The marine nitrogen cycle: new developments and global change

David A. Hutchins ✉ *and Douglas G. Capone* ✉

Abstract | The ocean is home to a diverse and metabolically versatile microbial community that performs the complex biochemical transformations that drive the nitrogen cycle, including nitrogen fixation, assimilation, nitrification and nitrogen loss processes. In this Review, we discuss the wealth of new ocean nitrogen cycle research in disciplines from metaproteomics to global biogeochemical modelling and in environments from productive estuaries to the abyssal deep sea. Influential recent discoveries include new microbial functional groups, novel metabolic pathways, original conceptual perspectives and ground-breaking analytical capabilities. These emerging research directions are already contributing to urgent efforts to address the primary challenge facing marine microbiologists today: the unprecedented onslaught of anthropogenic environmental change on marine ecosystems. Ocean warming, acidification, nutrient enrichment and seawater stratification have major effects on the microbial nitrogen cycle, but widespread ocean deoxygenation is perhaps the most consequential for the microorganisms involved in both aerobic and anaerobic nitrogen transformation pathways. In turn, these changes feed back to the global cycles of greenhouse gases such as carbon dioxide and nitrous oxide. At a time when our species casts a lengthening shadow across all marine ecosystems, timely new advances offer us unique opportunities to understand and better predict human impacts on nitrogen biogeochemistry in the changing ocean of the Anthropocene.

Research into the marine nitrogen cycle has a long history, dating back to the late 1800s and the first scientific consideration of the role of the ocean in the global processing of nitrogen and the regulation of phytoplankton production[1]. Subsequent research in the early 1900s focused on the stoichiometry of nitrogen uptake and regeneration (relative to phosphorus)[2] and on the identification of the various microorganisms involved in the limited number of nitrogen cycle reactions then recognized in the ocean[3].

Major components of the marine nitrogen cycle had been discovered by the mid-1900s, including the uptake of inorganic forms by phytoplankton, the oxidation of reduced inorganic forms such as ammonia and nitrite by bacterial chemoautotrophs termed nitrifiers, and the reduction of nitrate to nitrogen gas by denitrification (FIG. 1). The importance of other aspects of the nitrogen cycle in marine systems, such as nitrogen fixation (well established by that point as an important process in terrestrial environments)[4], remained to be resolved. Many advances in understanding marine nitrogen cycle biochemistry and biogeochemistry owed a large debt to early work using cultures or enrichments, often from wastewater samples or soils[5,6]. Moreover, novel pathways were yet to be discovered, as was the high phylogenetic diversity of microorganisms in all nitrogen cycle processes (FIG. 1), all of which are covered in this Review.

Despite this early progress, the modern era of marine nitrogen cycle research awaited the development of effective means of quantifying nitrogen cycle pathways using enzymatic and isotopic approaches as well as parallel advances in analytical instrumentation such as mass spectrometry and gas chromatography. Most recently, the infusion of molecular biological techniques into the field has fuelled a revolution in discerning the true biodiversity, distributions and functions of microorganisms involved in the ocean nitrogen cycle. Indeed, over the last several decades, we have discovered entirely new reactions, the involvement of microbial taxa in pathways that we had not suspected, and nitrogen cycle functions occurring in diverse and unexpected habitats (FIG. 1).

Historically, oceanographic observations have been highly constrained by the availability of ships, particularly in the open ocean. Vast areas of the sea remain chronically under-sampled both in time and space. However, another revolution is ongoing as the seascape of data on marine nitrogen cycling is now rapidly increasing. This is happening through a combination of satellite and drone-based remote sensing, autonomous samplers with advanced sensors (for example, biogeochemical Argo drifters)[7,8], and

Marine and Environmental Biology, University of Southern California, Los Angeles, CA, USA.

✉*e-mail: dahutch@usc.edu; capone@usc.edu*

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Haber–Bosch process
The industrial chemical process whereby ammonia for agricultural fertilizer is produced directly from hydrogen and nitrogen gas.

the substantial expansion of sampling on both oceanographic vessels (for example, the Tara Oceans project)[9] and ships of opportunity (for example, the Global Ocean Ship-based Hydrographic Investigations (GO-SHIP) repeat hydrography programme)[10,11].

Human agency has both direct and indirect effects on nitrogen biogeochemistry in the ocean. Probably the biggest direct anthropogenic change to the nitrogen cycle is through the release of nitrogen fertilizer produced by the Haber–Bosch process[12,13]. At the same time, marine nitrogen biogeochemistry is also responding to both first order (ocean acidification and warming) and second order (upper ocean stratification and deoxygenation) effects of climate change[14]. In this rapidly changing ocean environment, there is a pressing need for fresh perspectives on how the nitrogen cycle is adapting and evolving, and the implications of those responses for ocean biology and resources.

In this Review, we explore novel advances in marine nitrogen cycle concepts, methods, pathways and observations, with an emphasis on pelagic marine ecosystems. We conclude by considering open questions, future research directions and the developing opportunities that may help us to illuminate the shifting shape of the nitrogen cycle in the future changing ocean.

