Impact of intensifying nitrogen limitation on ocean net primary production is fingerprinted by nitrogen isotopes

Pearse J. Buchanan1✉, Olivier Aumont2, Laurent Bopp3, Claire Mahaffey1 & Alessandro Tagliabue1

The open ocean nitrogen cycle is being altered by increases in anthropogenic atmospheric nitrogen deposition and climate change. How the nitrogen cycle responds will determine long-term trends in net primary production (NPP) in the nitrogen-limited low latitude ocean, but is poorly constrained by uncertainty in how the source-sink balance will evolve. Here we show that intensifying nitrogen limitation of phytoplankton, associated with near-term reductions in NPP, causes detectable declines in nitrogen isotopes (δ15N) and constitutes the primary perturbation of the 21st century nitrogen cycle. Model experiments show that ~75% of the low latitude twilight zone develops anomalously low δ15N by 2060, predominantly due to the effects of climate change that alter ocean circulation, with implications for the nitrogen source-sink balance. Our results highlight that δ15N changes in the low latitude twilight zone may provide a useful constraint on emerging changes to nitrogen limitation and NPP over the 21st century.
Nitrogen limits phytoplankton growth in the low latitudes (45°S to 45°N), making the oceanic nitrogen cycle an important regulator of net primary production (NPP), which is essential for ecosystem health and carbon sequestration. Two major anthropogenic drivers, atmospheric nitrogen deposition and climate change, are altering the open-ocean nitrogen cycle. Atmospheric nitrogen deposition to the ocean has doubled since the preindustrial era and is currently the main input of anthropogenic nitrogen to the open ocean, causing documented increases in nitrate in certain locations. It is greatest in the Northern Hemisphere and is expected to peak by year 2030 as clean air initiatives are implemented. Meanwhile, climate change is accelerating and, by altering the properties and circulation of seawater, modifies biogeochemical processes and the distribution of bioavailable nitrogen. These anthropogenic drivers threaten to alter the twenty-first century nitrogen cycle and the nature of this alteration could either mitigate or amplify projected marine ecosystem productivity decline in the coming centuries.

Earth System Models (ESMs) are used to project anthropogenic trends, identify their drivers, and assess their detectability using concepts like the Time of Emergence (ToE), which quantify when anthropogenic signals emerge from natural variability. Although multi-century projections herald massive NPP declines associated with increasing nutrient limitation of phytoplankton, near-term ToE assessments suggest that variables related to nitrogen cycling, such as surface nitrate concentrations and NPP, only show detectable trends near the end of the twenty-first century, if at all. This highlights the challenge of detecting and predicting change in the nitrogen cycle, which is underpinned by a suite of overlapping biological processes that are highly sensitive to environmental change and may show strong variability. For instance, key nitrogen cycle processes will be altered directly as warming changes biogeochemical rates (i.e., metabolism) and indirectly as circulation alters substrate supply. Identifying the primary drivers and responses of the nitrogen cycle would facilitate improved understanding of the evolution of its source-sink balance and provide greater confidence in long-term projections of key ecosystem flows, such as NPP.

Nitrogen isotopes offer a sensitive means to detect such shifts. The isotopic composition of nitrogen ($\delta^{15}N$, where $\delta^{15}N = \left(\frac{^{15}N_{\text{sample}}}{^{14}N_{\text{standard}}} - 1\right) \times 1000$) is altered uniquely by different processes, such that nitrogen isotopes can record changes in the sources (biological nitrogen fixation and land-to-sea fluxes, including river input and atmospheric deposition), sinks (denitrification in the sediments and water column) and internal transformations (e.g., phytoplankton assimilation) of nitrogen. In general, nitrogen assimilation by phytoplankton and nitrogen sinks increase $\delta^{15}N$ of nitrate ($\delta^{15}N_{\text{NO3}}$), whereas sources of nitrogen decrease $\delta^{15}N_{\text{NO3}}$.

