Enrichment of ammonium in the future ocean threatens diatom productivity

Pearse James Buchanan¹, Juan J Pierella Karlusich², Robyn Elizabeth Tuerena³, Roxana Shafiee⁴, Malcolm Woodward⁵, Chris Bowler⁶, and Alessandro Tagliabue⁷

¹CSIRO

²FAS Division of Science, Harvard University
³Scottish Association for Marine Science
⁴Center for Environment, Harvard University
⁵Plymouth Marine Laboratory
⁶Institut de biologie de l'Ecole normale supérieure (IBENS), Ecole normale supérieure, CNRS, INSERM, PSL Université Paris 75005 Paris, France.
⁷University of Liverpool

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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.

1 Enrichment of ammonium in the future ocean threatens diatom productivity

2 Pearse J. Buchanan^{1,2,3}, Juan J. Pierella Karlusich^{4,5}, Robyn E. Tuerena⁶, Roxana Shafiee⁷,

E. Malcolm S. Woodward⁸, Chris Bowler⁵, and Alessandro Tagliabue².

- 4 ¹CSIRO Environment, Hobart, 7004, Australia.
- ²Department of Earth, Ocean and Ecological Sciences, University of Liverpool; Liverpool, L69
 3GP, UK.
- ⁷ ³Department of Global Ecology, Carnegie Institution for Science; Stanford, CA, 94305, USA.
- ⁸ ⁴FAS Division of Science, Harvard University, Cambridge, MA, 02138, USA.
- 9 ⁵Institut de Biologie de l'École Normale Supérieure, Département de Biologie, École Normale
- 10 Supérieure, CNRS, INSERM, Université de Recherche Paris Sciences et Lettres, Paris, France.
- ¹¹ ⁶Scottish Association for Marine Science; Dunstaffnage, Oban, PA37 1QA, UK.
- ¹² ⁷Center for the Environment, Harvard University, Cambridge, MA, 02138.
- ¹³ ⁸Plymouth Marine Laboratory; Plymouth, PL1 3DH, UK.
- 14
- 15 Corresponding author: Pearse J Buchanan (<u>pearse.buchanan@csiro.au</u>)
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17 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.

24 Abstract

- 25 Diatoms are prominent eukaryotic photoautotrophs in today's oceans. While dominant in nitrate-
- 26 rich conditions, they face competitive exclusion by other phytoplankton when ammonium forms
- 27 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
- 29 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
- 31 reduces diatom prevalence in marine ecosystems at the global-scale. Under a high emission 32 scenario, we anticipate 98% of the euphotic zones to experience ammonium enrichment by 2081-
- 32 scenario, we anticipate 56% of the explore zones to experience anticontum enrichment by 2081 33 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
- 36 diatoms and ocean ecosystems globally.
- 37

38 Plain Language Summary

This work investigates how a type of microscopic algae called diatoms are affected by changes 39 40 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 41 42 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 43 44 observations and modelling to understand how a widespread future enrichment of ammonium within marine ecosystems might affect diatom relative abundance. We attribute that the 45 enrichment of ammonium can explain 70% of the projected losses to diatom relative abundance 46 by the end of the 21st century if greenhouse gas emissions continue unabated. The form of 47 nitrogen, whether oxidized or reduced, is thus an important control on diatom relative 48 abundance. 49

50

51 **1 Introduction**

- 52 Diatoms are among the most successful and diversified eukaryotic photoautotrophs in the
- 53 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
- ⁵⁵ et al., 2003; Carter et al., 2005; Donald et al., 2013; Fawcett et al., 2011; Glibert et al., 2016;
- 56 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" (NO₃⁻-fueled) primary production (Fawcett et al.,
- 59 2011). As new production is linked to the rate of organic carbon export to the ocean interior
- 60 (Dugdale & Goering, 1967), diatoms also contribute significantly to oceanic carbon dioxide
- 61 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 62 are competitively excluded by other phytoplankton when the primary substrate for growth is 63 ammonium (NH₄⁺). While diatoms tend to have a higher affinity for NO_3^- than other 64 phytoplankton, making then adept competitors for NO₃⁻ when NO₃⁻ is the primary nitrogen 65 substrate, investigations into the kinetics of nutrient uptake have identified that diatoms have a 66 lower affinity for NH₄⁺ then other major groups of phytoplankton (Litchman et al., 2007) (Fig. 67 1a). Their low affinity for NH₄⁺ means that diatoms tend to be competitively excluded by other 68 phytoplankton taxa, such as the smaller (although not always (Arsenieff et al., 2020; Leblanc et 69 al., 2018; Pierella Karlusich et al., 2020)) cyanobacteria and green algae, when nitrogen is 70 limiting and NH₄⁺ is the dominant source of nitrogen (Litchman et al., 2007). 71 Variations in circulation and biogeochemical processes control the form of nitrogen that supports 72 primary production in the sunlit upper ocean (Fig. 1b). As mixing injects NO₃⁻ from deeper 73 74 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, NH₄⁺ and other 75 76 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 77 restricted by a lack of vertical mixing, consequently depleted, and demand is instead satisfied by 78 NH4⁺ through an intense heterotrophic recycling of organic matter. Although nutrient stocks are 79 80 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 81 (Bender & Jönsson, 2016; Matsumoto et al., 2016; Rii et al., 2016; Yang et al., 2019). Intense 82 competition for NH₄⁺ in these environments not only excludes the less competitive 83 phytoplankton species, but also the archaea and bacteria that are responsible for ammonia 84 oxidation, which would otherwise resupply nitrite and nitrate and alter the form of nitrogen 85 available for growth (Xianhui Sean Wan et al., 2018; Zakem et al., 2018). Thus, while nitrogen 86 concentrations are low in stratified systems, there is intense competition for a rapid supply of 87 NH_4^+ . 88



90 Fig. 1. Competitive outcomes for phytoplankton dependent on regimes of nitrogen cycling

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91 in the upper ocean. (a), Example limitation of diatoms (black) and other generic phytoplankton
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- 92 (green) by nitrate (solid lines) and ammonium (dashed lines) as a function of changing
- 93 NH_4^+ :DIN ratios. NH_4^+ :DIN ratios (x-axis) are altered by increasing NO_3^- while holding NH_4^+
- 94 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
- 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
- 98 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
- 100 (regenerated production).
- 101
- 102 Ongoing and projected climate change is expected to alter both circulation and biogeochemical
- 103 processes and consequently alter the relative availability of NH_4^+ in marine environments.

Hereafter, we use the NH₄⁺ to dissolved inorganic nitrogen ratio (NH₄⁺:DIN), where DIN = NH₄⁺ 104 $+ NO_2 + NO_3$, as a measure of this relative availability in the form of nitrogen. When we refer 105 to enrichment of NH₄⁺, we specifically mean an increase in the amount of DIN that is NH₄⁺, with 106 an enrichment consistent with a higher proportion of primary production supported through 107 regeneration (i.e., NH4⁺-based). Physical changes, including a changing oceanic circulation 108 (Sallée et al., 2021), is expected to limit inputs of NO₃⁻ from deeper waters to further intensify 109 nitrogen limitation of phytoplankton communities (Bopp et al., 2005; Buchanan et al., 2021). 110 Climate warming is expected to accelerate the metabolism of phytoplankton (Eppley, 1972) and 111 thereby increase nitrogen demand and recycling rates (Cherabier & Ferrière, 2022). Meanwhile, 112 ocean acidification may decelerate rates of microbial ammonia oxidation (Beman et al., 2011) 113 (the first step of nitrification), elevating NH_4^+ concentrations at the expense of NO_3^- . All of these 114 changes are expected to increase NH4⁺:DIN ratios in marine environments. However, the 115 magnitude of NH₄⁺ enrichment and its dominant drivers remain unquantified. Moreover, we lack 116 a general understanding as to the degree to which diatoms are negatively affected by NH₄⁺ 117 enrichment at the global scale. This represents an important knowledge gap as to how climate 118 119 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 120 of phytoplankton relative abundance data and an ocean-biogeochemical model to quantify future 121 NH_4^+ enrichment and its effects on diatoms within the global ocean. 122

2 Materials and Methods 123

2.1 The biogeochemical model 124

125 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 126 Nucleus for European Modelling of the Ocean (NEMO-v4.0). We chose a 2° nominal horizontal 127 resolution with 31 vertical levels with thicknesses ranging from 10 meters in the upper 100 128 129 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. 130 We updated the standard PISCES-v2 for the purposes of this study. This model explicitly

131

resolves the pools of ammonium (NH_4^+) , nitrite (NO_2^-) , nitrate (NO_3^-) , two kinds of 132

133 phytoplankton biomass (nanophytoplankton and diatoms), two kinds of zooplankton biomass

134 (micro- and meso-zooplankton), small and large pools of particulate organic matter, and

135 dissolved organic matter. Nitrogen is added to the ocean via biological nitrogen fixation, riverine

136 fluxes, and atmospheric deposition. Nitrogen is removed from the ocean via denitrification,

137 anaerobic ammonium oxidation (anammox) and burial. The internal cycling of nitrogen involves

assimilation by phytoplankton in particulate organic matter, grazing and excretion by

139 zooplankton, solubilization of particulates to dissolved organics, ammonification of dissolved

140 organic matter to NH_4^+ , followed by nitrification of NH_4^+ and NO_2^- via ammonia oxidation and

141 nitrite oxidation.

142 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 143 assimilation, ammonia oxidation and anammox (Fig. S1). Each process is dependent on other 144 145 tracers and seawater properties (described in Aumont et al. (2015)). However, we briefly detail the contribution to the NH_4^+ budget (mean \pm standard deviation) as well as primary dependencies 146 of the most important processes. Ammonification ($69 \pm 13\%$ of NH₄⁺ sources) rates are highest 147 in productive oceanic regions with high concentrations of dissolved organic compounds. 148 Excretion of NH₄⁺ by zooplankton ($30 \pm 13\%$ of sources) is modelled as a fraction of their 149 grazing rate, with this fraction ranging between 0.21 to 0.42 as phytoplankton become more 150 151 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

153 phytoplankton biomass, and subsequently applying limitations associated with nutrient

availability. Ammonia oxidation $(38 \pm 27\% \text{ of sinks})$ is modelled by multiplying a temperature-

dependent growth rate against the concentration of NH₄⁺ and applying observationally-informed

- 156 limitation terms associated with NH₄⁺ affinity, light intensity, and pH (Text S1). Phytoplankton
- assimilation was a greater proportion of sinks in stratified, oligotrophic environments (Fig. S1).
- 158 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 163 conditions, and a climate change run where these factors changed according to historical

164 observations from 1850 to 2005 and according to the high emissions Representative

165 Concentration Pathway 8.5 from 2006 to 2100 (RCP8.5) (Riahi et al., 2011). We chose a high

166 emissions scenario to emphasize the clearest degree of anthropogenic changes, and thus

167 maximize anthropogenic effects. However, we acknowledge that the RCP8.5 is considered an

168 extreme scenario under present development pathways (Riahi et al., 2017).

169 In addition, we performed parallel experiments that isolated the individual effects of our three

170 anthropogenic stressors: a changing circulation ("Phys"), warming on biological metabolism

171 ("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 theirpreindustrial state.

