Convergent Estimates of Marine Nitrogen Fixation

Wei-Lei Wang[1] J. Keith Moore[1], Adam C. Martiny[1,2], François W. Primeau[1]*

Abstract

Uncertainty in the global patterns of marine nitrogen fixation limits our understanding of the response of the ocean's nitrogen and carbon cycles to environmental change. The geographical distribution and ecological controls on nitrogen fixation are difficult to constrain with limited in-situ measurements. Here we present convergent estimates of nitrogen fixation from an inverse biogeochemical and a prognostic ocean model. Our results demonstrate strong spatial variability in the nitrogen to phosphorus ratio of exported organic matter that greatly increases the global nitrogen-fixation rate. We find that new nitrogen supports up to 50% of export in subtropical gyres, that nitrogen fixation and denitrification are spatially decoupled and that current-era nitrogen sources and sinks largely balance on multidecadal timescales. Moreover, we propose a role for top-down grazing control in shaping the global patterns of nitrogen fixation. Our findings suggest higher than expected ocean carbon export and weaker stabilizing nitrogen-cycle feedbacks than previously thought.

Main

Great uncertainty in global patterns of marine nitrogen fixation limits our ability to build mechanistic models that reliably predict the response of the ocean's nitrogen and carbon cycles to environmental change. Field N_2-fixation measurements are challenging to scale up because they have poor spatial coverage with high spatio-temporal variability, spanning 6 orders of magnitude[1, 2, 3, 4]. Estimates from geochemical inverse models can use the more abundant hydrographic nitrate and phosphate concentration measurements to infer global rates of N_2 fixation. However, the existing P^* method[5, 6, 7] predicts a geographical distribution that conflicts with in-situ measurements and prognostic biogeochemistry models. For example, in-situ measurements in the tropical Pacific Ocean, yield rates that are high in the west and low in the east but the P^* method predicts the opposite

[1] _Department of Earth System Science, University of California Irvine, Irvine, CA 92617, USA
[2] Department of Ecology and Evolutionary Biology, University of California Irvine, Irvine, CA 92697, USA
* Corresponding author

pattern[8, 9]. On larger-scales, observations and models suggest relatively high rates of tropical-Atlantic N_2 fixation, whereas the P^* method predicts relatively low rates[4,7,10,11].

The P^* method attempts to diagnose N_2-fixation rates with a tracer, $P^* \equiv [PO_4^{3-}] - [NO_3^-]/16$, from observed surface phosphate and nitrate concentrations and its computed divergence using an ocean general circulation model (OGCM). Assuming that non-diazotrophic production follows a constant N:P ratio of 16:1, P^* is unaffected by biological production so that any P^* divergences indicate the addition of new fixed N.

Errors in the computed P^* divergence – either due to circulation or the nutrient data – could explain the conflicting estimates. Coarse-resolution OGCMs have significant biases, and P^*, being computed as a concentration difference, tends to have larger relative errors than either $[PO_4^-]$ or $[NO_3^-]$ alone. Furthermore, the low nitrate and phosphate concentrations in oligotrophic surface waters are often below the detection limits of traditional measurement techniques.

Another source of error is the assumption that organic matter produced by non-diazotrophic plankton follows fixed Redfield (16N:1P) stoichiometry. While the P^* N_2-fixation estimate accounted for preferential remineralization of dissolved organic phosphorus (DOP) compared to nitrogen (DON), it did not consider the large-scale stoichiometric diversity of phytoplankton[7]. The impact of non-Redfield plankton cycling could be important. Model studies show that it greatly changes the amount of N_2 fixation necessary to explain observed P^* patterns while also modifying the size of the marine nitrogen reservoir[12-14] with similar impacts from non-Redfield cycling of DON and DOP[10,11]. Given recently documented C:N:P variations in particulate and dissolved organic matter as well as in the organic-matter export flux[15-19], it is important to construct models that do not assume constant stoichiometry.

Our global inversion diagnoses N_2 fixation by tracking the circulation of N and P separately through their organic and inorganic forms without assuming a constant N:P ratio in plankton or exported organic matter. It is based on a data-constrained circulation model[20, 21] to minimize prognostic-model biases and uses the full water-column nitrate and phosphate measurements[22] to reduce the sensitivity to larger surface-water P^* errors.