Results

Anthropogenic alteration. To assess the impact of atmospheric nitrogen deposition and climate change on the marine nitrogen cycle and its isotopes, we performed four simulations using the Pelagic Interactions Scheme for Carbon and Ecosystem Studies version 2 (PISCES-v2) biogeochemical model forced by output from the Institut Pierre-Simon Laplace Climate Model 5A (IPSL-CM5A). These simulations included a preindustrial control scenario (1801–2100), an anthropogenic scenario that combined historical (1851–2005) and future projections (2006–2100) of atmospheric nitrogen deposition and climate change (using the high emissions RCP8.5 scenario), as well as two additional simulations with each anthropogenic driver considered in isolation (see ‘Methods’). The anthropogenic effects on nitrogen cycling were quantified by comparing mean conditions at the end of the twenty-first century (2081–2100) with mean conditions at the end of the preindustrial control simulation.

The combination of anthropogenic nitrogen deposition and climate change had strong effects on the modelled nitrogen cycle when compared to the preindustrial control. Nitrogen deposition increased from 16.1 Tg N yr$^{-1}$ between 1801 and 1850 to 41.9 Tg N yr$^{-1}$ by 2030, and declined thereafter to 40.0 Tg N yr$^{-1}$ by 2081–2100 (Fig. 1a and Supplementary Fig. 4). The Northern Hemisphere received the highest deposition rates, in particular the west Pacific in agreement with recent observations. New nitrogen supply from biological nitrogen fixation declined from 78.8 to 73.9 Tg N yr$^{-1}$ (−6% of its preindustrial rate) by 2081–2100, consistent with other ESM simulations that considered increasing nitrogen deposition, and displayed a clear tropical to subtropical shift (Fig. 1b). Declines in NPP of between 5% and 60% developed across the lower latitudes by 2081–2100, which drove a global decline in nitrogen consumption by phytoplankton of 297 Tg N yr$^{-1}$ (−5%), consistent with other ESM projections. Declines in nitrogen utilization by zooplankton grazing (Fig. 1d) were consistent with trophic amplification, whereas denitrification changes (in both the water column and sediments; Fig. 1e, f) depended on local changes in particulate organic matter export, a dependency consistent with field investigations and data-constrained modelling. Overall, the combination of nitrogen deposition and climate change increased bioavailable nitrogen sources by 19.2 Tg N yr$^{-1}$, whereas decreasing bioavailable nitrogen sinks by 8.3 Tg N yr$^{-1}$, resulting in net gains of 27.5 Tg N yr$^{-1}$ by 2081–2100 (Fig. 1g). Although these gains in the global marine nitrogen budget are greater than those reported previously, a common inter-model response to anthropogenic impacts appears to be a shift towards nitrogen accumulation.

An important point is that climate change dominated the alteration of the marine nitrogen budget. By 2081–2100, climate change had increased the bioavailable nitrogen budget by 23.7 Tg N yr$^{-1}$ in the absence of historical and future increases in nitrogen deposition. This increase is explained by an increase in nitrogen fixation (+7.0 Tg N yr$^{-1}$) and a decrease in sinks (denitrification (−13.6 Tg N yr$^{-1}$) and burial (−3.1 Tg N yr$^{-1}$). Supplementary...
Fig. 1 Anthropogenic perturbation (Δ) of the marine nitrogen cycle by 2081–2100. Change is relative to the preindustrial control simulation. Top row shows major sources: a nitrogen deposition; b nitrogen fixation. Upper middle row shows internal cycling: c net primary production; d zooplankton grazing. Lower middle row shows major sinks: e water column denitrification; f sedimentary denitrification. Burial of nitrogen in sediments is not shown. Globally integrated changes are shown above each panel. Note the different scale for internal cycling. g Change in global nitrogen budget (sources minus sinks) due to anthropogenic drivers.