The effect of climate change at the end of the 21^{st} century (mean conditions 2081-2100) was

176 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

179 end of the 21st century and eliminated the effect of model drift. We calculated changes at each

180 grid cell by averaging over the euphotic zone, which was defined as those depths where total

181 phytoplankton biomass was greater than 0.1 mmol C m⁻³. In addition, we compared the

182 preindustrial simulation with observations to explore broad patterns in NH₄⁺ and NH₄⁺: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 NH₄⁺ 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}".

188

2.3 Nutrient and rate data

189 Measured NH_4^+ concentrations (N=692) were used for model-data assessment (Fig. S2-S3).

190 Nutrients were collated from published work (Buchwald et al., 2015; Mdutyana et al., 2020;

191 Newell et al., 2013; Raes et al., 2020; A. E. Santoro et al., 2013; Alyson E. Santoro et al., 2021;

- 192 Shiozaki et al., 2016; Tolar et al., 2016; Xianhui S. Wan et al., 2021; Xianhui Sean Wan et al.,
- 193 2018), and oceanographic cruises AR16 (<u>https://www.bco-dmo.org/deployment/747056</u>), 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
- 196 NO₃⁻. If NO₃⁻ measurements were not made alongside NH₄⁺, then NO₃⁻ concentrations were
- 197 extracted from the World Ocean Atlas 2018 (Garcia et al., 2019) monthly climatology at the
- 198 closest grid cell. These data are available in Data Set S1.
- 199 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
- 201 (Clark et al., 2021; Dore & Karl, 1996; Mdutyana et al., 2020; Newell et al., 2013; Raes et al.,
- 202 2020; Raimbault et al., 1999; A. E. Santoro et al., 2013; Alyson E. Santoro et al., 2021; Shiozaki
- 203 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.
- 205 Measurements of NH_4^+ and NO_3^- concentrations alongside NH_4^+ and NO_3^- -fueled primary
- 206 production (μ mol m⁻³ day⁻¹) were used to determine the relationship between NH₄⁺:DIN ratios
- and the proportion of net primary production that is fueled by NH_4^+ (Fig. S6). While coincident
- 208 measurements of these properties are not common, we compiled data from nine studies
- 209 (Fernández et al., 2009; Joubert et al., 2011; Mdutyana et al., 2020; Metzler et al., 1997;
- 210 Philibert, 2015; Rees et al., 2006; Thomalla et al., 2011; Xianhui Sean Wan et al., 2018;
- 211 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
- 213 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
- 216 S3.
- 217 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.,
- 219 2011) by extraction from the text (where values were given) and from figures using the
- 220 WebPlotDigitizer tool (<u>https://automeris.io/WebPlotDigitizer/</u>). 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

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

In addition, we analyzed the metagenomic read abundances for the single-copy photosynthetic gene *psbO*, an approach that covers both cyanobacteria and eukaryotic phytoplankton and provides a more robust picture of phytoplankton cell abundances than rRNA gene methods (Pierella Karlusich et al., 2022). We retrieved the abundance tables from samples obtained from 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:

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

Where Y is the predicted value of the response variable, α is the intercept, $s_n(x_n)$ is the nth thin-241 plate spline of the nth independent variable, and ε is the population error around the prediction. 242 Independent variables were mixed-layer depth (m), phosphate (µM), silicate (µM), dissolved 243 244 iron (µM), and the NH₄⁺:DIN ratio. Mixed layer depth, phosphate and silicate was measured in situ at the sample locations of Tara Oceans, while dissolved iron and NH₄⁺:DIN ratios were 245 provided by the model. In addition, phosphate and silicate concentrations were available as 246 interpolated products from the World Ocean Atlas (Garcia et al., 2019). An alternative estimate 247 of NH₄⁺:DIN ratios was provided by the Darwin model (Follows et al., 2007). Predictor variables 248 from models and World Ocean Atlas were extracted at the locations and months of sampling. 249

Mixed-layer depth, nutrients (phosphate, silicate and NH₄⁺:DIN) and the relative abundance of 250

phytoplankton taxa were log₁₀-transformed prior to model building to ensure homogeneity of 251

variance. 252

Before model testing, we calculated the variance inflation factors (VIFs) of independent 253

variables to avoid multi-collinearity. All covariate VIFs were < 3. GAMs were computed using a 254

low spline complexity (k = 3) that prevented overfitting. We fit GAMs using all predictors (full 255 model), then assessed the deviance explained by each predictor by fitting subsequent GAMS

256

with each predictor in isolation, and by removing the predictor in question from the full model. 257

258 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 259

assessed via the percent of deviance explained by the model. 260

261 A two-sided Mann-Whitney U test was used to test for differences between the two distributions

of diatom relative abundance separated by NH₄⁺:DIN ratios < 4% and > 4% presented in Figure 262

2b. The 4% threshold was used because it split the dataset in half and aligned with the point at 263

which primary production transitioned from mostly new (NO₃⁻-fueled) to regenerated (NH₄⁺-264

fueled) (Fig. S6). This non-parametric test (performed with the scipy package in python) returned 265

highly significant two-sided p-values (p < 0.0001) where indicated by *** in Figure 2c 266

- **3** Results and Discussion 267
- 268

3.1 NH₄⁺ enrichment and diatom relative abundance

The competitive exclusion of diatoms by other phytoplankton in NH₄⁺ enriched waters suggests 269

that declines in diatom relative abundance should be associated with increases in NH₄⁺:DIN. 270

While shown theoretically (Glibert et al., 2016; Litchman, 2007; Litchman et al., 2007) and in 271

restricted locations (Berg et al., 2003; Carter et al., 2005; Donald et al., 2013; Fawcett et al., 272

2011; Klawonn et al., 2019; Van Oostende et al., 2017; Selph et al., 2021; Tungaraza et al., 273

2003; Xianhui Sean Wan et al., 2018), this relationship is yet to be observed at the large scale. 274

The *Tara* Oceans global survey offers 144 stations encompassing equatorial to polar marine 275

environments (Ibarbalz et al., 2019). We used two proxies of diatom relative abundance from 276

this dataset: 18S rRNA gene metabarcodes for estimating relative abundance among eukaryotic 277

278 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 NH₄⁺:DIN was used to predict diatom relative abundance in

285 Generalized Additive Models (GAMs), along with other bottom-up drivers of phytoplankton

community composition (see Methods).

287 Our analysis revealed that elevated NH₄⁺: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

290 predictor variables: whether model-derived, in situ measurements, interpolated products (Garcia

et al., 2019), or when switching out NH₄⁺:DIN as predicted by our biogeochemical model with

that provided by another (Follows et al., 2007) (Table S1). Importantly, the relationship between

293 NH₄⁺: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). NH₄⁺:DIN also offered large

296 explanatory power for diatom abundance compared to the other predictor variables, explaining

between 18-30% of the deviance in the data (Table S1).

298 The association between diatoms and NH_4^+ :DIN was strong compared with the other major

299 phytoplankton taxa (Table S2). Only dinoflagellates (18S metabarcoding), *Prochlorococcus* and

300 chlorophytes (*psbO*) showed similarly strong associations (Fig. S14-S15). These associations are

also expected. *Prochlorococcus* was positively related to NH₄⁺:DIN, reflecting their superior

affinity for NH₄⁺ 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 NH₄⁺:DIN and positively related to phosphate, reflecting their prominence in nutrient-

rich waters (Vannier et al., 2016). The positive relationship between dinoflagellates and

306 NH₄⁺: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 309 biogeochemical model (model_{control}; black line in Fig. 2a). This model imbues its diatoms with a 310 known competitive disadvantage for NH_4^+ (Fig. 1a; Fig. S4). If competition for NH_4^+ is an 311 important control on diatom relative abundance in the model, we should therefore see a strong 312 negative relationship between the NH4⁺:DIN ratio and diatom relative abundance. We stress here 313 that if diatoms had an equal affinity for NH₄⁺ as other phytoplankton, then they would not be 314 outcompeted (as shown later). As expected, diatom relative abundance was negatively related to 315 NH_4^+ :DIN (deviance explained = 70%; p-value < 0.001). Interestingly, the relationship was also 316 strongly non-linear and similar to that seen in the Tara Oceans data, with rapid losses of diatoms 317 as NH₄⁺:DIN became greater than 4%. This threshold, where NH₄⁺ becomes 4% of total nitrogen 318 stocks, aligns with the point at which primary production becomes dominated by regenerated 319 production (Fig. S6). This result not only showcases the intense recycling of NH₄⁺ in the marine 320 environment and competition for this coveted nutrient, but also showcases how diatoms are 321 322 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 323 324 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 325 (Fig. 2b,c,d; Mann-Whitney U pair-wise tests). Both modelled and Tara Oceans data predicted 326 similar values of diatom relative abundance within communities where NH₄⁺:DIN was less than 327 328 4%, as well as in communities where NH₄⁺:DIN was greater than 4% (Fig. 2b,e). Overall, the modelled and observed changes in diatom relative abundance associated with NH₄⁺:DIN appear 329 statistically indistinguishable. Since our biogeochemical model explicitly accounts for 330 competitive exclusion of diatoms as NH₄⁺:DIN increases, this similarity may mean that the 331 negative relationship apparent in both may originate from the same mechanism, specifically 332 333 being a competitive disadvantage for NH₄⁺.



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Fig. 2. Effects of NH4⁺ enrichment on primary production and diatom relative abundance. (a), Partial dependence plot from the 335 generalized additive model (GAM) showing the relationship between the NH4⁺ to DIN ratio and the percent relative abundance of 336 diatoms. Blue round markers and blue line fit are percent among eukaryotic phytoplankton (18S rRNA metabarcodes). Red star 337 markers and red line fit are percent among all phytoplankton (psbO gene counts). Solid and dashed black lines are output from the 338 ocean-biogeochemical model with and without competitive exclusion of diatoms for NH₄⁺. The vertical dotted line delineates when 339 NH₄⁺ is 4% of DIN. The inset map shows the locations of *Tara* Oceans samples. (b), Boxplots of the raw partial residuals from panel 340 (a) but separated either side of the 4% NH₄⁺ to DIN threshold for percent among eukaryotic phytoplankton (blue), all phytoplankton 341 (red), the ocean-biogeochemical model (solid black), and model without competitive exclusion of diatoms for NH4⁺ (dashed black). 342 Whiskers correspond to the 5th and 95th percentiles. Tables on the right denote significant pair-wise differences (Mann-Whitney U) 343 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). 344

345 3.2 Future enrichment of NH₄⁺ in the ocean

Given the importance of NH₄⁺ enrichment for influencing primary production and phytoplankton 346 community composition, we explored the potential impact of anthropogenic climate change on 347 NH4⁺:DIN across the global ocean. Using a high emissions climate change scenario from 1851 to 348 349 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 350 data-constrained slowdown of ammonia oxidation by ocean acidification (Fig. S16) in our ocean-351 biogeochemical model. By the end of the 21st century (2081-2100), these factors increased 352 NH4⁺:DIN in over 98% of the upper ocean euphotic layer (Fig. 3a). On average, the fraction of 353 DIN present as NH_4^+ increased by 6 ± 6 %, with enrichment exceeding 20% in regions with 354 pronounced DIN gradients, such as oceanographic fronts. The enrichment of NH4⁺ caused an 355 expansion of regenerated production across the ocean, such that NH₄⁺ overtook NO₃⁻ as the main 356 nitrogen substrate for phytoplankton growth in an additional 13% of the ocean. The greatest 357 change occurred within the 21st century (Fig. 3b), indicating a direct relationship between the 358 severity of climate change and the magnitude of NH₄⁺ enrichment. 359

