



NutGENIE 1.0: nutrient cycle extensions to the cGENIE Earth system model to examine the long-term influence of nutrients on oceanic primary production

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Abstract. Understanding the nuances of the effects of nutrient limitation on oceanic primary production has been the focus of many bioassay experiments by oceanographers. A theme of these investigations is that they identify the currently limiting nutrient at a given location, or in other words they identify the proximate limiting nutrient (PLN). However, the ultimate limiting nutrient (ULN; the nutrient whose supply controls system productivity over extensive timescales) can be different from the PLN. Our motivation is to investigate the identity of the ULN. To facilitate this the carbon-centric **Grid Enabled Integrated Earth** system model (cGENIE) **nutrient** cycles have been extended to create NutGENIE. NutGENIE incorporates the nutrients nitrogen, phosphorus, and iron. The impacts of diazotrophs, capable of fixing nitrogen, are represented alongside those of other phytoplankton. NutGENIE is capable of extended model simulations necessary to investigate the ULN while, at the same time, including iron as a potentially limiting nutrient. NutGENIE will be described, with particular focus on the biogeochemical cycles of iron, nitrogen and phosphorus. Model results are compared to ocean observational data to assess the degree of realism. Model-data comparisons include physical properties, nutrient concentrations, and process rates (e.g., export and nitrogen fixation). These comparisons support the conclusion that NutGENIE is appropriate for the investigation of the ULN.



1 Introduction

1.1 The importance of oceanic primary production

25 Photosynthetic phytoplankton that inhabit the sunlit ocean surface, the euphotic zone, are responsible for the majority of ocean
 primary production (PP) and form the base of marine food webs. These photosynthetic phytoplankton, photoautotrophs, use
 light to fix dissolved carbon dioxide (CO₂) and other nutrients into biomass that fuels the pelagic ecosystem, and ultimately
 leads to the export of carbon to depth via a process known as the biological carbon pump (BCP) (Chisholm, 2000; Boyd et al.,
 30 2019). The strength of the BCP can influence atmospheric concentrations of CO₂ and therefore Earth's carbon cycle and
 climate (Sarmiento et al., 1998; Hain et al., 2014; Galbraith and Skinner, 2020). Net primary production (NPP) is total rate of
 organic carbon production minus the rate of respiration by phytoplankton; it therefore represents the rate that phytoplankton
 produces biomass (Sigman and Hain, 2012). Estimates of global marine NPP based on satellite, float or ecosystem models are
 ~ 50 - 60 petagrams of carbon per year (Pg C yr⁻¹) (Carr et al., 2006; Silsbe et al., 2016; Johnson and Bif, 2021). Ocean uptake
 of CO₂, mostly through abiotic processes, has contributed to mitigating much of the impact of anthropogenic CO₂ emissions
 35 with approximately half taken up by a combination of land and ocean carbon reservoirs (Ballantyne et al., 2012; Friedlingstein
 et al., 2022). Understanding of the controls on ocean NPP levels can provide insights into Earth's past, current and potential
 future carbon cycle. Nutrient supply to the euphotic zone acts as fundamental control on ocean PP levels, this supply and
 subsequent growth limitation are the focus of the model extensions we present here.

1.2 Factors limiting primary production

40 Predation or grazing from higher trophic levels can be categorised as 'top-down' control of phytoplankton PP; by reducing
 phytoplankton populations, grazing reduces the total amount of photosynthesis. When not at optimal levels, light, temperature,
 and nutrients cause realised growth rates to be below the maximum growth rate of a phytoplankton population and can be
 considered as 'bottom-up' controls on PP. Light as a source of energy is an obvious potential limitation to photosynthetic
 phytoplankton. The nature of light limitation has been considered and methods of modelling it developed (e.g. Marra et al.,
 45 1985; Yang et al., 2020). Temperature also regulates biological rates as individual species have a relatively narrow optimal
 temperature range with growth declining rapidly outside this range (Gillooly et al., 2002). When community production is
 considered, growth rates have an exponential growth with temperature as species with higher optimal growth ranges are
 favoured (Eppley, 1972). Again, studies have proposed methods of modelling temperature limitation (e.g. Grimaud et al.,
 2017; O'Donnell et al., 2018).

50 Elements (C, H, N, P, O and S) obtained from nutrients are essential components of macro-molecules such as proteins, nucleic
 acids, etc. (Moore et al., 2013). Nutrient limitation is a condition or state where addition of a nutrient would stimulate growth
 (Cullen, 1991; de Baar, 1994). Nutrient stress refers to a physiological response to nutrient shortage (Cullen et al., 1992).
 Nutrient deficiency refers to the lack of one nutrient relative to others (Cullen, 1991). Nutrient co-limitation is a condition
 where the addition of multiple nutrients stimulates more growth than addition of any one nutrient alone (Arrigo, 2005; Saito
 55 et al., 2008). Addition of the proximate limiting nutrient (PLN), stimulates immediate growth, whereas addition of the ultimate
 limiting nutrient (ULN) enhances total system productivity over extensive timescales (Cullen, 1991; Tyrrell, 1999).
 Much work has been conducted to describe the nature of phytoplankton nutrient requirements (Redfield, 1934, 1958) and
 subsequent limitation of growth (Sommer, 1986; Timmermans et al., 2004; Flynn, 2010; Bestion et al., 2018). Moore et al.
 (2013) and Browning and Moore (2023) conducted extensive analysis to compare nutrient availability to phytoplankton
 60 nutrient requirements. This work enabled the determination of spatial variations of proximate nutrient limitations. Further
 analysis linked nutrient deficiencies to large-scale ocean physical–chemical–biological processes (Moore, 2016).
 Oceanographers have conducted numerous experiments to investigate nutrient limitation of oceanic PP. A great deal of this
 work has involved the use of bioassay experiments that consist of the addition of nutrients to samples of surface ocean water



to determine which stimulates the greatest phytoplankton growth (Mills et al., 2004; Bonnet et al., 2008; Moore et al., 2008).

65 The concept of iron fertilisation also gained focus following the work of Martin (1990), prompting a range of iron fertilisation experiments. These experiments involved in situ iron fertilisation (Martin et al., 1994; Boyd and Abraham, 2001; Hoffmann et al., 2006) - in effect field bioassay experiments. The implications of many bioassay and fertilisation experiments was summarised and synthesised by Moore et al. (2013), who were able to identify primary, secondary, and co-limiting nutrients across many regions. Moore (2016) compared the stoichiometry of the elemental requirements of phytoplankton to the

70 elemental composition of ocean basins' deep water, that acts to supply nutrients to surface water. Browning and Moore (2023) conducted further synthesis of over 150 bioassay and fertilisation experiments, identifying three dominant nutrient limitation regimes. The stratified subtropical gyres and summertime Arctic Ocean are nitrogen limited, upwelling regions are typically iron limited and remaining regions are most commonly co-limited by iron and nitrogen (Browning and Moore, 2023). The underlying bioassay experiments and analysis mentioned here have a common theme in that they focus on the immediate

75 nutrient deficiency situation in a temporal sense, and often focus on a specific ocean location. This focus on the immediate nutrient deficiency identifies the PLN.

Tyrrell (1999) used a box model approach to identify nitrate as the PLN and phosphate as the ULN. In contrast, Falkowski (1997) argued that the dynamics of the nitrogen cycle, with particular emphasis on the limiting role iron has on nitrogen fixation, has ultimate control over phytoplankton productivity. Deutsch et al. (2007) concluded that nitrogen fixation stabilises

80 the oceanic fixed nitrogen inventory over time but that water column denitrification rather than atmospheric inputs of iron determine nitrogen fixation rates. Moore and Doney (2007) concluded that for much of the global ocean iron is the ultimate limiting nutrient. There were some shortcomings in prior work to identify the ULN: (a) Tyrrell (1999) did not include iron, consequently the high iron requirements of the enzyme nitrogenase central to nitrogen fixation were not captured; (b) Falkowski (1997) provided an analysis based on the evolution of biogeochemical cycles, without supporting the analysis with

85 modelling; (c) The modelling of Deutsch et al. (2007) was only conducted over short timescales to a modern ocean steady-state; and (d) Moore and Doney (2007) focused primarily on the nutrient regime of the Southern Ocean.

These shortcomings and other considerations suggest the desirability of a new modelling approach to the ULN question in which the model used possesses the following characteristics: (1) cycling and biological uptake of (and potential limitation by) all three nutrients (N, P, Fe), (2) nitrogen-fixing as well as non-fixing phytoplankton, (3) spatial resolution, as opposed,

90 for instance, to representing the whole surface ocean with one box, (4) but at the same time the ability to carry out model runs exceeding the residence times of all three nutrients, and (5) external inputs (e.g. delivery of nutrients down rivers) and external outputs (e.g. delivery of nutrients to seafloor sediments via burial) in an 'open' model allowing total ocean inventories of nutrients to change over time

1.3 Investigating the Ultimate Limiting Nutrient

95 One way of modelling a system is to represent it by a mathematical model. The model abstraction can allow focus on features of interest. Models represent fundamental processes through a series of mathematical equations and parameterisations. Models provide insight into processes that are difficult or expensive to observe or even immeasurable. They give spatial and temporal coverage that would otherwise be unavailable. Through hypothesis testing, it is possible to examine *what if?* questions that would be impossible or undesirable to investigate in the real ocean. Models also allow an analysis of past events and insight

100 into potential future scenarios that without a model would be unavailable.

Here we propose to establish a model approach that can be used subsequently to study the long-term influence of nutrients on PP and diagnose the ULN. Such investigations will require full ocean investigations to be executed over tens of thousands of years, given the long residence times of nutrients in the global ocean (phosphorus: several tens of thousands years (Delaney, 1998), nitrogen: a few thousand years (Gruber, 2004) and iron: tens to hundreds years (Hayes et al., 2018)). For that to be

105 successful the carbon-centric **Grid Enabled Integrated Earth** system model (cGENIE), has been configured and modified to



include the three nutrients nitrate, phosphate, and iron (Sect. 2) to create a **nutrient-centric Grid Enabled Integrated Earth** system model (NutGenIE).

A background overview of the NutGenIE model framework is provided in Sect. 2.2, followed by detailed descriptions of the critical aspects of NutGenIE nutrient cycles that have been configured to support the ongoing analysis. Details of the validation approach (Sect. 3.1) and subsequent results (Sect. 3.2 to **Error! Reference source not found.**) and discussion follow.

2 Model description

2.1 Physical model of cGenIE

The ocean physics and climate model in cGenIE are based on the fast climate model ‘C-GOLDSTEIN’ of Edwards and Marsh (2005). C-GOLDSTEIN is comprised of a reduced physics (frictional geostrophic) 3-D ocean circulation model coupled to a 2-D energy–moisture balance model (EMBM) and a dynamic–thermodynamic sea ice model (Edwards and Marsh, 2005; Marsh et al., 2011). The ocean model calculates the horizontal and vertical transport of heat, salinity, and biogeochemical tracers using a parameterisation for isoneutral diffusion and eddy-induced advection (Edwards and Marsh, 2005; Marsh et al., 2011). The ocean model additionally determines heat and moisture exchanges with the atmosphere, sea ice, and land, and is forced at the ocean surface by zonal and meridional wind stress according to a specified wind field. Horizontal transport of sea ice is resolved by the sea ice model in addition to the exchange of heat and fresh water with the ocean and atmosphere. A full description of the C-GOLDSTEIN model can be found in Edwards and Marsh (2005) and, with updates, in Marsh et al. (2011). The ocean model is configured on a 36x36 equal-area horizontal grid. The grid is uniform in longitude (10° increments) and uniform in the sine of latitude (resulting in latitude increments of approximately 3.2° at the Equator increasing to 19.2° at the highest latitude). The ocean has 16 logarithmically spaced z-coordinate levels in the vertical. The thickness of the vertical levels increases with depth, from 80.8 m at the surface to 765 m at the deepest level. The configured representation of the grid and bathymetry is shown in Fig. 1. C-GOLDSTEIN is run with 96 time steps per year and is configured based on the parameterisation detailed in the fifth row (GENIE-16) of Table 1 of Cao et al. (2009).

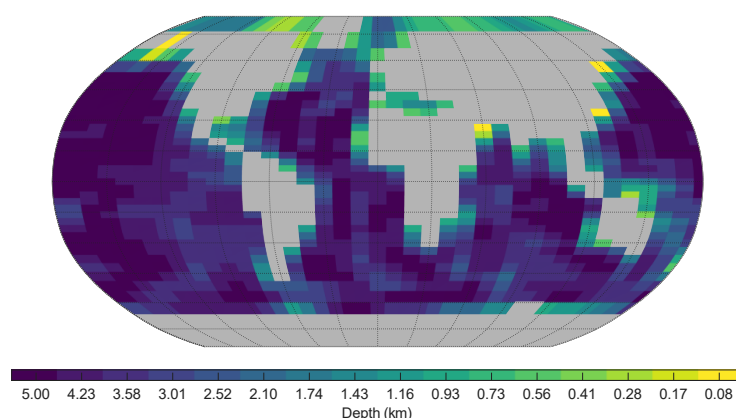


Figure 1. The modern cGenIE gridded continental configuration and ocean bathymetry (depth in km). Based on 16 depth levels and a 36 x 36 equal area grid of cGenIE. Exact depths at the bottom of each depth level are provided in Table S1.

2.2 Biogeochemistry framework (BioGEM)

cGenIE includes a series of geochemical tracers within the biogeochemical model component referred to as BIOGEM (Ridgwell et al., 2007). The biological part of BIOGEM is abstracted relative to reality and does not maintain explicit biomass tracers (such as phytoplankton concentrations) for ocean life (Ridgwell et al., 2007). Biological activity is estimated from



surface nutrient uptake which in turn is immediately converted to particulate and dissolved organic matter (POM and DOM) in the surface ocean (Ridgwell et al., 2007). The subsequent processing associated with POM and DOM is discussed in detail in Sect. 2.3. This abstracted approach results in a computationally efficient model that represents biogenically induced chemical fluxes (Maier-Reimer, 1993) and capable of execution timescales required to investigate the ULN. The basis of the biological nutrient uptake and export scheme is similar to that of Parekh et al. (2005). This has in turn been developed subsequently by work of others including Monteiro et al. (2012) and Reinhard et al. (2020). Three tracer categories (atmospheric, oceanic, and sedimentary) track biogeochemical processes within the cGenIE model. Atmospheric tracers include carbon dioxide and oxygen. A more extensive range of ocean tracers is used: dissolved inorganic carbon (DIC) and dissolved oxygen; the nutrient framework of fixed nitrogen or dissolved inorganic nitrogen ($\text{DIN} = \text{NO}_3 + \text{NH}_4$), phosphate (PO_4), and iron (Fe); dissolved organic matter, partitioned between carbon (DOC), nitrogen (DON), phosphorus (DOP), and iron (DOFe); tracers associated with the iron cycle to track ligands and complexed ligand-bound iron; and additional tracers that include dissolved N_2 , ammonia, calcium and sulphate. Ocean tracers for POM are not used as POM is immediately remineralised following the scheme set out in Sect. 2.3.4 Sedimentary tracers include POM (partitioned by nutrient), calcium carbonate and detrital material. By default, results are output as annual average figures, however the BIOGEM module computes tracers at 48 time steps per year giving the possibility of results output relating to shorter timeframes.