Fig. 5). In contrast, the anthropogenic increase in nitrogen deposition without climate change led to a small change in the budget of +4.9 Tg N yr\(^{-1}\) (Fig. 1g) due to strong compensatory feedbacks, consistent with other ESMs\(^{33-35}\), wherein newly deposited nitrogen either replaced nitrogen previously provided by nitrogen fixation (−12.0 Tg N yr\(^{-1}\)) or was rapidly removed by a local acceleration of denitrification (+6.4 Tg N yr\(^{-1}\)) and burial (+2.8 Tg N yr\(^{-1}\); Supplementary Fig. 6). The individual effects of climate change (+23.7 Tg N yr\(^{-1}\)) and nitrogen deposition (+4.9 Tg N yr\(^{-1}\)), while not perfectly additive, combined to cause the net accumulation of nitrogen in the ocean (+27.5 Tg N yr\(^{-1}\)).

Isotopic signals. By 2081–2100, the combination of climate change and nitrogen deposition caused widespread, detectable declines in δ\(^{15}\)N of nitrate (δ\(^{15}\)N\(_{\text{NO}_3}\); Fig. 2a) and particulate organic matter (δ\(^{15}\)N\(_{\text{POM}}\); Fig. 3a) across the lower ocean relative to the historical period (1986–2005), when most baseline isotopic measurements were taken\(^{20}\) and against which twenty-first-century trends might be assessed. Declines in δ\(^{15}\)N\(_{\text{POM}}\) developed in both the euphotic and twilight zones (see ‘Methods’ and Supplementary Fig. 7), whereas declines in δ\(^{15}\)N\(_{\text{NO}_3}\) were clearest in the twilight zone (Fig. 2a and Supplementary Fig. 8). Changes in δ\(^{15}\)N\(_{\text{NO}_3}\) in the euphotic zone were highly variable, as small changes in nitrogen cycling amid low nitrate concentrations altered \(^{15}\)N:\(^{14}\)N ratios substantially. In contrast, twilight zone δ\(^{15}\)N\(_{\text{NO}_3}\) declined more uniformly by >0.2‰ across the tropical and subtropical Pacific and the Atlantic by 2081–2100 (Fig. 2a), with stronger signals in the gyres where nitrate concentrations are lowest (Supplementary Fig. 9). Unlike the euphotic zone, these declines in the twilight zone are within detection limits of observational methods, as concentrations of nitrate exceed the 0.3 mmol m\(^{-3}\) threshold required for isotopic measurement\(^{43}\).

Declines in nitrogen isotopes emerged more rapidly from background variability than other metrics related to the nitrogen cycle. By 1960–2000, trends in twilight zone δ\(^{15}\)N\(_{\text{NO}_3}\) had emerged over much of the North Pacific, western equatorial Pacific, Arabian Sea and Atlantic Oceans (Fig. 2b). By year 2020, both δ\(^{15}\)N\(_{\text{NO}_3}\) and δ\(^{15}\)N\(_{\text{POM}}\) had emerged across 50% of the lower latitude ocean, increasing to 77–82% by 2081–2100 (Fig. 2c). Isotopic trends developed earlier and were more widespread than other variables, including NO\(_3\) concentrations and the N* tracer (N* = nitrate–phosphate · 16) in both the euphotic and twilight zones, as well as vertically integrated NPP and nitrogen fixation (Fig. 2c).

Although both contributed to the isotopic declines, the influence of climate change exceeded nitrogen deposition during the twenty-first century. The impact of nitrogen deposition on δ\(^{15}\)N\(_{\text{NO}_3}\) began in 1950 and showed little additional effect after 2050 in our model (Fig. 2d–f). In contrast, climate change impacts were only noticeable after 1975 and emerged across 60% of the lower latitude ocean in the twenty-first century (Fig. 2g–i). By 1986–2005, nitrogen deposition was responsible for emergent δ\(^{15}\)N\(_{\text{NO}_3}\) trends across 29–41% of the lower latitude twilight zone (Fig. 2f), compared with only 3–10% due to climate change (Fig. 2i). In the northwest Pacific, a strong decline in δ\(^{15}\)N\(_{\text{POM}}\) recorded in corals has been attributed to the rise in nitrogen deposition in recent decades\(^{31}\) and our simulations support this attribution. However, in the four decades from 2020–2060 (dotted areas), the pattern was reversed, with 31.9% of the ocean showing emergent trends due to climate change compared to only 14.2% due to nitrogen deposition. The dominance of climate
change continued to 2081–2100 with an additional emergence of 10–20% (Fig. 2i), compared to only 2–4% due to nitrogen deposition (Fig. 2f). Climate change was particularly important for emergences in the Southern Hemisphere (Fig. 2g) where rates and changes in nitrogen deposition were minimal (Fig. 1a).