Nitrogenous nutrient uptake and assimilation

Perhaps the most studied and best understood aspect of marine nitrogen cycling is the uptake of nitrogenous nutrients by phytoplankton[15] (FIG. 1), going back to Hensen who pondered the relationships between nutrient distributions in the upper ocean and phytoplankton assemblages[1]. Nonetheless, there remain surprises to be uncovered. It has long been recognized that, in addition to inorganic forms of nitrogen such as nitrate and ammonia, small organic molecules such as urea are potential substrates to satisfy phytoplankton nutritional nitrogen demands[16]. Recent efforts have applied stable isotope probing methods to understand the importance of specific functional and phylogenetic

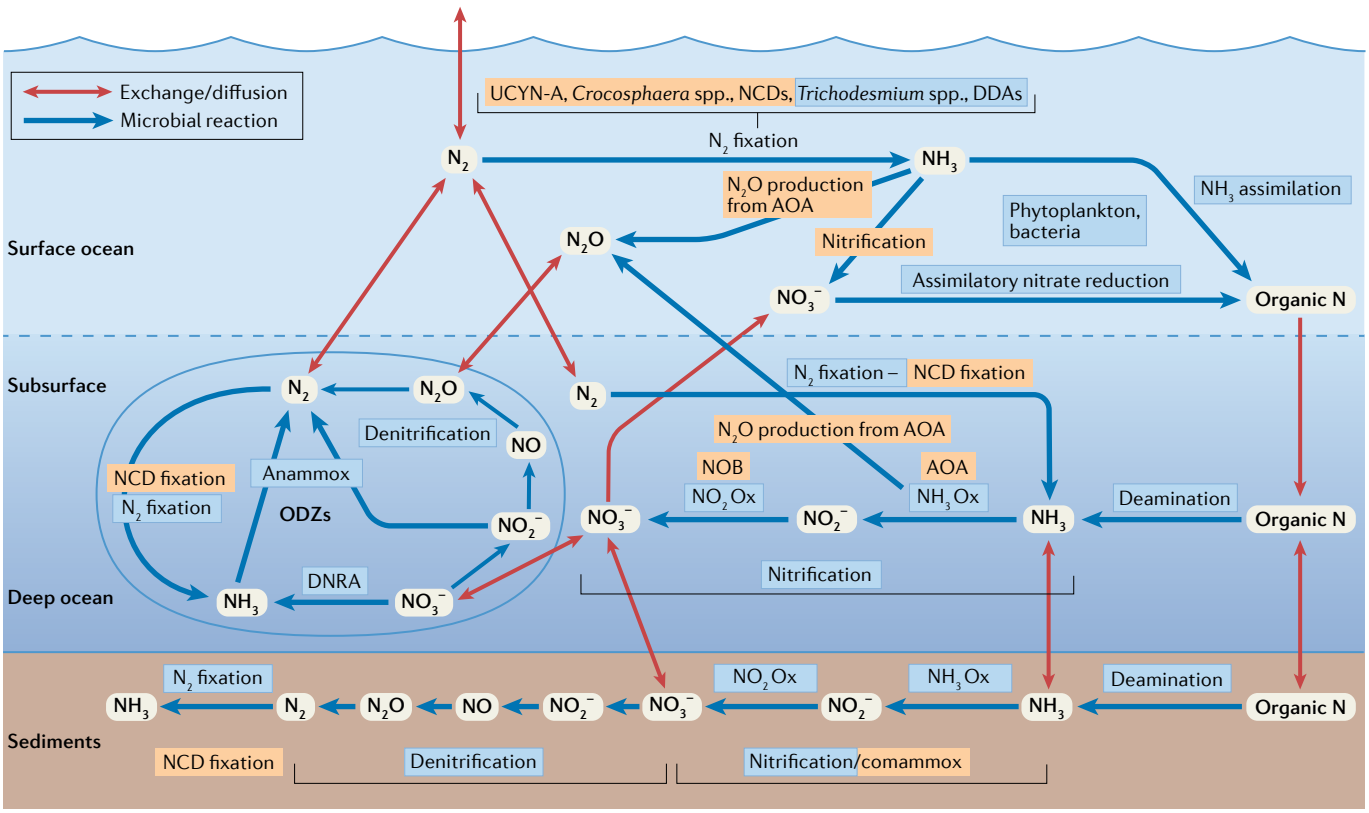

Fig. 1 | **The marine nitrogen cycle.** The figure highlights new and recently recognized features and players. Red arrows indicate transfers or exchanges. Blue arrows indicate microbial transformations and are not intended to be quantitative with respect to size. Labels in orange indicate relatively recent discoveries of new groups or of novel aspects within known groups of nitrogen-transforming microorganisms. For organizational simplicity, four ocean realms are represented: (1) the upper sunlit (photic) ocean, typically the upper 100 m or less, where photosynthesis occurs along with assimilatory processes such as nitrogen fixation, nitrate reduction and ammonia uptake; (2) the subsurface aphotic and largely oxic water column down to the deep sea, where heterotrophic nitrogen-regenerative (for example, deamination) and chemoautotrophic pathways, such as nitrification, predominate; (3) the anoxic water column pockets or O_2-depleted zones (ODZs), where anaerobic metabolic pathways, such as dissimilatory nitrate reduction, denitrification and anammox, predominate; and (4) the benthic or seafloor environment. In shallow coastal areas, the benthic environment intersects the photic zone with a similar array of processes to the photic water column. However, most of the ocean's benthic environments are aphotic and dominated by heterotrophic and chemoautotrophic processes. Where the organic flux to the sediments is high (for example, on continental shelf sediments), O_2 diffusing into the sediments is rapidly consumed and depleted, and anaerobic processes predominate. AOA, ammonia-oxidizing archaea; DDA, diatom–diazotroph association; DNRA, dissimilatory nitrate reduction to ammonia; NCD, non-cyanobacterial diazotroph; NOB, nitrite-oxidizing bacteria; Ox, oxidation; UCYN-A, unicellular cyanobacteria group A.