2.3 Biogeochemistry extensions (NutGenIE)

NutGenIE is an extension to the BioGEM module within cGenIE. The novel features of the configuration of NutGenIE described here includes a) the concurrent use of three nutrients (N, P and Fe) when determining phytoplankton growth (surface nutrient uptake) and b) the representation of a second iron binding ligand class with stronger binding in the upper water column. In this section we detail the most pertinent feature of BioGEM alongside the extensions made in NutGenIE.

In NutGenIE, nutrients taken up by phytoplankton are converted to POM and DOM in the surface ocean. The ratio of POM to DOM is set by a configuration option calibrated against nutrient observations in Ridgwell et al. (2007). POM is subject to immediate gravitational sinking to the ocean interior, without lateral advection, where it is immediately remineralised. DOM is subject to ocean circulation and mostly retained in the surface ocean. DOM has an assumed lifetime governed by a degradation rate constant (λ , 0.5 yr^{-1}) with remineralisation occurring as outlined in Sect. 2.3.4 (Reinhard et al., 2020).

The nutrient uptake processes differ for the two classes of phytoplankton considered within the model. Diazotrophs (designated by the superscript Diaz) are those phytoplankton capable of nitrogen fixation. The other phytoplankton class (designated by the superscript OPhy) are not capable of nitrogen fixation and must source nitrogen from the DIN in the surface waters. Nutrient uptake by other phytoplankton (Γ^{OPhy}) is described in Sect. 2.3.2; similarly, nutrient uptake by diazotrophs (Γ^{Diaz}) is described in Sect. 2.3.3. The nutrient uptake terms (Γ^{OPhy} and Γ^{Diaz}) only have a value in the surface layer.

We intend to use the model to investigate the ULN and for this purpose it is essential that nutrient cycles are open. Therefore, in NutGenIE a removal (burial) flux is applied by removing a fixed proportion (k_{BF}) of nutrient uptake by other phytoplankton and diazotrophs from the modelled ocean. This represents a simplified instantaneous sediment burial term that is not coupled to POM remineralisation dynamics. External inputs are also applied, via rivers and/or the atmosphere and seafloor. The combined nutrient uptake by other phytoplankton and diazotrophs after the application of the burial removal flux is represented by Γ^{All} (Eq. (1)). Setting k_{BF} to a value of zero would negate this removal flux.

$$\Gamma^{\text{All}} = (1 - k_{BF})(\Gamma^{\text{OPhy}} + \Gamma^{\text{Diaz}}) \quad (1)$$

The understanding of the oceanic iron cycle has developed in recent years; a comprehensive summary is provided in Figure 2 of Tagliabue et al. (2017). Tagliabue et al. (2017) identify aeolian dust deposition, rivers, sea-ice, hydrothermal systems and sediments as sources of iron. The iron cycle of NutGenIE has been extended so that it includes surface dust deposition, a



surface flux that represents riverine inputs and a benthic flux to represent hydrothermal systems and sediments as sources of iron.

Nitrogen cycling within NutGenIE represents the various forms of nitrogen; that is, nitrate, ammonium, dinitrogen, and organic nitrogen. The cycling is achieved by the processes of uptake of nitrate and ammonium by other phytoplankton, nitrogen fixation by diazotrophs, denitrification, and nitrification (Monteiro et al., 2012). However, in reality in oxygen minimum zones additional removal pathways exist, for instance dissimilatory nitrate reduction to ammonia and anaerobic ammonium oxidation (anammox) (Lam et al., 2009). Like denitrification Anammox converts DIN to dinitrogen, i.e. reducing the inventory of DIN (Lam et al., 2009). It is therefore noted that anammox is not represented by the NutGenIE denitrification process that is solely based on organic matter remineralisation.

The structure of the phosphorus, nitrate and iron cycles in NutGenIE are shown in Fig. 2. Input and output fluxes associated with each nutrient are shown alongside the primary processes that influence nutrient concentrations. Each nutrient cycle is discussed in more detail in following sections, the spatial distribution of input fluxes (RP, RN, DDFe and BFe) shown in Fig. S1 to S3.

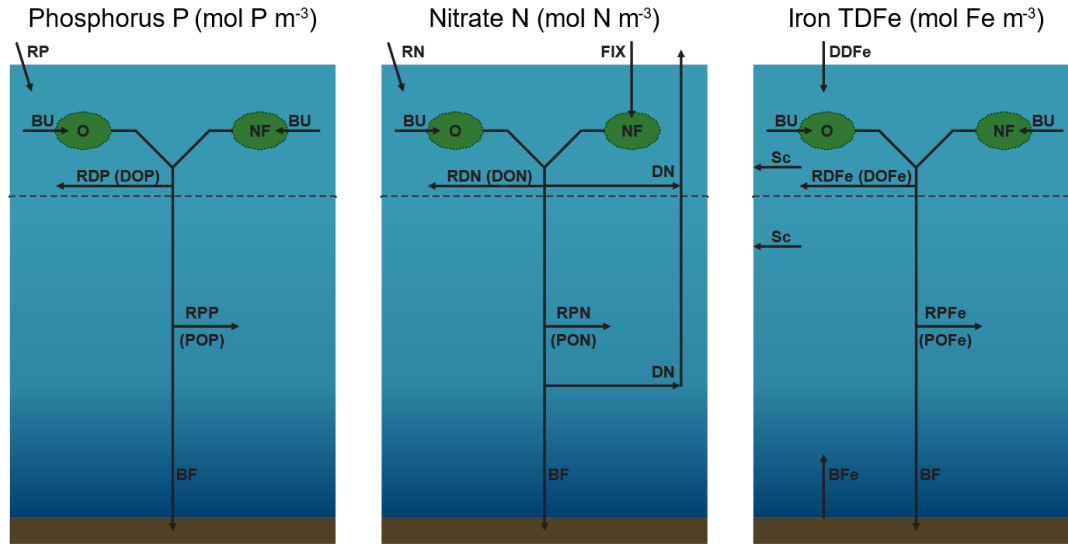


Figure 2. Structure of NutGenIE nutrient cycles. BU, biological uptake of nutrients by O, other phytoplankton and NF, nitrogen fixers (diazotrophs) occurs in the surface ocean layer. River inputs (RP and RN) and dust deposition of iron (DDFe) are input fluxes to the surface ocean; BFe, Benthic (seafloor) flux of iron; FIX, nitrogen fixation; DN, denitrification; Sc, scavenging of iron; BF, burial fraction; RDP, RDN and RDFe are remineralisation of dissolved organic phosphate, nitrate and iron respectively. RPP, RPN and RPF are remineralisation of particulate organic phosphate, nitrate and iron respectively. Remineralisation of dissolved and particulate organic matter occurs throughout the water column.

2.3.1 Nutrients and dissolved organic matter

Here we cover the main governing equations in NutGenIE. For each nutrient an equation is provided for it, alongside an equation for its dissolved organic matter, e.g., for phosphorus the equations for phosphate and DOP are provided. These equations represent the mechanism employed in NutGenIE to maintain the tracer concentrations throughout the water column. Note that the transport terms calculated by the ocean circulation model (Edwards and Marsh, 2005) are omitted.

$$\frac{\delta P_{O_4}}{\delta t} = -\Gamma_P^{OPhy} - \Gamma_P^{Diaz} + \lambda DOP + S_{PO_4} \quad (2)$$

$$\frac{\delta DOP}{\delta t} = \nu \Gamma_P^{All} - \lambda DOP \quad (3)$$

Γ_P^{OPhy} is the biological uptake of PO_4 by other phytoplankton as described in Sect. 2.3.2. Similarly, Γ_P^{Diaz} is the biological uptake of PO_4 by diazotrophs and is described in Sect. 2.3.3. A proportion (ν) of the nutrients taken up by diazotrophs and



other phytoplankton (Γ_P^{All}) is partitioned into DOM. This DOM is subsequently remineralised with a time constant (λ). The remaining proportion ($1 - v$) of the nutrient uptake is partitioned into POM that undergoes water column remineralisation as detailed in Sect. 2.3.4. The values of v and λ , are configurable, but in NutGenIE are given default values of $v = 0.66$ and $\lambda = 0.5 \text{ yr}^{-1}$ following the OCMIP-2 protocol (Najjar and Orr, 1999). S_{PO_4} represents a surface input flux of PO_4 such as riverine

210 inputs. The magnitude of this flux is configurable via a parameter.

NutGenIE governing equations for NO_3 and Fe are provided below.

$$\frac{\delta NO_3}{\delta t} = -\Gamma_N^{OPhy} + \Delta^{Nit} - R_{NO_3} + \lambda DON + S_{NO_3} \quad (4)$$

$$\frac{\delta DON}{\delta t} = v\Gamma_N^{All} - \lambda DON \quad (5)$$

Δ^{Nit} and R_{NO_3} represent the processes of nitrification and denitrification and are outlined in Sect. 2.3.6 and 2.3.4 respectively.

$$215 \quad \frac{\delta Fe}{\delta t} = -\Gamma_{Fe}^{OPhy} - \Gamma_{Fe}^{Diaz} + \lambda DOFe + DD_{Fe} + B_{Fe} - k_{sc} Fe' \quad (6)$$

$$\frac{\delta DOFe}{\delta t} = v\Gamma_{Fe}^{All} - \lambda DOFe \quad (7)$$

The governing equation for iron contains an additional term, DD_{Fe} , that represents iron supplied via dust deposition. B_{Fe} represent an additional configurable input flux of iron applied to the seafloor layer. The prescribed dust deposition is achieved by a NutGenIE forcing mechanism following a re-gridding from Mahowald et al. (2006). The processes associated with iron
 220 follow the methodology of Parekh et al. (2005). k_{sc} is a scavenging rate term that acts on free dissolved iron III (Fe') throughout the water column. Honeyman et al. (1988) observed that particle concentration influences scavenging; its rate in NutGenIE takes this into account by using a power law function to determine the scavenging rate:

$$k_{sc} = \tau k_0 (C_p)^\phi \quad (8)$$

where k_0 is the scavenging rate (when particles are abundant), C_p is the particle concentration, and ϕ is a constant coefficient.

225 As Honeyman et al. (1988) empirically determined k_0 and ϕ using thorium, the scavenging rate is scaled by τ (Parekh et al., 2005). The processes associated with ligand complexation are discussed in Sect. 2.3.7.

2.3.2 Other phytoplankton nutrient uptake

NutGenIE accounts for primary production (PP) via the production of organic matter resulting from the uptake of nutrients. The nutrient framework is configurable but here it is DIN ($= NO_3 + NH_4$), PO_4 and Fe. Nutrient uptake by non-diazotrophs
 230 (other phytoplankton) results in the production of organic matter (Γ^{OPhy}) at a rate subject to Eq. (9) (Monteiro et al., 2012).

$$\Gamma^{OPhy} = V_{max}^{OPhy} (1 - f_{ice}) \gamma^T \gamma^I \min \left[\frac{PO_4}{PO_4 + K_P}; \frac{DIN}{DIN + K_N}; \frac{Fe}{Fe + K_{Fe}} \right] \min \left[PO_4; \frac{DIN}{R_N^{OPhy}}; \frac{Fe}{R_{Fe}^{OPhy}} \right] \quad (9)$$

V_{max}^{OPhy} is the maximum net nutrient uptake rate of other phytoplankton. f_{ice} is the fraction of the surface ocean covered in ice. γ^T is a temperature limitation function based on an Eppley curve, $\gamma^T = Ae^{T/b}$, where T is the temperature ($^{\circ}C$) and A and b the associated Eppley constants. γ^I is the light limitation function ($\gamma^I = I/I_0$, where I is the amount of light and I_0 the solar
 235 constant). Nutrient limitation follows Michaelis-Menten kinetics with a minimum law of nutrients. K_P , K_N , and K_{Fe} are the other phytoplankton half-saturation constants for phosphate, fixed nitrogen, and iron, respectively. The concentration of the limiting nutrient is used to determine the other phytoplankton biomass, as often assumed in biogeochemical modelling (Maier-Reimer, 1993; Doney et al., 2006; Monteiro et al., 2012). The uptake by other phytoplankton is in units of phosphorus. Therefore, DIN and Fe are scaled by the other phytoplankton elemental composition ($R_N^{OPhy} = N:P$ and $R_{Fe}^{OPhy} = Fe:P$).

240 2.3.3 Nitrogen fixation and diazotrophs nutrient uptake

The activity of diazotrophs in NutGenIE is also accounted for by the production of organic matter resulting from the uptake of nutrients. The availability of dinitrogen (N_2) supplied via atmospheric transfer, is deemed to be unlimited so that the production of organic matter (Γ^{Diaz}) is at a rate subject to Eq. (10).



$$\Gamma^{Diaz} = V_{max}^{Diaz} (1 - f_{ice}) \gamma^T \gamma^I \min \left[\frac{PO_4}{PO_4 + K_P}; \frac{Fe}{Fe + K_{Fe}^{Diaz}} \right] \min \left[PO_4; \frac{Fe}{R_{Fe}^{Diaz}} \right] \quad (10)$$

245 But only if $\frac{DIN}{R_N^{OPhy}} < \min \left[PO_4; \frac{Fe}{R_{Fe}^{OPhy}} \right]$ and $DIN < N_{thresh}$, otherwise the rate is zero. Together these two conditions only allow nitrogen fixation if DIN is scarce and it is the limiting nutrient for other phytoplankton.

V_{max}^{Diaz} is the maximum net nutrient uptake of diazotrophs and is assumed to be lower than V_{max}^{OPhy} because of the energy demands of the process of N_2 fixation. The ice fraction, temperature and light limitation aspects are the same as for other phytoplankton (Eq. (9) above). A higher Fe requirement for diazotrophs is consistent with the iron demands of the nitrogenase enzyme (Berman-Frank et al., 2007).