Fig. 2 Anthropogenic trends of nitrogen isotopes in the twilight zone and their Time of Emergence. a End of twenty-first century (2081–2100) minus turn of the century (1986–2005) twilight zone $\delta^{15}$N$_{NO_3}$ due to both anthropogenic drivers. b Time of Emergence of twilight zone $\delta^{15}$N$_{NO_3}$. c Percentage of the low-latitude ocean (45°S–45°N) with emergent trends in biogeochemical variables related to the marine nitrogen cycle. They include vertically integrated net primary production (NPP) and nitrogen fixation ($N_2$ fixation), nitrate (NO$_3$) concentrations in both the euphotic zone (EZ) and twilight zone (TZ), $\delta^{15}$N$_{NO_3}$ and $\delta^{15}$N$_{POM}$. d–f Same as a–c but for experiment with nitrogen deposition only. g–i, Same as a–c but for experiment with climate change only.

Fig. 3 Biogeochemical control on the nitrogen cycle perturbation. a Climate change effect on euphotic zone $\delta^{15}$N$_{POM}$. b Climate change effects on twilight zone $\delta^{15}$N$_{NO_3}$ due to biogeochemical processes only. c Change in euphotic zone bioavailable nitrogen (nitrate plus ammonium). d Schematic describing a major mechanism of $\delta^{15}$N depletion in our experiments. Less upwelled bioavailable nitrogen (N) within a water parcel travelling from an upwelling zone (1) to the subtropical gyres (3) leads to lower $\delta^{15}$N$_{POM}$ outside of the productive zone. Greater nitrogen limitation of phytoplankton generates less enrichment of $^{15}$N in unused nitrogen (1), leading to a lower peak in $\delta^{15}$N$_{NO_3}$ and $\delta^{15}$N$_{POM}$ at the boundary between nitrogen-replete and nitrogen-limited regimes (2). A sharp depletion in $\delta^{15}$N$_{NO_3}$ is recorded in the area where the nitrogen-replete to nitrogen-limited transition was previously located under historical conditions. This depleted signal is carried laterally into the nitrogen-limited gyres (3) and delivered to the twilight zone via remineralization of low $\delta^{15}$N$_{POM}$. Future $\delta^{15}$N$_{POM}$ may be higher in regions near to upwelling (equatorial Pacific and Benguela upwelling in a), because nitrogen limitation decreases fractionation by phytoplankton, meaning that more $^{15}$N is assimilated into organic matter and removed from the euphotic zone. The schematic in d was made using GIMP version 2.10.6 (https://www.gimp.org/).

Linking nitrogen cycling and isotopic signals. Although low $\delta^{15}$N from nitrogen deposition was important for twentieth century declines in $\delta^{15}$N$_{NO_3}$, consistent with previous modelling, climate-driven declines in $\delta^{15}$N$_{NO_3}$ during the twenty-first century potentially involved changes to numerous
nitrogen cycle processes, the individual effects of which are difficult to isolate. Potential contributors include nitrogen limitation of phytoplankton, which limits the rate and strength of their fractionation, an increase in nitrogen fixation, an increase in zooplankton recycling, a decrease in denitrification or a physical redistribution of the dissolved nitrogen compounds by a changing circulation (or any combination of these processes). Here we demonstrate that changes ultimately linked to increasing nitrogen limitation were responsible for the broad, simulated δ15NNO3 declines that emerged in the twilight zones of the low-latitude oceans. Namely, a decrease in phytoplankton production and fractionation potentially supplemented by a tropical-subtropical shift of nitrogen fixation.

