Enrichment of ammonium in the future ocean threatens diatom productivity

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Key Points:

- An ocean biogeochemical model shows an enrichment in ammonium relative to total nitrogen in over 98% of the surface ocean.
- *Tara* Oceans data reveals a global negative relationship between diatoms and ammonium to total nitrogen ratios.
- We attribute 70% of future losses in diatom relative abundance in marine ecosystems to ammonium enrichment.

Abstract

Diatoms are prominent eukaryotic photoautotrophs in today's oceans. While dominant in nitrate-rich conditions, they face competitive exclusion by other phytoplankton when ammonium forms the bulk of bioavailable nitrogen. The extent to which this competitive exclusion defines diatom abundance worldwide and the consequences of potential future ammonium enrichment remain unexplored and unquantified. Here, using phytoplankton abundance proxies from the *Tara* Oceans dataset and an ocean-biogeochemical model, we demonstrate that ammonium enrichment reduces diatom prevalence in marine ecosystems at the global-scale. Under a high emission scenario, we anticipate 98% of the euphotic zones to experience ammonium enrichment by 2081-2100 and attribute a majority (70%) of future diatom displacement to competitive exclusion by other phytoplankton as bioavailable nitrogen supply shifts from nitrate to ammonium. Overall, the form of nitrogen emerges as a significant but previously underestimated stressor affecting diatoms and ocean ecosystems globally.

Plain Language Summary

This work investigates how a type of microscopic algae called diatoms are affected by changes in the form of nitrogen that is available in the sunlit surface ocean. Diatoms are crucial for ocean health and carbon cycling because they grow and sink rapidly. Diatoms typically thrive in waters with high concentrations of nitrate, an oxidized form of nitrogen, but they are outcompeted by other algae when ammonium, a reduced form, is the primary source of nitrogen. We use both observations and modelling to understand how a widespread future enrichment of ammonium within marine ecosystems might affect diatom relative abundance. We attribute that the enrichment of ammonium can explain 70% of the projected losses to diatom relative abundance by the end of the 21st century if greenhouse gas emissions continue unabated. The form of nitrogen, whether oxidized or reduced, is thus an important control on diatom relative abundance.

1 Introduction

Diatoms are among the most successful and diversified eukaryotic photoautotrophs in the present-day ocean (Armbrust, 2009; Pierella Karlusich et al., 2020). Part of their success is due to their competitive edge for growth on nitrate (NO_3^-) as a source of bioavailable nitrogen (Berg et al., 2003; Carter et al., 2005; Donald et al., 2013; Fawcett et al., 2011; Glibert et al., 2016; Klawonn et al., 2019; Litchman, 2007; Van Oostende et al., 2017; Selph et al., 2021; Tungaraza et al., 2003; Xianhui Sean Wan et al., 2018), which also underpins their role as disproportionately large contributors to "new" (NO_3^--fueled) primary production (Fawcett et al., 2011). As new production is linked to the rate of organic carbon export to the ocean interior (Dugdale & Goering, 1967), diatoms also contribute significantly to oceanic carbon dioxide sequestration and the ocean's most productive fisheries (Cushing, 1989; Legendre, 1990;

Tréguer et al., 2018). However, this apparent preference for NO_3^- may instead reflect that they are competitively excluded by other phytoplankton when the primary substrate for growth is ammonium (NH_4^+). While diatoms tend to have a higher affinity for NO_3^- than other phytoplankton, making then adept competitors for NO_3^- when NO_3^- is the primary nitrogen substrate, investigations into the kinetics of nutrient uptake have identified that diatoms have a lower affinity for NH_4^+ then other major groups of phytoplankton (Litchman et al., 2007) (Fig. 1a). Their low affinity for NH_4^+ means that diatoms tend to be competitively excluded by other phytoplankton taxa, such as the smaller (although not always (Arsenieff et al., 2020; Leblanc et al., 2018; Pierella Karlusich et al., 2020)) cyanobacteria and green algae, when nitrogen is limiting and NH_4^+ is the dominant source of nitrogen (Litchman et al., 2007).

Variations in circulation and biogeochemical processes control the form of nitrogen that supports primary production in the sunlit upper ocean (Fig. 1b). As mixing injects NO_3^- from deeper waters, it becomes the dominant form in areas of upwelling, especially when limitation by iron, light or grazing pressure slows uptake by phytoplankton. In stratified systems, NH_4^+ and other forms of reduced nitrogen (e.g., urea and other organics, which can be important nitrogen sources (Morando & Capone, 2018)) dominate the bioavailable nitrogen pool. Nitrate supply is restricted by a lack of vertical mixing, consequently depleted, and demand is instead satisfied by NH_4^+ through an intense heterotrophic recycling of organic matter. Although nutrient stocks are low, the rapidity of this recycling supports net autotrophy and “normal” rates of primary production as measured via carbon uptake incubations and isotopes in the subtropical gyres (Bender & Jönsson, 2016; Matsumoto et al., 2016; Rii et al., 2016; Yang et al., 2019). Intense competition for NH_4^+ in these environments not only excludes the less competitive phytoplankton species, but also the archaea and bacteria that are responsible for ammonia oxidation, which would otherwise resupply nitrite and nitrate and alter the form of nitrogen available for growth (Xianhui Sean Wan et al., 2018; Zakem et al., 2018). Thus, while nitrogen concentrations are low in stratified systems, there is intense competition for a rapid supply of NH_4^+.