The conditions associated with Eq. (10) restrict nitrogen fixation to occurring in oligotrophic environments where DIN is the most limiting nutrient (defined as $DIN/R_N^{OPhy} < \min [PO_4; Fe/R_{Fe}^{OPhy}]$ for other phytoplankton). Oligotrophic environments are defined as having $DIN < N_{thresh}$ with N_{thresh} discussed in Sect. 2.3.5.

250 The computations associated with Eq. (9 and 10) are executed each time step, that is, 48 times per year. The values of V_{max}^{OPhy} and V_{max}^{Diaz} are 16 yr^{-1} and 0.7 yr^{-1} respectively; the maximum computed values of the associated limiting terms γ^T , γ^I , $\min \left[\frac{PO_4}{PO_4 + K_P}; \frac{DIN}{DIN + K_N}; \frac{Fe}{Fe + K_{Fe}} \right]$, and $\min \left[\frac{PO_4}{PO_4 + K_P}; \frac{Fe}{Fe + K_{Fe}^{Diaz}} \right]$ are 4.3, 0.8, 0.7, and 0.5 respectively. Therefore, the maximum percentage of the grid cell nutrient concentration taken up by other phytoplankton each time step is 80% (2.5% by diazotrophs).

2.3.4 Organic matter (OM) remineralisation

260 OM is split into two fractions, labile and refractory (refrac). OM is remineralised through the water column according to Eq. (11), an exponential function of depth (Monteiro and Ridgwell, 2023).

$$F^{POM}(z) = F^{POM}(z = z_0) \left(r_{labile}^{POM} e^{\left[\frac{z_0 - z}{l_{labile}} \right]} + (1 - r_{labile}^{POM}) e^{\left[\frac{z_0 - z}{l_{refrac}} \right]} \right) \quad (11)$$

$F^{POM}(z)$ is the POM flux at depth z . z_0 is the depth of the base of the photic zone. The labile fraction of POM is r_{labile}^{POM} , consequently, the refractory fraction of POM is $(1 - r_{labile}^{POM})$. l_{labile} and l_{refrac} are the e-folding depths of remineralisation for labile POM and refractory POM.

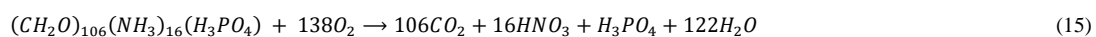
265 OM decomposition is partitioned via a series of redox reactions: initially aerobic respiration utilising O_2 as the electron acceptor, secondly denitrification utilising NO_3 as the electron acceptor, and lastly sulfate reduction utilising SO_4 as the electron acceptor. Electron acceptors (O_2 , NO_3 , and SO_4) are consumed according to decreasing free energy yields (Froelich et al., 1979). Consumption rates of electron acceptors in the process of OM remineralisation follow Eq. (12 to 14) and take account of both electron acceptors abundance and the inhibitory effect of electron acceptors with higher free energy yield
270 (Reinhard et al., 2020). Equation (12) can be considered to represent aerobic respiration, Eq. (13) represents nitrate reduction / denitrification, and Eq. (14) represents sulfate reduction.

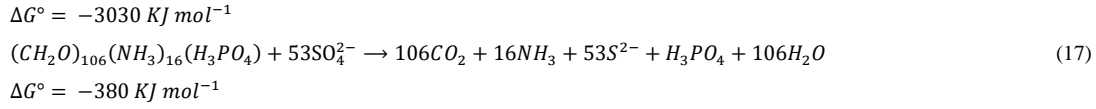
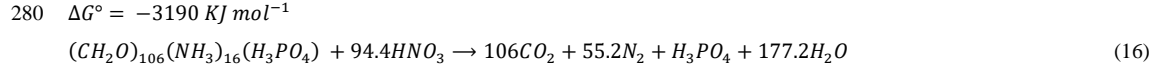
$$R_{O_2} = \frac{[O_2]}{K_{O_2} + [O_2]} \quad (12)$$

$$R_{NO_3} = \frac{[NO_3]}{K_{NO_3} + [NO_3]} \frac{K_{O_2}^i}{K_{O_2}^i + [O_2]} \quad (13)$$

$$R_{SO_4} = \frac{[SO_4]}{K_{SO_4} + [SO_4]} \frac{K_{O_2}^i}{K_{O_2}^i + [O_2]} \frac{K_{NO_3}^i}{K_{NO_3}^i + [NO_3]} \quad (14)$$

275 where R_i indicates the relative fraction of each electron acceptor consumed, K_i are the half-saturation constants for each redox reaction and K_i^i are the inhibition constants to reduce redox reactions of lower yielding free energy. Redfield stoichiometry defines the elemental ratios of OM (C:N:P = 106:16:1) with the following redox pathways (Froelich et al., 1979).





285 In each of Eq. (15 to 17), OM is represented by $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)$ and ΔG° is the Gibbs free energy yield (Froelich et al., 1979). OM decomposition by bacteria when oxygen levels are low leads to the use of nitrate as an alternative electron acceptor. Therefore, Eq. (13) above represents denitrification in NutGenIE.

2.3.5 Threshold for nitrogen fixation in oligotrophic environments

For the modern ocean a threshold can be constrained by observations leading to a fixed threshold $N_{\text{thresh}} \approx 2 \mu\text{mol DIN l}^{-1}$
 290 (Monteiro et al., 2011). For paleo-ocean settings the competition between other phytoplankton and diazotrophs changes with environments leading to a dynamic threshold. However, the dynamic threshold is only applicable in paleoclimate reconstruction when iron is not included and hence is not relevant here.

2.3.6 Nitrification

In NutGenIE, nitrification is considered the process of oxidising ammonia to nitrate, $\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$.
 295 The rate of nitrification (Δ^{Nit}) allows for the limitations by ammonium and oxygen and employs a Michaelis-Menten formulation for a two-substrate reaction (Monteiro and Ridgwell, 2023).

$$\Delta^{\text{Nit}} = V_{\text{max}}^{\text{Nit}} \frac{O_2 \times \text{NH}_4}{(K_{O_2}^{\text{Nit}} \times K_{\text{NH}_4}^{\text{Nit}}) + (K_{O_2}^{\text{Nit}} \times \text{NH}_4) + (K_{\text{NH}_4}^{\text{Nit}} \times O_2) + (O_2 \times \text{NH}_4)} \min \left[\text{NH}_4, \frac{16}{138} O_2 \right] \quad (18)$$

$V_{\text{max}}^{\text{Nit}}$ is the maximum rate of nitrification. $K_{O_2}^{\text{Nit}}$ and $K_{\text{NH}_4}^{\text{Nit}}$ are the half-saturation constants for oxygen and ammonium, respectively.

300 2.3.7 Ligand scheme enhancement in NutGenIE

The iron cycle involves two processes that act on Fe' that are not like other cycles, scavenging and complexation. Fe' can be scavenged and is lost as particulate iron, which is there after not available for biological uptake. Secondly, Fe' can be complexed with a ligand (L') to form complexed iron (FeL). Complexed iron can in turn disassociate, reverting to free iron and a ligand. An equilibrium is established so that $\text{Fe}' + \text{L}' \rightleftharpoons \text{FeL}$. Both Fe' and FeL are available for biological uptake. Scavenging, 305 complexation, and biological uptake processes are shown in Fig. 3. Total iron (Fe_T) is the sum of free and complexed iron $\text{Fe}_T = \text{Fe}' + \text{FeL}$. Total ligand (L_T) is the sum of free and complexed ligands $\text{L}_T = \text{L}' + \text{FeL}$.

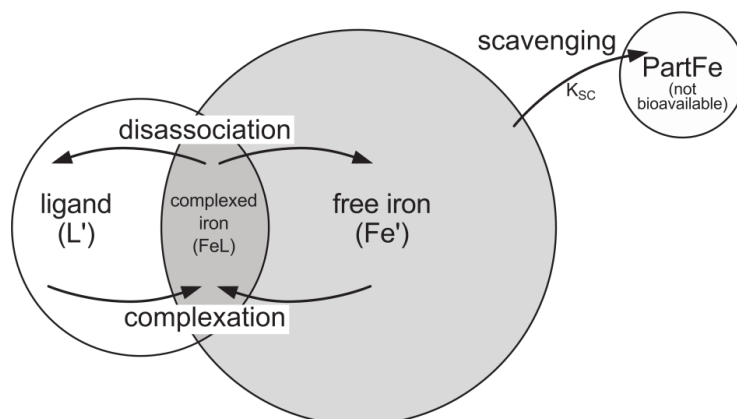


Figure 3 Schematic of iron scavenging, complexation, and biological availability. The rate of scavenging is represented by K_{sc} . Both Fe' and FeL are biologically available (shaded area). Complexation is the combination of Fe' and L' to form complexed iron (FeL). FeL can disassociate to Fe' and L' . Complexation of Fe' and L' to FeL occurs on the timescales of minutes to hours (Witter et al., 2000) such that it is valid to assume that the complexation reaction goes to equilibrium. An equilibrium relationship constant (k_{FeL}), where $k_{FeL} = [FeL]/[Fe'][L']$, can be used to determine the speciation of iron (Parekh et al., 2004). A ligand strength, or stability constant, ($\log(k_{FeL}) = 11.0$) is used which is based on field and laboratory studies and sensitivity analysis (Parekh et al., 2004). Higher values of the stability constant, $\log(k_{FeL})$, imply a stronger binding ligand, and lower values a weaker binding ligand. The ligand scheme described above is based on the work of Archer and Johnson (2000), Parekh et al. (2004) and Parekh et al. (2005).

Research has indicated differing ligand classes with differing binding strengths as well as a varying distribution of ligands through the water column. Schemes with dual ligand classes have been proposed with a strong binding ligand L_1 in surface waters and a moderate binding class L_2 throughout the water column (Hunter and Boyd, 2007; Ye et al., 2009; Misumi et al., 2013; Völker and Tagliabue, 2015). Differing distributions of L_1 and L_2 are of interest when considering global modelling (Misumi et al., 2013; Völker and Tagliabue, 2015; Boyd and Tagliabue, 2015; Ye et al., 2020). The behaviour of ligand class L_2 is analogous with the single ligand class scheme described above (Parekh et al., 2005). The net effect of schemes with dual ligand classes is to have strong binding ligands at the surface.

The binding characteristics of ligands is represented by a stability constant (k_{FeL}) which, in NutGenIE, has been made configurable independently for each depth level rather than homogeneous which would dictate a uniform ligand binding scheme. A default value k_{FeL} is configured with the ability to override this at each depth level by providing a depth level specific stability constant k_{FeL}^n , where n has a value of 16 (surface layer) to 1 (deepest layer). The existence of a strong binding ligand class predominantly present in the upper water column is represented by setting a higher value of k_{FeL}^{16} in the surface layer of NutGenIE.

2.3.8 NutGenIE configuration parameters

The NutGenIE model has an implicit ecosystem and therefore appropriate values for constants are not immediately apparent from observations or experimental outputs. The constants associated with the processes set out in sections above are based on previous calibrations of cGenIE (Ridgwell et al., 2007; Monteiro et al., 2012; Reinhard et al., 2020; van de Velde et al., 2021) with adjustments associated with the three-nutrient configuration. The parameters associated with nutrient tracers, nutrient uptake, remineralisation, nitrification, and iron cycle are outlined in Tables 1 to 5. Monteiro and Ridgwell (2023) carried out significant work in the addition of the nitrogen cycle to cGenIE; parameter values used in their work were the initial values used for the NutGenIE configuration. The atmosphere of NutGenIE is set to and maintained at a pre-industrial CO_2 concentration of 278 part per million (ppm).



340 In many cases parameters, particularly those associated with nutrient uptake, have been determined as the result of a calibration or tuning exercise. Parameters were adjusted to result in a combination that showed best agreement with the concentrations of nutrients, the scale of pertinent processes (e.g., export and nitrogen fixation), and the spatial variations of nutrient uptake limitations. The determination of the best parameter combination used the techniques outlined in Sect. 3.

345 **Table 1** Biogeochemical parameters of NutGENIE relating to nutrient tracers. These parameters relate to Eq (1 to 8). Where the model value of the parameter differs from the literature reference value, the literature value is provided.

Name	Model value	Unit	Description and literature reference
k_{BF}	0.0048	-	Burial fraction, 0.0016 (Schlesinger, 1991).
λ	0.5	yr^{-1}	Remineralised time constant (Najjar and Orr, 1999).
v	0.66	-	DOM Partition (Najjar and Orr, 1999).
$1 - v$	0.34	-	POM Partition.
k_0	0.079	d^{-1}	Initial scavenging rate (Honeyman et al., 1988).
ϕ	0.58	-	Exponent coefficient (Honeyman et al., 1988).
τ	0.505	-	Scavenging scaling factor 0.2 (Parekh et al., 2005).



Table 2 Biogeochemical parameters of NutGenIE relating to nutrient uptake. These parameters relate to Eq. (9 and 10). Where the model value of the parameter differs from the literature reference value, the literature value is provided.

Name	Model value	Unit	Description and literature reference
V_{max}^{OPhy}	16	yr^{-1}	Maximum net nutrient uptake (removal) rate by other phytoplankton.
A	0.59	-	First temperature-dependent uptake rate modifier (Bissinger et al., 2008).
b	15.8	-	Second temperature-dependent uptake rate modifier (Bissinger et al., 2008).
I_0	1,368	$W m^{-2}$	Solar constant (light).
K_P	0.14	$\mu mol P kg^{-1}$	Phosphate half-saturation constant.
K_N	3.3	$\mu mol N kg^{-1}$	Nitrate half-saturation constant.
K_{Fe}	0.27	$nmol Fe kg^{-1}$	Iron half-saturation constant.
R_N^{OPhy}	16	-	Other phytoplankton N:P elemental ratio (Redfield, 1934, 1958).
R_{Fe}^{OPhy}	1.93×10^{-3}	-	Other phytoplankton Fe:P elemental ratio. Determined from K_{Fe} / K_P .
V_{max}^{Diaz}	0.67	yr^{-1}	Maximum net nutrient uptake (removal) rate by diazotrophs
K_{Fe}^{Diaz}	0.54	$nmol Fe kg^{-1}$	Iron half-saturation constant for diazotrophs.
R_{Fe}^{Diaz}	3.86×10^{-3}	-	Diazotrophs Fe:P elemental ratio. Determined from K_{Fe}^{Diaz} / K_P .

350

Table 3 Biogeochemical parameters of NutGenIE relating to remineralisation. These parameters relate to Eq. (11 to 14). Where the model value of the parameter differs from the literature reference value, the literature value is provided.