We present data-constrained estimates of (1) the spatially-variable N:P ratio of exported organic matter, (2) global patterns of N_2 fixation and denitrification, (3) the fraction of export production supported by new fixed nitrogen, and (4) the degree to which N sources and sinks balance in the current era. By construction, the inverse model is agnostic to the biological underpinnings that control N_2 fixation. To identify the mechanisms driving the inferred N_2-fixation patterns, we compare with results from the Community Earth System Model (CESM) ocean component,

also modified to allow for variable N:P in phytoplankton and sinking organic matter, building on the non-Redfield treatment of DOM[11, 17]. CESM produces a geographic distribution of N_2 fixation remarkably similar to the one inferred from the inverse model, and provides insights into the geochemical and ecological constraints on diazotrophs that drive global N_2-fixation patterns.

Nitrogen fluxes and transformations

The inverse model is based on a system of conservation equations relating rates of losses of fixed N due to denitrification and anammox, physical transport due to circulation and gravitational settling of particles, biogeochemical transformations of N and P between organic and inorganic forms and between dissolved and particulate phases, and external inputs of fixed N (Fig. 1). The solution of these equations yields six state variables, which are the concentrations of dissolved inorganic nitrogen and phosphorus ([DIN], [DIP]), and the dissolved and particulate phases of organic nitrogen and phosphorus ([DON], [DOP], [PON], [POP]). The biogeochemical transformation rates are parameterized using only 13 parameters (Table S1), which are constrained by a hydrographic database of [DIN], [DIP], and [DON][17, 22] (supplementary materials Fig. S1). The fluxes and transformations inferred by the model are estimated under the assumption that the marine N cycle is in steady state and therefore balanced. We relax this assumption in the uncertainty analysis (see Methods).

N:P ratio of exported organic matter

The inversion yields a molar N:P ratio for the combined export from particulate and dissolved organic matter, denoted $(N:P)_{exp}$, ranging from more than 26:1 in the most nutrient-depleted gyres to less than 12:1 in nutrient-rich upwelling regions (Fig.2a). We find a close correspondence between the inferred $(N:P)_{exp}$ and the N:P ratios measured in suspended particles[18, 19, 23] (Fig.2b), similar to previous results examining C:P ratios[16]. The agreement suggests that at least part of the variance in the relative export of N compared to P originates in the stoichiometric diversity of plankton, rather than being entirely due to differential N and P remineralization[11, 24]. We do find evidence for the preferential remineralization of P. The optimal parameter estimates indicate a shallower dissolution of POP compared to PON and a faster degradation of DOP compared to DON (*c.f.* the optimal values of b_P, b_N, κ_{dP} and κ_{dN}, in Table S1).

The globally-integrated ratio of biological export of N and P is 17.3:1, above the Redfield value of 16:1. The ratio is less than a simple averaging of the regional ratios shown in Fig. 2a would suggest due to the unequal regional contributions to total export. The elevated N:P ratios in the subtropical gyres are similar to those assumed in previous studies[12,13] but our estimates for the non-gyre regions are considerably higher, with mean ratios only modestly below Redfield. A global N:P

export ratio of 17.3:1 is also much higher than the ratio of the oceanic reservoir of nitrogen and phosphorus which is 14.3:1[13]. While it is argued that the difference between these two ratios is a signature of denitrification, this is only partly true. In the presence of spatially-varying N:P ratios, the average residence time of remineralized N need not equal that of P because of regional differences in the time for respired products to return to the surface[25,26].

Geographic distribution of N_2 fixation

The inversion reveals high N_2-fixation rates in the subtropical gyres where surface nutrients are depleted (and export N:P ratios are high) and low fixation rates in upwelling regions where surface macro nutrients are abundant (Figs. 3a,S6). The most intense N_2- fixation rates are found downstream of the low-latitude upwelling regions in all basins. This pattern differs from the *P** estimate [7], which predicts the highest fixation rates in the eastern tropical Pacific upwelling regions and relatively low rates in the Atlantic.

Our global inversion is in good agreement with regional inversions for the Atlantic Ocean derived from isotope budgets [27]. Northward of 24°N, 11°S, and 30°S we estimate N_2-fixation rates of $4.5^{7.0}_{3.1}$, $27.9^{38.1}_{21.3}$, and $36.2^{50.9}_{26.9}$ TgN/yr respectively, whereas, Ref. [27] estimated 3.0$\pm$0.5, 27.1$\pm$4.3, and 30.5$\pm$4.9 TgN/yr.

Our inversion generally supports the idea that little N_2 fixation occurs at temperatures below 20℃ [28]. The one exception to this is elevated N_2 fixation in the Arctic Ocean, where detectable N_2-fixation rates have been measured[29]. Our inverse estimates in this region must be interpreted cautiously because the data constraining the circulation and nutrient-cycling are sparse (Fig. S1).