Cyanate
An anion consisting of a C atom tripled-bonded to an N atom and single-bonded to an O atom in a linear configuration.

Diazotrophs
Organisms that are capable of fixing atmospheric N_2 gas into bioavailable ammonia.

Cosmopolitan
A descriptor for a group of organisms that is universally distributed across a range of environments.

Coccolithophorids
A group of unicellular, photosynthetic phytoplankton in the division Haptophyta, with cells that are covered by overlapping calcium carbonate plates or 'coccoliths'.

Combined nitrogen
Inorganic forms of soluble nitrogen that are covalently bonded to other elements (typically O or H), including the highly bioavailable compounds nitrate, nitrite and ammonia.

groups to nitrogenous substrate uptake in the upper water column[17]. New evidence indicates that cyanate can also be an important substrate for phytoplankton in certain systems[18].

Nitrogen fixation

Marine nitrogen fixers (diazotrophs) provide an irreplaceable lifeline to marine ecosystems through their unique ability to convert atmospheric N_2 gas, which is inaccessible to most organisms, to bioavailable nitrogen in the form of NH_3 (FIG. 1). In oligotrophic environments, nitrogen fixation can supply up to 50% of the new (or exogenous) nitrogen entering the system[19] and, at global scales, it accounts for 100–200 Tg N per year[20], offsetting losses by nitrogen removal processes.

Diazotrophy relies on the prokaryotic enzyme nitrogenase, which is easily inactivated by O_2 and so requires cellular protective strategies in aerobic environments. Nitrogenase has an extraordinarily high catalytic iron requirement[21]; therefore, diazotrophy is often limited by this essential trace metal in the open ocean. In regimes with higher iron inputs, such as the North Atlantic[22], phosphorus can also limit marine nitrogen fixation. Important diazotrophs in the ocean include a number of free-living and symbiotic cyanobacteria groups as well as some non-photosynthetic diazotrophs (termed non-cyanobacterial diazotrophs (NCDs)) (FIG. 1). The central role of nitrogen fixation in ocean biogeochemistry means it has long been a priority research focus for marine microbiologists, and it continues to be a very active area of research, with recent advances ranging from the molecular to the global scale[20,23].

Nitrogen-fixing microorganisms. One of the major recent advances has been the discovery of a cyanobacterial symbiotic association as a predominant component of upper ocean diazotrophic communities (FIG. 1). Unicellular cyanobacteria group A (UCYN-A) were first detected in molecular analyses of samples from Station Aloha near Hawaii[24]. Subsequent research shows that they are cosmopolitan and found in a range of surface waters, from the nutrient-poor tropics to the polar regions[25,26]. The cyanobacteria are photoheterotrophic symbionts of a eukaryotic prymnesiophyte alga closely related to coccolithophorids[27,28], and the metabolic cycles of the partners in the symbiosis are interdependent[29]. Very recent evidence indicates that, although the distribution of UCYN-A overlaps somewhat with that of the well-studied filamentous cyanobacterium *Trichodesmium* spp., they often occupy separate ecological niches[30–32]. The long-familiar *Trichodesmium* genus (FIG. 1) still offers new surprises too as metagenomic studies have recently revealed the unexpected finding that broadly distributed non-diazotrophic species co-exist with diazotrophic forms[33], as was hinted at by an earlier study[30].

Other microbial diazotrophic symbiotic associations have been long been recognized in the pelagic tropical ocean. These include diatom–diazotroph associations between the heterocystous cyanobacterium *Richelia intracellularis* and certain oligotrophic diatoms such as *Rhizosolenia* and *Hemiaulus*[34] (FIG. 1). A diatom–diazotroph association between a rhopalodiacean diatom and a small, spherical diazotrophic non-photosynthetic cyanobacterium was first discovered in a freshwater system[35] but has now been reported to also occur in the sea[36].

