon uptake by 0.01 PgC/year (assuming global N limitation) or 0.1 PgC/year (assuming global P limitation) resulting in net ocean uptake of 5.2–5.3 PgC/year in the 2090s.

The total 21st century underestimation of ocean carbon uptake by a comparative fixed stoichiometry model is estimated at between 2.0 PgC (assuming global N limitation) and 15.1 PgC (assuming global P limitation; Figure 7b). These estimates are calculated by applying the annual anomaly in global carbon export efficiency relative to the 1850–1900 mean, to the annual atmosphere-ocean CO<sub>2</sub> flux and integrating over the 21st century. Given that PISCES-QUOTA projects total 21st century ocean carbon uptake of 426.5 PgC, the potential underestimation of this by a fixed stoichiometry model is 0.5–3.5% under RCP8.5. We note that this represents a likely upper limit on the potential ocean carbon uptake bias of fixed phytoplankton stoichiometry models. Critically, it assumes that the projected increase in carbon export efficiency provides a long-term enhancement of the vertical dissolved inorganic carbon profile with all additional exported carbon remaining in the deep ocean. In reality, over the multiple timescales that this deep water is recirculated into the upper ocean, the enhanced vertical dissolved inorganic carbon profile would be diminished, reducing ocean carbon uptake and the estimated bias between variable and fixed stoichiometry models. Furthermore, this estimate only accounts for the direct effect of stoichiometrically altered export material. The additional indirect effects of changing food quality and community composition, which will principally affect the magnitude and not the efficiency of export production, are unaccounted for. A shift to smaller particle cell sizes due to phytoplankton community composition shifts, for example, can reduce the efficiency of the biological carbon pump (Bopp et al., 2005), while a decrease in phytoplankton food quality can increase carbon regeneration in the upper ocean if the excess carbon that zooplankton consume is respired.

Observations of phosphate frugal phytoplankton in the low latitude oceans that export more carbon per unit P, have been previously invoked to suggest that the projected expansion of nutrient-depleted waters could result in a shift to more efficient carbon export, that somewhat compensates for the expected decline in productivity (Teng et al., 2014). While PISCES-QUOTA projections support this hypothesis, the estimated impact of variable phytoplankton stoichiometry on global ocean carbon uptake is relatively limited on the centennial timescale considered here. This does not, however, preclude the likelihood that over glacial-interglacial timescales, the impact on atmospheric CO<sub>2</sub> could be substantially larger as has been suggested by box models (Galbraith & Martiny, 2015). We also note

that as PISCES-QUOTA zooplankton are considered to have fixed stoichiometry, which may not be the case on the centennial timescale considered (Talmy et al., 2016), the model may be underestimating the potential contribution of zooplankton to more efficient future carbon export.

## 5. Conclusion

We find that over the 21st century, the impact of accounting for variable phytoplankton stoichiometry on global carbon cycle feedbacks is potentially limited. Based on changes in the stoichiometry of export material in the PISCES-QUOTA model, we estimate that fixed stoichiometry models may be underestimating the integrated 21st century ocean carbon uptake by up to 0.5–3.5%. While further studies are required to validate this, it suggests that from the perspective of informing global climate policy and emissions reduction targets, the inclusion of quota ocean biogeochemistry in ESMs may not be a high priority given the associated increase in computational cost.

Nonetheless, variable stoichiometry can have a large impact on projections of climate impacts on the marine environment. As with the majority of current generation fixed stoichiometry models (Bopp et al., 2013), PISCES-QUOTA projects global NPP declines driven by reductions in the low latitudes. However, picophytoplankton declines in the low latitudes are less extensive than those of other PFTs, in part due to their stoichiometric flexibility under nutrient limitation. We also find that the phytoplankton food quality available to higher trophic levels can be substantially reduced throughout the 21st century. At the global scale declines in phytoplankton N and P content are 1.3% and 7.8%, respectively; however, reductions can exceed 20% in oligotrophic gyres and the Arctic, and this could have major implications for regional ecosystems. Such projections are not permissible within a fixed stoichiometry model framework and highlight the importance of models such as PISCES-QUOTA in informing climate impact assessments.

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