Water-column losses are inferred to be highest in suboxic waters ($[O]_2$<5 mmol/m^3) flanking the equator in the eastern tropical Pacific and in the northern Indian Ocean, where column-integrated rates can exceed 440 mmol/m^2/yr (Fig. 3c). The inferred water-column losses extend over the much larger volume of hypoxic waters ($[O]_2$ < 60 mmol/m^3) albeit at a lower rate, with non-negligible integrated water-column losses at oxygen concentrations above 20 mmol/m^3 (Fig. S7a,b) supporting the idea that substantial anaerobic respiration occurs within particle microenvironments in hypoxic waters[30] (but see also Fig. S7c,d and S14-S16). Benthic losses are highest along continental margins where more sinking organic matter reaches the bottom (Fig. 3d).

Our inversion reveals the importance of large-scale inter-basin transport of nitrogen for maintaining a globally balanced fixed-N budget (Table 1). The Atlantic Ocean for example maintains its balance by exporting ~15TgN/yr (33% of its N input). This result has been anticipated by prognostic model simulations and box-model budgets[31,32] and is consistent with strong evidence for P-limitation in the North

Atlantic[33-35]. The Pacific Ocean supplies more than half of the fixed-N inputs, but also contributes disproportionately to losses because of intense water-column denitrification in the east Pacific low-oxygen zones, with a net basin-scale deficit of ~10 TgN/yr in agreement with Ref.[31]. The Indian Ocean has a nearly balanced N budget (Table 1).

Microbial N_2 fixation supports more than 30% of the export production in all subtropical gyres and more than 50% in the N. Pacific and S. Atlantic (Fig. 4). These estimates are in agreement with independent budgets based on $\delta^{15}N$ measurements. At the Bermuda Atlantic Time-series Study (BATS) station in subtropical Atlantic (32°10′N 64°30′W), a $\delta^{15}N$ budget suggests that no input of new N is needed to close the N budget[36] – our inversion shows a negligible contribution of N_2 fixation. Similarly a $\delta^{15}N$ budget for the Hawaii Ocean Time-series (HOT) (22°45′N 158°00′W) suggests that 30%–50% of export production is sustained by new N[37] – we estimate 30%–40%(Fig. 4). Globally, we find that N_2 fixation supports ~8% of the global carbon export production, which is inferred by our inverse-model to be ~12 PgC/yr.

Globally-integrated marine N cycle budget

We estimate that N_2 fixation plus external inputs (Fig.3b), delivers 200 TgN/yr to the ocean. This input is balanced by water-column and benthic losses of 68 and 132 TgN/yr (Table 1).

The uncertainty for our global N_2-fixation rate estimate of 163 TgN/yr is approximately $\pm$30% (Table 1). The globally-integrated N_2-fixation and N-loss rates in our steady-state model can be scaled up or down with only modest changes in the spatial distribution of nutrients and N_2 fixation (Figs S12 and S13). Thus, while the nutrient data provides strong constraints on the spatial pattern of N_2 fixation it provides only weak bounds for the globally-integrated rate. Our uncertainty estimate for the globally-integrated rates therefore relies on ^{15}N isotopic constraints[38,39], which require a benthic to water-column loss ratio between 1.3 and 3.0. This constraint means that we cannot scale the benthic-loss function up or down by more than 20% (Table S2), leading to uncertainties of $\pm$40% and $\pm$12% for the globally-integrated benthic and water-column loss rates (Table 1). In comparison, the uncertainty due to the other parameters is small, typically contributing relative errors of less than 2% in basin-integrated rates. External inputs due to rivers and atmospheric deposition are small in comparison to the sedimentary losses and therefore contribute relatively less uncertainty[31]. An alternative inversion based on pre-industrial atmospheric deposition [40], yields a N_2-fixation rate that is ~10% higher than the one for the present-day deposition (Table S4) with only modest changes in the pattern of N_2 fixation (Fig. S9). This ~10% decrease in N_2 fixation associated with increased atmospheric deposition is similar to what has been found in previous modeling studies, which found strong

negative feedbacks limiting the impact of atmospheric deposition[41,42]. We don't explicitly estimate organic N burial in sediments, but this would be a similarly small fraction of our inferred benthic fixed N loss.

The uncertainty due to the relaxation of the steady-state assumption by allowing for slowly-evolving nutrient fields (see Methods) has a modest impact on the parametric uncertainty. The most probable non-steady state model has a global nitrogen budget, with a 1 TgN/yr increment in the estimated benthic loss, an 11 TgN/yr reduction in water-column denitrification, and a 16TgN/yr reduction in fixation, leaving a global source-sink imbalance of only 6 TgN/yr (Tables 1 and S3). Because the inversion could have returned a much larger N-cycle imbalance, this suggests that our model is robust to undetected slowly-evolving trends in the marine N cycle and that for the current era there is no evidence for large imbalances on multidecadal timescales.