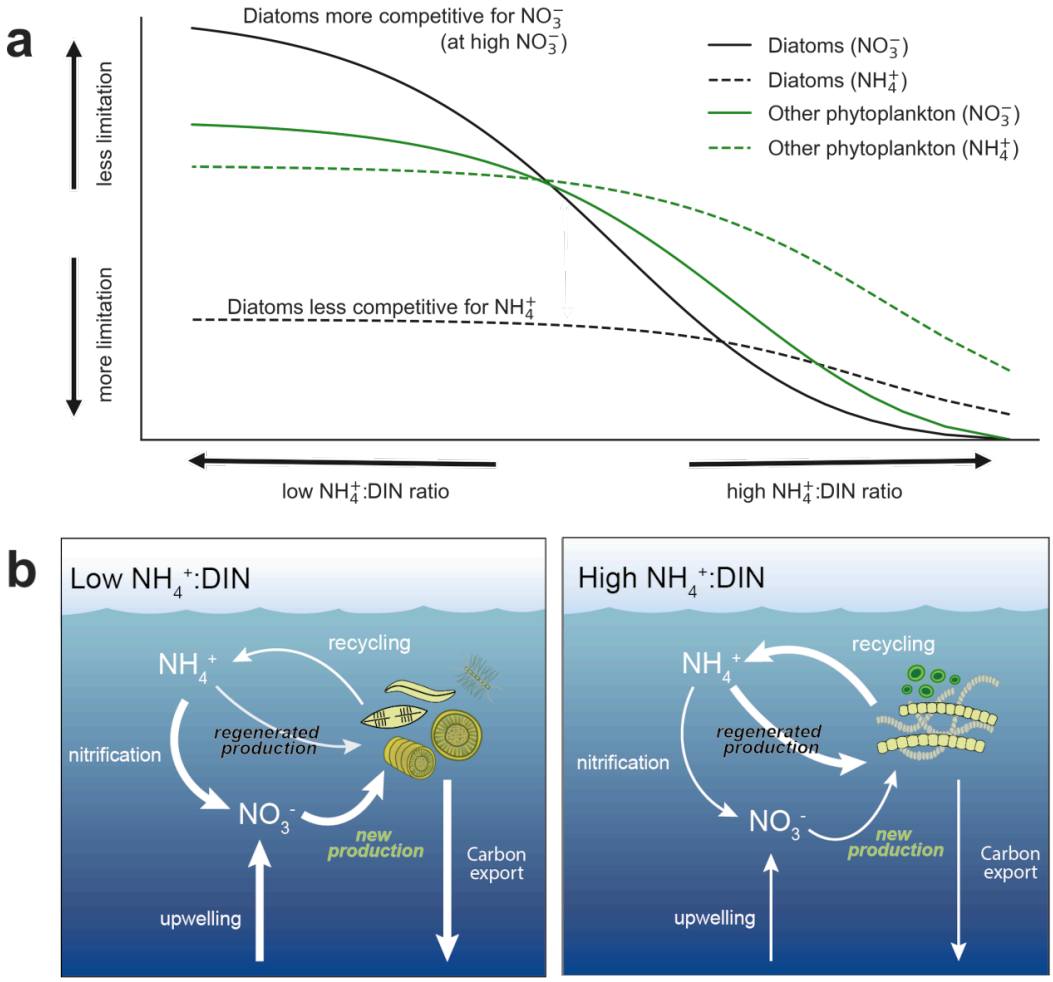


Fig. 1. Competitive outcomes for phytoplankton dependent on regimes of nitrogen cycling in the upper ocean. (a), Example limitation of diatoms (black) and other generic phytoplankton (green) by nitrate (solid lines) and ammonium (dashed lines) as a function of changing NH_4^+:DIN ratios. NH_4^+:DIN ratios (x-axis) are altered by increasing NO_3^- while holding NH_4^+ constant. Diatoms are always more limited by growth on NH_4^+ than other phytoplankton groups. These limitation functions are integrated within the biogeochemical model. (b), Two regimes of nitrogen cycling with low and high NH_4^+:DIN ratios. Nitrogen in the form of NO_3^- is mixed into the euphotic zone, taken up by phytoplankton, including diatoms, to produce organic matter (new production). Organic matter sinks and contributes to carbon export or is consumed by heterotrophs and recycled to NH_4^+. NH_4^+ may be nitrified to NO_3^- or consumed by phytoplankton (regenerated production).

Ongoing and projected climate change is expected to alter both circulation and biogeochemical processes and consequently alter the relative availability of NH_4^+ in marine environments.

Hereafter, we use the NH_4^+ to dissolved inorganic nitrogen ratio (NH_4^+:DIN), where DIN = NH_4^+ + NO_2^- + NO_3^-, as a measure of this relative availability in the form of nitrogen. When we refer to enrichment of NH_4^+, we specifically mean an increase in the amount of DIN that is NH_4^+, with an enrichment consistent with a higher proportion of primary production supported through regeneration (i.e., NH_4^+-based). Physical changes, including a changing oceanic circulation (Sallée et al., 2021), is expected to limit inputs of NO_3^- from deeper waters to further intensify nitrogen limitation of phytoplankton communities (Bopp et al., 2005; Buchanan et al., 2021). Climate warming is expected to accelerate the metabolism of phytoplankton (Eppley, 1972) and thereby increase nitrogen demand and recycling rates (Cherabier & Ferrière, 2022). Meanwhile, ocean acidification may decelerate rates of microbial ammonia oxidation (Beman et al., 2011) (the first step of nitrification), elevating NH_4^+ concentrations at the expense of NO_3^-. All of these changes are expected to increase NH_4^+:DIN ratios in marine environments. However, the magnitude of NH_4^+ enrichment and its dominant drivers remain unquantified. Moreover, we lack a general understanding as to the degree to which diatoms are negatively affected by NH_4^+ enrichment at the global scale. This represents an important knowledge gap as to how climate change will affect the upper ocean nitrogen cycle and phytoplankton community composition, with implications for carbon export and fisheries productivity. In this work, we use compilations of phytoplankton relative abundance data and an ocean-biogeochemical model to quantify future NH_4^+ enrichment and its effects on diatoms within the global ocean.

2 Materials and Methods

2.1 The biogeochemical model

The biogeochemical model is the Pelagic Interactions Scheme for Carbon and Ecosystem Studies version 2 (PISCES-v2) (Aumont et al., 2015). This model is embedded within version 4.0 of the Nucleus for European Modelling of the Ocean (NEMO-v4.0). We chose a 2° nominal horizontal resolution with 31 vertical levels with thicknesses ranging from 10 meters in the upper 100 meters to 500 meters below 2000 meters. Due to the curvilinear grid, horizontal resolution increases to 0.5° at the equator and to near 1° poleward of 50°N and 50°S.

We updated the standard PISCES-v2 for the purposes of this study. This model explicitly resolves the pools of ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-), two kinds of

phytoplankton biomass (nanophytoplankton and diatoms), two kinds of zooplankton biomass (micro- and meso-zooplankton), small and large pools of particulate organic matter, and dissolved organic matter. Nitrogen is added to the ocean via biological nitrogen fixation, riverine fluxes, and atmospheric deposition. Nitrogen is removed from the ocean via denitrification, anaerobic ammonium oxidation (anammox) and burial. The internal cycling of nitrogen involves assimilation by phytoplankton in particulate organic matter, grazing and excretion by zooplankton, solubilization of particulates to dissolved organics, ammonification of dissolved organic matter to NH_4^+, followed by nitrification of NH_4^+ and NO_2^- via ammonia oxidation and nitrite oxidation.