Name	Model value	Unit	Description and literature reference
r_{labile}^{POM}	0.945	-	Labile fraction of POM (Reinhard et al., 2020).
r_{refrac}^{POM}	0.055	-	Refractory fraction of POM (Reinhard et al., 2020).
l_{labile}	590	m	e-folding depth of remineralisation for labile POM (Reinhard et al., 2020).
l_{refrac}	10^6	m	e-folding depth of remineralisation for refractory POM (Reinhard et al., 2020).
K_{O_2}	29.16	$\mu mol kg^{-1}$	half-saturation constant for aerobic respiration (Monteiro and Ridgwell, 2023).
$K_{O_2}^i$	4.50	$\mu mol kg^{-1}$	inhibition constant for aerobic respiration (Monteiro and Ridgwell, 2023).
K_{NO_3}	81.54	$\mu mol kg^{-1}$	half-saturation constant for nitrate reduction (denitrification) (Monteiro and Ridgwell, 2023).
$K_{NO_3}^i$	81.54	$\mu mol kg^{-1}$	inhibition constant for nitrate reduction (denitrification) (Monteiro and Ridgwell, 2023).
K_{SO_4}	500	$\mu mol kg^{-1}$	half-saturation constant for sulfate reduction (Olson et al., 2016).
$K_{SO_4}^i$	1000	$\mu mol kg^{-1}$	inhibition constant for sulfate reduction (Olson et al., 2016).

Table 4 Biogeochemical parameters of NutGenIE relating to Nitrification. The parameters relate to Eq. (18).

Name	Model value	Unit	Description and literature reference
V_{max}^{Nit}	7.3	yr^{-1}	Nitrification maximum constant rate (Monteiro and Ridgwell, 2023).
$K_{O_2}^{Nit}$	0.02	$\mu mol kg^{-1}$	Nitrification half-saturation constant for oxygen (Monteiro and Ridgwell, 2023).
$K_{NH_4}^{Nit}$	0.01	$\mu mol kg^{-1}$	Nitrification half-saturation constant for ammonium (Monteiro and Ridgwell, 2023)

355

Table 5 Biogeochemical parameters of NutGenIE relating to the iron cycle. The parameters relate to the text of Sect. 2.3.7.

Name	Model value	Unit	Description and literature reference
$\log(k_{FeL})$	11	-	Default log of association constant for ligands.
$\log(k_{FeL}^{16})$	11.4	-	Log of association constant related to ligands in surface waters.



3 Model validation results

The cGenIE model has been used extensively, with many studies examining the validity of the cGenIE approach and experiment results (Ridgwell et al., 2007; Monteiro et al., 2012; Tagliabue et al., 2016; Reinhard et al., 2020; van de Velde et al., 2021). A complete validation analysis of cGenIE and its capabilities of representing the ocean and its processes is not undertaken here. The aim in the validation in this paper is to assess the pertinent biogeochemical distributions and processes that are relevant to the proposed use of NutGenIE. NutGenIE will be used to consider the effect nutrient supply has on PP and this informs the biogeochemical processes considered in the validation process. Nutrient concentrations and distributions are evaluated because they influence PP which is central to the intended purpose (identification of the ULN). The processes of photosynthesis, respiration and remineralisation occur at differing depths of the ocean water column and each exert an influence on the concentration of dissolved oxygen. The concentration of dissolved oxygen is therefore a useful indicator of biogeochemical processes and, hence, also worthy of evaluation here. In Sect. 2.2 above, the concept that NutGenIE represents PP by nutrient uptake and the subsequent formation of organic matter was discussed. In NutGenIE a proportion of this organic matter sinks from the ocean surface and therefore POC export is also compared to observations.

3.1 Datasets and methods

The World Ocean Atlas (WOA) 2018 provides annual climatology data based on observed ocean properties that are utilised for comparison purposes. These properties include temperature (Locarnini et al., 2018), salinity (Zweng et al., 2018), phosphate concentrations (Garcia et al., 2018a), nitrate concentrations (Garcia et al., 2018a) and dissolved oxygen concentrations (Garcia et al., 2018b). The WOA datasets are provided with a spatial resolution of $1^\circ \times 1^\circ$ grid and 102 depth levels from surface to 500 m.

The GEOTRACES dataset contains data from cruises measuring multiple hydrographic parameters, trace metals, and isotopes (Schlitzer, 2014). GEOTRACES provides depth profiles of ocean dissolved iron concentration measurements in the Atlantic, Pacific and Southern Oceans that were compared to NutGenIE concentrations using depth profiles. Cruises GA02 (Mar 2011 – Apr 2011) and GIPY05 (Feb 2008 – Apr 2008) covered the Atlantic Ocean and Southern Ocean respectively while GPc06 (Aug 2005 – Sep 2005) and GP19 (Dec 2014 – Feb 2015) provided coverage of the Pacific Ocean.

The Oregon State University Ocean Productivity group (Ocean Productivity, 2024) provide computations, based on observational data, of vertically integrated net PP (NPP). Differing methodologies for the computation of NPP are supported by the Ocean Productivity group. The observational rate of NPP ($\text{g C m}^{-2} \text{ d}^{-1}$) used for comparison purposes here is the mean of values from the VGPM (Behrenfeld and Falkowski, 1997), Eppley-VGPM (Carr et al., 2006) and CbPM (Westberry et al., 2008) methodologies. The observation-based estimates are provided with a spatial resolution of $\frac{1}{2}^\circ \times \frac{1}{2}^\circ$ grid, that is, a 2160×1080 grid.

3.1.1 Rates and distribution of nitrogen fixation and denitrification

It is important that the model has a realistic level of nitrogen fixation as the dynamic between diazotrophs and other phytoplankton will influence how the model reacts to nutrient perturbations. Estimates of ocean N_2 fixation have tended to increase over the previous three decades with some key global marine values being (all values provided in Tg N yr^{-1}) 125 ± 41 (Gruber and Sarmiento, 1997); 132 (Codispoti et al., 2001); 121 (Galloway et al., 2004); 135 ± 51 (Gruber, 2004); 140 ± 9 (Luo et al., 2012); and $163 \pm 30\%$ (Wang et al., 2019).

Alongside work to constrain the scale of global marine N_2 fixation, work has progressed to determine the spatial distribution of diazotrophs. Spatial restrictions on the prevalence of marine nitrogen fixation have been summarised in Figure 2 of Sohm et al. (2011), Figure 3a of Wang et al. (2019), and Figure 4 of Zehr and Capone (2020). In each of these figures marine nitrogen fixation is mostly limited to within 30° either side of the equator. Sohm et al. (2011) and Wang et al. (2019) both indicate that in the Pacific and Atlantic basins nitrogen fixation rates are elevated in the northern hemisphere compared to the southern



hemisphere. Wang et al. (2019) and Zehr and Capone (2020) highlight that whilst marine nitrogen fixation is mostly limited to a band from 30° N to 30° S it is somewhat reduced at the equator, and this is particularly so in the Pacific Ocean. The area of reduced nitrogen fixation in the equatorial Pacific Ocean corresponds to an area of nutrient supply from deep water upwelling.

Estimates of denitrification are routinely greater than those for N₂ fixation in marine nitrogen budgets. Example of annual global marine denitrification are 175 ± 28 (Gruber and Sarmiento, 1997); 450 (Codispoti et al., 2001); 322 (Galloway et al., 2004); 245 ± 54 (Gruber, 2004); and 200 ± 26% (Wang et al., 2019) (all values provided in Tg N yr⁻¹). Wang et al. (2019) provide location of fixed nitrogen due to a) water column denitrification and anammox and b) sedimentary denitrification and anammox. Areas of significant water column denitrification include the northern Indian Ocean, northern Pacific Ocean, eastern equatorial Pacific Ocean and the eastern equatorial Atlantic Ocean (Wang et al., 2019). Sedimentary denitrification is more evenly distributed across the ocean basins with intensification closer to coastal locations (Wang et al., 2019).

3.1.2 Comparison techniques

WOA and Ocean Productivity datasets are re-gridded both horizontally and vertically to match NutGenIE prior to comparison. Hereafter comparisons which utilise the re-gridded datasets are referred to as WOAR and OPR for WOA and Ocean Productivity respectively.

Thermohaline transects are used to represent and compare properties of the ocean interior following a similar approach to that detailed by Yool et al. (2021). The aim of the transects is to generally follow water masses from recently ventilated young deep water in the North Atlantic, through the Southern Ocean, to older deep waters in the North Pacific, and basin zonal means are used throughout the transect. For reference, NutGenIE age of water (i.e., years since ventilation) details are provided in Fig. S4.

3.1.3 Statistical evaluation

The alignment processes detailed in the previous two sections also facilitated statistical analysis of properties common to NutGenIE and WOAR, that is temperature, salinity, [PO₄], [NO₃] and [O₂]. The statistical analysis was conducted for the surface ocean as well as for the thermohaline transects. The statistical calculation only considers cells that are present in both the NutGenIE and WOAR datasets and computes the mean and standard deviation for each dataset. Correlation analysis between the two datasets can then provide a Pearson correlation coefficient (*r*) and a *p*-value resulting from a test of the null hypothesis that there is no relationship between the datasets.

Normalising each dataset by calculating the ratio of each model standard deviation to the observed standard deviation, when combined with correlation coefficients, allows a graphical representation of the skill of NutGenIE using a Taylor diagram (Taylor, 2001). The normalised NutGenIE standard deviation will vary either side of 1, with a value of 1 indicating the same standard deviation in the model results as in the observed data. The correlation is indicated by the *r* value, angular distance *θ* from the origin is controlled by the normalised standard deviation and the correlation coefficient, with a correlation of 1 on the *x*-axis. The normalised centred root-mean-square (RMS) difference between NutGenIE results and observed data is proportional to the distance from points on the plot of perfect agreement.

3.1.4 Spatial variation of limiting factors and nutrients

Given the proposed use of the model to investigate the nature of nutrient limitation, additional diagnostic outputs have been added. The diagnostics are based on the nutrient uptake equations for other phytoplankton and diazotrophs (Eq. (9 and 10) respectively). The temperature component γ^T can have values greater than one, therefore the temperature limiting factor (LF_{Temp}) is determined as the minimum of γ^T and 1. This ensures that LF_{Temp} only detects scenarios where temperature acts to constrain nutrient uptake. It is then possible to represent each of these limiting factors on a single figure by setting them



each to represent a channel of RGB colour. Nutrient limitation is represented by green; temperature limitation is represented by red; and light limitation is represented by blue. Limitation by multiple factors is represented by the resulting mixed colour as displayed on the Maxwell triangle. The limiting factor values are calculated as follows at each time step of the model processing.

$$LF_{Temp} = \min[\gamma^T, 1] \quad (19)$$

$$LF_{Light} = \gamma^I \quad (20)$$

$$LF_{Nut}^{OPhy} = \min\left[\frac{PO_4}{PO_4+K_P}; \frac{DIN}{DIN+K_N}; \frac{Fe}{Fe+K_{Fe}}\right] \quad (21)$$

$$445 \quad LF_{Nut}^{Diaz} = \min\left[\frac{PO_4}{PO_4+K_P}; \frac{Fe}{Fe+K_{Fe}^{Diaz}}\right] \quad (22)$$

In a similar manner, the limiting nutrient at each time step of model processing is determined by considering each Michaelis-Menten term; this facilitates determination of the PLN at each time step. For each cell and time step the nutrient identified as the PLN is assigned 1, the other nutrients are assigned 0. This facilitates the determination of a limiting nutrient term (e.g., LN_p^{OPhy}) as outlined in Eq. (23 to 27).

$$450 \quad \text{if } \frac{PO_4}{PO_4+K_P} < \frac{DIN}{DIN+K_N} \text{ and } \frac{PO_4}{PO_4+K_P} < \frac{Fe}{Fe+K_{Fe}} \text{ then } LN_p^{OPhy} = 1 \text{ else } LN_p^{OPhy} = 0 \quad (23)$$

$$\text{if } \frac{DIN}{DIN+K_N} < \frac{PO_4}{PO_4+K_P} \text{ and } \frac{DIN}{DIN+K_N} < \frac{Fe}{Fe+K_{Fe}} \text{ then } LN_N^{OPhy} = 1 \text{ else } LN_N^{OPhy} = 0 \quad (24)$$

$$\text{if } \frac{Fe}{Fe+K_{Fe}} < \frac{PO_4}{PO_4+K_P} \text{ and } \frac{Fe}{Fe+K_{Fe}} < \frac{DIN}{DIN+K_N} \text{ then } LN_{Fe}^{OPhy} = 1 \text{ else } LN_{Fe}^{OPhy} = 0 \quad (25)$$

$$\text{if } \frac{PO_4}{PO_4+K_P} < \frac{Fe}{Fe+K_{Fe}^{Diaz}} \text{ then } LN_p^{Diaz} = 1 \text{ else } LN_p^{Diaz} = 0 \quad (26)$$

$$\text{if } \frac{Fe}{Fe+K_{Fe}^{Diaz}} < \frac{PO_4}{PO_4+K_P} \text{ then } LN_{Fe}^{Diaz} = 1 \text{ else } LN_{Fe}^{Diaz} = 0 \quad (27)$$

455 For each nutrient, annual mean values are then calculated for each cell. The PLN is then represented on a figure that utilises a RGB colour mechanism in which Fe PLN is represented by green, PO_4 PLN is represented by red, and NO_3 PLN is represented by blue.

3.1.5 Model initialisation and steady state.

The NutGenIE spin up experiment was executed for 50 kyr, sufficient for the N, P and Fe cycles to reach equilibrium and in excess of the residence time of each nutrient. The concentrations of global mean nutrients and dissolved oxygen throughout that spin up are provided in Fig. S5. The end state concentrations of nutrients and dissolved oxygen are as follows: global mean $[PO_4] = 2.14$ micromoles per kilogram ($\mu\text{mol kg}^{-1}$); global mean $[NO_3] = 28.5$ $\mu\text{mol kg}^{-1}$; global mean $[TDFe] = 0.73$ micromoles per kilogram (nmol kg^{-1}); and global mean $[O_2] = 176$ $\mu\text{mol kg}^{-1}$. The NutGenIE budget for each nutrient at steady state at the end of the 50 kyr spin up experiment is shown below.