A potentially important source of uncertainty that we are unable to quantify in our annually-averaged inverse model is the neglect of the seasonal cycle. However, because the model is constrained by data from the full water column, we expect that the muted seasonality at the base of the thermocline and deeper waters will anchor the inversion to produce the correct annually averaged fluxes. Further reductions in the uncertainty of the inverse estimates of N_2 fixation will require a seasonally varying circulation model that better resolves the coastal shelf regions and the oxygen minimum zones. Better data coverage in the Arctic would help reduce large uncertainties in polar waters.

Ecological controls on N_2 fixation patterns

Our inverse model is largely agnostic about the biological underpinnings driving N_2 fixation. This is a positive feature as it reduces the chances that the answer is built into the model structure. To understand the mechanisms driving N_2-fixation patterns, we compare with biogeochemical simulations from the CESM ocean component, modified to allow for variable N:P ratios in phytoplankton and organic-matter export. The CESM-simulated N_2-fixation pattern is remarkably similar to the inverse-model estimate ($R^2 = 0.47$, cf. Figs. 3a, 5a). In both the prognostic and inverse models, N_2-fixation rates are suppressed directly above the coastal and equatorial upwelling zones, with strong spatial decoupling of N_2 fixation and water-column denitrification associated with upwelling zones in the eastern tropical Pacific and Arabian Sea. Maximum N_2-fixation rates in both models are in downstream waters, advected away from the upwelling zones. The decoupling between upwelling zones and N_2 fixation occurs over much larger spatial scales in the Pacific, due to iron-limitation in the offshore waters. N_2 fixation and the drawdown of "excess" P are hampered by iron-limitation, pushing the highest N_2-fixation rates to the western tropical Pacific, where iron concentrations are higher, in line with field observations and previous modeling studies[11, 32, 43, 44].

N_2-fixation patterns in CESM are driven by bottom-up limitations on diazotroph growth and top-down grazing by zooplankton. Previous studies have focused on bottom-up controls (influences of nutrients, light, and temperature) to explain global N_2-fixation patterns[11, 13, 14, 43, 44]. Diazotrophs need sufficient phosphorus and iron for growth, and benefit from competitors' N-limitation. In regions with high dust-input rates in the North Atlantic and northern Indian Ocean, diazotrophs tend to be phosphorus limited, with iron availability constraining growth over much of the remaining low-latitude ocean (Fig.5b).

Nutrient dynamics are important controls on diazotrophy, but we also suggest a key role for grazing, based on both first principles and the CESM results. Diazotroph growth rates are inherently slower than those of key microzooplankton grazers, which have growth rates similar to the fastest growing phytoplankton[45, 46]. This suggests that diazotrophs will always be in the density-dependent part of the grazing rate versus prey biomass curve, unlikely to escape grazing control and bloom. Furthermore, as diazotrophs typically account for only a small fraction of the phytoplankton community (in CESM up to ~10% of NPP in the most strongly N-limited regions and less than 3% in upwelling zones), it will be the growth of the more abundant and faster-growing, non-diazotrophic phytoplankton that determines zooplankton biomass, indirectly influencing the top-down grazing experienced by diazotrophs.

In CESM, diazotroph biomass is elevated and N_2-fixation rates are highest in the most N-limited regions where zooplankton biomass is low (Figs. 5a, S21a). In the Indian basin, western Pacific, and coastal upwelling zones, diazotrophs are not strongly nutrient-limited (Fig.5b). Top-down grazing pressure is keeping diazotroph biomass low, despite ambient nutrient concentrations that support near-maximal growth rates. The lowest diazotroph biomass is seen in the coastal upwelling zones, where other phytoplankton groups are blooming and zooplankton biomass is elevated (Fig. S21a,c). A sensitivity experiment with the maximum grazing rate on diazotrophs reduced by a factor of 0.63, giving them the same maximum-grazing-rate to maximum-growth-rate ratio as diatoms, results in massive diazotroph blooms in the low-latitude coastal upwelling zones, boosting global N_2 fixation by 62% (Fig. 5c, S21b,d and SI). The high N_2-fixation rates in upwelling regions in this reduced-grazing simulation are similar to the P^* estimate. Thus, the CESM results suggest grazing plays a key role in the spatial decoupling of N_2 fixation and denitrification, and prevents the runaway denitrification losses that could occur with high N_2-fixation rates directly above the OMZs[47]. These results are not dependent on the highly-parameterized treatment of zooplankton and grazing in CESM, but should always arise in models that assume slower maximum growth rates for diazotrophic phytoplankton along with a grazing pressure similar to other phytoplankton.