Physical changes, a warming-induced stimulation of microbial metabolism and ocean 360 acidification all played a role in increasing NH₄⁺:DIN. Among these factors, physical changes 361 had the largest contribution, accounting for 55% of future trends (Fig. 3b), followed by ocean 362 acidification (25%) and stimulated metabolism (13%). Physical changes decreased DIN to cause 363 increases in NH4⁺:DIN in many regions (Fig 3c; Fig. S16) and occurred either through reduced 364 physical supply (e.g., North Atlantic (Whitt & Jansen, 2020)) or increased demand and export of 365 organic nitrogen in regions experiencing an increase in primary production due to losses in sea 366 ice and increases in light (e.g., Arctic (Comeau et al., 2011)). Ocean acidification increased 367 NH4⁺:DIN everywhere, but had the greatest effect in oligotrophic settings where DIN 368 369 concentrations are lower, and minimal effects in eutrophic regions (Fig 3c; Fig. S16). We do 370 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 371 exploring a much weaker relationship between pH and ammonia oxidation that reduced the 372 contribution of acidification to NH₄⁺ enrichment by 10% or more and increased the contribution 373 of the other stressors (Fig. S17). However, as pH decline was most strongly influential to 374



- 376 NH₄⁺:DIN ratios in eutrophic regions where diatoms form an important component on the
- 377 community. Warming stimulated the nutrient demand of phytoplankton, which reduced DIN, a
- 378 mechanism consistent with the effects of temperature on marine microbial recycling (Cherabier
- 879 & Ferrière, 2022). While its global contribution was small at 13% (Fig. 3b), warming had
- 380 important effects at the boundaries of NO₃⁻-rich regions by contracting their areal extent, turning
- 381 NO₃⁻-rich waters to NO₃⁻-poor waters (Fig. 3c; Fig. S16). Altogether, the individual contributions
- 382 of physical change, acidification and stimulated metabolism diagnosed via our sensitivity
- experiments explained 93% of the full change in NH₄⁺:DIN, indicating that a linear combination
- 384 of the three drivers accounted for near the full response.



Fig. 3. Anthropogenic impacts on the NH₄⁺ to DIN ratio. (a), The difference in the NH₄⁺ to DIN ratio averaged over the euphotic zone at the end of the 21^{st} century (2081-2100) with all anthropogenic impacts. (b), Global mean trends in euphotic zone NH₄⁺ to DIN ratio in the different experiments: preindustrial control (grey), ocean acidification (OA; green), warming on metabolic rates (Warm; red), physical changes (Phys; blue) and all effects (All; black) according to the RCP8.5 climate change scenario. (c), Increases in the NH₄⁺ to DIN ratio due to physical 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

Our climate change simulations predict a future decline in the abundance of diatoms and their 396 representation within phytoplankton communities, particularly in the subantarctic, tropical, North 397 Atlantic, North Pacific and Arctic Oceans where declines sometimes exceeded 20% (Fig. 4a; Fig. 398 S18). Diatoms are currently major contributors to net primary production in these regions 399 (Armbrust, 2009; Tréguer et al., 2018; Uitz et al., 2010). The decline in diatom relative 400 401 abundance was driven by a combination of stimulated microbial metabolism (60%) and physical changes (40%), while ocean acidification had negligible effects (Figure 4c) because of its limited 402 effect on NH₄⁺:DIN outside of the oligotrophic gyres where diatoms are already a small 403 proportion of communities (Fig. S17). However, we recognize that other influential bottom-up 404 and top-down stressors, such as growth limitation by other nutrients (Taucher et al., 2022), shifts 405 in the light environment, and/or grazing pressure (Brun et al., 2015; Margalef, 1978; Taucher et 406 al., 2022) are also influential to structuring phytoplankton communities. Furthermore, we 407 acknowledge that the negative relationship that we observe between NH₄⁺:DIN and diatom 408 relative abundance in both the *Tara* Oceans datasets and the model (Figure 2a) may be 409 influenced by these or other covarying factors. This includes increases or decreases in the total 410 availability of DIN, namely being NO₃⁻. If other factors are covarying with NH₄⁺:DIN but are 411 more influential to diatom relative abundance, this may lead to the erroneous attribution of a 412 causative relationship between diatom relative abundance and NH₄⁺:DIN ratios (i.e., a false 413 positive). 414



Fig. 4. Impact of NH₄⁺ enrichment within DIN on diatom relative abundance. (a), Mean 416 change (Δ) in the relative abundance of diatoms (%) by the end of the 21st century (2081-2100) 417 as predicted by the control run of the ocean-biogeochemical model (model_{control}) under the 418 RCP8.5 scenario and averaged over the euphotic zone. (b), Same as in (a), but for the model 419 420 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), 421 warming effects on metabolic rates (red), ocean acidification effect on ammonia oxidation 422 (green) and all stressors (black) for model_{control}. (d), The same as in (c), but for model_{compete}. 423 Shading shows the change between (c) and (d). 424 425

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 432 NH_4^+ , but still suffered their unique limitations associated with light, silicate, phosphate, nitrate 433 (Fig. 1a) and iron availability, as well as grazing pressure.

Making diatoms equally competitive for NH_4^+ mitigated the losses of diatom representation 434 within future phytoplankton communities by 70%. While phytoplankton biomass, including 435 diatoms, largely declined everywhere outside of the polar regions (Fig. S18), the losses in diatom 436 relative abundance were reduced from a global mean of 3.2% to 0.9% by 2081-2100 (Fig. 4c). 437 Physical changes no longer exerted a global negative effect on their total nor relative abundance, 438 while the negative effect of elevated microbial metabolism on relative abundance was 439 440 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 441 Pacific, the Arabian Sea, the North Atlantic, and the southern subtropics. Outside of the Southern 442 Ocean and the eastern boundary upwelling systems, physical changes that tended to reduce DIN 443 444 concentrations now favored diatoms, while elevated metabolism now had positive, rather than negative, effects in the tropical Pacific. 445

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

⁴⁴⁸ NH₄⁺: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.

450 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}

452 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 454 the negative relationship between NH₄⁺:DIN and diatom relative abundance was reversed in 455 model_{compete} (black dotted line in Fig. 2a). Now positive rather than negative, this relationship 456 differed statistically from those predicted from Tara Oceans data (Figure 2b-e). This strongly 457 suggests that competition for NH₄⁺ independently controls diatom relative abundance. We stress 458 that in this experiment both diatoms and other phytoplankton maintained the same affinity for 459 NO_3^- . While we acknowledge that decreases in NO_3^- were a major cause of NH_4^+ enrichment in 460 461 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

statistical similarity between the *in situ* (*Tara* Oceans) and *in silico* (model_{control}) relationships,

this implicates NH_4^+ : DIN as a key underlying driver of diatom relative abundance in the world

467 ocean.

468 **4 Conclusions**

Our results show that the form of bioavailable nitrogen exerts a strong influence on the 469 competitive niche of diatoms, and that this niche is therefore tied to the upper ocean nitrogen 470 cycle. Our modelling suggests an enrichment of NH₄⁺ in over 98% of ocean euphotic zones by 471 the end of the 21st century under a high emissions scenario (Riahi et al., 2011). In those places 472 where nitrogen availability limits growth, diatoms suffer displacement by phytoplankton taxa 473 474 with a greater affinity for NH₄⁺. The warming and physical changes that drive NH₄⁺ enrichment and diatom displacement are expected (Bindoff et al., 2019) and the link between NH4⁺ 475 enrichment and diatom displacement is demonstrated herein at the global scale. However, we 476 acknowledge that the link between environmental change and NH₄⁺ enrichment rests on 477 processes that are still not fully understood. For instance, an observed increase in summertime 478 mixed layer depths may counter the effect of a strengthening pycnocline (Sallée et al., 2021) to 479 increase NO₃⁻ injection into euphotic zones. Another key contributor to this uncertainty is the 480 microbial loop, driven by heterotrophic bacteria, which resupplies NH_4^+ through mineralization 481 of organic matter (Fig. 1b). The microbial loop is not yet incorporated in detail within earth 482 system models but its response to warming can either elevate or depress regenerated production 483 depending on assumptions made about the bacterial physiology (Cherabier & Ferrière, 2022). 484 The future balance of reduced (NH4⁺ and organic forms) to oxidized nitrogen and its impact on 485 the state of marine ecosystems hinges on a suite of unexplored feedbacks between the marine 486 487 microbial loop and environmental change.

Overall, the open ocean habitat appears to be becoming more challenging for diatoms. Iron stress is growing in the Southern Ocean (Ryan-Keogh et al., 2023), silicic acid limitation is prospect across the ocean in response to ocean acidification (Taucher et al., 2022), and growing nitrogen limitation may make diatoms less adaptable as temperatures rise (Aranguren-Gassis et al., 2019). Furthermore, diatoms may be even more susceptible to increases in NH_4^+ :DIN in temperate 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 NO₃⁻-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
- 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

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525 **Open Research**

- 526 All data and materials used in the analysis are freely available. Nutrient data, nitrification rates,
- 527 coincident nutrient concentrations with regenerated/new primary production rates, and ammonia
- 528 oxidation rates relative to pH variations are provided in Supplementary Data 1-4. The biological
- 529 data from the *Tara* Oceans sampling program are available at
- 530 https://zenodo.org/record/3768510#.Xraby6gzY2w and https://ftp.ebi.ac.uk/biostudies/nfs/S-
- 531 <u>BSST/761/S-BSST761/</u>. The model output and scripts to reproduce the analysis are available at
- 532 <u>https://doi.org/10.5281/zenodo.7630283</u>. Developments to the PISCESv2 ocean-biogeochemical
- 533 model code are freely available for download at
- 534 <u>https://github.com/pearseb/ORCA2_OFF_PISCESiso-N</u>.
- 535

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1 Enrichment of ammonium in the future ocean threatens diatom productivity

2 Pearse J. Buchanan^{1,2,3}, Juan J. Pierella Karlusich^{4,5}, Robyn E. Tuerena⁶, Roxana Shafiee⁷,

E. Malcolm S. Woodward⁸, Chris Bowler⁵, and Alessandro Tagliabue².

- 4 ¹CSIRO Environment, Hobart, 7004, Australia.
- ²Department of Earth, Ocean and Ecological Sciences, University of Liverpool; Liverpool, L69
 3GP, UK.
- ⁷ ³Department of Global Ecology, Carnegie Institution for Science; Stanford, CA, 94305, USA.
- ⁸ ⁴FAS Division of Science, Harvard University, Cambridge, MA, 02138, USA.
- 9 ⁵Institut de Biologie de l'École Normale Supérieure, Département de Biologie, École Normale
- 10 Supérieure, CNRS, INSERM, Université de Recherche Paris Sciences et Lettres, Paris, France.
- ¹¹ ⁶Scottish Association for Marine Science; Dunstaffnage, Oban, PA37 1QA, UK.
- ¹² ⁷Center for the Environment, Harvard University, Cambridge, MA, 02138.
- ¹³ ⁸Plymouth Marine Laboratory; Plymouth, PL1 3DH, UK.
- 14
- 15 Corresponding author: Pearse J Buchanan (<u>pearse.buchanan@csiro.au</u>)
- 16

17 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.