The role of heterotrophic and chemoautotrophic nitrogen fixers (NCD groups) has also been a subject of much research[37,38], particularly with regard to their contribution to aphotic zone activity[39,40]. Sequences of NCD *nifH* genes (which encode a nitrogenase subunit) have been obtained from diverse pelagic marine environments globally[41] and transcription of NCD genes has been reported[37]. Emerging data sets from recent global expeditions are revealing geographical patterns of diazotroph abundances and the identity of particular NCDs such as the Gamma-A group, which are most abundant near the surface and in size fractions up to 20 µm (REFS[42,43]). These results are consistent with recent modelling efforts indicating that NCDs in the water column may be largely particle associated[44]. Methodological limitations remain with identifying the broader range of bacterial or archaeal NCD groups or measuring and correlating their absolute abundance and nitrogen fixation rates. Single-cell analyses, such as those recently applied to cyanobacterial diazotrophs[45,46], may help to better resolve the role and quantitative contribution of NCDs to marine diazotrophy[37,47]. Group-specific estimates of N inputs on larger scales may lack consideration of NCD contributions but geochemically derived estimates should include and integrate the contribution of NCDs[23]. This is because these basin-scale and global-scale calculations do not rely on quantifying functional groups but are based on spatial gradients of stoichiometric deviations from average regeneration ratios of inorganic N and P (REFS[48,49]) or on N natural isotope abundance[50].

Marine environments. One pelagic environment that has been receiving special attention with regard to the importance of NCDs are the O_2-depleted zones (ODZs; those areas where nitrate is the predominant electron acceptor)[51] of the world ocean such as the Arabian Sea, Eastern Tropical North Pacific (ETNP)[52] and Eastern Tropical South Pacific (ETSP)[53,54] systems. Globally, ODZs are expanding in volume as a result of climate change[55]. These regimes represent ideal environments for nitrogen fixers as reduced O_2 levels benefit the O_2-sensitive nitrogenase enzyme. At the same time, low combined nitrogen (that is, nitrate, nitrite and ammonia) concentrations due to elevated removal processes make diazotrophy a highly favourable ecological niche.

Nitrogen fixation has also been extensively examined in a wide range of benthic environments, including seagrass meadow[56] and coral reef[57] ecosystems. Symbiotic associations with chemoautotrophic diazotrophs have been discovered in lucinid clams in seagrass communities[58] and in cold water corals[59]. A specific association between the tropical seagrass *Posidonia oceanica* and a gammaproteobacterium that occurs in high densities in its roots has very recently been discovered[60]. Exciting recent work has identified cold seeps, whale falls and deep sea sediments in general as sites of active and diverse diazotrophic populations[45,61].

Tow-Fish
An oceanographic method whereby a pumped seawater sampling intake system is towed behind a research vessel at a controlled depth and speed.

Methodological advances. An ongoing challenge has been the quantification of nitrogen fixation rates as well as the distributions of diazotrophs in the upper ocean based on spatially and temporally limited field observations. Advances in old methodologies and the introduction of new approaches are improving the relatively low resolution of traditional shipboard sampling techniques, enabling the identification of diazotrophic assemblage compositions and their quantitative contributions to new nitrogen supplies. The recent global surveys mentioned above have steadily improved our understanding of the biogeographical distributions of major groups of near-surface diazotrophs at both regional and global scales[11,36,62]. Indeed, nitrogen fixation occurs in a much broader array of environments than traditionally thought, including coastal waters[63,64] and higher latitudes[26].

Several issues have been indicated with the standard $^{15}N_2$ uptake approaches, including contaminated stocks of commercial $^{15}N_2$ gas[65] as well as concerns about underestimating nitrogen fixation rates due to slow dissolution of $^{15}N_2$ when added as a bubble[66] while assuming rapid and complete dissolution. However, most current practitioners measure dissolved $^{15}N_2$ enrichments directly using membrane inlet mass spectrometry[32,39], eliminating this problem.

High-throughput molecular methods for characterizing DNA phylogenies and the abundance and transcription of diazotroph-specific *nifH* genes are now available and are being applied over broad regional geographic ranges[63,67] (FIG. 2). In parallel, shipboard procedures for underway determination of nitrogen fixation rates have been developed[68] and deployed using a Tow-Fish together with a system to analyse *nifH* genes and certain nutrient stress genes by quantitative PCR and gene transcript analysis[63,67] (FIG. 2). Molecular biology approaches have also been adapted to autonomous platforms, such as the Environmental Sample Processor, allowing automated sampling of diazotrophic populations[69].

Rapidly progressing molecular advances have enabled unprecedented recent insights into the hidden regulatory mechanisms underlying diazotrophy in the ocean. For instance, in situ assessment of the factors limiting nitrogen fixation is being aided by the application of transcriptomics to metabolic pathways linked to diazotrophy[32]. Nutrient limitation biomarker abundances in North Atlantic metaproteome data sets have shown that *Trichodesmium* spp. experience chronic Fe and P co-limitation in this region[32,70].

Remote sensing is also contributing to an expanded understanding of the distribution of nitrogen fixation in the upper ocean. The ability to discriminate certain cyanobacterial diazotrophs, such as *Trichodesmium* spp., in the surface ocean from their signature pigments and characteristic high reflectance[71] has allowed satellite mapping of surface blooms over broad spatial and temporal scales[72,73]. Deployment of spectroradiometers, fluorometers and other sensors on remote-control aerial vehicles is opening up a new dimension of remote sensing capabilities[74].