Marine diazotrophs comprise a highly diverse group of organisms, but much of the pelagic N_2 fixation is thought to be by relatively slow-growing, *Trichodesmium spp.* and small unicellular diazotrophs[46]. The top-down grazing argument is particularly applicable to unicellular diazotrophs, even if only a fraction of the microzooplankton community was preying on them. *Trichodesmium spp.* may have more specialized predators, but grows extremely slowly[46,48]. Copepods were recently shown to graze on all diazotroph types present in mesocosm experiments as primary or secondary consumers, with 28% of zooplankton N biomass coming from diazotrophy[49]. More studies of grazing impacts on plankton community composition and diazotrophy are needed.

Convergent Estimates of N_2 Fixation

Our results present convergent global estimates of marine N_2 fixation from two independent methods, an inverse model that infers N inputs from the observed nutrient concentrations and a prognostic Earth System Model that explicitly resolves diazotrophic growth and N_2-fixation rates as a function of ambient nutrients, temperature, and light, in the context of grazing and competition. The prognostic model provides plausible mechanistic controls that lead to the N_2-fixation pattern deduced by the inverse model. The export of excess fixed N from the Atlantic basin (~15 TgN/yr) shows that a substantial amount of N_2 fixation is geographically uncoupled from oxygen minimum zones, suggesting some stabilizing nitrogen-cycle feedbacks might be weaker and slower than previously thought.

There is a strong similarity between the N:P of sinking organic matter inferred from the inverse model and simulated with CESM (R^2 = 0.76, Fig. S19). Both models have elevated ratios in the subtropical gyres and N:P ratios only modestly below the Redfield value elsewhere. Prior studies have imposed significantly lower N:P ratios in the more productive regions[12,13]. To capture the observed higher N:P ratios in the gyres, N:P ratios in nutrient-rich regions had to be set very low to maintain an assumed 16:1 global mean for non-diazotrophs[13]. Our results suggest that the observed nutrient distributions are not compatible with a mean N:P ratio in organic matter export of 12:1 or lower in upwelling zones. Thus, given mean N:P export ratios in the gyres above 20:1, global-mean N:P export ratio is greater than the Redfield value at 17.3:1 in our most-probable inverse estimate and 20.0:1 in CESM. The higher mean N:P ratio in sinking organic matter and excessively high, water-column denitrification (134 TgN/yr) in CESM relative to the inverse model, leads to a higher total N_2 fixation of 238 TgN/yr, with benthic denitrification losses of 160 TgN/yr (Fig. S17). The discrepancy is largely attributable to the coarse resolution in CESM, which does not capture the narrow, equatorial sub-surface jets critical for ventilating the OMZs[50].

Accounting for N:P variability in organic-matter export boosts global N_2 fixation, by 63% in the inverse model and by 50% in CESM, when compared to simulations with fixed Redfield stoichiometry (Table S7, Figs.S10, S20). Spatially-variable N:P ratios for plankton and exported organic-matter allows global marine N-cycle models to be reconciled with ocean observations, and significantly impacts the marine carbon cycle. Variable N:P ratios boost global POC export by 12% in CESM relative to fixed Redfield simulation. Earth System Models must include explicit representation of this stoichiometric variability to capture the observed biogeochemical patterns, and to accurately predict the response and feedbacks of ocean biogeochemistry to ongoing global warming.

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Contributions

All authors contributed to the design of the study. W.L.W. and F.W.P. built the inverse model and analyzed its results. J.K.M. performed the CESM simulations and analyzed its output. F.W.P., W.L.W. and J.K.M. wrote the manuscript. All authors participated in the discussion of the results and commented on the manuscript.

Competing Interests

The authors declare that they have no competing financial interests.

Correspondence

Correspondence and requests for materials should be addressed to F. Primeau (email: fprimeau@uci.edu).

Biologically available nitrogen budget

Basin	Input			Loss		Net
	Atm. Dep.	River Input	Microbial N Fix.	Water Col.	Sedim.	
Pacific	12.0	3.3	$100.6\,^{132.8}_{78.9}$	$54.6^{58.1}_{42.7}$	$70.9^{106.6}_{48.2}$	$-9.7^{-9.2}_{-19.9}$
Atlantic	8.3	4.4	$34.0^{49.5}_{24.0}$	$0.3^{0.3}_{0.1}$	$31.0^{45.0}_{21.8}$	$15.3^{17.7}_{13.6}$
Indian	4.5	2.9	$26.6^{37.2}_{19.5}$	$13.8^{14.5}_{12.5}$	$22.8^{34.3}_{15.5}$	$-2.6^{-1.5}_{-3.3}$
Arctic	0.4	0.4	$1.8^{2.9}_{1.1}$	$0.0^{0.0}_{0.0}$	$5.8^{7.2}_{4.6}$	$-3.2^{-2.7}_{-3.9}$
Med.	0.7	0.2	$0.2^{0.6}_{0.0}$	$0.0^{0.0}_{0.0}$	$0.9^{1.3}_{0.7}$	$0.2^{1.0}_{0.1}$
Global	25.8	11.2	$163.2^{222.9}_{125.6}$	$68.6^{72.9}_{55.8}$	$131.5^{194.5}_{90.7}$	$-5.7^{-0.4}_{-6.4}$