First, the presence of 15N-depleted organic matter sinking from the overlying euphotic zone is a first-order driver of the δ15NNO3 declines in the twilight zone. Widespread declines in euphotic zone δ15NPOM (Fig. 3a) thus delivered less 15N to twilight zones across large parts of the lower latitude ocean following the remineralization of sinking organic material. This driver was further supported by an offline analysis of purely biogeochemical 15NNO3 fluxes in our global model. The only internal biogeochemical source of nitrate is from nitrification of the ammonium that forms following remineralization, whereas the main sinks are primary production and denitrification. By isolating the fluxes of these individual sources and sinks within each grid cell, we disentangled local biogeochemical effects from circulation effects (see ‘Methods’). Biogeochemical fluxes tended to deplete δ15NNO3 across the tropics and subtropics, and the ensuing changes to δ15NNO3 were greater than observed in the full model (Fig. 3b). This indicates that physical sources and sinks (i.e., ocean transports) partially compensated for the biogeochemical effects. Smoothing of the strong gradients set by biogeochemical processes under otherwise preindustrial conditions to the global model, we expect δ15NPOM declines of 0.1–0.8‰ for bioavailable nitrogen declines of 5–40%, which agrees broadly with the results of the full model by 2081–2100 (Fig. 2c). Furthermore, the local enrichment of δ15NPOM in the upwelling region in both our 0D model (compare solid and dashed lines in Fig. 3d) and in the tropical Pacific in our global model (Fig. 3a) clearly signifies the existence of this mechanism, where more 15N was removed from upwelling zones due to nitrogen limitation of phytoplankton (it is noteworthy that this feature was absent in the Atlantic due to local declines in denitrification; Fig. 1g). Ultimately, the biogeochemical consequences of increasing nitrogen limitation appeared to be the primary cause of the widespread isotopic declines.

Warming vs. circulation changes. We examined the direct (i.e., warming on biogeochemical rates) and indirect effects (i.e., circulation altering nutrient supply) of climate change in two additional experiments. First, warming was imposed on biogeochemical processes under otherwise preindustrial conditions to mimic its effect on rates. Second, preindustrial temperatures were imposed, while climate change altered the circulation to mimic its effect on substrate availability (see ‘Methods’). Direct effects of warming on biogeochemical processes showed a limited ability to reproduce the full suite of climate-driven trends, with the exception of the poleward shift in nitrogen fixers (Fig. 4). In contrast, changes to ocean circulation (e.g., stratification) in the indirect effect simulation replicated changes in euphotic zone nitrate (Spearman’s rank correlation; rs = 0.94), twilight zone δ15NNO3 (rs = 0.94), twilight zone δ15NPOM (rs = 0.95), and NPP (rs = 0.69), zooplankton grazing (rs = 0.69) and water column denitrification (rs = 0.88) and sedimentary denitrification (rs = 0.69).
stratification) on phytoplankton in the low latitudes over the preindustrial period. Central to the climate-driven perturbation is the fact that nitrogen deposition since the preindustrial period has increased by a factor of 2.5. This has led to a shift in the sources and sinks of nitrogen, and the accompanying changes in nitrogen isotopes that fingerprint the response of the nitrogen cycle.

Discussion

Our experiments demonstrate the dominant role of climate change in the twenty-first century alteration of the marine nitrogen cycle, despite a 2.5-fold increase in atmospheric nitrogen deposition since the preindustrial period. Central to the climate-driven perturbation is the fact that nitrogen limitation of phytoplankton in the low latitudes due to changes in ocean circulation, likely due to increasing stratification, is ongoing and expected to intensify in the future. Importantly, these changes are clearly fingerprinted by detectable changes in the isotopic composition of nitrate and particulate organic matter within twilight zones across much of the lower latitude ocean. The ocean twilight zone is emerging as an important depth stratum to detect trends in nitrogen cycling. Signals may be larger in the euphotic zone, but detection is severely challenged by high-frequency variability. In contrast, the twilight zone collects euphotic zone signals through sinking and remineralization of organic matter and acts as a low-pass filter to record large-scale, multi-annual changes in upper-ocean-biogeochemical processes. The relative stability of the twilight zone is demonstrated by the low variability of modern-day δ¹⁵N recorded in sub-euphotic foraminifera. As foraminifera are now routinely used to reconstruct δ¹⁵N for studies of the past oceanic nitrogen cycle, our results suggest that sedimentary archives of sub-euphotic foraminifera may provide an opportunity to investigate past variations in nitrogen availability across the low latitudes. If we consider the coming decades, the strong sensitivity of nitrogen isotopes to large-scale changes in nitrogen cycling mean that repeat hydrographic surveys and multi-decadal time series can complement remote sensing and bioArgo floats to constrain the impacts of climate change and natural variability, providing an important means to assess model projections of NPP and an enigmatic marine nitrogen cycle.