Data streams from all of these many and diverse sources have increased exponentially in the past decade. These inputs have been incorporated into ecosystem models with explicit representations of diazotrophs and their contributions to nitrogen fixation[75,76]. This, in turn, has greatly improved our understanding of diazotroph distributions in the current ocean[77] and the key factors determining their biogeography[49,78]. Models have

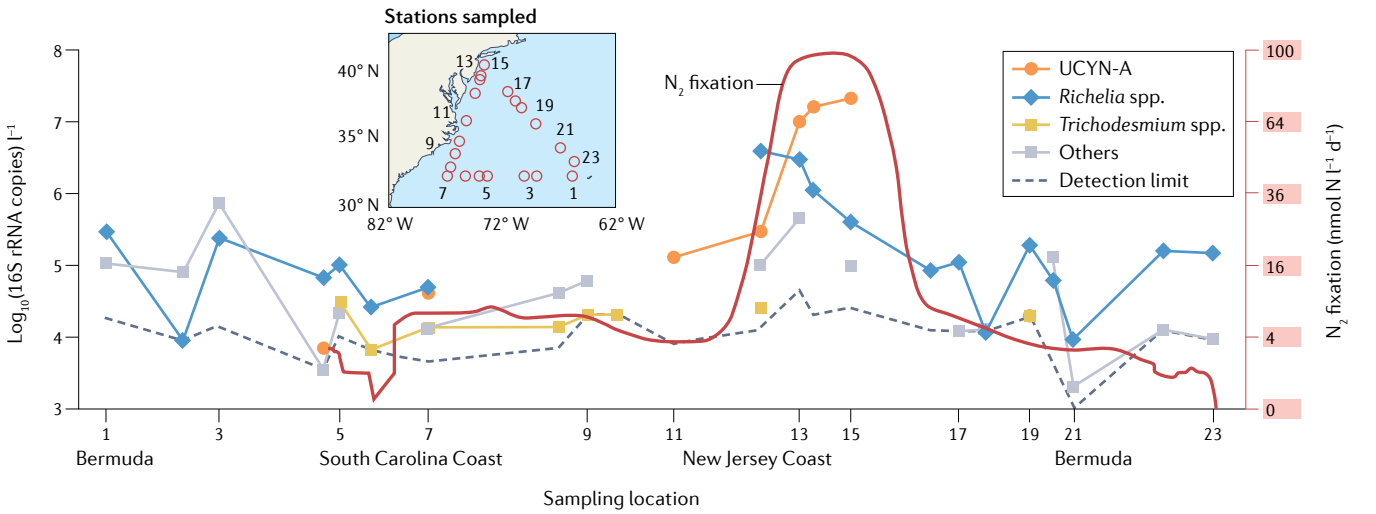

Fig. 2 | **Nitrogen fixation rates and abundance of dominant diazotrophs in coastal and open ocean regimes of the northwest Atlantic Ocean.** Integrated daily measurements of surface water shipboard underway sampling for whole community nitrogen fixation rates are shown in red. Cyanobacterial N_2-fixing groups quantified using 16S rRNA amplicon sequencing include the free-living colonial *Trichodesmium* spp. (yellow), the photoheterotrophic phytoplankton symbiont unicellular cyanobacteria group A (UCYN-A; orange), and the photosynthetic symbiont *Richelia intracellularis* found in diatom–diazotroph associations (blue). The 'Others' category (grey) includes several genera of heterotrophic proteobacterial diazotrophs collectively known as non-cyanobacterial diazotrophs. The dotted line indicates the limit of detection for diazotrophs and their hosts. By using a novel combination of real-time underway analyses of nitrogen fixation rates and rapid shipboard determinations of taxon-specific gene abundance, fine-scale shifts in diazotrophic community structure and new nitrogen inputs can be compared in unprecedented detail. Adapted from REF.[67], CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

also allowed us to make more informed basin-scale and global-scale estimates using biogeochemical proxies based on N to P stoichiometries and isotopic mass balances of the natural abundance of ^{15}N in relevant pools (for example, N_2, NO_3 and particulate organic N)[79] as well as offering predictions of how nitrogen fixation may change in the future ocean[80,81].

Nitrification

Nitrification is a two-step process that transforms fully reduced nitrogen (NH_3 or NH_4^+) into to a completely oxidized form (NO_3^-), and so ultimately controls the availability of nitrate, the nitrogen source that is usually most available to marine phytoplankton. The chemolithoautotrophic, exclusively prokaryotic nitrification process begins with the oxidation of ammonia to nitrite. In the open ocean, this is carried out mostly by ammonia-oxidizing archaea (AOA) (FIG. 1). In addition to ammonia, it has recently been shown that some AOA can also use urea, cyanate and polyamines as substrates for energy and/or growth[82,83], thus expanding the repertoire of reduced nitrogenous substrates they can exploit as well as their role in dissolved organic nitrogen cycling. Nitrite-oxidizing bacteria (NOB) are primarily responsible for the subsequent oxidation of nitrite to nitrate in the oxic ocean[84] (FIG. 1). The main marine nitrite oxidizers are members of the phylum Nitrospinae[83], whereas other NOB groups are diverse but much less abundant.