Table 1: Biologically available nitrogen budget. All numbers are in TgN/yr and correspond to the most probable value from the posterior probability distribution for the steady state model. The only exception is the entry for the net global imbalance which corresponds to the most probable value for the model in which we allowed for a slowly evolving disequilibrium. The upper and lower limits correspond to the upper and lower bounds obtained by combining inversions in which we relaxed the steady state assumption to allow for a slowly decaying disequilibrium and inversions in which we scaled the rate coefficient for sedimentary denitrification by $\pm 20\%$, which produced a sedimentary to water column denitrification ratio in the range of 1.3 to 3.0 in accord with the ^{15}N isotopic constraints.

Figure Legends

Figure 1: Schematic representation of the P-cycle model (left) and N-cycle model (right). The dissolved tracers DIP, DOP, DIN, and DON are affected by advection and diffusion whereas the particulate tracers POP and PON are affected by gravitational settling. See Methods and Supplementary Information for the detailed mathematical formulation of the model and Bayesian inversion procedure.

Figure 2: N:P ratio of exported organic material. (a) Map of the N:P ratio of exported organic material ($(N:P)_{exp}$) inferred from the inverse model. The numbers within the delineated regions correspond to the ratio of the integrated export of N to the integrated export of P. (b) Comparison of the measured N:P ratio in the stock of suspended particulate organic matter (POM) to that of the flux of exported organic matter inferred from the inverse model. (c) Comparison of the measured C:P ratio in the stock of suspended POM to that in the flux of exported organic matter. For the calculation of the P:C export ratio a C:N ratio of 106:16 is assumed. The export flux includes the contributions from both sinking POM and the downward mixing of DOM and the box plot summarizes the distribution of all 2°× 2° grid boxes that fall in each phosphate concentration bin. The boxplots show the 25, 50 and 75 percentiles binned according to the phosphate concentration in the water. The whiskers cover 99.3 of the data with the remaining points shown with the diamond symbols. Out of 1774 POM data points 77 outliers are not shown in order to keep the vertical axis in a reasonable range. Note that the left axis for panels (b) and (c) for the P:N and P:C ratios has a linear scale whereas the right axis has a hyperbolic scale.

Figure 3: Maps of the column integrated sources and sinks of fixed nitrogen. (a) Input due to microbial N_2 fixation. (b) Combined external input due to the present-day atmospheric deposition and river fluxes[24, 25]. (c) Loss due to water column denitrification and anammox. (d) Loss due to sedimentary denitrification and anammox. Note that the color scales are non-linear in order to make the lower rates visible. We note that while the spatial pattern of N_2 fixation is quite robust, the pattern of water-column denitrification is rather more uncertain. See Supplementary Information for alternate patterns of water-column denitrification that are also consistent with the DIN and DIP constraints

Figure 4: Contribution of new N to export production. (a) Fraction of export production supported by the input of new N including microbial fixation, atmospheric deposition (present day), and river inputs. (b) Fraction of export production supported by microbial N2 fixation alone.

Figure 5: Prognostic model simulations of diazotrophs and N_2 fixation. (a) Rates of N_2 fixation simulated by the CESM. (b) Diazotroph growth limitation patterns. Nutrient replete is where ambient nutrients could support growth at more than 90% of the maximum growth rate. (c) Rates of N_2 Fixation simulated by CESM with reduced grazing pressure, similar to that experienced by the diatoms (maximum grazing rate on diazotrophs reduced by a factor of 0.63).

Methods

Inverse model

Ocean Circulation

The ocean circulation model used in this study was optimized using climatological observations of temperature, salinity, natural (pre-bomb) radiocarbon, sea surface height, phosphate, heat and fresh water fluxes, as well as the transient CFC-11 observations[20, 21].

Biogeochemical fluxes and transformations

The biogeochemical conservation equations keep track of six nutrient pools, dissolved inorganic phosphorus and nitrogen (DIP & DIN), dissolved organic phosphorus and nitrogen (DOP & DON) and sinking particulate organic phosphorus and nitrogen (POP & PON).