Methods

Modelling approach. We used the PISCES-v2 biogeochemical model, attached to the Nucleus for European Modelling of the Ocean version 4.0 (NEMO-v4) general ocean circulation model. PISCES-v2 includes five nutrients pools (nitrate, ammonium, phosphate, silicate, and nitrite) and 52 species. The model is run in a range of 0°C to 4°C, with a horizontal resolution of 1° latitude by 1° longitude and a vertical resolution of 20 layers. The model is forced by observed and predicted sea surface temperature, salinity, and wind stress. The model is run for 100 years, with the first 50 years used for model spin-up and the last 50 years used for model output. The model is run for both control and climate change experiments. The climate change experiments are run for 2100, relative to preindustrial conditions. If nitrogen sinks do decline as less organic matter sinks out of the euphotic zone, then our results suggest that the bioavailable nitrogen reservoir may accumulate. Although the response of hypoxic zones, and hence nitrogen sinks, to climate change is subject to considerable uncertainty, the shift towards accumulation is consistent with previous modelling and may be reinforced by including currently unrepresented processes, such as the stimulation of nitrogen fixation by increasing pCO₂ and anthropogenic iron deposition. Net accumulation of bioavailable nitrogen in the twenty-first century, if realized, may mitigate or even counteract the multi-centennial declines in NPP that are projected as a result of nutrient trapping in the deep ocean and potentially represents an important self-stabilizing mechanism for ocean productivity on multi-centennial timescales. Importantly, our results suggest that this response will be fingerprinted by δ¹⁵N in sedimentary archives of NPP and an enigmatic marine nitrogen cycle.

Fig. 4 Direct and indirect effects of climate change on the nitrogen cycle. How well the direct effects (warming on biogeochemical rates) and indirect effects (circulation changes, including stratification) of climate change reproduce changes in the nitrogen cycle and its isotopes in the full model. Agreement is measured as a cell-to-cell comparison using Spearman’s rank correlation between the climate change experiment and these experiments, comparing 2D fields of euphotic zone nitrate (NO₃), twilight zone δ¹⁵NNO₃, eutrophic zone δ¹⁵NPO₄, and sedimentary archives of δ¹⁵NPO₄.
phosphate, silicic acid and dissolved iron), dissolved oxygen, the full carbon system and subtropical waters, and were shallowest in equatorial and temperate waters (Supplementary Fig. 7).

**Time of emergence.** ToE calculations determined when anthropogenic, anomalous trends emerged from the noise of background variability. ToE was calculated at each grid cell within both the euphotic and twilight zones (depth-averaged) and using annually averaged fields of ocean tracers. We therefore ignored temporal trends and variability at seasonal and sub-seasonal scales. Raw time series were first detrended and normalized using the linear slope and mean of the preindustrial control experiment, such that the preindustrial control time series varied about zero, while anomalous trends in experiments with climate change and/or nitrogen deposition deviated from zero. These detrended and normalized time series were smoothed using a boxcar (flat) moving average with a window of 11 years to filter decadal variability (Supplementary Fig. 12). Differences with the preindustrial control experiment were then computed.

To determine whether the differences with the preindustrial control experiment were anomalous, we calculated a measure of noise from the raw, inter-annual time series of the preindustrial control experiment (1801–2100). A signal emerged from the noise if it exceeded 2 SDs, a threshold that represents with 95% confidence that a value was anomalous and is therefore a conservative envelope to distinguish normality from anomaly.