Of relevance to this study are the sources and sinks of NH_4^+. Sources of NH_4 are ammonification, zooplankton excretion and nitrogen fixation, while sinks are phytoplankton assimilation, ammonia oxidation and anammox (Fig. S1). Each process is dependent on other tracers and seawater properties (described in Aumont et al. (2015)). However, we briefly detail the contribution to the NH_4^+ budget (mean ± standard deviation) as well as primary dependencies of the most important processes. Ammonification (69 ± 13% of NH_4^+ sources) rates are highest in productive oceanic regions with high concentrations of dissolved organic compounds. Excretion of NH_4^+ by zooplankton (30 ± 13% of sources) is modelled as a fraction of their grazing rate, with this fraction ranging between 0.21 to 0.42 as phytoplankton become more nutrient limited and are of poorer food quality. Phytoplankton assimilation of NH_4^+ (62 ± 27% of sinks) is modelled by multiplying a temperature- and light-dependent growth rate against phytoplankton biomass, and subsequently applying limitations associated with nutrient availability. Ammonia oxidation (38 ± 27% of sinks) is modelled by multiplying a temperature-dependent growth rate against the concentration of NH_4^+ and applying observationally-informed limitation terms associated with NH_4^+ affinity, light intensity, and pH (Text S1). Phytoplankton assimilation was a greater proportion of sinks in stratified, oligotrophic environments (Fig. S1).

2.2 Model experiments

To quantify the impact of anthropogenic activities on NH_4^+:DIN ratios, we performed transient simulations by forcing the biogeochemical model with monthly physical outputs produced by the Institut Pierre-Simon Laplace Climate Model 5A (Dufresne et al., 2013). Simulations included a preindustrial control where land-use, greenhouse gases and ozone remained at preindustrial

conditions, and a climate change run where these factors changed according to historical observations from 1850 to 2005 and according to the high emissions Representative Concentration Pathway 8.5 from 2006 to 2100 (RCP8.5) (Riahi et al., 2011). We chose a high emissions scenario to emphasize the clearest degree of anthropogenic changes, and thus maximize anthropogenic effects. However, we acknowledge that the RCP8.5 is considered an extreme scenario under present development pathways (Riahi et al., 2017).

In addition, we performed parallel experiments that isolated the individual effects of our three anthropogenic stressors: a changing circulation ("Phys"), warming on biological metabolism ("Warm"), and acidification effects on ammonia oxidation ("OA"). The experiment with all anthropogenic effects was termed "All". These experiments involved altering the factor of interest in line with the historical and RCP8.5 scenario while holding the other factors at their preindustrial state.

The effect of climate change at the end of the 21st century (mean conditions 2081-2100) was quantified by comparing with the preindustrial control simulation. This preindustrial control simulation was run parallel to the climate change simulations (i.e., 1850-2100), but without anthropogenic forcings. This allowed a direct comparison to be made between experiments at the end of the 21st century and eliminated the effect of model drift. We calculated changes at each grid cell by averaging over the euphotic zone, which was defined as those depths where total phytoplankton biomass was greater than 0.1 mmol C m^{-3}. In addition, we compared the preindustrial simulation with observations to explore broad patterns in NH_4^+ and NH_4^+:DIN ratios, averaged over the euphotic zone (Text S2; Fig. S2-S3).

Finally, we repeated the set of experiments described above (All, Phys, Warm and OA) but with an alternative parameterization where diatoms were made to have the same growth limitation on NH_4^+ as other phytoplankton (Fig. S4). This experiment was called "model$_{compete}$", while the model with the default parameterization for nitrogen limitation was termed "model$_{control}$".

2.3 Nutrient and rate data

Measured NH_4^+ concentrations (N=692) were used for model-data assessment (Fig. S2-S3). Nutrients were collated from published work (Buchwald et al., 2015; Mdutyana et al., 2020; Newell et al., 2013; Raes et al., 2020; A. E. Santoro et al., 2013; Alyson E. Santoro et al., 2021;

Shiozaki et al., 2016; Tolar et al., 2016; Xianhui S. Wan et al., 2021; Xianhui Sean Wan et al., 2018), and oceanographic cruises AR16 (https://www.bco-dmo.org/deployment/747056), JC156, and JC150. Coincident NO_2^- and NO_3^- were used to compute NH_4^+ to DIN ratios. If coincident measurements of NO_2^- were not available, then NH_4^+ to DIN ratios were calculated with only NO_3^-. If NO_3^- measurements were not made alongside NH_4^+, then NO_3^- concentrations were extracted from the World Ocean Atlas 2018 (Garcia et al., 2019) monthly climatology at the closest grid cell. These data are available in Data Set S1.

Measured ammonia oxidation rates (N=696) were also used for model-data assessment and showed broad agreement with the model (Fig. S5). Data were collated from published work (Clark et al., 2021; Dore & Karl, 1996; Mdutyana et al., 2020; Newell et al., 2013; Raes et al., 2020; Raimbault et al., 1999; A. E. Santoro et al., 2013; Alyson E. Santoro et al., 2021; Shiozaki et al., 2016; Tolar et al., 2016; Xianhui S. Wan et al., 2021; Xianhui Sean Wan et al., 2018) and are available in Data Set S2.

Measurements of NH_4^+ and NO_3^- concentrations alongside NH_4^+- and NO_3^--fueled primary production ($\mu mol\ m^{-3}\ day^{-1}$) were used to determine the relationship between NH_4^+:DIN ratios and the proportion of net primary production that is fueled by NH_4^+ (Fig. S6). While coincident measurements of these properties are not common, we compiled data from nine studies (Fernández et al., 2009; Joubert et al., 2011; Mdutyana et al., 2020; Metzler et al., 1997; Philibert, 2015; Rees et al., 2006; Thomalla et al., 2011; Xianhui Sean Wan et al., 2018; Yingling et al., 2021) providing 190 data points that together encompassed oligotrophic to eutrophic conditions from the tropics to the Southern Ocean. Measurements from the Gulf of Mexico (Yingling et al., 2021) were unique in that nutrient concentrations and uptake rates were not measured at precisely the same depths or stations. Coincident values were determined by calculating trends in depth via linear interpolation (Fig. S7). These data are available in Data Set S3.

Ammonia oxidation rates data from experiments involving pH changes were acquired directly from the papers presenting the results (Beman et al., 2011; Huesemann et al., 2002; Kitidis et al., 2011) by extraction from the text (where values were given) and from figures using the WebPlotDigitizer tool (https://automeris.io/WebPlotDigitizer/). Changes in ammonia oxidation rates were normalized to a pH of 8 (Fig. S8). These data are available in Data Set S4.

222 ### 2.4 Phytoplankton relative abundance data

223 *Tara* Oceans expeditions between 2009 and 2013 performed a worldwide sampling of plankton
224 in the upper layers of the ocean (Pierella Karlusich et al., 2020). We mined the 18S rRNA gene
225 (V9 region) metabarcoding data set (Ibarbalz et al., 2019; de Vargas et al., 2015) by retrieving
226 the operational taxonomic units (OTUs) assigned to eukaryotic phytoplankton from samples
227 obtained from 144 stations (https://zenodo.org/record/3768510#.Xraby6gzY2w). Barcodes with
228 greater than 85 % identity to phytoplankton sequences in reference databases were selected. The
229 total diatom barcode reads in each sample was normalized to the barcode read abundance of
230 eukaryotic phytoplankton. We exclusively used the data sets corresponding to surface samples
231 (5-9 m depth).