24 Abstract

- 25 Diatoms are prominent eukaryotic photoautotrophs in today's oceans. While dominant in nitrate-
- 26 rich conditions, they face competitive exclusion by other phytoplankton when ammonium forms
- 27 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
- 29 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
- 31 reduces diatom prevalence in marine ecosystems at the global-scale. Under a high emission 32 scenario, we anticipate 98% of the euphotic zones to experience ammonium enrichment by 2081-
- 32 scenario, we anticipate 56% of the explore zones to experience anticontum enrichment by 2081 33 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
- 36 diatoms and ocean ecosystems globally.
- 37

38 Plain Language Summary

This work investigates how a type of microscopic algae called diatoms are affected by changes 39 40 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 41 42 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 43 44 observations and modelling to understand how a widespread future enrichment of ammonium within marine ecosystems might affect diatom relative abundance. We attribute that the 45 enrichment of ammonium can explain 70% of the projected losses to diatom relative abundance 46 by the end of the 21st century if greenhouse gas emissions continue unabated. The form of 47 nitrogen, whether oxidized or reduced, is thus an important control on diatom relative 48 abundance. 49

50

51 **1 Introduction**

- 52 Diatoms are among the most successful and diversified eukaryotic photoautotrophs in the
- 53 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
- ⁵⁵ et al., 2003; Carter et al., 2005; Donald et al., 2013; Fawcett et al., 2011; Glibert et al., 2016;
- 56 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" (NO₃⁻-fueled) primary production (Fawcett et al.,
- 59 2011). As new production is linked to the rate of organic carbon export to the ocean interior
- 60 (Dugdale & Goering, 1967), diatoms also contribute significantly to oceanic carbon dioxide
- 61 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 62 are competitively excluded by other phytoplankton when the primary substrate for growth is 63 ammonium (NH₄⁺). While diatoms tend to have a higher affinity for NO_3^- than other 64 phytoplankton, making then adept competitors for NO₃⁻ when NO₃⁻ is the primary nitrogen 65 substrate, investigations into the kinetics of nutrient uptake have identified that diatoms have a 66 lower affinity for NH₄⁺ then other major groups of phytoplankton (Litchman et al., 2007) (Fig. 67 1a). Their low affinity for NH₄⁺ means that diatoms tend to be competitively excluded by other 68 phytoplankton taxa, such as the smaller (although not always (Arsenieff et al., 2020; Leblanc et 69 al., 2018; Pierella Karlusich et al., 2020)) cyanobacteria and green algae, when nitrogen is 70 limiting and NH₄⁺ is the dominant source of nitrogen (Litchman et al., 2007). 71 Variations in circulation and biogeochemical processes control the form of nitrogen that supports 72 primary production in the sunlit upper ocean (Fig. 1b). As mixing injects NO₃⁻ from deeper 73 74 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, NH₄⁺ and other 75 76 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 77 restricted by a lack of vertical mixing, consequently depleted, and demand is instead satisfied by 78 NH4⁺ through an intense heterotrophic recycling of organic matter. Although nutrient stocks are 79 80 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 81 (Bender & Jönsson, 2016; Matsumoto et al., 2016; Rii et al., 2016; Yang et al., 2019). Intense 82 competition for NH₄⁺ in these environments not only excludes the less competitive 83 phytoplankton species, but also the archaea and bacteria that are responsible for ammonia 84 oxidation, which would otherwise resupply nitrite and nitrate and alter the form of nitrogen 85 available for growth (Xianhui Sean Wan et al., 2018; Zakem et al., 2018). Thus, while nitrogen 86 concentrations are low in stratified systems, there is intense competition for a rapid supply of 87 NH_4^+ . 88



90 Fig. 1. Competitive outcomes for phytoplankton dependent on regimes of nitrogen cycling

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91 in the upper ocean. (a), Example limitation of diatoms (black) and other generic phytoplankton
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- 92 (green) by nitrate (solid lines) and ammonium (dashed lines) as a function of changing
- 93 NH_4^+ :DIN ratios. NH_4^+ :DIN ratios (x-axis) are altered by increasing NO_3^- while holding NH_4^+
- 94 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
- 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
- 98 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
- 100 (regenerated production).
- 101
- 102 Ongoing and projected climate change is expected to alter both circulation and biogeochemical
- 103 processes and consequently alter the relative availability of NH_4^+ in marine environments.

Hereafter, we use the NH₄⁺ to dissolved inorganic nitrogen ratio (NH₄⁺:DIN), where DIN = NH₄⁺ 104 $+ NO_2 + NO_3$, as a measure of this relative availability in the form of nitrogen. When we refer 105 to enrichment of NH₄⁺, we specifically mean an increase in the amount of DIN that is NH₄⁺, with 106 an enrichment consistent with a higher proportion of primary production supported through 107 regeneration (i.e., NH4⁺-based). Physical changes, including a changing oceanic circulation 108 (Sallée et al., 2021), is expected to limit inputs of NO₃⁻ from deeper waters to further intensify 109 nitrogen limitation of phytoplankton communities (Bopp et al., 2005; Buchanan et al., 2021). 110 Climate warming is expected to accelerate the metabolism of phytoplankton (Eppley, 1972) and 111 thereby increase nitrogen demand and recycling rates (Cherabier & Ferrière, 2022). Meanwhile, 112 ocean acidification may decelerate rates of microbial ammonia oxidation (Beman et al., 2011) 113 (the first step of nitrification), elevating NH_4^+ concentrations at the expense of NO_3^- . All of these 114 changes are expected to increase NH4⁺:DIN ratios in marine environments. However, the 115 magnitude of NH₄⁺ enrichment and its dominant drivers remain unquantified. Moreover, we lack 116 a general understanding as to the degree to which diatoms are negatively affected by NH₄⁺ 117 enrichment at the global scale. This represents an important knowledge gap as to how climate 118 119 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 120 of phytoplankton relative abundance data and an ocean-biogeochemical model to quantify future 121 NH_4^+ enrichment and its effects on diatoms within the global ocean. 122

2 Materials and Methods 123

2.1 The biogeochemical model 124

125 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 126 Nucleus for European Modelling of the Ocean (NEMO-v4.0). We chose a 2° nominal horizontal 127 resolution with 31 vertical levels with thicknesses ranging from 10 meters in the upper 100 128 129 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. 130 We updated the standard PISCES-v2 for the purposes of this study. This model explicitly

131

resolves the pools of ammonium (NH_4^+) , nitrite (NO_2^-) , nitrate (NO_3^-) , two kinds of 132

133 phytoplankton biomass (nanophytoplankton and diatoms), two kinds of zooplankton biomass

134 (micro- and meso-zooplankton), small and large pools of particulate organic matter, and

135 dissolved organic matter. Nitrogen is added to the ocean via biological nitrogen fixation, riverine

136 fluxes, and atmospheric deposition. Nitrogen is removed from the ocean via denitrification,

137 anaerobic ammonium oxidation (anammox) and burial. The internal cycling of nitrogen involves

assimilation by phytoplankton in particulate organic matter, grazing and excretion by

139 zooplankton, solubilization of particulates to dissolved organics, ammonification of dissolved

140 organic matter to NH_4^+ , followed by nitrification of NH_4^+ and NO_2^- via ammonia oxidation and

141 nitrite oxidation.

142 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 143 assimilation, ammonia oxidation and anammox (Fig. S1). Each process is dependent on other 144 145 tracers and seawater properties (described in Aumont et al. (2015)). However, we briefly detail the contribution to the NH_4^+ budget (mean \pm standard deviation) as well as primary dependencies 146 of the most important processes. Ammonification ($69 \pm 13\%$ of NH₄⁺ sources) rates are highest 147 in productive oceanic regions with high concentrations of dissolved organic compounds. 148 Excretion of NH₄⁺ by zooplankton ($30 \pm 13\%$ of sources) is modelled as a fraction of their 149 grazing rate, with this fraction ranging between 0.21 to 0.42 as phytoplankton become more 150 151 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

153 phytoplankton biomass, and subsequently applying limitations associated with nutrient

availability. Ammonia oxidation $(38 \pm 27\% \text{ of sinks})$ is modelled by multiplying a temperature-

dependent growth rate against the concentration of NH₄⁺ and applying observationally-informed

- 156 limitation terms associated with NH₄⁺ affinity, light intensity, and pH (Text S1). Phytoplankton
- assimilation was a greater proportion of sinks in stratified, oligotrophic environments (Fig. S1).
- 158 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 163 conditions, and a climate change run where these factors changed according to historical

164 observations from 1850 to 2005 and according to the high emissions Representative

165 Concentration Pathway 8.5 from 2006 to 2100 (RCP8.5) (Riahi et al., 2011). We chose a high

166 emissions scenario to emphasize the clearest degree of anthropogenic changes, and thus

167 maximize anthropogenic effects. However, we acknowledge that the RCP8.5 is considered an

168 extreme scenario under present development pathways (Riahi et al., 2017).

169 In addition, we performed parallel experiments that isolated the individual effects of our three

170 anthropogenic stressors: a changing circulation ("Phys"), warming on biological metabolism

171 ("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 theirpreindustrial state.

The effect of climate change at the end of the 21^{st} century (mean conditions 2081-2100) was

176 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

179 end of the 21st century and eliminated the effect of model drift. We calculated changes at each

180 grid cell by averaging over the euphotic zone, which was defined as those depths where total

181 phytoplankton biomass was greater than 0.1 mmol C m⁻³. In addition, we compared the

182 preindustrial simulation with observations to explore broad patterns in NH₄⁺ and NH₄⁺: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 NH₄⁺ 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}".