Furthermore, we required that anomalous values must consistently exceed the noise of the preindustrial control experiment until the end of the simulation (2100) to be registered as having emerged. Temporary emergences were therefore rejected, making our ToE estimates more conservative. A graphical representation of this process is shown in Supplementary Fig. 12.

**Isolating biogeochemical δ15NO3 fluxes.** We analysed the biogeochemical fluxes of δ15NO3 and NO3 into and out of each model grid cell within the twilight zone, to determine whether the trends in δ15NNO3 were related to biogeochemical or physical changes. Fluxes of δ15NO3 and NO3 included a net source from nitrification (NO3nitr) and net sinks due to new production (NO3new) and denitrification (NO3den). Although nitrification did not directly alter the 15N:NO ratio in our simulations, the release of δ15NO3 and NO3 by nitrification conveyed an isotopic signature determined by prior fractionation processes that produce ammonium (NH4). These processes include remineralization of particulate and dissolved organic matter, excetration by zooplankton and nitrogen fixation. The isotopic signatures of these processes were thus included implicitly in NO3nitr. For each grid cell, we calculated the biogeochemical tendency to alter δ15NNO3 based on the ratio of inputs minus outputs:

\[ \Delta \delta^{15}N_{NO_3} = \frac{\delta^{15}N_{NO_3} \text{-} \text{net} - \delta^{15}N_{NO_3} \text{-} \text{exported}}{\delta^{15}N_{NO_3} \text{-} \text{net} - \delta^{15}N_{NO_3} \text{-} \text{exported}} \times 1000 \]

(1)

This calculation excluded any upstream biological changes and circulation changes that might have altered δ15NNO3.

**0D water parcel model.** We simulated the nitrogen isotope dynamics in a recently upwelled water parcel during transit to the sub-tropics by building a 0D model. The model simulates state variables of dissolved inorganic nitrogen (DIN), particulate organic nitrogen (PON) and exported particulate nitrogen (ExpN), as well as their heavy isotopes (D15N, PO15N and Exp15N) in units of mmol N m−3 over 10 days given initial conditions and constants listed in Supplementary Table 1.

| reaction | equation |
|----------|----------|
| N uptake | DIN(t) − N uptake + N recycled |
| N recycled | DIN(t) − N uptake − N recycled |

(2)

(3)

(4)

(5)

(6)

(7)

DIN(t) was calculated as the maximum potential growth rate of phytoplankton (mu_max) in units of day−1 (Eq. 8) using temperature and then finds nitrogen uptake (N uptake, Eq. 10) using PON and limitation terms for nitrogen (Nlim, Eq. 9), light (Llim, Supplementary Table 1) and iron (Fe(III), Supplementary Table 1).

\[ \mu_{\text{max}} = 0.6 \text{day}^{-1}, \quad L_{\text{light}} \]  

(8)

(9)
\[ N_{\text{uptake}} = \mu_{\text{max}} \cdot \frac{1}{\text{DOM}} \cdot \min(F_{\text{DOM}}, N_{\text{lim}}) \cdot \text{PON} \]  

At a constant temperature of 18°C, \( \mu_{\text{max}} \) is equal to –1.9 day\(^{-1}\). Limitation terms for light and iron are set as constant and are used to prevent unrealistically high nitrogen uptake when nitrogen is high, such as occurs immediately following upwelling in the high-nutrient low-chlorophyll regions of the tropics. Fractionation by phytoplankton is calculated assuming an open system\(^{21}\), in this case where nitrogen can be lost through export of organic matter. To calculate the fractionation associated with uptake (\( \delta_{\text{Nup,exp}} \), Eq. 11), we multiply the total nitrogen uptake (\( N_{\text{uptake}} \), Eq. 10) by the heavy to light isotope ratio (\( r_{\text{DIN}}^{15} \), Eq. 12) and the fractionation factor (\( f_{\text{rec}} \), Supplementary Table 1), which is converted from units of per mil (‰) to a fraction relative to one. This fractionation factor (\( f_{\text{rec}} \)) is constant at 5% but is decreased towards 0% by the nitrogen limitation term (\( N_{\text{lim}} \), Eq. 9), such that when nitrogen is limiting to growth, the fractionation during uptake decreases (last term on the right-hand side approaches 1).