232 In addition, we analyzed the metagenomic read abundances for the single-copy photosynthetic
233 gene *psbO*, an approach that covers both cyanobacteria and eukaryotic phytoplankton and
234 provides a more robust picture of phytoplankton cell abundances than rRNA gene methods
235 (Pierella Karlusich et al., 2022). We retrieved the abundance tables from samples obtained from
236 145 stations (https://www.ebi.ac.uk/biostudies/studies/S-BSST761).

237 ### 2.5 Statistical analysis

238 We explored the environmental drivers of change in phytoplankton relative abundance data
239 (provided by *Tara* Oceans) with generalized additive models (GAMs) using the *mgcv* package in
240 R (Wood, 2006) according to the equation:

$$Y = \alpha + s_1(x_1) + s_2(x_2) + \cdots + s_n(x_n) + \varepsilon, \qquad 1$$

241 Where Y is the predicted value of the response variable, α is the intercept, $s_n(x_n)$ is the n^{th} thin-
242 plate spline of the n^{th} independent variable, and ε is the population error around the prediction.
243 Independent variables were mixed-layer depth (m), phosphate (µM), silicate (µM), dissolved
244 iron (µM), and the NH_4^+:DIN ratio. Mixed layer depth, phosphate and silicate was measured *in*
245 *situ* at the sample locations of Tara Oceans, while dissolved iron and NH_4^+:DIN ratios were
246 provided by the model. In addition, phosphate and silicate concentrations were available as
247 interpolated products from the World Ocean Atlas (Garcia et al., 2019). An alternative estimate
248 of NH_4^+:DIN ratios was provided by the Darwin model (Follows et al., 2007). Predictor variables
249 from models and World Ocean Atlas were extracted at the locations and months of sampling.

Mixed-layer depth, nutrients (phosphate, silicate and NH_4^+:DIN) and the relative abundance of phytoplankton taxa were log_{10}-transformed prior to model building to ensure homogeneity of variance.

Before model testing, we calculated the variance inflation factors (VIFs) of independent variables to avoid multi-collinearity. All covariate VIFs were < 3. GAMs were computed using a low spline complexity (k = 3) that prevented overfitting. We fit GAMs using all predictors (full model), then assessed the deviance explained by each predictor by fitting subsequent GAMS with each predictor in isolation, and by removing the predictor in question from the full model. The significance of a predictor was assessed by applying a smoothing penalty to only that predictor in the full model. Diagnostic plots were assessed visually, and predictive capacity was assessed via the percent of deviance explained by the model.

A two-sided Mann-Whitney U test was used to test for differences between the two distributions of diatom relative abundance separated by NH_4^+:DIN ratios < 4% and > 4% presented in Figure 2b. The 4% threshold was used because it split the dataset in half and aligned with the point at which primary production transitioned from mostly new (NO_3^--fueled) to regenerated (NH_4^+-fueled) (Fig. S6). This non-parametric test (performed with the *scipy* package in python) returned highly significant two-sided p-values ($p < 0.0001$) where indicated by *** in Figure 2c

3 Results and Discussion

3.1 NH_4^+ enrichment and diatom relative abundance

The competitive exclusion of diatoms by other phytoplankton in NH_4^+ enriched waters suggests that declines in diatom relative abundance should be associated with increases in NH_4^+:DIN. While shown theoretically (Glibert et al., 2016; Litchman, 2007; Litchman et al., 2007) and in restricted locations (Berg et al., 2003; Carter et al., 2005; Donald et al., 2013; Fawcett et al., 2011; Klawonn et al., 2019; Van Oostende et al., 2017; Selph et al., 2021; Tungaraza et al., 2003; Xianhui Sean Wan et al., 2018), this relationship is yet to be observed at the large scale. The *Tara* Oceans global survey offers 144 stations encompassing equatorial to polar marine environments (Ibarbalz et al., 2019). We used two proxies of diatom relative abundance from this dataset: 18S rRNA gene metabarcodes for estimating relative abundance among eukaryotic phytoplankton (de Vargas et al., 2015), and *psbO* gene counts for estimating relative abundance

among all phytoplankton (cyanobacteria and eukaryotes) (Pierella Karlusich et al., 2022). These estimates were combined with NH_4^+:DIN as predicted by a global ocean-biogeochemical model (Aumont et al., 2015) at the same location and month of sampling, since NH_4^+ measurements are scarce. This model effectively reproduced the sparse available datasets of NH_4^+ and NH_4^+:DIN, and is aligned with current understanding of how NH_4^+ cycles in the ocean (Supplementary Text; Fig. S1-S6). Model-derived NH_4^+:DIN was used to predict diatom relative abundance in Generalized Additive Models (GAMs), along with other bottom-up drivers of phytoplankton community composition (see Methods).

Our analysis revealed that elevated NH_4^+:DIN was consistently associated with declines in diatom relative abundance (Fig. 2a). This negative relationship was evident and significant in GAMs trained on both abundance proxies, as well as when using different combinations of predictor variables: whether model-derived, *in situ* measurements, interpolated products (Garcia et al., 2019), or when switching out NH_4^+:DIN as predicted by our biogeochemical model with that provided by another (Follows et al., 2007) (Table S1). Importantly, the relationship between NH_4^+:DIN and diatom relative abundance remained consistently negative and significant. This was not the case for other predictors, which were prone to insignificance or sign changes depending on the combination of predictors used (Fig. S9-S13). NH_4^+:DIN also offered large explanatory power for diatom abundance compared to the other predictor variables, explaining between 18-30% of the deviance in the data (Table S1).

The association between diatoms and NH_4^+:DIN was strong compared with the other major phytoplankton taxa (Table S2). Only dinoflagellates (18S metabarcoding), *Prochlorococcus* and chlorophytes (*psbO*) showed similarly strong associations (Fig. S14-S15). These associations are also expected. *Prochlorococcus* was positively related to NH_4^+:DIN, reflecting their superior affinity for NH_4^+ and dominance in oligotrophic gyres (Herrero et al., 2001; Litchman, 2007; Litchman et al., 2007; Matsumoto et al., 2016; Rii et al., 2016). Chlorophytes were negatively related to NH_4^+:DIN and positively related to phosphate, reflecting their prominence in nutrient-rich waters (Vannier et al., 2016). The positive relationship between dinoflagellates and NH_4^+:DIN within eukaryotic phytoplankton likely reflects the inclusion of non-photosynthetic dinoflagellate lineages with the 18S metabarcoding method (Pierella Karlusich et al., 2022) and the proliferation of these types within systems enriched in reduced nitrogen (Glibert et al., 2016).