188

2.3 Nutrient and rate data

189 Measured NH_4^+ concentrations (N=692) were used for model-data assessment (Fig. S2-S3).

190 Nutrients were collated from published work (Buchwald et al., 2015; Mdutyana et al., 2020;

191 Newell et al., 2013; Raes et al., 2020; A. E. Santoro et al., 2013; Alyson E. Santoro et al., 2021;

- 192 Shiozaki et al., 2016; Tolar et al., 2016; Xianhui S. Wan et al., 2021; Xianhui Sean Wan et al.,
- 193 2018), and oceanographic cruises AR16 (<u>https://www.bco-dmo.org/deployment/747056</u>), 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
- 196 NO₃⁻. If NO₃⁻ measurements were not made alongside NH₄⁺, then NO₃⁻ concentrations were
- 197 extracted from the World Ocean Atlas 2018 (Garcia et al., 2019) monthly climatology at the
- 198 closest grid cell. These data are available in Data Set S1.
- 199 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
- 201 (Clark et al., 2021; Dore & Karl, 1996; Mdutyana et al., 2020; Newell et al., 2013; Raes et al.,
- 202 2020; Raimbault et al., 1999; A. E. Santoro et al., 2013; Alyson E. Santoro et al., 2021; Shiozaki
- 203 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.
- 205 Measurements of NH_4^+ and NO_3^- concentrations alongside NH_4^+ and NO_3^- -fueled primary
- 206 production (μ mol m⁻³ day⁻¹) were used to determine the relationship between NH₄⁺:DIN ratios
- and the proportion of net primary production that is fueled by NH_4^+ (Fig. S6). While coincident
- 208 measurements of these properties are not common, we compiled data from nine studies
- 209 (Fernández et al., 2009; Joubert et al., 2011; Mdutyana et al., 2020; Metzler et al., 1997;
- 210 Philibert, 2015; Rees et al., 2006; Thomalla et al., 2011; Xianhui Sean Wan et al., 2018;
- 211 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
- 213 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
- 216 S3.
- 217 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.,
- 219 2011) by extraction from the text (where values were given) and from figures using the
- 220 WebPlotDigitizer tool (<u>https://automeris.io/WebPlotDigitizer/</u>). 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

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

In addition, we analyzed the metagenomic read abundances for the single-copy photosynthetic gene *psbO*, an approach that covers both cyanobacteria and eukaryotic phytoplankton and provides a more robust picture of phytoplankton cell abundances than rRNA gene methods (Pierella Karlusich et al., 2022). We retrieved the abundance tables from samples obtained from 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:

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

Where Y is the predicted value of the response variable, α is the intercept, $s_n(x_n)$ is the nth thin-241 plate spline of the nth independent variable, and ε is the population error around the prediction. 242 Independent variables were mixed-layer depth (m), phosphate (µM), silicate (µM), dissolved 243 244 iron (µM), and the NH₄⁺:DIN ratio. Mixed layer depth, phosphate and silicate was measured in situ at the sample locations of Tara Oceans, while dissolved iron and NH₄⁺:DIN ratios were 245 provided by the model. In addition, phosphate and silicate concentrations were available as 246 interpolated products from the World Ocean Atlas (Garcia et al., 2019). An alternative estimate 247 of NH₄⁺:DIN ratios was provided by the Darwin model (Follows et al., 2007). Predictor variables 248 from models and World Ocean Atlas were extracted at the locations and months of sampling. 249

Mixed-layer depth, nutrients (phosphate, silicate and NH₄⁺:DIN) and the relative abundance of 250

phytoplankton taxa were log₁₀-transformed prior to model building to ensure homogeneity of 251

variance. 252

Before model testing, we calculated the variance inflation factors (VIFs) of independent 253

variables to avoid multi-collinearity. All covariate VIFs were < 3. GAMs were computed using a 254

low spline complexity (k = 3) that prevented overfitting. We fit GAMs using all predictors (full 255 model), then assessed the deviance explained by each predictor by fitting subsequent GAMS

256

with each predictor in isolation, and by removing the predictor in question from the full model. 257

258 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 259

assessed via the percent of deviance explained by the model. 260

261 A two-sided Mann-Whitney U test was used to test for differences between the two distributions

of diatom relative abundance separated by NH₄⁺:DIN ratios < 4% and > 4% presented in Figure 262

2b. The 4% threshold was used because it split the dataset in half and aligned with the point at 263

which primary production transitioned from mostly new (NO₃⁻-fueled) to regenerated (NH₄⁺-264

fueled) (Fig. S6). This non-parametric test (performed with the scipy package in python) returned 265

highly significant two-sided p-values (p < 0.0001) where indicated by *** in Figure 2c 266

- **3** Results and Discussion 267
- 268

3.1 NH₄⁺ enrichment and diatom relative abundance

The competitive exclusion of diatoms by other phytoplankton in NH₄⁺ enriched waters suggests 269

that declines in diatom relative abundance should be associated with increases in NH₄⁺:DIN. 270

While shown theoretically (Glibert et al., 2016; Litchman, 2007; Litchman et al., 2007) and in 271

restricted locations (Berg et al., 2003; Carter et al., 2005; Donald et al., 2013; Fawcett et al., 272

2011; Klawonn et al., 2019; Van Oostende et al., 2017; Selph et al., 2021; Tungaraza et al., 273

2003; Xianhui Sean Wan et al., 2018), this relationship is yet to be observed at the large scale. 274

The *Tara* Oceans global survey offers 144 stations encompassing equatorial to polar marine 275

environments (Ibarbalz et al., 2019). We used two proxies of diatom relative abundance from 276

this dataset: 18S rRNA gene metabarcodes for estimating relative abundance among eukaryotic 277

278 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 NH₄⁺:DIN was used to predict diatom relative abundance in

285 Generalized Additive Models (GAMs), along with other bottom-up drivers of phytoplankton

community composition (see Methods).

287 Our analysis revealed that elevated NH₄⁺: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

290 predictor variables: whether model-derived, in situ measurements, interpolated products (Garcia

et al., 2019), or when switching out NH₄⁺:DIN as predicted by our biogeochemical model with

that provided by another (Follows et al., 2007) (Table S1). Importantly, the relationship between

293 NH₄⁺: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). NH₄⁺:DIN also offered large

296 explanatory power for diatom abundance compared to the other predictor variables, explaining

between 18-30% of the deviance in the data (Table S1).

298 The association between diatoms and NH_4^+ :DIN was strong compared with the other major

299 phytoplankton taxa (Table S2). Only dinoflagellates (18S metabarcoding), *Prochlorococcus* and

300 chlorophytes (*psbO*) showed similarly strong associations (Fig. S14-S15). These associations are

also expected. *Prochlorococcus* was positively related to NH₄⁺:DIN, reflecting their superior

affinity for NH₄⁺ 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 NH₄⁺:DIN and positively related to phosphate, reflecting their prominence in nutrient-

rich waters (Vannier et al., 2016). The positive relationship between dinoflagellates and

306 NH₄⁺: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 309 biogeochemical model (model_{control}; black line in Fig. 2a). This model imbues its diatoms with a 310 known competitive disadvantage for NH_4^+ (Fig. 1a; Fig. S4). If competition for NH_4^+ is an 311 important control on diatom relative abundance in the model, we should therefore see a strong 312 negative relationship between the NH4⁺:DIN ratio and diatom relative abundance. We stress here 313 that if diatoms had an equal affinity for NH₄⁺ as other phytoplankton, then they would not be 314 outcompeted (as shown later). As expected, diatom relative abundance was negatively related to 315 NH_4^+ :DIN (deviance explained = 70%; p-value < 0.001). Interestingly, the relationship was also 316 strongly non-linear and similar to that seen in the Tara Oceans data, with rapid losses of diatoms 317 as NH₄⁺:DIN became greater than 4%. This threshold, where NH₄⁺ becomes 4% of total nitrogen 318 stocks, aligns with the point at which primary production becomes dominated by regenerated 319 production (Fig. S6). This result not only showcases the intense recycling of NH₄⁺ in the marine 320 environment and competition for this coveted nutrient, but also showcases how diatoms are 321 322 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 323 324 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 325 (Fig. 2b,c,d; Mann-Whitney U pair-wise tests). Both modelled and Tara Oceans data predicted 326 similar values of diatom relative abundance within communities where NH₄⁺:DIN was less than 327 328 4%, as well as in communities where NH₄⁺:DIN was greater than 4% (Fig. 2b,e). Overall, the modelled and observed changes in diatom relative abundance associated with NH₄⁺:DIN appear 329 statistically indistinguishable. Since our biogeochemical model explicitly accounts for 330 competitive exclusion of diatoms as NH₄⁺:DIN increases, this similarity may mean that the 331 negative relationship apparent in both may originate from the same mechanism, specifically 332 333 being a competitive disadvantage for NH₄⁺.



334

Fig. 2. Effects of NH4⁺ enrichment on primary production and diatom relative abundance. (a), Partial dependence plot from the 335 generalized additive model (GAM) showing the relationship between the NH4⁺ to DIN ratio and the percent relative abundance of 336 diatoms. Blue round markers and blue line fit are percent among eukaryotic phytoplankton (18S rRNA metabarcodes). Red star 337 markers and red line fit are percent among all phytoplankton (psbO gene counts). Solid and dashed black lines are output from the 338 ocean-biogeochemical model with and without competitive exclusion of diatoms for NH₄⁺. The vertical dotted line delineates when 339 NH₄⁺ is 4% of DIN. The inset map shows the locations of *Tara* Oceans samples. (b), Boxplots of the raw partial residuals from panel 340 (a) but separated either side of the 4% NH₄⁺ to DIN threshold for percent among eukaryotic phytoplankton (blue), all phytoplankton 341 (red), the ocean-biogeochemical model (solid black), and model without competitive exclusion of diatoms for NH4⁺ (dashed black). 342 Whiskers correspond to the 5th and 95th percentiles. Tables on the right denote significant pair-wise differences (Mann-Whitney U) 343 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). 344

345 3.2 Future enrichment of NH₄⁺ in the ocean

Given the importance of NH₄⁺ enrichment for influencing primary production and phytoplankton 346 community composition, we explored the potential impact of anthropogenic climate change on 347 NH4⁺:DIN across the global ocean. Using a high emissions climate change scenario from 1851 to 348 349 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 350 data-constrained slowdown of ammonia oxidation by ocean acidification (Fig. S16) in our ocean-351 biogeochemical model. By the end of the 21st century (2081-2100), these factors increased 352 NH4⁺:DIN in over 98% of the upper ocean euphotic layer (Fig. 3a). On average, the fraction of 353 DIN present as NH_4^+ increased by 6 ± 6 %, with enrichment exceeding 20% in regions with 354 pronounced DIN gradients, such as oceanographic fronts. The enrichment of NH4⁺ caused an 355 expansion of regenerated production across the ocean, such that NH₄⁺ overtook NO₃⁻ as the main 356 nitrogen substrate for phytoplankton growth in an additional 13% of the ocean. The greatest 357 change occurred within the 21st century (Fig. 3b), indicating a direct relationship between the 358 severity of climate change and the magnitude of NH₄⁺ enrichment. 359

Physical changes, a warming-induced stimulation of microbial metabolism and ocean 360 acidification all played a role in increasing NH₄⁺:DIN. Among these factors, physical changes 361 had the largest contribution, accounting for 55% of future trends (Fig. 3b), followed by ocean 362 acidification (25%) and stimulated metabolism (13%). Physical changes decreased DIN to cause 363 increases in NH4⁺:DIN in many regions (Fig 3c; Fig. S16) and occurred either through reduced 364 physical supply (e.g., North Atlantic (Whitt & Jansen, 2020)) or increased demand and export of 365 organic nitrogen in regions experiencing an increase in primary production due to losses in sea 366 ice and increases in light (e.g., Arctic (Comeau et al., 2011)). Ocean acidification increased 367 NH4⁺:DIN everywhere, but had the greatest effect in oligotrophic settings where DIN 368 369 concentrations are lower, and minimal effects in eutrophic regions (Fig 3c; Fig. S16). We do 370 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 371 exploring a much weaker relationship between pH and ammonia oxidation that reduced the 372 contribution of acidification to NH₄⁺ enrichment by 10% or more and increased the contribution 373 of the other stressors (Fig. S17). However, as pH decline was most strongly influential to 374



- 376 NH₄⁺:DIN ratios in eutrophic regions where diatoms form an important component on the
- 377 community. Warming stimulated the nutrient demand of phytoplankton, which reduced DIN, a
- 378 mechanism consistent with the effects of temperature on marine microbial recycling (Cherabier
- 879 & Ferrière, 2022). While its global contribution was small at 13% (Fig. 3b), warming had
- 380 important effects at the boundaries of NO₃⁻-rich regions by contracting their areal extent, turning
- 381 NO₃⁻-rich waters to NO₃⁻-poor waters (Fig. 3c; Fig. S16). Altogether, the individual contributions
- 382 of physical change, acidification and stimulated metabolism diagnosed via our sensitivity
- experiments explained 93% of the full change in NH₄⁺:DIN, indicating that a linear combination
- 384 of the three drivers accounted for near the full response.