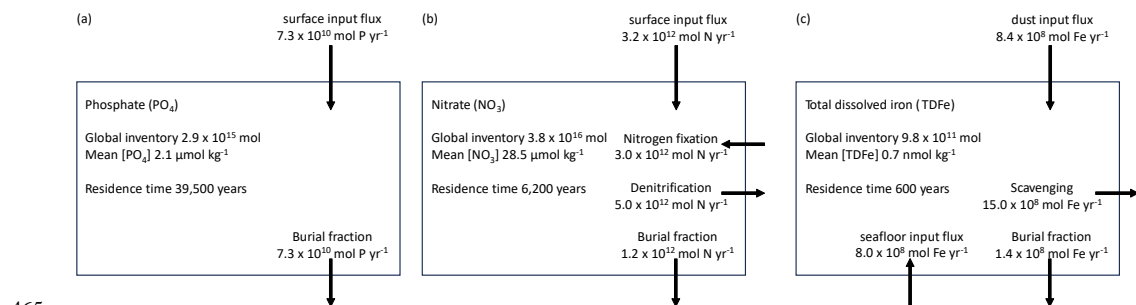


Figure 4 NutGenIE nutrient budgets at end of 50 kyr spin up. (a) Phosphate budget. (b) Nitrate budget. (c) Total dissolved iron budget.



3.2 Physical evaluation

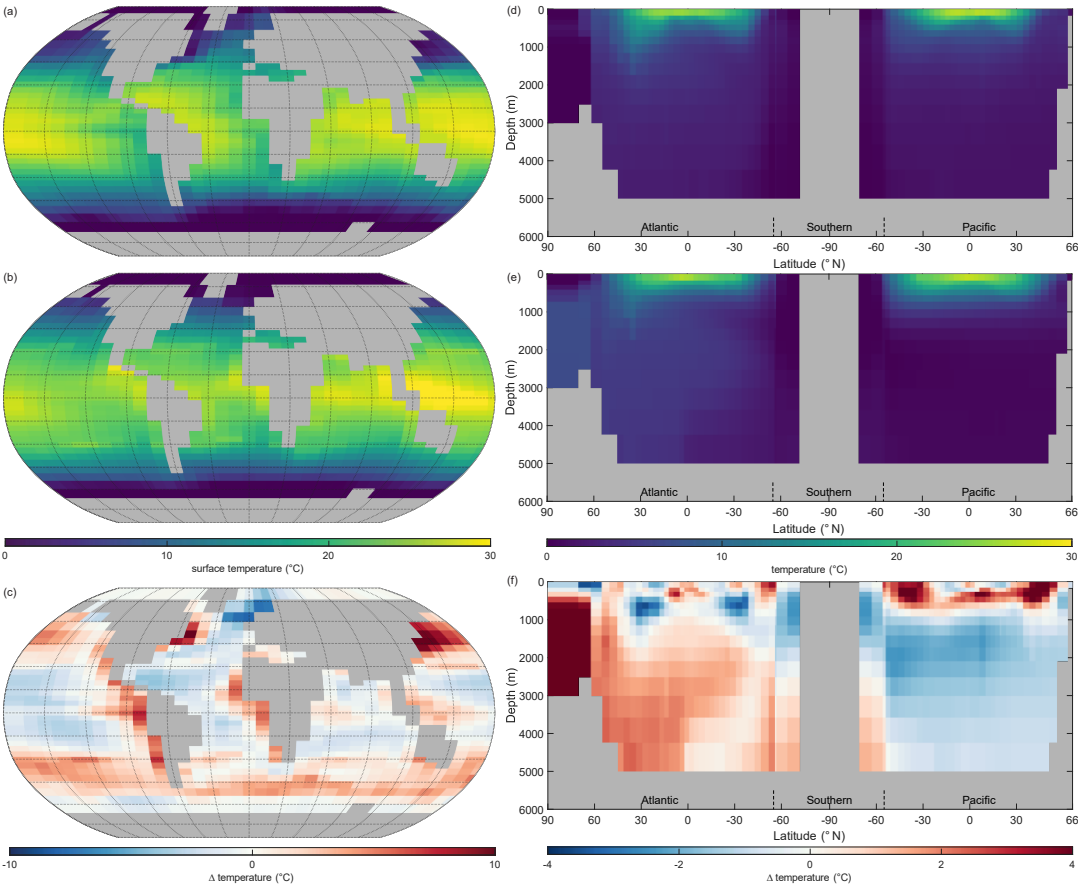


Figure 5 Annual mean global temperature. (a) Observed (WOAR) sea surface temperature (SST). (b) NutGenIE SST. (c) Delta SST (NutGenIE - WOAR). (a-c) based on surface level 0 – 80.8 m depth level. (d) Observed (WOAR) thermohaline transect zonal mean temperature. (e) NutGenIE thermohaline transect zonal mean temperature. (f) Thermohaline transect temperature delta (NutGenIE - WOAR). Temperature (and difference) in °C.

Figure 5 shows the observations from the WOAR dataset, NutGenIE results and deltas (differences between the two) for annual mean global sea surface temperature and thermohaline transects. It is noted that WOAR temperatures are in situ temperature, whereas potential temperature is used in NutGenIE; however, the differences will be minimal and do not require an alignment conversion. NutGenIE results are compared to WOAR salinity data in Fig. 6. NutGenIE represents temperature and salinity reasonably well, but ocean physics is not the focus here, so the properties are not described in detail. Mean surface and interior (thermohaline transect) temperature and salinity values for both NutGenIE and WOAR are provided in Table 6.

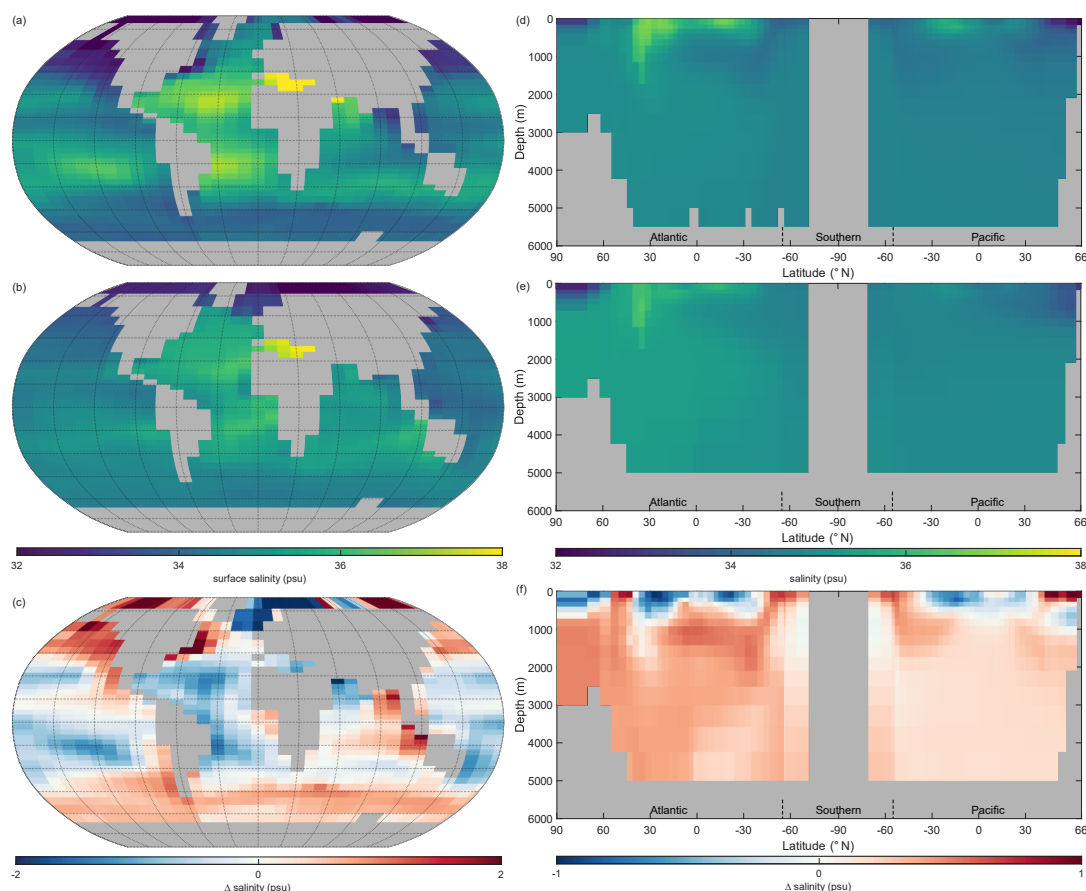


Figure 6 Annual mean global salinity. (a) Observed (WOAR) sea surface salinity (SSS). (b) NutGenIE SSS. (c) Delta SSS (NutGenIE - WOAR). (a-c) based on surface level 0 – 80.8 m depth level. (d) Observed (WOAR) thermohaline transect zonal mean salinity. (e) NutGenIE thermohaline transect zonal mean salinity. (f) Thermohaline transect salinity delta (NutGenIE - WOAR). Salinity (and difference) in psu.

3.3 Biogeochemistry tracer evaluation (nutrients, oxygen)

3.3.1 Phosphate

The representation of phosphate and the other nutrients by NutGenIE is particularly important if the model is to be suitable for experiments that examine the impacts of variations in nutrient supply. We have seen that the end state global mean concentration of phosphate is $2.14 \mu\text{mol kg}^{-1}$; we now consider the spatial variation and compare to observational data. The surface phosphate concentrations of NutGenIE are largely a good representation of the observed concentration from WOAR. In general, NutGenIE surface $[\text{PO}_4]$ is slightly greater than observed $[\text{PO}_4]$ at low latitudes and slightly less than observed $[\text{PO}_4]$ at higher latitudes (Fig. 7 a-c). The magnitude of differences in surface $[\text{PO}_4]$ between NutGenIE and observations are almost universally less than $0.5 \mu\text{mol kg}^{-1}$. There are some specific differences to be noted; NutGenIE surface $[\text{PO}_4]$ is lower than observed in the North Pacific; between 45°S and 60°S NutGenIE surface $[\text{PO}_4]$ is lower than observed; and NutGenIE does not fully represent the supply of nutrients in upwelling areas of the equatorial Pacific and Benguela. The mean NutGenIE annual mean global surface $[\text{PO}_4]$ is $0.52 \mu\text{mol kg}^{-1}$ with a standard deviation of 0.36 which compare to WOAR mean and standard deviations of 0.58 and $0.54 \mu\text{mol kg}^{-1}$ respectively.

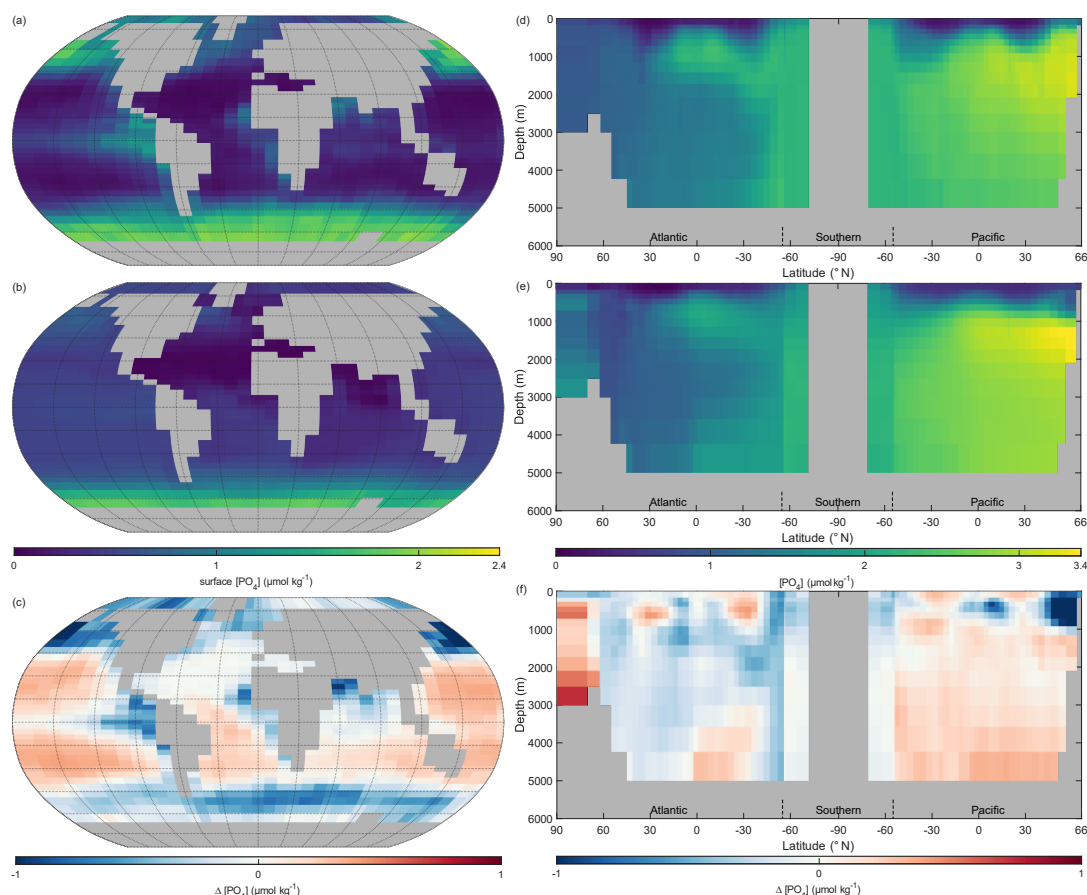


Figure 7 Annual mean global phosphate concentration (PO_4). (a) Observed (WOAR) surface PO_4 . (b) NutGenIE surface PO_4 . (c) Delta surface PO_4 (NutGenIE - WOAR). (a-c) based on surface level 0 – 80.8 m depth level. (d) Observed (WOAR) thermohaline transect zonal mean PO_4 . (e) NutGenIE thermohaline transect zonal mean PO_4 . (f) Thermohaline transect PO_4 delta (NutGenIE - WOAR). PO_4 (and difference) in $\mu\text{mol kg}^{-1}$.

Ocean interior representation of phosphate by NutGenIE is also successfully aligned to observed concentrations (Fig. 7 (d to f)). The Atlantic sector has somewhat lower PO_4 than the Southern Ocean and PO_4 is further elevated in the Pacific Ocean, reflecting the age of water masses, and increasing remineralisation. NutGenIE also represents well the differing water masses in the Atlantic Ocean with the tongue of northward flowing Antarctic Intermediate Water rich in nutrients. Differences between NutGenIE and observations are minimal apart from the northern Pacific Ocean at depths less than 1 000 m where NutGenIE PO_4 are approximately $1.2 \mu\text{mol kg}^{-1}$ less than observed concentrations. In general, NutGenIE has a slight negative bias in PO_4 in the Atlantic Ocean and a slight positive bias in PO_4 in the Pacific Ocean. NutGenIE represents the PO_4 in the Southern Ocean in alignment with observations and there are consequently minimal differences in that sector of the thermohaline transect. The mean NutGenIE annual mean PO_4 of the thermohaline transect is $2.0 \mu\text{mol kg}^{-1}$ with a standard deviation of $0.73 \mu\text{mol kg}^{-1}$ which compare to WOAR mean and standard deviations of 2.0 and $0.64 \mu\text{mol kg}^{-1}$ respectively.