We performed the same GAM analysis on diatom relative abundances predicted by our biogeochemical model ($model_{control}$; black line in Fig. 2a). This model imbues its diatoms with a known competitive disadvantage for NH_4^+ (Fig. 1a; Fig. S4). If competition for NH_4^+ is an important control on diatom relative abundance in the model, we should therefore see a strong negative relationship between the NH_4^+:DIN ratio and diatom relative abundance. We stress here that if diatoms had an equal affinity for NH_4^+ as other phytoplankton, then they would not be outcompeted (as shown later). As expected, diatom relative abundance was negatively related to NH_4^+:DIN (deviance explained = 70%; p-value < 0.001). Interestingly, the relationship was also strongly non-linear and similar to that seen in the *Tara* Oceans data, with rapid losses of diatoms as NH_4^+:DIN became greater than 4%. This threshold, where NH_4^+ becomes 4% of total nitrogen stocks, aligns with the point at which primary production becomes dominated by regenerated production (Fig. S6). This result not only showcases the intense recycling of NH_4^+ in the marine environment and competition for this coveted nutrient, but also showcases how diatoms are outcompeted as more primary production becomes regenerated. On the other hand, this also showcases how diatom are major contributors to new primary production in the ocean (Fawcett et al., 2011). Importantly, on either side of this 4% threshold, the GAM predictions built from both the biogeochemical model and *Tara* Oceans data could not be statistically differentiated (Fig. 2b,c,d; Mann-Whitney U pair-wise tests). Both modelled and *Tara* Oceans data predicted similar values of diatom relative abundance within communities where NH_4^+:DIN was less than 4%, as well as in communities where NH_4^+:DIN was greater than 4% (Fig. 2b,e). Overall, the modelled and observed changes in diatom relative abundance associated with NH_4^+:DIN appear statistically indistinguishable. Since our biogeochemical model explicitly accounts for competitive exclusion of diatoms as NH_4^+:DIN increases, this similarity may mean that the negative relationship apparent in both may originate from the same mechanism, specifically being a competitive disadvantage for NH_4^+.

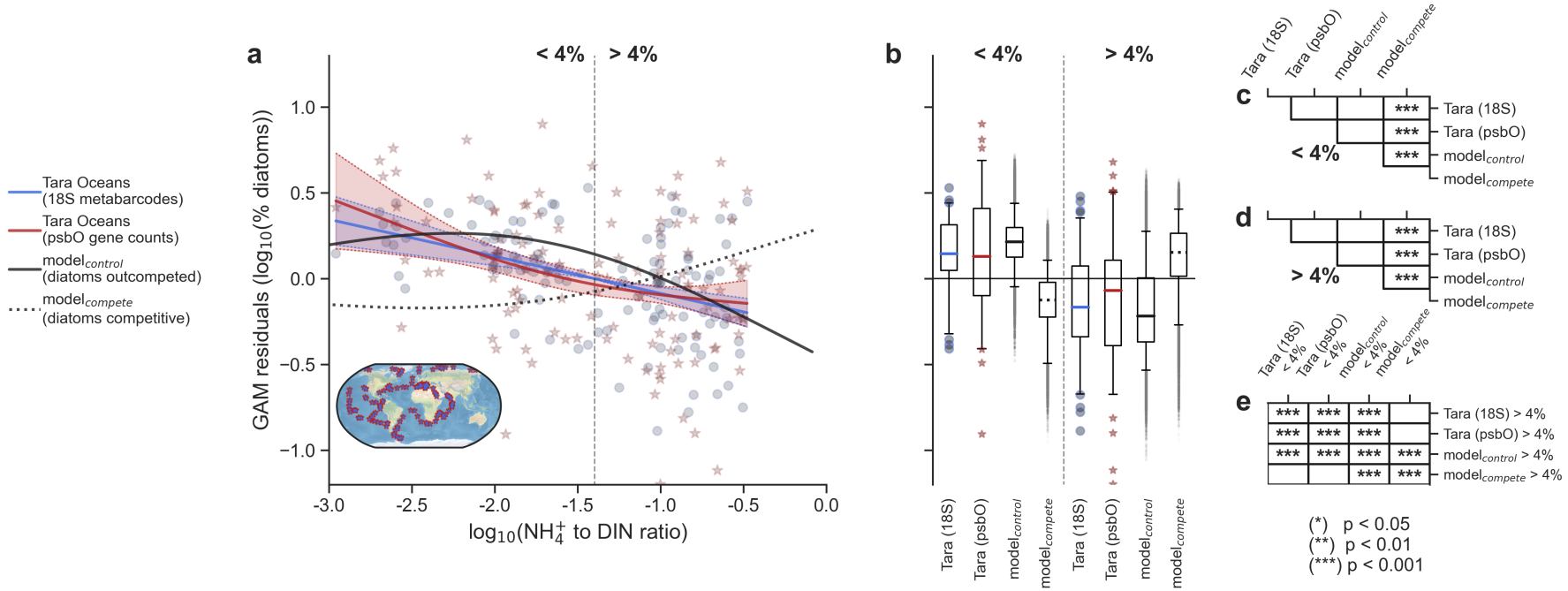


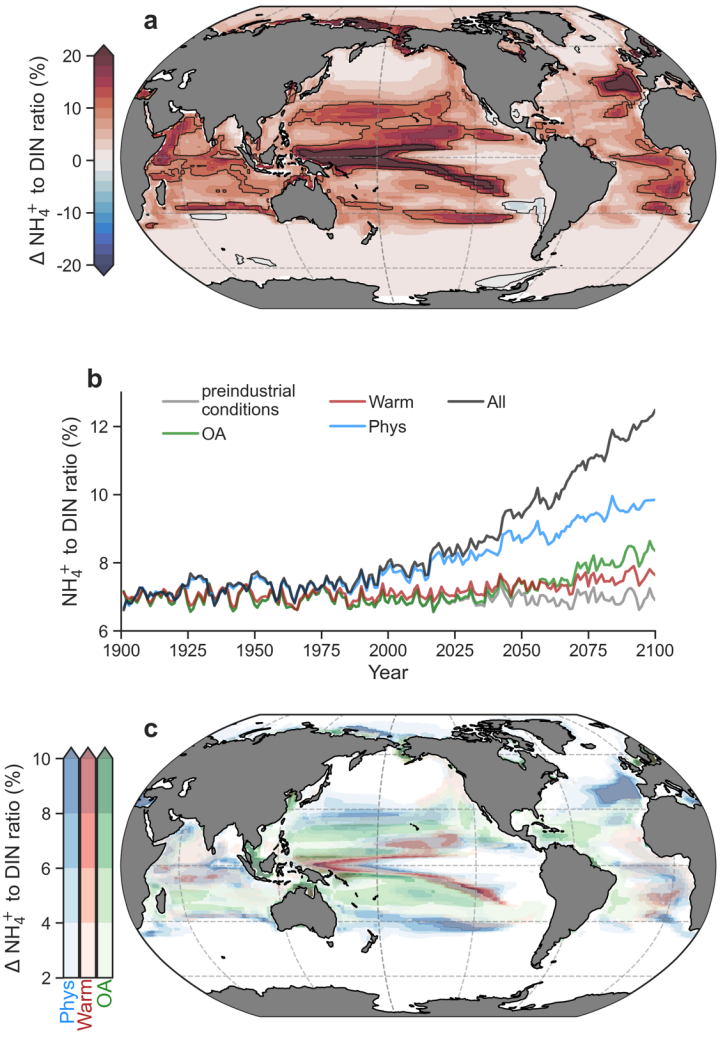
Fig. 2. Effects of NH_4^+ enrichment on primary production and diatom relative abundance. (**a**), Partial dependence plot from the generalized additive model (GAM) showing the relationship between the NH_4^+ to DIN ratio and the percent relative abundance of diatoms. Blue round markers and blue line fit are percent among eukaryotic phytoplankton (18S rRNA metabarcodes). Red star markers and red line fit are percent among all phytoplankton (*psbO* gene counts). Solid and dashed black lines are output from the ocean-biogeochemical model with and without competitive exclusion of diatoms for NH_4^+. The vertical dotted line delineates when NH_4^+ is 4% of DIN. The inset map shows the locations of *Tara* Oceans samples. (**b**), Boxplots of the raw partial residuals from panel (**a**) but separated either side of the 4% NH_4^+ to DIN threshold for percent among eukaryotic phytoplankton (blue), all phytoplankton (red), the ocean-biogeochemical model (solid black), and model without competitive exclusion of diatoms for NH_4^+ (dashed black). Whiskers correspond to the 5th and 95th percentiles. Tables on the right denote significant pair-wise differences (Mann-Whitney U) amongst datasets when NH_4^+:DIN is less than 4% (**c**), when it is more than 4% (**d**) and when comparing < 4% with > 4% datasets (**e**).