Fig. 3. Anthropogenic impacts on the NH₄⁺ to DIN ratio. (a), The difference in the NH₄⁺ to DIN ratio averaged over the euphotic zone at the end of the 21^{st} century (2081-2100) with all anthropogenic impacts. (b), Global mean trends in euphotic zone NH₄⁺ to DIN ratio in the different experiments: preindustrial control (grey), ocean acidification (OA; green), warming on metabolic rates (Warm; red), physical changes (Phys; blue) and all effects (All; black) according to the RCP8.5 climate change scenario. (c), Increases in the NH₄⁺ to DIN ratio due to physical 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

Our climate change simulations predict a future decline in the abundance of diatoms and their 396 representation within phytoplankton communities, particularly in the subantarctic, tropical, North 397 Atlantic, North Pacific and Arctic Oceans where declines sometimes exceeded 20% (Fig. 4a; Fig. 398 S18). Diatoms are currently major contributors to net primary production in these regions 399 (Armbrust, 2009; Tréguer et al., 2018; Uitz et al., 2010). The decline in diatom relative 400 401 abundance was driven by a combination of stimulated microbial metabolism (60%) and physical changes (40%), while ocean acidification had negligible effects (Figure 4c) because of its limited 402 effect on NH₄⁺:DIN outside of the oligotrophic gyres where diatoms are already a small 403 proportion of communities (Fig. S17). However, we recognize that other influential bottom-up 404 and top-down stressors, such as growth limitation by other nutrients (Taucher et al., 2022), shifts 405 in the light environment, and/or grazing pressure (Brun et al., 2015; Margalef, 1978; Taucher et 406 al., 2022) are also influential to structuring phytoplankton communities. Furthermore, we 407 acknowledge that the negative relationship that we observe between NH4⁺:DIN and diatom 408 relative abundance in both the *Tara* Oceans datasets and the model (Figure 2a) may be 409 influenced by these or other covarying factors. This includes increases or decreases in the total 410 availability of DIN, namely being NO₃⁻. If other factors are covarying with NH₄⁺:DIN but are 411 more influential to diatom relative abundance, this may lead to the erroneous attribution of a 412 causative relationship between diatom relative abundance and NH₄⁺:DIN ratios (i.e., a false 413 positive). 414



Fig. 4. Impact of NH₄⁺ enrichment within DIN on diatom relative abundance. (a), Mean 416 change (Δ) in the relative abundance of diatoms (%) by the end of the 21st century (2081-2100) 417 as predicted by the control run of the ocean-biogeochemical model (model_{control}) under the 418 RCP8.5 scenario and averaged over the euphotic zone. (b), Same as in (a), but for the model 419 420 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), 421 warming effects on metabolic rates (red), ocean acidification effect on ammonia oxidation 422 (green) and all stressors (black) for model_{control}. (d), The same as in (c), but for model_{compete}. 423 Shading shows the change between (c) and (d). 424 425

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 432 NH_4^+ , but still suffered their unique limitations associated with light, silicate, phosphate, nitrate 433 (Fig. 1a) and iron availability, as well as grazing pressure.

Making diatoms equally competitive for NH_4^+ mitigated the losses of diatom representation 434 within future phytoplankton communities by 70%. While phytoplankton biomass, including 435 diatoms, largely declined everywhere outside of the polar regions (Fig. S18), the losses in diatom 436 relative abundance were reduced from a global mean of 3.2% to 0.9% by 2081-2100 (Fig. 4c). 437 Physical changes no longer exerted a global negative effect on their total nor relative abundance, 438 while the negative effect of elevated microbial metabolism on relative abundance was 439 440 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 441 Pacific, the Arabian Sea, the North Atlantic, and the southern subtropics. Outside of the Southern 442 Ocean and the eastern boundary upwelling systems, physical changes that tended to reduce DIN 443 444 concentrations now favored diatoms, while elevated metabolism now had positive, rather than negative, effects in the tropical Pacific. 445

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

⁴⁴⁸ NH₄⁺: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.

450 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}

452 and model_{compete} predicted contrasting outcomes, the form of nitrogen, specifically NH_4^+ :DIN

453 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 454 the negative relationship between NH₄⁺:DIN and diatom relative abundance was reversed in 455 model_{compete} (black dotted line in Fig. 2a). Now positive rather than negative, this relationship 456 differed statistically from those predicted from Tara Oceans data (Figure 2b-e). This strongly 457 suggests that competition for NH₄⁺ independently controls diatom relative abundance. We stress 458 that in this experiment both diatoms and other phytoplankton maintained the same affinity for 459 NO_3^- . While we acknowledge that decreases in NO_3^- were a major cause of NH_4^+ enrichment in 460 461 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

statistical similarity between the *in situ* (*Tara* Oceans) and *in silico* (model_{control}) relationships,

this implicates NH_4^+ : DIN as a key underlying driver of diatom relative abundance in the world

467 ocean.

468 **4 Conclusions**

Our results show that the form of bioavailable nitrogen exerts a strong influence on the 469 competitive niche of diatoms, and that this niche is therefore tied to the upper ocean nitrogen 470 cycle. Our modelling suggests an enrichment of NH₄⁺ in over 98% of ocean euphotic zones by 471 the end of the 21st century under a high emissions scenario (Riahi et al., 2011). In those places 472 where nitrogen availability limits growth, diatoms suffer displacement by phytoplankton taxa 473 474 with a greater affinity for NH₄⁺. The warming and physical changes that drive NH₄⁺ enrichment and diatom displacement are expected (Bindoff et al., 2019) and the link between NH4⁺ 475 enrichment and diatom displacement is demonstrated herein at the global scale. However, we 476 acknowledge that the link between environmental change and NH₄⁺ enrichment rests on 477 processes that are still not fully understood. For instance, an observed increase in summertime 478 mixed layer depths may counter the effect of a strengthening pycnocline (Sallée et al., 2021) to 479 increase NO₃⁻ injection into euphotic zones. Another key contributor to this uncertainty is the 480 microbial loop, driven by heterotrophic bacteria, which resupplies NH_4^+ through mineralization 481 of organic matter (Fig. 1b). The microbial loop is not yet incorporated in detail within earth 482 system models but its response to warming can either elevate or depress regenerated production 483 depending on assumptions made about the bacterial physiology (Cherabier & Ferrière, 2022). 484 The future balance of reduced (NH4⁺ and organic forms) to oxidized nitrogen and its impact on 485 the state of marine ecosystems hinges on a suite of unexplored feedbacks between the marine 486 487 microbial loop and environmental change.

Overall, the open ocean habitat appears to be becoming more challenging for diatoms. Iron stress is growing in the Southern Ocean (Ryan-Keogh et al., 2023), silicic acid limitation is prospect across the ocean in response to ocean acidification (Taucher et al., 2022), and growing nitrogen limitation may make diatoms less adaptable as temperatures rise (Aranguren-Gassis et al., 2019). Furthermore, diatoms may be even more susceptible to increases in NH_4^+ :DIN in temperate 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 NO₃⁻-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
- 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

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525 **Open Research**

- 526 All data and materials used in the analysis are freely available. Nutrient data, nitrification rates,
- 527 coincident nutrient concentrations with regenerated/new primary production rates, and ammonia
- 528 oxidation rates relative to pH variations are provided in Supplementary Data 1-4. The biological
- 529 data from the *Tara* Oceans sampling program are available at
- 530 https://zenodo.org/record/3768510#.Xraby6gzY2w and https://ftp.ebi.ac.uk/biostudies/nfs/S-
- 531 <u>BSST/761/S-BSST761/</u>. The model output and scripts to reproduce the analysis are available at
- 532 <u>https://doi.org/10.5281/zenodo.7630283</u>. Developments to the PISCESv2 ocean-biogeochemical
- 533 model code are freely available for download at
- 534 <u>https://github.com/pearseb/ORCA2_OFF_PISCESiso-N</u>.
- 535

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Supporting Information for

Enrichment of ammonium in the future ocean threatens diatom productivity

Pearse J. Buchanan^{1,2,3}, Juan J. Pierella Karlusich^{4,5}, Robyn E. Tuerena⁶, Roxana Shafiee⁷, E. Malcolm S. Woodward⁸, Chris Bowler⁵, and Alessandro Tagliabue².

¹CSIRO Environment, Hobart, 7004, Australia.

²Department of Earth, Ocean and Ecological Sciences, University of Liverpool; Liverpool, L69 3GP, UK.

³Department of Global Ecology, Carnegie Institution for Science; Stanford, CA, 94305, USA.

⁴FAS Division of Science, Harvard University, Cambridge, MA, 02138, USA.

⁵Institut de Biologie de l'École Normale Supérieure, Département de Biologie, École Normale Supérieure, CNRS, INSERM, Université de Recherche Paris Sciences et Lettres, Paris, France.

⁶Scottish Association for Marine Science; Dunstaffnage, Oban, PA37 1QA, UK.

⁷Center for the Environment, Harvard University, Cambridge, MA, 02138.

⁸Plymouth Marine Laboratory; Plymouth, PL1 3DH, UK.

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Introduction

In Text S1 we provide additional information on how ammonia oxidation and nitrite oxidation is computed within the ocean biogeochemical model. In Text S2 we evaluate the ocean biogeochemical model against observational nutrient and rate datasets (provided in Data S1-S4). Figures S1-S20 and Tables S1-S3 are provided to support the conclusions of the main text.

Text S1.

Nitrification in PISCES-v2 was previously treated as a one-step conversion of NH_4^+ to NO_3^- but was split into its two component steps (ammonia and nitrite oxidation) for the purposes of this study. Both steps were simulated implicitly by multiplying a maximum growth rate μ^{max} (day⁻¹) by the concentration of substrate (μ M) to return a maximum potential rate (μ M day⁻¹). This was then multiplied by limitation terms (L^X) representing the effect of environmental conditions to return the realized rate.