3.3.2 Nitrate

Surface nitrate concentrations of NutGenIE largely follow the spatial patterns of the observed concentration (Fig. 8 (a to c)). In general, NutGenIE surface NO_3 are lower than the observed NO_3 , although this is less evident at low latitudes. The magnitude of differences in surface NO_3 between NutGenIE and observations are almost universally less than $10 \mu\text{mol kg}^{-1}$. There are some specific differences to be noted which are similar to those identified for phosphate; NutGenIE surface NO_3



are lower than observed in the North Pacific; between 45° S and 60° S NutGenIE surface $[\text{NO}_3]$ are $\approx 10 \mu\text{mol kg}^{-1}$ lower than observed; and NutGenIE does not fully represent the supply of nutrients in upwelling areas of the equatorial Pacific and Benguela. The mean NutGenIE annual mean global surface $[\text{NO}_3]$ is $3.0 \mu\text{mol kg}^{-1}$ with a standard deviation of $4.68 \mu\text{mol kg}^{-1}$ which compare to WOAR mean and standard deviations of 6.0 and $7.99 \mu\text{mol kg}^{-1}$ respectively.

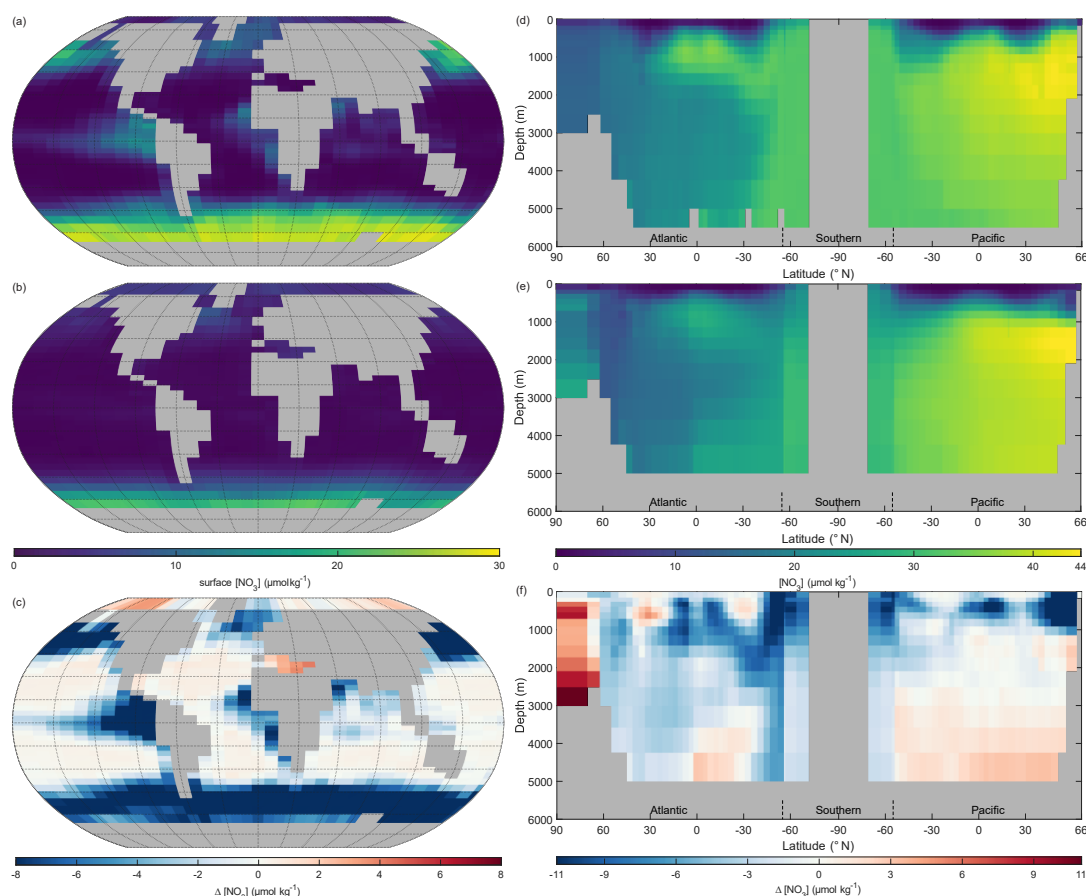


Figure 8 Annual mean global nitrate concentration ($[\text{NO}_3]$). (a) Observed (WOAR) surface $[\text{NO}_3]$. (b) NutGenIE surface $[\text{NO}_3]$. (c) Delta surface $[\text{NO}_3]$ (NutGenIE - WOAR). (a-c) based on surface level 0 – 80.8 m depth level. (d) Observed (WOAR) thermohaline transect zonal mean $[\text{NO}_3]$. (e) NutGenIE thermohaline transect zonal mean $[\text{NO}_3]$. (f) Thermohaline transect $[\text{NO}_3]$ delta (NutGenIE - WOAR). $[\text{NO}_3]$ (and difference) in $\mu\text{mol kg}^{-1}$.

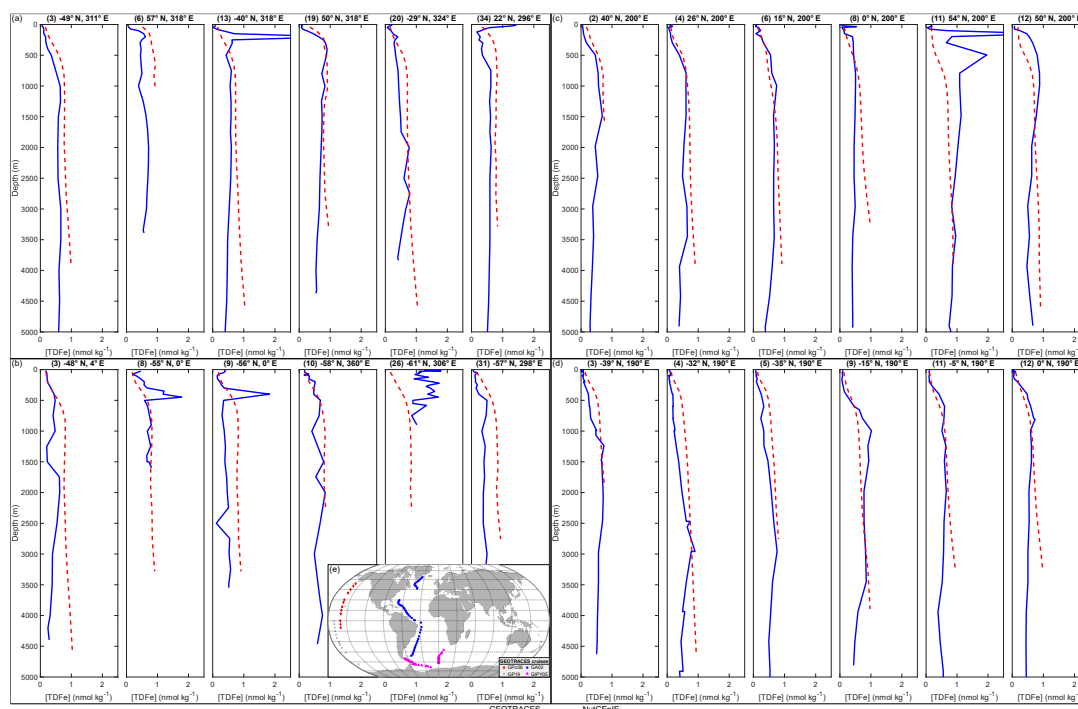
Ocean interior representation of nitrate by NutGenIE are aligned to observation concentrations (Fig. 8 (d to f)). The Atlantic sector has somewhat lower $[\text{NO}_3]$ than the Southern Ocean and $[\text{NO}_3]$ are further elevated in the Pacific Ocean, this again reflects the age of water masses, and increasing remineralisation. NutGenIE also successfully represents differing water masses in the Atlantic Ocean with the tongue of northward flowing Antarctic Intermediate Water rich in nutrients. Differences between NutGenIE and observations are less than $5 \mu\text{mol kg}^{-1}$ apart from the northern Pacific Ocean at depths less than 1 000 m where NutGenIE $[\text{NO}_3]$ are as much as $18 \mu\text{mol kg}^{-1}$ less than observed concentrations. In general, NutGenIE has a positive bias in $[\text{NO}_3]$ in the Arctic, a negative bias in the Atlantic Ocean, a minimal negative bias in the Southern Ocean, and a positive bias in $[\text{NO}_3]$ in the Pacific Ocean below 1 000 m. The mean NutGenIE annual mean $[\text{NO}_3]$ of the thermohaline transect is $26.5 \mu\text{mol kg}^{-1}$ with a standard deviation of $9.95 \mu\text{mol kg}^{-1}$ which compare to WOAR mean and standard deviations of 28.3 and $9.0 \mu\text{mol kg}^{-1}$ respectively.



535 3.3.3 Iron

In general, NutGenIE broadly represents the observed iron depth profiles from the four GEOTRACES cruises (Fig. 9). A sample of 6 profiles for each cruise are shown here (the complete set of depth profiles for each cruise are available in supplementary information Fig. S6 to S24). The simplified bathymetry associated with the NutGenIE 36 x 36 x 16 structure does result in several profiles where the depth of the NutGenIE grid cell is significantly shallower than the specific ocean depth, for example Fig. 9(a) profile (6) and Fig. 9(c) profile (2). There are, however, a total of 107 profiles across the four cruises which provide sufficient opportunities to consider the ability of NutGenIE to represent ocean iron concentrations. It is important to note that the GEOTRACES based profiles represent a specific point in time whereas the NutGenIE profiles represent annual mean concentrations.

There are 47 profiles associated with cruise GA02 covering a transect in the Atlantic Ocean from 64° N to 60° S. There are two instances where the depth profiles of NutGenIE do not follow the observed profiles. Firstly, where the observed profile has a subsurface peak or maximum in the TDFe concentration (e.g., Fig. 9(a) profile (13)). Secondly, where the observed profile has an elevated surface TDFe concentration (e.g., Fig. 9(a) profile (34)), potentially related to an episodic input of iron from dust. At depths below 1 000 m there is strong alignment between the NutGenIE profiles and the observed profiles.



550 Figure 9 Sample iron depth profiles for GEOTRACES cruises. (a) NutGenIE and GEOTRACES GA02 cruise. (b) NutGenIE and GEOTRACES GIPY05 cruise. (c) NutGenIE and GEOTRACES GPC06 cruise. (d) NutGenIE and GEOTRACES GP19 cruise. (a-d) Total dissolved iron (TDFe) in nmol kg⁻¹. Blue line represents GEOTRACES observations of [TDFe], red dashed line represents NutGenIE [TDFe]. (e) Location of GEOTRACES cruises and stations used here for comparison to the NutGenIE model. Cruise station locations are shown as follows: GPC06 – red diamonds, GP19 – black circles, GA02 – blue squares and GIPY05 – magenta triangles.

There are 35 profiles associated with cruise GIPY05 covering two transects in the Atlantic sector of the Southern Ocean. The latitude range of these profiles is between 42° S and 68° S with longitudes ranging between 66° W and 9° E. There are some profiles where NutGenIE does not accurately represent the observed profiles; examples include Fig. 9(b) profiles (8), (9), and (26). However, as with cruise GA02, NutGenIE depth profiles of TDFe associated with cruise GIPY05 provide a reasonable representation of the observed depth profiles.



560 GEOTRACES cruise GPc06 and GP19 were both undertaken in the Pacific Ocean and have 12 and 13 depth profiles of TDFe, respectively. Cruise GPc06 covered a range of latitudes from 54° N to 10° S at a longitude of 200° E. The TDFe depth profiles associated with cruise GPc06 (Fig. 9(c)) highlight reasonable alignment between NutGenIE and the observed TDFe concentrations. The one exception to this is profile (11) where the observed profile shows elevated [TDFe] between 100 and 1 000m. This profile is the most northerly, 54° N, and associated with an area of the North Pacific where NutGenIE is less accurate in the representation of both phosphate and nitrate (Fig. 7 and 8 respectively).

565 Cruise GP19 covered the more southerly latitudes of the Pacific Ocean from the equator to 64° S at a longitude of 200° E. One profile occurs when the cruise travelled to a more westerly location at 30° S, 174° E. The TDFe depth profiles associated with cruise GP19 (Fig. 9(d)) highlight reasonable alignment between NutGenIE and the observed TDFe concentrations. In summary the depth profiles of TDFe concentrations associated with GEOTRACES cruises GA02, GIPY05, GPc06, and GP19 indicate that NutGenIE can successfully reflect average observations.

For each of the 107 depth profiles mean values of [TDFe] were calculated for both GEOTRACES and NutGenIE. For these profiles the NutGenIE mean [TDFe] ranged from 0.45 to 0.90 nmol kg⁻¹. The mean [TDFe] for GEOTRACES ranged from 0.16 to 1.25 nmol kg⁻¹. The NutGenIE mean [TDFe] were on average 0.14 nmol kg⁻¹ higher than measurements GEOTRACES recorded. The focus here has been to compare NutGenIE results to ocean observations, and this has been done using GEOTRACES depth profiles because WOA does not contain [TDFe] data. In addition, NutGenIE [TDFe] for the surface ocean and thermohaline transect are provided in Fig. S25.

3.3.4 Dissolved oxygen

It is known that gas solubility in seawater is a function of temperature, with gas solubility inversely correlated to temperature. Therefore, oxygen dissolves more readily in cooler seawater. It follows that the highest concentrations of surface dissolved oxygen should be observed in high latitude water and the surface dissolved oxygen reduce in each hemisphere moving towards the equator (Fig. 10 (a)). The representation of surface dissolved oxygen by NutGenIE also reflects the variation by latitude, with the maximum concentrations in the Arctic Ocean followed by the Southern Ocean. The difference figure (Fig. 10 (c)), highlights that in general NutGenIE has higher dissolved oxygen concentrations than observed. There are areas of the latitude ranges 30° N to 60° S and 30° N to 60° S in which NutGenIE dissolved oxygen concentrations are lower than observed.