3.2 Future enrichment of NH_4^+ in the ocean

Given the importance of NH_4^+ enrichment for influencing primary production and phytoplankton community composition, we explored the potential impact of anthropogenic climate change on NH_4^+:DIN across the global ocean. Using a high emissions climate change scenario from 1851 to 2100 (Representative Concentration Pathway 8.5 (Riahi et al., 2011)), we simulated physical changes (circulation change + sea-ice loss), the stimulation of metabolism by warming, and a data-constrained slowdown of ammonia oxidation by ocean acidification (Fig. S16) in our ocean-biogeochemical model. By the end of the 21st century (2081-2100), these factors increased NH_4^+:DIN in over 98% of the upper ocean euphotic layer (Fig. 3a). On average, the fraction of DIN present as NH_4^+ increased by 6 ± 6 %, with enrichment exceeding 20% in regions with pronounced DIN gradients, such as oceanographic fronts. The enrichment of NH_4^+ caused an expansion of regenerated production across the ocean, such that NH_4^+ overtook NO_3^- as the main nitrogen substrate for phytoplankton growth in an additional 13% of the ocean. The greatest change occurred within the 21st century (Fig. 3b), indicating a direct relationship between the severity of climate change and the magnitude of NH_4^+ enrichment.

Physical changes, a warming-induced stimulation of microbial metabolism and ocean acidification all played a role in increasing NH_4^+:DIN. Among these factors, physical changes had the largest contribution, accounting for 55% of future trends (Fig. 3b), followed by ocean acidification (25%) and stimulated metabolism (13%). Physical changes decreased DIN to cause increases in NH_4^+:DIN in many regions (Fig 3c; Fig. S16) and occurred either through reduced physical supply (e.g., North Atlantic (Whitt & Jansen, 2020)) or increased demand and export of organic nitrogen in regions experiencing an increase in primary production due to losses in sea ice and increases in light (e.g., Arctic (Comeau et al., 2011)). Ocean acidification increased NH_4^+:DIN everywhere, but had the greatest effect in oligotrophic settings where DIN concentrations are lower, and minimal effects in eutrophic regions (Fig 3c; Fig. S16). We do note, however, that there is much uncertainty in the relationship between pH and ammonia oxidation rates (Bayer et al., 2016; Kitidis et al., 2011). We performed an idealized experiment exploring a much weaker relationship between pH and ammonia oxidation that reduced the contribution of acidification to NH_4^+ enrichment by 10% or more and increased the contribution of the other stressors (Fig. S17). However, as pH decline was most strongly influential to

NH_4^+:DIN ratios in the subtropical gyres, the alternative parameterization did little to change NH_4^+:DIN ratios in eutrophic regions where diatoms form an important component on the community. Warming stimulated the nutrient demand of phytoplankton, which reduced DIN, a mechanism consistent with the effects of temperature on marine microbial recycling (Cherabier & Ferrière, 2022). While its global contribution was small at 13% (Fig. 3b), warming had important effects at the boundaries of NO_3^--rich regions by contracting their areal extent, turning NO_3^--rich waters to NO_3^--poor waters (Fig. 3c; Fig. S16). Altogether, the individual contributions of physical change, acidification and stimulated metabolism diagnosed via our sensitivity experiments explained 93% of the full change in NH_4^+:DIN, indicating that a linear combination of the three drivers accounted for near the full response.



386 **Fig. 3. Anthropogenic impacts on the NH_4^+ to DIN ratio. (a)**, The difference in the NH_4^+ to
387 DIN ratio averaged over the euphotic zone at the end of the 21st century (2081-2100) with all
388 anthropogenic impacts. (**b**), Global mean trends in euphotic zone NH_4^+ to DIN ratio in the
389 different experiments: preindustrial control (grey), ocean acidification (OA; green), warming on
390 metabolic rates (Warm; red), physical changes (Phys; blue) and all effects (All; black) according
391 to the RCP8.5 climate change scenario. (**c**), Increases in the NH_4^+ to DIN ratio due to physical
392 changes (blue), effect of warming on metabolic rates (red) and ocean acidification on ammonia
393 oxidation (green) from a multiple stressor perspective.

394

395 3.3 Impacts on future diatom abundance

396 Our climate change simulations predict a future decline in the abundance of diatoms and their
397 representation within phytoplankton communities, particularly in the subantarctic, tropical, North
398 Atlantic, North Pacific and Arctic Oceans where declines sometimes exceeded 20% (Fig. 4a; Fig.
399 S18). Diatoms are currently major contributors to net primary production in these regions
400 (Armbrust, 2009; Tréguer et al., 2018; Uitz et al., 2010). The decline in diatom relative
401 abundance was driven by a combination of stimulated microbial metabolism (60%) and physical
402 changes (40%), while ocean acidification had negligible effects (Figure 4c) because of its limited
403 effect on NH_4^+:DIN outside of the oligotrophic gyres where diatoms are already a small
404 proportion of communities (Fig. S17). However, we recognize that other influential bottom-up
405 and top-down stressors, such as growth limitation by other nutrients (Taucher et al., 2022), shifts
406 in the light environment, and/or grazing pressure (Brun et al., 2015; Margalef, 1978; Taucher et
407 al., 2022) are also influential to structuring phytoplankton communities. Furthermore, we
408 acknowledge that the negative relationship that we observe between NH_4^+:DIN and diatom
409 relative abundance in both the *Tara* Oceans datasets and the model (Figure 2a) may be
410 influenced by these or other covarying factors. This includes increases or decreases in the total
411 availability of DIN, namely being NO_3^-. If other factors are covarying with NH_4^+:DIN but are
412 more influential to diatom relative abundance, this may lead to the erroneous attribution of a
413 causative relationship between diatom relative abundance and NH_4^+:DIN ratios (i.e., a false
414 positive).