For ammonia oxidation ($[NH_4^+] \rightarrow [NO_2^-]$),

$$[\mathrm{NH}_{4}^{+}] \rightarrow [\mathrm{NO}_{2}^{-}] = \mu_{\mathrm{AO}}^{\mathrm{max}} \cdot [\mathrm{NH}_{4}^{+}] \cdot L_{\mathrm{AO}}^{\mathrm{NH}_{4}^{+}} \cdot L_{\mathrm{AO}}^{\mathrm{PAR}} \cdot L_{\mathrm{AO}}^{\mathrm{pH}}$$

$$\mu_{AO}^{\max} = \max(0.2, 0.029 \cdot T - 0.147)$$

$$L_{AO}^{NH_{4}^{+}} = \frac{NH_{4}^{+}}{NH_{4}^{+} + K_{AO}^{NH_{4}^{+}}}$$
3

$$L_{AO}^{PAR} = 1 - \frac{PAR}{PAR + K_{AO}^{PAR}}$$

$$L_{AO}^{pH} = \min\left(1, \frac{10^{(pH - pK_a)}}{10^{(R_{pH} - pK_a)}}\right)$$
5

In the above, μ_{AO}^{max} is estimated by a linear model with a floor of 0.2 day⁻¹ (Eqn. 2). This model was fit to the growth curves of three ecotypes of ammonia-oxidizing archaea (Qin et al., 2015) and returns rates of 0.8 day⁻¹ near 30°C (Fig. S20). A floor of 0.2 day⁻¹ was justified by relatively high rates observed in near-freezing waters (Tolar et al., 2016). The limitation term for NH₄⁺ uptake ($L_{AO}^{NH_4^+}$, Eqn. 3) assumes a constant half-saturation coefficient $K_{AO}^{NH_4^+}$ of 0.1 μ M, which is well reflective of both natural marine assemblages of archaea (Horak et al., 2013; Newell et al., 2013; Olson, 1981; Peng et al., 2016;

Xianhui Sean Wan et al., 2018) and the cultivated archaea *Nitrosopumilus maritimus* SCM1 (Martens-Habbena et al., 2009). Light limitation (L_{AO}^{PAR}) and effects of pH (L_{AO}^{pH}) are less well constrained, but nonetheless important. We set the half saturation term of photoinhibition $(K_{AO}^{PAR}, Eqn. 4)$ to 0.75 W m⁻², which accounted for an 80% reduction in rates at photosynthetically active radiation levels of 3 W m⁻² (Merbt et al., 2012). We set the reference pH (R_{pH}, Eqn. 5) below which negative effects on oxidation occur at 8.0, which reflects surface conditions of historical ocean and therefore the pH (i.e., NH₃ availability) that ammonia oxidizers are likely adapted to (Ward, 1987). With a pK_a of the NH₃-NH₄⁺ equilibrium equal to 9.3 (Zeebe & Wolf-Gladrow, 2001), this treatment reduced oxidation rates by 27.5% for a decline in pH of 0.14 units, which is a more conservative change than the 36-38% declines in oxidation reported by Beman et al. (2011) for the same pH change.

For nitrite oxidation ($[NO_2^-] \rightarrow [NO_3^-]$),

$$[NO_{2}^{-}] \rightarrow [NO_{2}^{-}] = \mu_{NO}^{max} \cdot [NO_{2}^{-}] \cdot L_{NO}^{NO_{2}^{-}} \cdot L_{NO}^{PAR}$$

$$L_{NO}^{NO_{2}^{-}} = \frac{NO_{2}^{-}}{NO_{2}^{-} + K_{NO}^{NO_{2}^{-}}}$$
7

$$L_{NO}^{PAR} = 1 - \frac{PAR}{PAR + K_{AO}^{PAR}}$$
8

The treatment of nitrite oxidation is like ammonia oxidation. However, there are two key differences. First, nitrite-oxidizing bacteria have lower growth yield per unit nitrogen oxidized compared to ammonia-oxidizing archaea (Bayer et al., 2022), which demands a slower growth rate in our model given that we are simulating this metabolism implicitly. Accordingly, we set the maximum growth rate of nitrite-oxidizing bacteria (μ_{NO}^{max}) to a constant 0.15 day⁻¹, informed by doubling times in excess of four days of marine cultures held at optimal conditions (Spieck & Lipski, 2011). Second, pH has no effect on NO₂⁻ concentrations. Otherwise, we maintain the same half-saturation coefficients for the substrate ($L_{NO}^{NO_2^-}$, Eqn. 7) and light limitation (L_{NO}^{PAR} , Eqn. 8) terms as for ammonia oxidizers, being 0.1 μ M for $K_{NO}^{NO_2^-}$ and 0.75 W m⁻² for K_{NO}^{PAR} (Table S3). All parameters for nitrification are presented in Table S3.

We did not include oxygen or iron limitation. Oxygen was ignored due to reports of high activity and biomass of nitrifiers in low oxygen zones, due perhaps to a combination of high cellular affinity for oxygen (Bristow et al., 2016) and potential anaerobic pathways of oxidation via alternative electron acceptors (Babbin et al., 2020; Kraft et al., 2022). We ignored iron limitation, despite its potential for limiting growth of ammonia oxidizers (Shafiee et al., 2019), because little is known regarding its effects on the growth of nitrite-oxidizing bacteria. In addition, changes to the availability of iron for biology in the future ocean are highly uncertain and models have little skill in this regard (Tagliabue et al., 2016). We acknowledge, however, that changes in both oxygen and iron availability may be important additional factors governing shifts in the NH4⁺ to DIN ratio in a future ocean.

Text S2.

Observations show that NH_4^+ concentrations of 0.1 µM or greater exist over continental shelves and in regions of strong mixing with high rates of primary production and subsequent heterotrophy. This accumulation of NH_4^+ in productive regions is reproduced by our model (Fig S2a). However, as high NH_4^+ co-occurs with high $NO_3^$ concentrations, NH_4^+ makes a small contribution to total DIN in these upwelling systems (Fig. S2b), which include the eastern tropical Pacific, eastern boundary upwelling systems, the northwest Indian Ocean, the subpolar gyres and the Southern Ocean (although the model underestimates NH_4^+ concentrations in the Southern Ocean). In contrast, low NH_4^+ concentrations of less than 0.05 µM pervade the oligotrophic gyres of the lower latitudes. As these regions also display very low NO_3^- concentrations, NH_4^+ makes up a much higher fraction of total DIN in both the observations and our model, with the NH_4^+ peak occurring deeper in the water column (Fig. S3).

Eutrophic upwelling systems and oligotrophic waters differed in the major sinks of NH_{4^+} (Fig. S1), consistent with available observations and constraints from theory. In eutrophic waters (defined by surface nitrate > 1 μ M), ammonia oxidation represented 49 \pm 29 % (mean \pm standard deviation) of NH_{4^+} sinks, but this dropped to 32 \pm 9 % in oligotrophic systems. Measured rates of ammonia oxidation showed a positive relationship with surface NO_{3^-} concentrations and this was reproduced by the model (Fig.

4

S4), indicating that ammonia oxidation was indeed a greater proportion of the overall NH₄⁺ budget in eutrophic regions. In agreement, isotopic methods have shown that the bulk of nitrogen assimilated by phytoplankton in oligotrophic waters is recycled (Eppley & Peterson, 1979; Fawcett et al., 2011; Klawonn et al., 2019; Van Oostende et al., 2017; Xianhui S. Wan et al., 2021), implying that most nitrogen cycling occurs without ammonia oxidation. Again, our model reproduces this feature of oligotrophic systems (Fig. S1).

Parallel observations of NH₄⁺ to DIN ratios and rates of new and regenerated production from studies spanning tropical to polar environments (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) show that there is a strong relationship between the NH₄⁺ to DIN ratio and the proportion of primary production that is regenerated (Fig. S6). This relationship is expected, in that high NH₄⁺ to DIN ratios should coincide with high rates of regenerated primary production. However, the nature of this relationship was sharp, and was well described by a quadratic Monod function with an optimal half-saturation constant of 0.2 ± 0.03 and an exponent of 0.5 ± 0.05 (Pearson's correlation = 0.69; R² (coefficient of determination) = 0.47; as compared to a linear relationship with an R² (coefficient of determination) = 1.13)). This quadratic function predicts that regenerated production contributes half of total net primary production when the standing stock of NH₄⁺ is only 4 ± 3 % of total DIN. Phytoplankton therefore grow principally on NO₃⁻ (new production dominates) only when NH₄⁺ is substantially depleted.

A similarly sharp relationship emerges from our global ocean-biogeochemical model (Aumont et al., 2015) (grey dots in Fig. S6) equipped with diatoms as an explicit phytoplankton functional type. In the model, all phytoplankton are parameterized to have higher affinities for NH₄⁺, and their growth is supported by NH₄⁺ until NO₃⁻ becomes sufficiently enriched that higher growth can be achieved on NO₃⁻ (Fig. S4). However, the transition at which growth on NO₃⁻ accelerates (cross-over of blue and yellow lines in Fig. S4) occurs at lower concentrations of NO₃⁻ for diatoms than other phytoplankton. This switch to NO₃⁻-fueled growth for diatoms occurs at a point where they are still outcompeted by other phytoplankton for nitrogen. All else being equal, diatoms therefore

suffer from greater growth limitation in low NO_3^- , high NH_4^+ regimes. Only when NO_3^- is truly plentiful (very low NH_4^+ to DIN ratios) do diatoms achieve the high growth rates that allow them to carve out a competitive niche. While other limiting factors such as silicate, iron and light are also influential, these differences in the growth response to NH_4^+ and NO_3^- , which reflect the measured affinities of diatoms and other major taxa (Litchman et al., 2007) and the universal preference for NH_4^+ at low NO_3^- (Flynn, 1999), contribute to the dominance of diatoms in upwelling systems and their competitive exclusion in relatively NH_4^+ -rich oligotrophic seas.



Figure S1. Global mean \pm standard deviations of NH₄⁺ fluxes separated into eutrophic and oligotrophic regions. Sources of NH₄⁺ are represented by positive values and sinks by negative values.



Figure S2. Global patterns of NH_4^+ concentrations and its contribution to DIN in the euphotic zone. (a) The simulated maximum NH_4^+ concentration within the euphotic zone. The maximum was chosen to emphasise basin-scale variations. (b) Average values of the NH_4^+ :DIN ratio. Modelled values are annual averages of the preindustrial control simulation between years 2081-2100. Observed values following linear interpolation between the surface and 200 metres depth are overlaid as coloured markers. Only those profiles with at least 3 data points within the upper 200 metres are shown.



Figure S3. Simulated and observed depth profiles of NH_4^+ at four locations in the North Pacific Ocean (Shiozaki et al., 2016).



Figure S4. Limitation of diatoms (solid) and other phytoplankton (dashed) in the oceanbiogeochemical model by NO_3^- (blue) and NH_4^+ (yellow) as a function of the NH_4^+ :DIN ratio on a log_{10} scale.



Figure S5. Measured (top) and modelled (bottom) ammonia oxidation rates from the global ocean plotted against the log₁₀ of nitrate (NO₃), which indicates a spectrum of oligotrophy-eutrophy from left to right along the x-axis.



Figure S6. Coincident measurements of the NH_4^+ to DIN ratio and the fraction of NPP fuelled by NH_4^+ from 9 studies (coloured dots) and as output by the model (grey dots). Black solid line is the best fit line to the observations and is described by the equation. Shading denotes one standard deviation.



Figure S1. Nutrient and community uptake rate data from the Gulf of Mexico (Yingling et al., 2021). Linear interpolations in depth are constructed and the interpolated values are used in Figure S6.



Figure S8. Parameterisation of ocean acidification on ammonia oxidation. Measurements of rate change in ammonia oxidation due to forced declines in pH (markers) are compared with a parameterisation for the relationship between pH and ammonia oxidation rate (solid line). This parameterisation returns a Pearson's correlation of 0.68 ($R^2 = 0.46$).