585 Region where NutGenIE dissolved oxygen concentrations are higher than observed (> 40 µmol kg⁻¹) are the North Atlantic to the east of Greenland, the northern Indian Ocean and the equatorial upwelling regions of the eastern Pacific and Indian Oceans. The mean NutGenIE annual mean global surface [O₂] is 249 µmol kg⁻¹ with a standard deviation of 44.60 µmol kg⁻¹ which compare to WOA mean and standard deviations of 239 and 44.64 µmol kg⁻¹ respectively.

When considering the ocean interior (Fig. 10 (d to f)) and comparing the observed dissolved oxygen concentrations to those of NutGenIE it is again the case that NutGenIE largely reflects the observed spatial variations. The Atlantic sector in both the observed and NutGenIE transects have generally higher dissolved oxygen concentrations than the Pacific Ocean, reflecting the fact the Pacific Ocean contains older water into which there has been greater remineralisation of organic matter. The tongue of AAIW with reduced dissolved oxygen concentrations is evident in both the observed and NutGenIE transects. In both the observed and NutGenIE transects the highest dissolved oxygen concentrations are seen towards the surface at high latitudes, that is, the Arctic Ocean, Southern Ocean, and North Pacific. The minimum dissolved oxygen concentrations, approaching 100 µmol kg⁻¹ are in the North Pacific at depths up to 3 000m in both the observed and NutGenIE transects. However, NutGenIE does not reflect the observed dissolved oxygen concentrations in the Arctic Ocean at depth well, with concentrations greater than 40 µmol kg⁻¹ below the observed concentrations. In addition, NutGenIE tends to have higher concentrations of dissolved oxygen (by up to 40 µmol kg⁻¹) in the upper 2 000 m of the water column and lower concentrations of dissolved oxygen (by up to 40 µmol kg⁻¹) at greater depths. The mean NutGenIE annual mean global interior [O₂] is 189 µmol kg⁻¹ with a standard deviation of 55 which compare to WOAR mean and standard deviations of 194 and 65 µmol kg⁻¹ respectively.

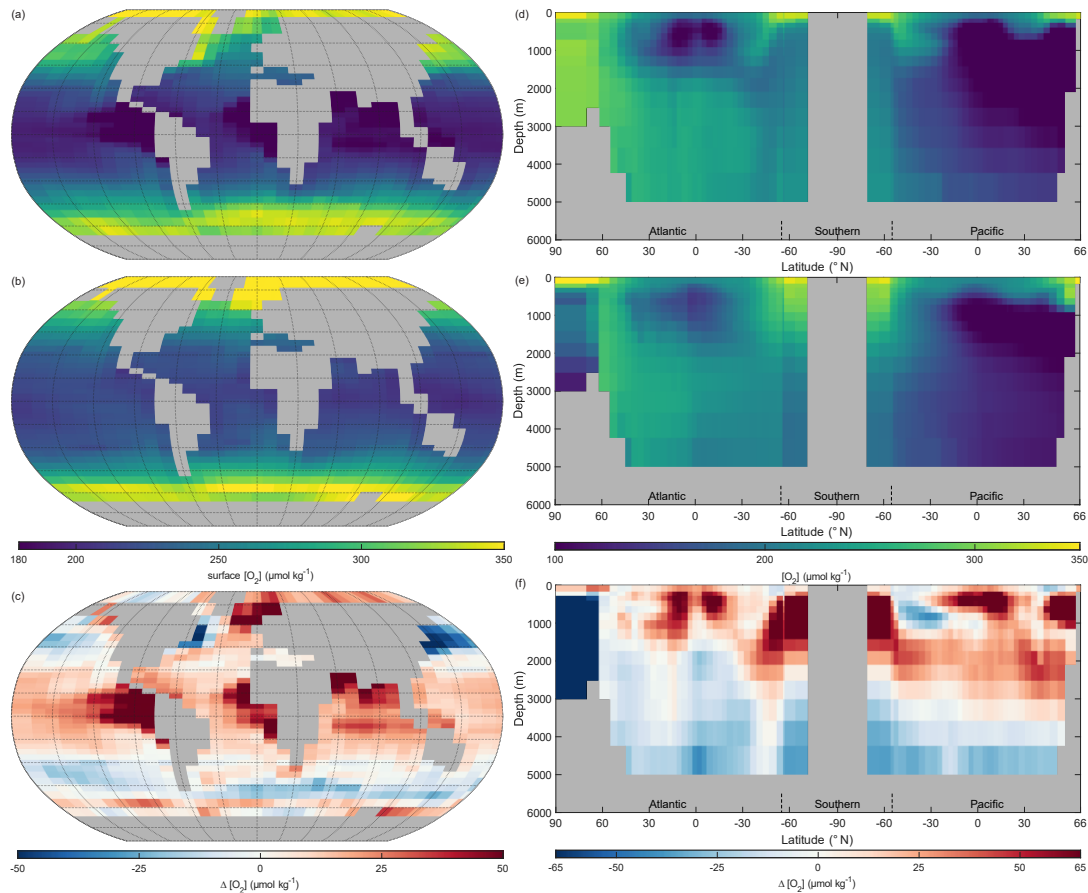


Figure 10 Annual mean global dissolved oxygen ([O₂]). (a) Observed (WOAR) surface [O₂]. (b) NutGenIE surface [O₂]. (c) Delta surface [O₂] (NutGenIE - WOAR). (a-c) based on surface level 0 – 80.8 m depth level. (d) Observed (WOAR) thermohaline transect zonal mean [O₂]. (e) NutGenIE thermohaline transect zonal mean [O₂]. (f) Thermohaline transect [O₂] delta (NutGenIE - WOAR). [O₂] (and difference) in $\mu\text{mol kg}^{-1}$.

3.3.5 Statistical analysis results

Statistical information, such as mean values, have in many cases been provided alongside the results associated with each ocean property; here we summarise the statistical and correlation results.

For all variable there is good agreement between the NutGenIE and WOAR mean values; all NutGenIE means are within one standard deviation of the observed WOAR mean. The NutGenIE datasets are derived from less granular grids and therefore it is understandable that in most cases the associated standard deviations are lower than the WOAR standard deviation. Correlation coefficients between NutGenIE and WOAR are reassuring with values ranging from 0.76 (surface [O₂]) to 0.97 (surface temperature). In all cases the correlation p-values are zero, indicating strong rejection of the null hypothesis that the NutGenIE and WOAR datasets are not correlated. Histograms of the NutGenIE and WOAR datasets for each of the variables in Table 6 also show reassuring similarities (supplementary information Fig. S26 to S35). A graphical representation of the skill of NutGenIE can be visualised using a Taylor diagram, Fig. 11.

Table 6 Statistical comparison of NutGenIE to WOAR. Surface values relate to level depth of 0 - 80.8 m. Interior values reflect the thermohaline transects as defined in Sect. 3.1.2. sd = standard deviation. All correlations have a p-value of 0.

Variable (units)	PO ₄ ($\mu\text{mol kg}^{-1}$)		NO ₃ ($\mu\text{mol kg}^{-1}$)		temperature (°C)		salinity (psu)		O ₂ ($\mu\text{mol kg}^{-1}$)	
	Surface	Interior	Surface	Interior	Surface	Interior	Surface	Interior	Surface	Interior
WOAR mean	0.58	2	6.0	28	17.5	3.2	35	35	240	194



NutGenIE mean	0.52	2	2.9	26	18	3.5	35	35	249	189
WOAR sd	0.54	0.64	7.99	9.00	9.56	3.72	1.19	0.33	52.91	64.55
NutGenIE sd	0.36	0.73	4.68	9.95	9.06	4.05	0.78	0.34	44.64	54.62
Pearson correlation coefficient (r)	0.82	0.92	0.88	0.90	0.97	0.93	0.77	0.82	0.94	0.76

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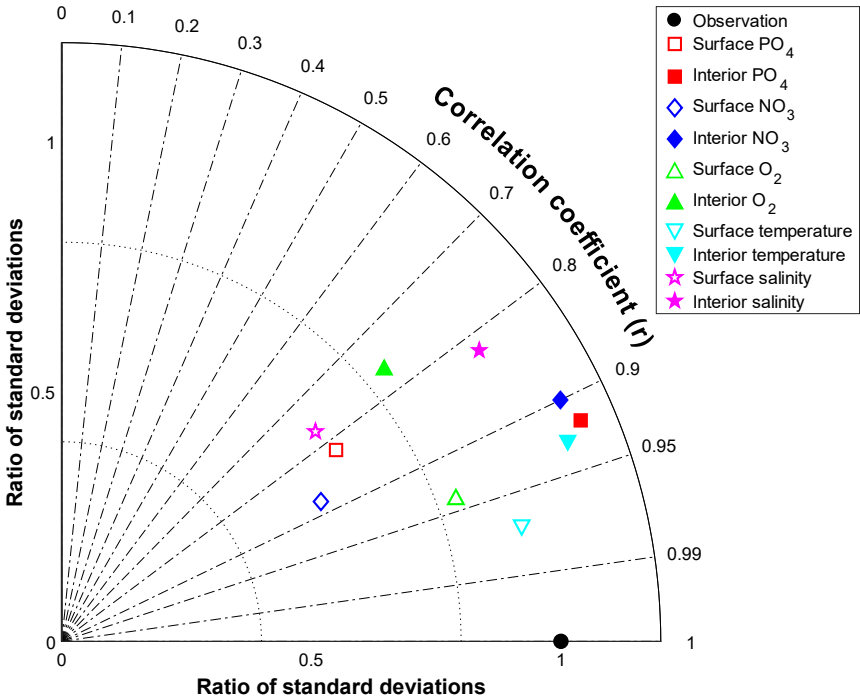


Figure 11 Taylor diagram of NutGenIE and observed (WOAR). Showing surface and interior temperature, salinity, [PO₄], [NO₃] and [O₂]. The RMS error and standard deviations have been normalised by the observed standard deviation of each field before plotting. Therefore, the RMS error and standard deviation indicate the ratio to the observed standard deviation. Angular distance θ is controlled by the correlation coefficient (r), with a correlation of 1 on the x-axis. The diagrams show NutGenIE results to observation (WOAR) comparisons based on annual average spatial fields.

625

3.3.6 Rates of PP

630 It was noted (Sect. 2.2) that NutGenIE does not explicitly model primary producer (phytoplankton) biomass. Nutrient uptake within the surface layer of NutGenIE is an output of the model. NutGenIE nutrient uptake is converted to the units ($\text{g C m}^{-2} \text{d}^{-1}$) of the Observation-based PP provided by the Oregon State University Ocean Productivity group (Ocean Productivity, 2024) and shown below (Fig. 12).

Large areas of the oceans away from the continental land masses have low levels of PP and this is reflected in both observations and NutGenIE (Fig. 12). A figure showing the base Ocean Productivity dataset prior to re-gridding is available in Fig. S36. PP is enhanced by upwelling, e.g., the equatorial Pacific and Eastern Atlantic, and this is reflected in both observations and NutGenIE. However, the highest observed rates of PP are seen immediately adjacent to the continental land masses. These elevated observed rates of PP are unable to be reflected accurately by NutGenIE given the 36×36 spatial resolution. NutGenIE also overestimates the rate of PP in the North Atlantic in an area south of Greenland and in a band close to 60°S .

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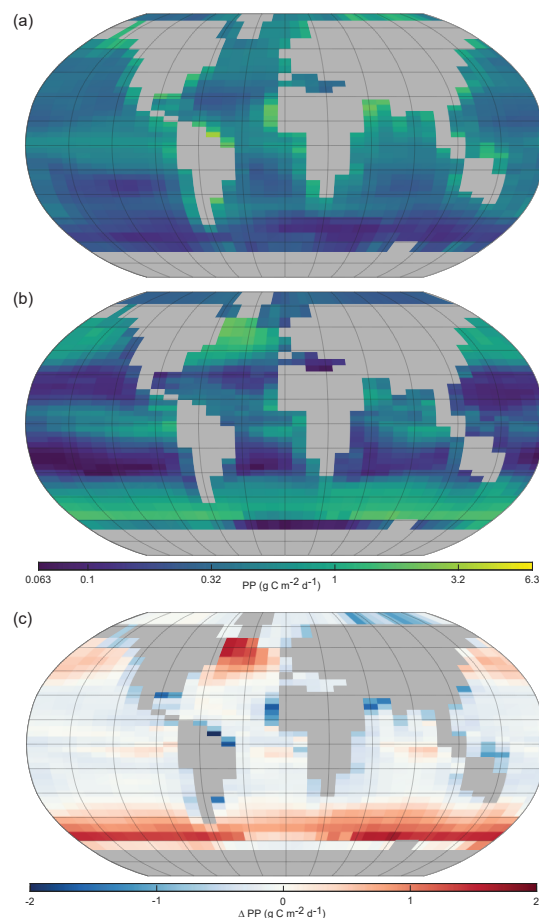


Figure 12 Annual mean global primary production. (a) Oregon State University Ocean Productivity (Ocean Productivity, 2024) re-gridded (OPR). (b) NutGenIE. (a) and (b) A log (base 10) scale is used. (c) Difference (NutGenIE - OPR). Primary production (and difference) in $\text{g C m}^{-2} \text{d}^{-1}$.

3.3.7 Nitrogen cycle processes

The NutGenIE global mean rate of marine nitrogen fixation is $3.0 \times 10^{12} \text{ mol N yr}^{-1}$ which equates to 84 Tg N yr^{-1} , with the majority occurring in the low latitudes, within 30° either side of the equator. The distribution of nitrogen fixation and associated rates in $\mu\text{mol N kg}^{-1} \text{yr}^{-1}$ can be seen in Fig. 13 (a). Higher rates of nitrogen fixation in each ocean basin are seen north of the equator than south of the equator. The highest rates of nitrogen fixation ($4.0 \mu\text{mol N kg}^{-1} \text{yr}^{-1}$) occur between the equator and 15° N in the Atlantic Ocean. A significant area of the Pacific Ocean either side of the equator has minimal or zero rates of nitrogen fixation.

Denitrification can occur throughout the water column. In NutGenIE denitrification occurs via the decomposition of organic matter by bacteria, when oxygen levels are low, which leads to the use of nitrate as an alternative electron acceptor. This in turn results in the conversion of nitrate to dinitrogen (Sect. 2.3.4). NutGenIE water column integrated denitrification is shown in Fig. 13 (b). The NutGenIE global mean rate of marine denitrification is $3.2 \times 10^{12} \text{ mol N yr}^{-1}$ which equates to 90 Tg N yr^{-1} .