Novel nitrifying microorganisms. Recently, comammox bacteria (*Nitrospira* spp.) that can fully oxidize ammonia to nitrate on their own (FIG. 1) have been found in marine wetlands, estuaries and coastal waters[85,86]. However, PCR-based and metagenomic surveys have so far failed to find comammox-specific genes in open ocean regimes[85,87]. The reason or reasons for the apparent inability of comammox bacteria to occupy this oceanic niche are presently unknown but could be related to competition with AOA and photoautotrophs for very low open-ocean concentrations of ammonia[85,88].

The metabolic diversity of some nitrite oxidizers has also been uncovered. Candidatus *Nitrotoga fabula*, isolated from activated sludge, prefers relatively high temperatures (>20 °C), has a unique nitrite oxidoreductase, tolerates high nitrite and nitrate concentrations, and can also use other electron donors such as H_2 and sulfite[89]. Studies examining the potential importance of the *Nitrotoga* clade in marine systems are ongoing[90,91].

Marine environments. Marine ammonia oxidation rates frequently peak just below the sunlit euphotic zone of the open ocean. This has led to past suggestions that AOA are directly inhibited by light, unable to deal with photochemically produced H_2O_2 due to a lack of catalase[92], or compete poorly for ammonia against phytoplankton in surface waters[93]. However, it is evident that AOA can be more abundant and active in the euphotic zone than previously thought[94,95]. Their presence can lead to rapid in situ cycling of regenerated nitrogen into oxidized forms, complicating estimates of new production based on the assumption that vertical advection is the primary or sole source of nitrate to phytoplankton communities.

Nitrification is among the most prominent biogeochemical processes in the dark mid-depths of the mesopelagic ocean[96] and ammonia oxidizers are the most abundant microbial functional group found in subsurface waters[96,97]. Less certain is how much of a contribution chemoautotrophy by the AOA and NOB found here makes to global oceanic CO_2 fixation and carbon sequestration. Estimates of the magnitude of global dark CO_2 fixation range from 1.2 to 11.0 Pg C per year (5–22% of the ocean's overall primary production budget) but, despite their abundance, AOA chemoautotrophy may account for only a relatively small fraction of this total (~2–9%)[98]. However, another estimate suggests that nitrite-oxidizing Nitrospinae NOB alone may be responsible for 15–45% of the total CO_2 fixation in the North Atlantic Ocean[99].

Nitrification and low O_2. The mesopelagic zone holds most of the ocean's low-O_2 waters in expansive ODZs. Perhaps surprisingly, recent work shows that this vast O_2-deficient mid-water habitat is a major stronghold of the obligately aerobic processes of nitrification[100]. Mesopelagic meta-omics surveys find that genes encoding the 3-hydroxypropionate or 4-hydroxybutyrate CO_2 fixation pathways used by AOA are most abundant around the periphery of ODZs. However, AOA are found in only low abundance within the anoxic core of ODZs[101], and substantial AOA-associated ammonia oxidation rates have rarely been reported here[102]. The reason for the presence of AOA in this environment is currently unknown.

By contrast, genes for the reductive tricarboxylic acid cycle employed by the nitrite-oxidizing bacterial phylum Nitrospinae are plentiful even in completely anoxic waters[103]. Recent metaproteomic evidence suggests that subunits of the key nitrite-oxidoreductase enzyme Nxr of Nitrospinae are hyperabundant proteins in ODZ environments, with enzyme copy numbers of more than 6×10^{10} per litre. As Nxr is an Fe-containing metalloenzyme, it may account for a large fraction of the particulate pool of this scarce micronutrient in ODZs[104] (FIG. 3). The highly abundant Nitrospinae from ODZs have not yet been obtained in pure cultures, and it is unclear how they remain active in the absence of O_2. In contrast to these low-O_2-adapted Nitrospinae, *Nitrospira* NOB isolated from oxic waters exhibit reduced yet appreciable nitrite oxidation rates when cultured at low O_2 levels. Under suboxic conditions, the abundance of their O_2-sensitive carbon fixation-related proteins and an oxidative stress-relieving superoxide dismutase both increase[105].

Together, these observations suggest that AOA and NOB have specific adaptations that allow them to couple ammonia and nitrite oxidation to autotrophy, even where O_2 is scarce to non-existent[106]. This ability may serve them well in an ocean where O_2 levels are rapidly declining and where future global expansion of ODZs is predicted[55,107]. This nitrifier attribute may imply a competitive interaction with anaerobic ammonium oxidation (anammox) bacteria (see below) and, along with alternative microbial metabolisms such as anaerobic nitrite oxidation[106], also has implications for the

Anammox
Anaerobic ammonium oxidation by chemoautotrophic bacteria of the phylum Planctomycetes, whereby nitrite and ammonium react directly to produce N_2 gas and water.