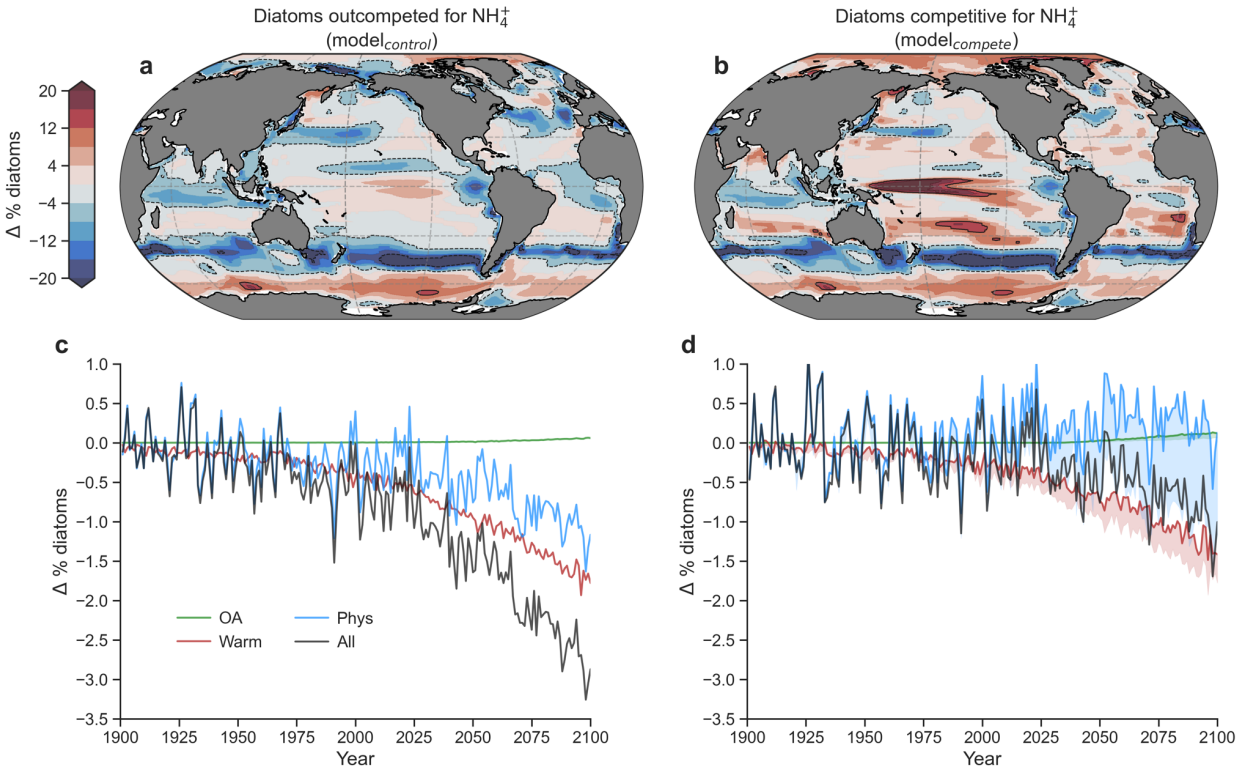


Fig. 4. Impact of NH_4^+ enrichment within DIN on diatom relative abundance. (**a**), Mean change (Δ) in the relative abundance of diatoms (%) by the end of the 21st century (2081-2100) as predicted by the control run of the ocean-biogeochemical model (model$_{control}$) under the RCP8.5 scenario and averaged over the euphotic zone. (**b**), Same as in (**a**), but for the model with equal affinities of diatoms and other phytoplankton for NH_4^+ (model$_{compete}$). (**c**), Global mean change in diatom relative abundance due to physical (circulation + light) changes (blue), warming effects on metabolic rates (red), ocean acidification effect on ammonia oxidation (green) and all stressors (black) for model$_{control}$. (**d**), The same as in (**c**), but for model$_{compete}$. Shading shows the change between (**c**) and (**d**).

To isolate the impact of competition for NH_4^+ specifically, and thus target the causative relationship between NH_4^+:DIN and diatom relative abundance, we performed idealized experiments that equalized diatom growth limitation on NH_4^+ with that of other phytoplankton (model$_{compete}$; equivalent to making the dashed lines in Figure 1a equivalent; Fig. S4). All other traits remained unchanged, including the different affinities of diatoms and other phytoplankton for NO_3^-. This experiment meant that when DIN was low, diatoms were equally competitive for

NH_4^+, but still suffered their unique limitations associated with light, silicate, phosphate, nitrate (Fig. 1a) and iron availability, as well as grazing pressure.

Making diatoms equally competitive for NH_4^+ mitigated the losses of diatom representation within future phytoplankton communities by 70%. While phytoplankton biomass, including diatoms, largely declined everywhere outside of the polar regions (Fig. S18), the losses in diatom relative abundance were reduced from a global mean of 3.2% to 0.9% by 2081-2100 (Fig. 4c). Physical changes no longer exerted a global negative effect on their total nor relative abundance, while the negative effect of elevated microbial metabolism on relative abundance was ameliorated by 25% (Fig. 4d; Fig. S18-19). Diatoms even showed increased total and/or relative abundance in regions where previously there were losses, including the Arctic, the tropical Pacific, the Arabian Sea, the North Atlantic, and the southern subtropics. Outside of the Southern Ocean and the eastern boundary upwelling systems, physical changes that tended to reduce DIN concentrations now favored diatoms, while elevated metabolism now had positive, rather than negative, effects in the tropical Pacific.

These experiments provide valuable insights into the factors controlling diatom niches. Regions where $model_{control}$ and $model_{compete}$ show similar changes are regions where other factors besides NH_4^+:DIN determine diatom competitiveness. In the Southern Ocean, iron, light and silicic acid are the major controls on diatom productivity and phytoplankton community composition (P. Boyd et al., 1999; P. W. Boyd et al., 2000; Krumhardt et al., 2022; Llort et al., 2019), and this is apparent in the matching outcomes of $model_{control}$ and $model_{compete}$. However, where $model_{control}$ and $model_{compete}$ predicted contrasting outcomes, the form of nitrogen, specifically NH_4^+:DIN and thus the intense competition for NH_4^+, exerted a dominant control.