\[ \delta_{\text{Nup,exp}} = N_{\text{uptake}} \cdot r_{\text{D}}^{15} \cdot \left( 1 - \frac{N_{\text{min}}}{\text{DOM}} \right) \]  

At each timestep, a fraction of the PON pool becomes detritus (Eq. 15) and this detritus is instantaneously recycled back to DIN or exported to ExpN and removed from the water parcel. The amount of detritus produced per timestep is calculated as the sum of linear respiration (Eq. 13) and quadratic mortality (Eq. 14) terms, where \( P_{\text{resp}} \) (units of day\(^{-1}\)), \( K_{\text{resp}} \) (units of mmol N m\(^{-3}\)) and \( P_{\text{mort}} \) (units of (mmol N m\(^{-3}\)) day\(^{-1}\)) are constants (Supplementary Table 1).

Respiration = \( P_{\text{resp}} \cdot \text{PON} \cdot \text{PON} \)/\( \text{PON} + K_{\text{resp}} \)  

Mortality = \( P_{\text{mort}} \cdot \text{PON}^2 \)  

Detritus = Respiration + Mortality  

Once we know the fraction of PON that becomes detritus at any given timestep, we must solve for the fraction of that detritus that becomes DIN through recycling (Eq. 19) and export (Eq. 20) fluxes. These, similar to \( 15N_{\text{up,exp}} \) (Eq. 11), are solved by multiplying against a standard ratio of heavy to light isotope (\( r_{\text{PON}}^{15} \), Eq. 21).

\[ N_{\text{recycled}} = N_{\text{recycled}} \cdot r_{\text{PON}}^{15} \]  

\[ N_{\text{exported}} = N_{\text{exported}} \cdot r_{\text{PON}}^{15} \]  

\[ r_{\text{PON}}^{15} = \frac{\text{PON}^{15} \cdot \text{PON}^{14}}{\text{PON}^{15} \cdot \text{PON}^{14}} \]  

Finally, we calculate the \( \delta^{15}N \) values of the major pools in the model (DIN, PON and ExpN) as output (Eqs. 22–24). We assume in this model that the major pools of DIN, PON and ExpN represent the total amount of the light isotope (\( V_{\text{DIN}} \)), whereas the DIN\(^{15}N \), PON\(^{15}N \) and ExpN\(^{15}N \) pools represent the relative enrichment in \( ^{15}N \) compared to a standard ratio. For simplicity, we make the standard ratio equal to 1. Therefore, taking the ratio of the DIN\(^{15}N \) to DIN pools and subtracting one returns the isotopic signature. Multiplying this by 1000 converts this signature to per mil units (‰).

\[ \delta^{15}N_{\text{DIN}} = \left( \frac{\text{DIN}^{15}N}{\text{DIN}} - 1 \right) \cdot 1000 \]  

\[ ^{15}N_{\text{DIN}} = \left( \frac{\text{Exp}^{15}N}{\text{ExpN}} - 1 \right) \cdot 1000 \]  

\[ ^{15}N_{\text{PON}} = \left( \frac{\text{PO}^{15}N}{\text{PON}} - 1 \right) \cdot 1000 \]  

**Data availability**

The data generated in this study have been deposited in the Zenodo database and are freely available at https://doi.org/10.5281/zenodo.5541332.

**Code availability**

The version of NEMO-PISCES used in this study can be downloaded with the following command: svn co https://forge.ipsl.jussieu.fr/nemo/svn/NEMO/releases/release-4.0 NEMO4.0. Additional development to include the isotopes can be merged into this version by contacting the lead author. Analyses and code to produce graphs were conducted using both Ferret and Python, and are available on GitHub at https://github.com/pearseb/PISCESsso_Ncyce_analysis and are citable https://doi.org/10.5281/zenodo.5545310.

Received: 28 January 2021; Accepted: 13 October 2021; Published online: 28 October 2021

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