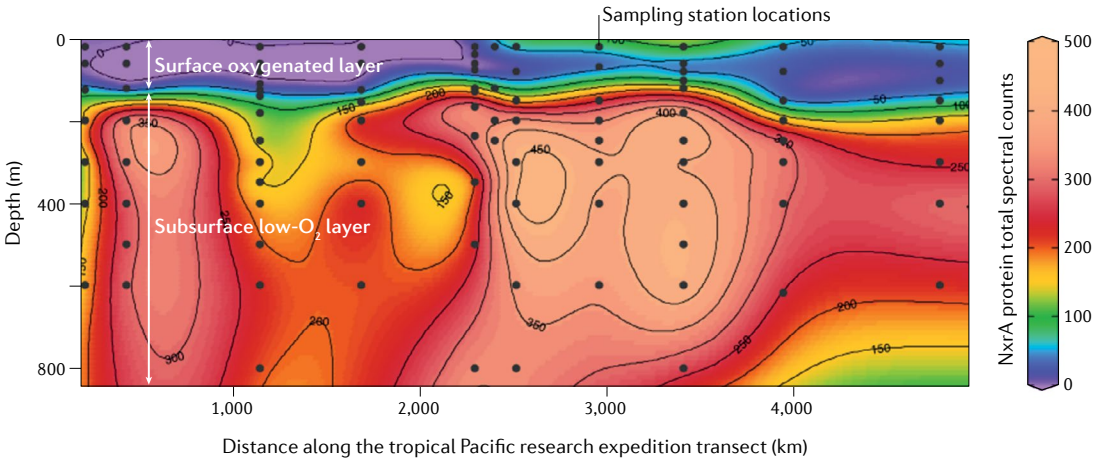

Fig. 3 | **Abundance of nitrite oxidoreductase proteins in low-O_2 subsurface waters of the Equatorial Pacific Ocean.** Shown are metaproteome total spectral counts of a protein subunit (NxrA) of the key enzyme that catalyses the oxidation of nitrite to nitrate by the nitrite-oxidizing bacterium *Nitrospina* spp. Warm colours denote higher spectral count abundance. Discrete metaproteome depth profile samples were collected from a research vessel at 11 stations down to 600–800 m (black circles) along a 5,000 km longitudinal transect across the tropical Pacific Ocean. NxrA subunit absolute abundances were determined by targeted metaproteomics using quadrupole-Orbitrap mass spectrometry and were plotted with data interpolation between stations using Ocean Data View. In this study, Nxr subunits constituted ~1.3% of the total protein measured in the 0.2–3.0 µm plankton size class, and they were the most abundant proteins detected in these mid-depth, low-O_2 open ocean waters. These results underscore the ecological dominance of nitrite-oxidizing bacterium throughout vast areas of the dark ocean and suggest that the iron-rich enzyme Nxr may account for a large fraction of the standing stock of this essential micronutrient here. Adapted from REF.[104], Springer Nature Limited.

maintenance of combined nitrogen stocks in low-O_2 environments.

Nevertheless, active nitrification requires at least trace levels of O_2, and it is not always clear what the source of this might be deep within ODZs. Nitrifiers may take advantage of a cryptic source of O_2 coming from photoautotrophs adapted to life in the dimly lit upper reaches of the ODZ, chiefly the ubiquitous tropical picocyanobacteria *Prochlorococcus* spp. However, this photosynthetically generated O_2 trickling down into the system never accumulates as demand by nitrifiers and other microaerophilic microorganisms consistently outstrips supply[108]. A recent study found elevated abundances of AOA and Nitrospinae NOBs in the upper ODZ of the ETNP, supported by O_2 produced by *Prochlorochoccus* spp. during autochthonous organic production within that layer[109]. New endogenous sources of O_2 from NO dismutation by bacteria of the NC10 candidate phylum[110,111] and even potentially by AOA within the ODZ[112] have been recently found.

An intriguing new discovery suggests that the first marine AOA to be cultured, *Nitrosopumilus maritimus* strain SCM1 (REF.[113]), produces both O_2 and N_2 when grown in the presence of nanomolar levels of O_2 (REF.[112]). The reaction, although not fully resolved, appears to involve NO and N_2O as intermediates, and the transformation of NH_3 all the way to N_2. This novel AOA pathway could be an unrecognized source of both N_2 and N_2O in low-O_2 regions, although indirect evidence suggests that the O_2 produced can also support substantial levels of ammonia oxidation. If AOA are capable of creating their own aerobic microenvironment for nitrification, this may help to explain how they thrive in the suboxic margins of ODZs. However, it also raises the following questions: why are AOA not doing the same thing in completely anoxic environments at the centre of ODZs, and what other capabilities may this unique metabolism provide for them?

Many of the diverse clades of NOB that have been detected along ODZ gradients, including fully anoxic zones[106], may also employ surprising metabolisms under suboxic conditions. For instance, in the absence of O_2, the NOB *Nitrococcus* spp. can grow heterotrophically while reducing nitrate (NO_3^-), apparently by reversing the nitrite (NO_2^-) oxidation reaction usually catalysed by NXR. Under low O_2 conditions, this NOB can also produce N_2O (REF.[114]).