The downward transport of P and N by the sinking and solubilization of POP and PON is treated in such a way as to produce power-law flux attenuation profiles, $(z/z_0)^{-b}$, with separate exponents b_P and b_N for P and N. The DOP and DON are respired back to DIP and DIN with separate rate constants κ_{dP} and κ_{dN}.

Biological production of organic phosphorus is modeled using a spatially variable uptake rate coefficient that is parameterized in terms of two adjustable parameters (α and β). Two additional parameters control the rate of dissolution of POP into DOP and the rate of DOP respiration ($b_P$and k_{dP}). A dynamically variable N:P ratio, $r_{\mathrm{N:P}}$, parameterized in terms of the local DIP concentration and two more adjustable parameters (*A* and *B*) relates the organic-phosphorus production to the organic-nitrogen production. As is the case for organic phosphorus, two adjustable parameters, ($b_N$and k_{dN}), control the rates of PON dissolution and DON respiration. We consider inputs of fixed N from N_2 fixation, atmospheric deposition, and rivers. Atmospheric and riverine inputs are prescribed[40, 51] and the input of N_2-fixation is diagnosed from the model solution (see Methods).

The net biological production of organic phosphorus in the euphotic zone is modeled using a spatially dependent uptake rate coefficient,

$$J_P = \gamma(\mathbf{r})[\mathrm{DIP}], \quad (1)$$

where $\gamma(\mathbf{r})$, is parameterize in terms of satellite-derived net primary production (NPP) and the observed phosphate concentration ($[\mathrm{DIP}]_{\mathrm{obs}}$) using two adjustable parameters, α and β, [Ref.S[16]], i.e.

$$\gamma(\mathbf{r}) = \begin{cases} \dfrac{\alpha\left[\dfrac{1}{r_{\mathrm{C:P}}}\dfrac{NPP(\mathbf{r})}{NPP_0}\right]^{\beta}}{\dfrac{[\mathrm{DIP}]_{\mathrm{obs}}(\mathbf{r})}{[\mathrm{DIP}]_0}}, & \text{if } z < z_c, \\ 0, & \text{otherwise,} \end{cases} \quad (2)$$

In (2), $\mathbf{r}$ denotes the position on our model grid, $[\mathrm{DIP}]_{\mathrm{obs}}$ is the objectively mapped phosphate concentration from the 2013 World Ocean Atlas and *NPP* is the satellite-derived carbon based net primary production (MODIS CbPM)[52,53], $r_{\mathrm{C:P}} = 106$ for the Redfield model and $r_{\mathrm{C:P}} = (c_1 + c_2[\mathrm{DIP}]_{obs})^{-1}$ with $c_1 = 0.006$ and $c_2 = 0.0069/(\mathrm{mmol\ P/\ m^3})$ for the variable stoichiometry model[23], z_c is euphotic zone depth, which is the depth of upper two model layers (~73m). $NPP_0 = 1\ \mathrm{mmol\ C\ m^{-2}s^{-1}}$ are used to ensure that α, has dimensions of inverse time. He full mathematical formulation of the P-cycle conservation equations are given in the Supplementary Information.

The net biological production of organic nitrogen is modeled using

$$J_N = r_{\mathrm{N:P}} J_P, \quad (3)$$

with N:P ratio parameterized in terms of the ambient DIP concentration according to

$$r_{\mathrm{N:P}} = A + B \cdot \Theta([DIP]; [DIP]_c, \Delta), \quad (4)$$

where A and B are adjustable parameters and where $[\mathrm{DIP}]_c$= 0.075 mmol/m^3 and $\Delta = 1$ mmol/m^3 are fixed parameters used to specify the limiter function

$$\Theta(x;\ x_c,\ \lambda) \equiv \frac{1}{2}\left[1 - \tanh\left(\frac{x - x_c}{\lambda}\right)\right]. \quad (5)$$

Sensitivity tests confirm that the inverse model solutions are not sensitive to $[DIP]_c$ (Supplementary Information).

The water-column loss of fixed N is proportional to the rate of organic-carbon respiration, limited to regions where dissolved oxygen concentrations are sufficiently low. Two adjustable parameters, ($[O_2]_c$ and Δ), control the shape of a limiter that ramps up the preference for nitrate over oxygen as the dominant oxidant. A third parameter, (k_w) scales the overall reaction rate.

Benthic losses occur in the bottom grid cells of each water column. They are modeled following an empirical function[54]. We added a parameter, (s), to scale the N-loss function, to account for uncertainties in this parameterization.