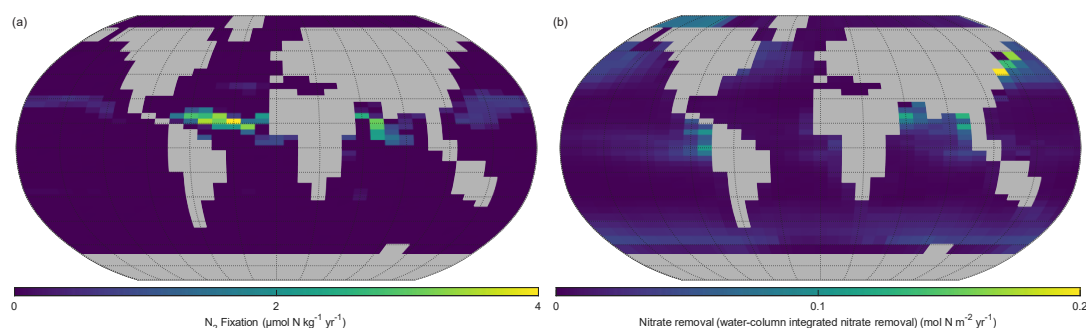


Figure 13 Annual mean distribution of NutGenIE nitrogen fixation and denitrification. (a) Surface level nitrogen fixation in $\mu\text{mol N kg}^{-1} \text{ yr}^{-1}$. (b) water column denitrification.

4 Discussion

4.1 Summary

We have presented the features of NutGenIE and carried our comparisons to datasets based on ocean observations. Focus on nutrient cycles and associated biogeochemical cycles has been vital with NutGenIE compared to both WOAR (phosphate, nitrate and dissolved oxygen) and GEOTRACES (iron) datasets. In addition, the WOA provides temperature and salinity datasets that have been compared with NutGenIE so give confidence that the fundamental physical properties are being well represented. NutGenIE has also been compared against ocean productivity data from the Oregon State University Ocean Productivity group. For each attribute the comparisons have shown that NutGenIE is a effective representation rather than a perfect replication of the oceans which would be unrealistic.

The NutGenIE steady state nutrient global inventories (Fig. 4) are well aligned to ocean estimates; this is also evident in the comparisons of interior nutrient concentrations. Fluxes associated with each NutGenIE nutrient cycle, considering the simplified cycles, are close to literature estimates of ocean nutrient budgets. NutGenIE residence times (phosphate $\sim 40,000$ years, nitrate $\sim 6,000$ years and iron < 1000 years) are of the expected order of magnitude, although iron is slightly higher than global ocean estimates tens to hundreds years (Delaney, 1998; Gruber, 2004; Hayes et al., 2018). This supports the conclusion that NutGenIE nutrient cycles as configured here are a reasonably accurate representation of the oceans.

The mechanisms that maintain NutGenIE ocean nutrient concentrations are pertinent to the intended investigations and, therefore, significant discrepancies would be worrying. Annual mean concentrations of phosphate and nitrate both compare successfully to the WOAR. Those comparisons have considered both the areas with first order impact to ocean PP, that is, the surface ocean and the ocean interior that has longer term impact on PP in terms of nutrient replenishment. Differences in both nutrients' concentrations have been identified and noted; however, there are no significant flaws in NutGenIE distributions related to phosphate and nitrate.

In summary, the validation of NutGenIE results against ocean observations suggest that NutGenIE represents the ocean successfully. In particular, the representation of nutrient concentrations give confidence that NutGenIE will be suitable for the intended study of long-term influence of nutrients on oceanic PP. There are, however, aspects of NutGenIE as configured here that do not represent reality as successfully and these are noted below. The representation of the Arctic Ocean has highlighted discrepancies relating to temperature, salinity, and dissolved oxygen below the surface. In general, NutGenIE nutrient concentrations in the upper 1000m of the northern Pacific Ocean are lower than observed concentrations. The derived NutGenIE NPP used here results in an overestimate in an area of the North Atlantic close to Greenland and a band close to 60° S . Whilst these discrepancies are noted, the ability of NutGenIE to successfully represent Earth's oceans and processes indicate that NutGenIE will be useful for the future investigations into the long-term influence of nutrients on oceanic primary production.

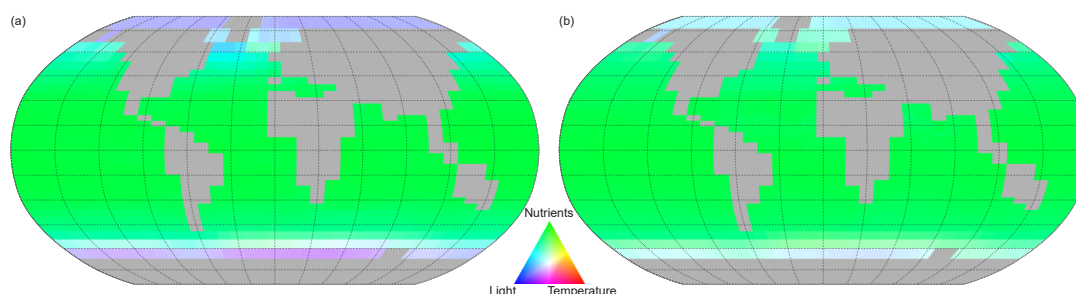


690 4.2 Spatial variation of limitations

The comparisons to ocean observations detailed in the results have not considered the limiting factors that act to control PP. Here, we briefly review those limiting factors and in particular the spatial variation of nutrient limitation to ensure that NutGenIE is realistic as these aspects will be vital in the proposed investigations of the ULN.

The nature of light and temperature limitations are such that they exert the greatest restriction on nutrient uptake in the higher latitudes. The comparative limitations of nutrient uptake by light, temperature, and nutrient supply are shown in Fig. 14 for both other phytoplankton and diazotrophs. For both phytoplankton classes a combination of light, temperature, and nutrient supply limit nutrient uptake in the high latitudes. The nutrient uptake at low and mid latitudes is controlled by nutrient availability. The spatial variability of nutrient limitation is shown in Fig. 15 that displays the PLN for each phytoplankton class.

700 Other phytoplankton nutrient uptake is limited by a combination of nutrients. PO_4 is the PLN in 1 % of the surface ocean, NO_3 is the PLN for 71 % and Fe limiting in the remaining 28 %. PO_4 limitation is restricted to the Mediterranean Sea and a small area of the Caribbean. The areas where Fe acts as the PLN are the Southern Ocean, south of 40° S, and north of 40° N in both the Pacific and Atlantic Oceans.



705 **Figure 14 Spatial variation of the limiting factor for nutrient uptake**, (a proxy for phytoplankton growth in NutGenIE). For (a) other phytoplankton and (b) diazotrophs. Red = temperature limitation, green = Nutrient limitation, blue = light limitation.

Figure 14 facilitates the representation of the three limiting factors on a single figure, however, the colours used are not favourable to readers with colour vision deficiencies. Figures showing individual limiting factors are available in supplementary information Fig. S37 to S45.

710 Nutrient uptake by diazotrophs will only be limited by either Fe or PO_4 (dinitrogen is freely available for nitrogen fixation). In this configuration of NutGenIE, Fe is the PLN for diazotrophs across 93 % of the surface ocean, with PO_4 being the PLN in the remaining 7 %. The areas where PO_4 acts as the PLN for diazotrophs are restricted to the northern hemisphere and are the Atlantic Ocean from 15° N to 40° N; the Mediterranean Sea; and a section of the Indian Ocean from the equator to 30° N.

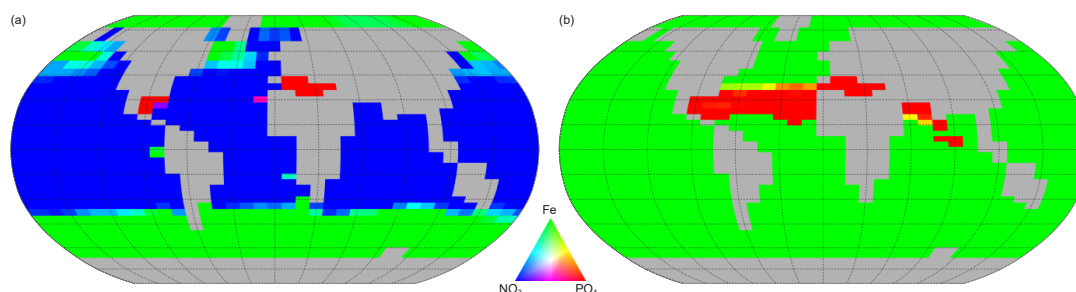


Figure 15 Spatial variation of the limiting factor for nutrient uptake (a proxy for phytoplankton growth in NutGenIE). For (a) other phytoplankton and (b) diazotrophs (will not be limited by NO_3 as nitrogen is considered freely available via fixation). Red = PO_4 limitation, green = Fe limitation, blue = NO_3 limitation.

Figure 15 shows the limiting nutrient in each surface cell, in addition, supplementary figures providing the calculated limiting value for each nutrient are available in Fig. S46 to S49.

The additional diagnostic tools that have allowed the spatial variations in the limiting factors (Fig. 14) and PLN (Fig. 15) to be visualised are also reassuring. Given the proposed use of this configuration of NutGenIE to investigate long term nutrient limitation of PP it is important that the spatial variations are realistic. Mahowald et al. (2017) (see Fig. 3 therein) produced schematic distributions of factor and nutrient limitation for differing phytoplankton classes. The results of NutGenIE compare well to the schematics of Mahowald et al. (2017).

4.3 The ULN and future work

The flexibility NutGenIE model allows for different continental configurations alongside varying atmospheric conditions that would allow investigations of the impact of nutrient supply on PP in paleo-worlds scenarios (e.g. Wilson et al., 2018). NutGenIE would also facilitate experiments or simulations that consider differing nutrient input fluxes and or residence times or differing nutrient requirements of phytoplankton.

Earlier we considered the distinction between the PLN and the ULN for oceanic PP. The limitations of previous work to identify the ULN have also been discussed along with required characteristic of any model intended to investigate the ULN (Sect. 1.3). Aspects relating to the biogeochemical cycles of NutGenIE and the ability to represent reality are summarised above. However, two additional critical aspects when investigating the ULN were detailed in Sect 1.3, the importance of an open system model and for model run times to considerably exceed the residence times of all nutrients. The open nutrient cycles have been detailed in Sect. 2.3 and NutGenIE model runs in excess of 100 kyr are feasible. NutGenIE run times indicate simulations of 100 kyr would complete within a two-week duration.

Comparisons between NutGenIE and real ocean data (encompassing physical processes, nutrients, and BGC processes) have been made and in each case the comparisons indicate that as configured here NutGenIE is a suitable tool for the study of the ULN question. The proposed use here is to consider the limiting influences that nutrients have on ocean PP over the long term, therefore realistic surface nutrient concentrations are vital. Surface nutrient concentrations are influenced by both physical and BGC processes, hence the relevance in reviewing those aspects. The NutGenIE model as configured here is representing Earth's oceans (area of $\sim 361 \times 10^{12} \text{ m}^2$, volume of $\sim 135 \times 10^{16} \text{ m}^3$) by a 36×36 grid with 16 depth levels. This level of abstraction will not be able to accurately reproduce the complexities of ocean processes; it is however important that the most relevant processes are included with sufficient detail. Therefore, we have focused on whether a good representation rather than a perfect replication of the oceans has been obtained.



5 Conclusions

Our motivation has been to create a model, NutGENIE, that can be used to investigate the ULN for oceanic PP for the nitrogen, phosphorus and iron cycles. A key development has been to ensure that the modelled iron cycle is realistic by including a dynamic ligand mechanism. We have conducted an extensive validation of biogeochemical aspects of NutGENIE by comparing
750 pertinent tracers to real ocean observations in both surface waters and the ocean interior. This review has highlighted areas of discrepancies but, more importantly, supports the fact that, overall, NutGENIE reflects the processes and state of the ocean with a high degree of accuracy. Statistical comparisons of NutGENIE properties to ocean observation have provided strong evidence that this configuration of NutGENIE is suitable to conduct the planned nutrient limitation analysis. We believe these validations support the suggestion that NutGENIE can be used for that purpose and to investigate other questions related to the
755 role of nutrients on oceanic biogeochemical processes.

The primary motivation behind establishing this configuration is to analyse the long-term influence of nutrient limitation on oceanic PP and we conclude that NutGENIE, as configured and evaluated here, can support such a study. This configuration of NutGENIE can also be useful in the analysis of the dynamics of nutrient supply and oceanic PP in past, present or future scenarios.

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Code availability

Code and data are available via a zenodo repository. The draft version for review purposes can be accessed at https://zenodo.org/records/14766197?preview=1&token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6IjRhYTlIMWlwLTQzMdctNDAwMy05MDE2LTM4YmMyMDAzNWFiNSIsImRhdGEiOnt9LCJyYW5kb20iOiIzMzkzMDg1Zjg1MzFkYjU5MzBmNDdkMjlxOWZlZW10Sj9rByAMfulbvDCoAAAdCmbmSP_eRveQ8zPelBdVbAXPkfcEtDQfgIwJnqzot9zNyLtHv_NX0vSKmJil6eSvK7oYw

Data availability

Code and data are available via a zenodo repository. The draft version for review purposes can be accessed at https://zenodo.org/records/14766197?preview=1&token=eyJhbGciOiJIUzUxMiJ9.eyJpZCI6IjRhYTlIMWlwLTQzMdctNDAwMy05MDE2LTM4YmMyMDAzNWFiNSIsImRhdGEiOnt9LCJyYW5kb20iOiIzMzkzMDg1Zjg1MzFkYjU5MzBmNDdkMjlxOWZlZW10Sj9rByAMfulbvDCoAAAdCmbmSP_eRveQ8zPelBdVbAXPkfcEtDQfgIwJnqzot9zNyLtHv_NX0vSKmJil6eSvK7oYw

Author contribution

DS developed the model and conducted the analysis with input from all authors. All authors wrote the manuscript.

Competing interests

Some authors are members of the editorial board of journal Geoscientific Model Development. The authors have no other competing interests to declare.

Disclaimer

Acknowledgements

The authors acknowledge and thank the entire cGenIE development community. These model enhancements have depended on the contributions of others in maintaining and developing the cGenIE model. The model enhancement developments and simulation executions were carried out on the University of Bristol's Sprout cluster, for which the authors are grateful for the provision and management. The validation work relied on datasets provided by World Ocean Atlas, GEOTRACES, and the Oregon State University Ocean Productivity group. The authors thank those groups and acknowledge their efforts in providing these datasets

D. A. Stappard was supported in this work by the Natural Environmental Research Council [grant number NE/S007210/1]. For the purpose of open access, the author has applied a CC BY public copyright licence to any Author Accepted Manuscript version arising from this submission.

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