The importance of phytoplankton's competitive ability for NH_4^+ is exemplified by the fact that the negative relationship between NH_4^+:DIN and diatom relative abundance was reversed in $model_{compete}$ (black dotted line in Fig. 2a). Now positive rather than negative, this relationship differed statistically from those predicted from *Tara* Oceans data (Figure 2b-e). This strongly suggests that competition for NH_4^+ independently controls diatom relative abundance. We stress that in this experiment both diatoms and other phytoplankton maintained the same affinity for NO_3^-. While we acknowledge that decreases in NO_3^- were a major cause of NH_4^+ enrichment in our experiments, we emphasize that the mechanism by which diatoms decline in the community

462 is due to their poor competitive ability for growth on NH_4^+, not because of increases or decreases
463 in total NO_3^- concentration. Changes in NO_3^- certainly affect diatom growth, but only do so
464 indirectly by shifting the regime away from or towards intense competition for NH_4^+. Given the
465 statistical similarity between the *in situ* (*Tara* Oceans) and *in silico* ($model_{control}$) relationships,
466 this implicates NH_4^+:DIN as a key underlying driver of diatom relative abundance in the world
467 ocean.

468 **4 Conclusions**

469 Our results show that the form of bioavailable nitrogen exerts a strong influence on the
470 competitive niche of diatoms, and that this niche is therefore tied to the upper ocean nitrogen
471 cycle. Our modelling suggests an enrichment of NH_4^+ in over 98% of ocean euphotic zones by
472 the end of the 21st century under a high emissions scenario (Riahi et al., 2011). In those places
473 where nitrogen availability limits growth, diatoms suffer displacement by phytoplankton taxa
474 with a greater affinity for NH_4^+. The warming and physical changes that drive NH_4^+ enrichment
475 and diatom displacement are expected (Bindoff et al., 2019) and the link between NH_4^+
476 enrichment and diatom displacement is demonstrated herein at the global scale. However, we
477 acknowledge that the link between environmental change and NH_4^+ enrichment rests on
478 processes that are still not fully understood. For instance, an observed increase in summertime
479 mixed layer depths may counter the effect of a strengthening pycnocline (Sallée et al., 2021) to
480 increase NO_3^- injection into euphotic zones. Another key contributor to this uncertainty is the
481 microbial loop, driven by heterotrophic bacteria, which resupplies NH_4^+ through mineralization
482 of organic matter (Fig. 1b). The microbial loop is not yet incorporated in detail within earth
483 system models but its response to warming can either elevate or depress regenerated production
484 depending on assumptions made about the bacterial physiology (Cherabier & Ferrière, 2022).
485 The future balance of reduced (NH_4^+ and organic forms) to oxidized nitrogen and its impact on
486 the state of marine ecosystems hinges on a suite of unexplored feedbacks between the marine
487 microbial loop and environmental change.

488 Overall, the open ocean habitat appears to be becoming more challenging for diatoms. Iron stress
489 is growing in the Southern Ocean (Ryan-Keogh et al., 2023), silicic acid limitation is prospect
490 across the ocean in response to ocean acidification (Taucher et al., 2022), and growing nitrogen
491 limitation may make diatoms less adaptable as temperatures rise (Aranguren-Gassis et al., 2019).

492 Furthermore, diatoms may be even more susceptible to increases in NH_4^+:DIN in temperate
493 waters, as cooler conditions appear to amplify their growth dependence on NO_3^- (Glibert et al.,
494 2016; Parker & Armbrust, 2005). In addition to these stressors, the climate-driven expansion of
495 NH_4^+-enriched oligotrophic gyres, as well as the potential for a NO_3^--limited Arctic, will further
496 disadvantage diatoms. Notwithstanding the potential for evolution, these and other rapid changes
497 may reduce diatom diversity (Lampe et al., 2018; Sugie et al., 2020), making diatoms susceptible
498 to extirpation (Cael et al., 2021). If this is realized, ocean ecosystems may shift towards longer,
499 less productive food-chains underpinned by smaller, slower-growing phytoplankton (Sommer et
500 al., 2002), with severe implications for the health of important fisheries and carbon storage.
501 Further work is urgently needed to understand how this key marine phytoplankton group might
502 respond to these growing challenges in an integrated manner.

503

504 **Acknowledgments**

505 Simulations and development were undertaken on Barkla, part of the High-Performance
506 Computing facilities at the University of Liverpool. The authors wish to acknowledge use of the
507 Ferret program (http://ferret.pmel.noaa.gov/Ferret/), climate data operators
508 (https://code.mpimet.mpg.de/projects/cdo/), NetCDF Operators (http://nco.sourceforge.net/) and
509 Python (www.python.org) for the analysis and graphics in this paper. Thanks to Xianhui Wan,
510 Carolyn Buchwald and Alyson Santoro who shared data, and ongoing discussions with Elena
511 Litchman. PJB, RET and AT were supported by the ARISE project (NE/P006035/1), part of the
512 Changing Arctic Ocean programme, jointly funded by the UKRI Natural Environmental
513 Research Council (NERC) and the German Federal Ministry of Education and Research
514 (BMBF). JJPK was supported by the Moore-Simons Project on the Origin of the Eukaryotic Cell,
515 Simons Foundation (735929LPI). EMSW and AT acknowledge support from the UKRI NERC
516 grant NE/N009525/1, the Mid Atlantic Ridge project (FRidge). EMSW was also supported by
517 the UKRI NERC grant NE/N001079/1 (Zinc, Iron and Phosphorus in the Atlantic). CB
518 acknowledges support from FEM (Fonds Francais pour l'Environnement Mondial), the French
519 Government 'Investissements d'Avenir' programs OCEANOMICS (ANR-11-BTBR-0008),
520 FRANCE GENOMIQUE (ANR-10-INBS-09-08), MEMO LIFE (ANR-10-LABX-54), and PSL
521 Research University (ANR-11-IDEX-0001-02), the European Research Council (ERC) under the

European Union's Horizon 2020 research and innovation program (Diatomic; grant agreement No. 835067), and project AtlantECO.

Open Research

All data and materials used in the analysis are freely available. Nutrient data, nitrification rates, coincident nutrient concentrations with regenerated/new primary production rates, and ammonia oxidation rates relative to pH variations are provided in Supplementary Data 1-4. The biological data from the *Tara* Oceans sampling program are available at https://zenodo.org/record/3768510#.Xraby6gzY2w and https://ftp.ebi.ac.uk/biostudies/nfs/S-BSST/761/S-BSST761/. The model output and scripts to reproduce the analysis are available at https://doi.org/10.5281/zenodo.7630283. Developments to the PISCESv2 ocean-biogeochemical model code are freely available for download at https://github.com/pearseb/ORCA2_OFF_PISCESiso-N.

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