Figure S9. Key predictors of diatom relative abundance as a proportion of eukaryotic phytoplankton (blue) and all phytoplankton (red) generated by a GAM. The predictors are the log₁₀ transformed silicic acid concentration (*in situ*), ratio of NH₄⁺:DIN (model-derived), phosphate concentration (*in situ*), dissolved iron concentration (model-derived) and mixed layer depth (*in situ*). Dots are the partial residuals of the fitted GAM. The deviance explained and significance of each predictor are reported in Table S1.



Figure S10. Key predictors of diatom relative abundance as a proportion of eukaryotic phytoplankton (blue) and all phytoplankton (red) generated by a GAM. The predictors are the log₁₀ transformed silicic acid concentration (WOA18 (Garcia et al., 2019)), ratio of NH₄⁺:DIN (model-derived), phosphate concentration (WOA18 (Garcia et al., 2019)), dissolved iron concentration (model-derived) and mixed layer depth (*in situ*). Dots are the partial residuals of the fitted GAM. The deviance explained and significance of each predictor are reported in Table S1.



Figure S11. Key predictors of diatom relative abundance as a proportion of eukaryotic phytoplankton (blue) and all phytoplankton (red) generated by a GAM. The predictors are the log_{10} transformed silicic acid concentration (model-derived), ratio of NH₄⁺:DIN (model-derived), phosphate concentration (model-derived), dissolved iron concentration (model-derived) and mixed layer depth (*in situ*). Dots are the partial residuals of the fitted GAM. The deviance explained and significance of each predictor are reported in Table S1.


Figure S12. Key predictors of diatom relative abundance as a proportion of eukaryotic phytoplankton (blue) and all phytoplankton (red) generated by a GAM. The predictors are the log_{10} transformed silicic acid concentration (model-derived), ratio of NH₄⁺:DIN (Darwin model), phosphate concentration (model-derived), dissolved iron concentration (model-derived) and mixed layer depth (*in situ*). Dots are the partial residuals of the fitted GAM. The deviance explained and significance of each predictor are reported in Table S1.



Figure S13. Key predictors of diatom relative abundance as a proportion of eukaryotic phytoplankton (blue) and all phytoplankton (red) generated by a GAM. The predictors are the log_{10} transformed silicic acid concentration (*in situ*), ratio of NH₄⁺:DIN (Darwin model), phosphate concentration (*in situ*), dissolved iron concentration (model-derived) and mixed layer depth (*in situ*). Dots are the partial residuals of the fitted GAM. The deviance explained and significance of each predictor are reported in Table S1.

18S metabarcodes



Figure S13. GAM relationships between NH_4^+ to DIN ratios and the relative abundance of each major phytoplankton taxa from the 18S metabarcoding estimates. Dots are the partial residuals of the fitted GAM. Each colour indicates a different combination of predictor variables.



Figure S15. GAM relationships between NH_4^+ to DIN ratios and the relative abundance of each major phytoplankton taxa from the *psbO* gene count estimates. Dots are the partial residuals of the fitted GAM. Each colour indicates a different combination of predictor variables.



Figure S16. Anthropogenic impacts on concentrations of NH_4^+ , DIN and NH_4^+ :DIN ratios. a-c, The difference in concentrations and the NH_4^+ to DIN ratio averaged over the euphotic zone at the end of the 21^{st} century (2081-2100) with all anthropogenic impacts (All). d-f, same as a-c but for physical changes (circulation + light) only (Phys). g-i, same as a-c but for warming effects on metabolism only (Warm). j-l, same as a-c but for ocean acidification only (OA).



Figure S17. Alternative parameterisation of pH effect on ammonia oxidation. a, The alternative parameterisation (dashed line), which includes a weaker effect of pH decline on ammonia oxidation. b, How the weaker relationship between pH and ammonia oxidation ameliorates the increases in NH_4^+ :DIN. As NH_4^+ :DIN increases almost everywhere in these experiments, we only show how this alternative parameterisation works to reduce the increase.



Figure S18. Anthropogenic impacts on concentrations of other phytoplankton, diatoms and the relative abundance of diatoms. a-c, Concentrations and the relative abundance of diatoms are averaged over the depths at which total phytoplankton concentrations are greater than 0.1 μ M of carbon at the end of the 21st century (2081-2100) with all anthropogenic impacts (All). d-f, same as a-c but for physical changes (circulation + light) only (Circ). g-i, same as a-c but for warming effects on metabolism only (Warm). j-l, same as a-c but for ocean acidification only (OA).



Figure S19. Impact of NH_4^+ enrichment within DIN on diatom abundance. (a), Mean change (Δ) in the abundance of diatoms (μ M C) 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 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).



Figure S20. Temperature dependence of the maximum growth rate (μ) of ammonia oxidising archaea ecotypes (Qin et al., 2015).

significance	18S metabarcodes					
Predictor	Model- derived	WOA	in situ	Darwin NH₄⁺:DIN	Darwin + <i>in situ</i>	
Si	***	ns	*	**	ns	
NH4 ⁺ :DIN	<mark>* * *</mark>	<mark>* * *</mark>	<mark>* * *</mark>	<mark>***</mark>	<mark>***</mark>	
PO4 ²⁻	* * *	*	*	ns	* *	
dFe	ns	ns	*	ns	**	
MLD	* * *	*	**	* *	**	
significance		psbO gene counts				
Predictor	Model- derived	WOA	in situ	Darwin NH₄⁺:DIN	Darwin + <i>in situ</i>	
Si	**	ns	ns	**	ns	
NH4 ⁺ :DIN	**	*	**	* * *	<mark>***</mark>	
PO4 ²⁻	ns	**	**	ns	**	
dFe	ns	**	<mark>* * *</mark>	ns	***	
MLD	<mark>* * *</mark>	**	***	<mark>* * *</mark>	**	
% Deviance		18S metabarcodes				
explained						
Predictor	Model-	WOA	in situ	Darwin	Darwin +	
	derived			NH4 ⁺ :DIN	in situ	
Si	24 (5)	21 (1)	17 (2)	<mark>24</mark> (4)	17 (2)	
NH4 ⁺ :DIN	<mark>30 (16)</mark>	<mark>30 (4)</mark>	<mark>29 (7)</mark>	22 <mark>(6)</mark>	<mark>24</mark> (2)	
PO4 ²⁻	11 (8)	32 (3)	24 (3)	11 (1)	<mark>24</mark> (4)	
dFe	4 (0)	4 (1)	5 (5)	4 (2)	5 (<u>4)</u>	
MLD	17 (6)	17 (3)	19 (5)	18 (5)	19 <mark>(5)</mark>	
% Deviance explained	psbO gene counts					
Predictor	Model-	WOA	in situ	Darwin	Darwin +	
	derived		5104	NH4 ⁺ :DIN	in situ	
Si	<mark>25</mark> (1)	17 (1)	13 (0)	<mark>25</mark> (2)	13 (0)	
NH4 ⁺ :DIN	18 (2)	18 (2)	18 (3)	24 (4)	<mark>30</mark> (3)	
PO4 ²⁻	15 (0)	<mark>27</mark> (4)	15 (4)	15 (0)	15 <mark>(3)</mark>	
dFe	7 (1)	7 (6)	13 (13)	7 (0)	13 <mark>(8)</mark>	
MLD	19 <mark>(9)</mark>	19 <mark>(5)</mark>	<mark>21 (7)</mark>	19 <mark>(6)</mark>	21 (6)	

Table S1. Generalized Additive Model (GAM) results for predictions of the relative abundance of diatoms. Data provided by *Tara* Oceans 18S rRNA gene metabarcoding and *psbO* gene counts. Rows are the different predictor variables. Si = Silicate, $PO_4^{2^-}$ = Phosphate, dFe = dissolved iron, MLD = mixed layer depth. Significance is assessed by applying a smoothing penalty to the predictor in question. Deviance explained is calculated by fitting a GAM with only the predictor in question, and by removing the predictor from the full model and comparing the difference in deviance explained with the full model (this result is provided in the parantheses). The most significant or most

explanatory are highlighted. (*) p-value < 0.05. (**) p-value < 0.01. (***) p-value < 0.001.

18S metabarcodes

Таха	Model-derived	Darwin model	
Diatoms	29.9% (***)	21.6% (***)	
Cryptophytes	2.4%	4.3% (*)	
Chlorophytes	2.6%	1.6%	
Dinoflagellates	36.8% (***)	30.6% (***)	
Haptophytes	4.3% (*)	5.9% (**)	
Dictyochophytes	9.1% (**)	11.4% (***)	
Pelagophytes	0.0%	6.8% (**)	
psbO gene counts			
Таха	Model-derived	Darwin model	
Diatoms	17.6 (***)	24.3% (***)	
Prochlorococcus	23.4% (***)	16.0% (***)	
Synechococcus	5.9% (**)	7.7% (**)	
Chlorophytes	13.2% (***)	21.2% (***)	
Dinoflagellates	1%	0.0%	
Haptophytes	13.6% (***)	1.2%	
Pelagophytes	11 70/ /***)	17 E0/ (***)	
	11.2% (****)	12.5% (***)	
Trichodesmium	11.2% (****) 4%	9.3% (**)	

Table S2. Deviance explained from the Generalized Additive Models using NH_4^+ :DIN as the sole predictor of the relative abundance of different eukaryotic phytoplankton taxa. Data provided by *Tara* Oceans 18S rRNA gene metabarcoding and *psbO* gene counts. Significance of NH_4^+ :DIN as a predictor of diatom relative abundance is denoted by the number of *. No * means p-value > 0.05. (*) p-value < 0.05. (**) p-value < 0.01. (***) p-value < 0.001. NH_4^+ :DIN may be model-derived from PISCES-v2 or from the Darwin model (Follows et al., 2007).

Parameter	Description	Value	Units
μ_{AO}^{max}	Maximum rate of ammonia oxidation	Eqn. 2	day ⁻¹
$K_{AO}^{\rm NH_4^+}$	Ammonia oxidation half- saturation constant for ammonium	0.1	mmol m ⁻ 3
K ^{PAR} A0	Ammonia oxidation half- saturation constant for photosynthetically active radiation	0.75	W m ⁻²
R_{AO}^{pH}	Reference pH below which ammonia oxidation is limited	8.0	pH units
рК _а	pH at which all NH_x is NH_3	9.3	pH units
μ_{NO}^{max}	Maximum rate of nitrite oxidation	0.15	day⁻¹
$K_{NO}^{NO_2^-}$	Nitrite oxidation half-saturation constant for nitrite	0.1	µmol m ⁻³
K ^{PAR} NO	Nitrite oxidation half-saturation constant for photosynthetically active radiation	0.75	W m⁻²

Table S3. Parameters and their values used to simulate ammonia and nitrite oxidation in the PISCES-v2 ocean biogeochemical model, detailed in equations 1-8. Values are informed by field and laboratory studies cited in the methods.

Data Set S1. Nutrient concentration data.

Data Set S2. Ammonia oxidation rate data.

Data Set S3. Coincident nutrient and regenerated to new primary production rate data.

Data Set S4. Variations in ammonia oxidation rates for pH changes. Rates normalized to a pH of 8.