Due to the loss of fixed N in low-oxygen environments, recycled and external N sources can only support a fraction of the biological production of organic N implied by

the organic P production and local value of $r_{N:P}$. We therefore introduce a limiter that ramps down the uptake of DIN as its concentration approaches zero. The shape of this limiter is controlled by one last parameter ($[DIN]_c$). Importantly, the limiter acts only on the drawdown of DIN and not on the production of new organic N. The difference between drawdown and production is the inferred rate of N_2 fixation.

$$\begin{aligned} J_{FIX} &= Net\ Production - Uptake \\ &= \Theta([DIN]; [DIN]_c, \Gamma) J_N, \end{aligned} \qquad (6)$$

The full conservation equations the are given in the Supplementary Information.

The inversion process proceeds as follows: We use the model solution for the [DIN], [DIP], and [DON] state variables to define the mean of a joint probability function that we assign to the [DIN], [DIP], and [DON] observational data (See Supplementary Information). This probability function is conditioned on the model's parameters. We then use Bayes' rule to invert the probability function, to obtain the posterior probability for the unknown parameters conditioned on the known data. Finally, we draw samples from the posterior parameter distribution, which we then feed into the model equations to generate a probabilistic sample of the unobserved geochemical rates of interest. To make the computation feasible, we approximate the posterior probability for the parameters using a multivariate normal distribution. Because the normal approximation is poor for the benthic scaling parameter s and the critical oxygen concentration, $[O_2]_c$, we separate the analysis into two levels of inference. At the first level we find the conditional probability of the parameters conditioned on s and $[O_2]_c$. At the second level of inference we vary s and $[O_2]_c$ and compare the relative posterior probability for these parameters after marginalizing out all the other unknown parameters. Separating the analysis in this way has the advantage of making the parameter optimization more efficient and allows us to directly analyze the marginal sensitivity of our inferences to the overall benthic N loss rate and to the overall water-column N loss rates.

Even if we can neglect the uncertainty due to the missing seasonal cycle, there is still the possibility that the system is not in steady state. There is likely strong variability over shorter timescales impacted by ENSO events and inter-annual variability in climate forcings[41]. Our inverse model results must therefore be viewed as a climatological estimate that averages over this type of variability. But there could also be weak longer term trends in the nutrient fields that invalidate out the steady-state assumption. To address this issue we augmented the model's list of adjustable parameters to include the amplitudes of the 263 eigenmodes of the linearized model that have e-folding decay timescales of 20 years or more (Supplementary Information). The long decay timescale of these modes would make them difficult to detect in a time-series that is only a few decades long. Furthermore, because these modes are only weakly damped they are more likely to become excited by short term variability[41]. We then jointly re-optimized

the full list of parameters. The inclusion of the extra degrees of freedom had only a modest impact on the optimal values for most of the biogeochemical parameters. The only exceptions were for b_P, whose value decreased by 16% implying a deeper dissolution of POP, and κ_{dP} whose value increased fivefold, implying a very rapid remineralization of DOP. The impact on the inferred large-scale patterns of N_2 fixation due to these changes was small as were the changes to the basin wide budgets (Tables S3).

Prognostic CESM model simulations

The prognostic nitrogen cycle simulations were conducted using a modified version of the ocean component of the Community Earth System Model (CESM)[55, 56]. The model includes representations of four phytoplankton functional groups (diatoms, diazotrophs, calcifiers, and smaller pico- to nano-sized phytoplankton). The model also includes multiple potentially growth-limiting nutrients (nitrogen, phosphorus, iron, and silicon). It has been well validated[55,56] and is often a component of CESM climate simulations[57,58]. The version of the model used here was modified to include variable plankton phosphorus cell quotas, in response to ambient phosphate concentrations after Ref.[23], but with a minimum N:P ratio imposed, and to allow for variable N:P in the sinking particulate export. These modifications were included in CESM2. The CESM model results correspond to the average of the last 20 years of a 310-year simulation. More details are given in the Supplementary Methods.

Comparison of $(N:P)_{exp}$ to N:P of suspended POM

The particulate organic matter data used for the comparison between the N:P of suspended particulate organic matter with the inferred N:P of exported organic matter shown in Fig. 2 is from [Ref. 59].

Method References.

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Data Availability Statement

The code for the inverse model is available at DOI: 10.5281/zenodo.2020377. The optimized tracer transport operator used to run the inverse model is available upon request by contacting F.W.P. (fprimeau@uci.edu). All other data used to constrain the inverse model are publicly available (see Supplementary Materials). The particulate organic matter data used for the comparison between the N:P of suspended particulate organic matter with the inferred N:P of exported organic matter shown in Fig. 2 is from [Ref. 59]. The model output for generating all the other figures is available upon request.