Nitrogen loss pathways

Denitrification and anammox. Removal of inorganic forms of nitrogen used by planktonic organisms (nitrate and ammonia) occurs via two prokaryotic pathways. Conventional denitrification is the sequential reduction of nitrate, nitrite, nitric oxide and nitrous oxide to N_2 gas that is carried out by certain bacteria and even some eukaryotes and is used by these organisms as an alternative respiratory pathway when O_2 is depleted[115] (FIG. 1). Anammox, performed by specific chemoautotrophic planctomycete bacteria, oxidizes ammonia with nitrite, forming N_2 (REF.[116]) (FIG. 1). Recent findings indicate that anammox bacteria can also directly couple nitric oxide reduction to ammonia oxidation[117], and can also produce nitrate[118]. Both bacterial groups are widely distributed in ODZs and anoxic marine sediments, which have been the subject of much work on denitrification and anammox[115,119]. Early geochemical studies focused on nitrate deficits in these systems, and the results of more recent approaches based on measuring excess N_2

Autochthonous organic production
Primary production that occurs locally, within the environment being considered.

relative to argon seem consistent with these previous extrapolations[120]. New evidence also suggests that microbial organic oxidation rates[121] and nitrogen removal by denitrification[122] and anammox[123] may be enhanced in the sediments of some of the deepest parts of the ocean (the hadal zones, >5,000 m in depth).

Although not strictly a nitrogen loss pathway, dissimilatory nitrate reduction to ammonia (with nitrate being the electron acceptor) is used by many chemoorganotrophic bacteria[124], and can ecologically serve to retain combined nitrogen in ODZs or in anoxic sediments. There is evidence for the importance of this pathway in the ETSP[125], which could account for a substantial fraction of the NH_3 substrate for anammox. However, more recent studies found only low abundances of the key enzyme of the nitrite reductase pathway (NrfA, which catalyses the production of ammonia) in microbial populations of the ETNP[126], with rates below limits of detection in the ETSP[127].

Nitrogen losses and deoxygenation. Recent research has focused on the relative balance and role of denitrification and anammox in nitrogen removal in several major ODZs. Anammox is a substantial contributor to nitrogen removal in ODZs, such as the Benguela Current[128] and ETSP[125] regimes, whereas it has been suggested that denitrification is dominant in the Arabian Sea[129]. Variations in the relative importance of these two processes among and within ODZs may be a function of the intensity of seasonal supplies of organic carbon[129]. Other factors are likely the relative sensitivity of each process to O_2[130,131] and the differences in intrinsic growth rates and responses to environmental variables, including their respective substrates[129]. A recent modelling study provided a context for the oscillatory behaviour of denitrifiers and anammox bacteria in idealized ODZ systems[132].

As noted above, another group that is enriched in ODZs and whose activities may contribute to nitrogen removal processes is the NC10 bacterial candidate phylum, typified by *Methylomirabilis oxyfera*, which oxidizes CH_4 with NO_2 as a reductant, and the product NO is dismutated to N_2 and O_2 (REFS[110,133]).

Patterns of both short-term and long-term climatic variability in denitrification have been described in different systems. Detailed modelling studies of the Eastern Tropical Pacific have found that ODZ water column denitrification peaks during La Niña periods and is depressed during the El Niño phase of the El Niño Southern Oscillation cycle[134]. In the eastern Arabian Sea, two recent studies of shelf sediment cores show that water column denitrification appears to expand in volume and intensity during interglacial periods, and is strongly reduced during glacial periods[135,136].

Recent work shows that, although the Bay of Bengal in the Indian Ocean is suboxic, it does not yet seem to be a major sink for nitrate. Nitrogen gas production rates may be limited by the availability of nitrite[137]. Five years of data from profiling floats suggests that, although the Bay of Bengal is poised to become another major ODZ, high variability in O_2 concentrations may have overridden denitrification from becoming firmly established and precluded substantial nitrate losses to date[8].

El Niño Southern Oscillation cycle
La Niña and El Niño are alternate phases of the natural global climate cycle known as the El Niño Southern Oscillation, with contrasting global wind, precipitation and temperature trends.

Particles as nitrogen loss hotspots. Several studies have examined the role of particles in the water column in providing a low-O_2 environment for denitrifiers and anammox bacteria. In the ETNP, genes for denitrification are enriched in >30 µm particles in both oxic and anoxic zones, but anammox genes are not enriched. This is perhaps not surprising as, unlike anammox bacteria, many denitrifiers are facultative aerobes. For some genes, such as N_2O reductase (*nosZ*), that are associated with distinct phylotypes, specific homologs are associated with free-living forms whereas others are associated with particles. Patterns with other key genes associated with nitrogen cycle pathways occurring in ODZs have also emerged[126]. A modelling study that also considered the role of particles as an important niche for denitrification in the much greater volume of hypoxic waters (compared to anoxic ODZs) predicted that consideration of this habitat would double existing estimates of denitrification, which consider only ODZs[138]. Most recently, a study[139] found a strong correspondence between rates of anammox and small particles. Although anammox bacteria have generally been found to be free living[140], the particles likely provide a source of ammonia for the anammox reaction[139].

The future of the ocean nitrogen cycle

Marine nitrogen biogeochemistry has some surprising implications for human technological advances, resource harvesting, and even potentially for environmental remediation and mitigation strategies (BOX 1). Moreover, new research approaches are examining how anthropogenic stressors, such as sea surface warming and ocean acidification, affect the current marine nitrogen cycle. A primary goal of the rapidly developing field of ocean global change microbiology is to predict the trajectory of key biogeochemical cycles in a more extreme future ocean[141] (FIG. 4).

Microbial adaptation to global change. Laboratory experimental evolution methods developed in other microbiology disciplines[142] can help predict how marine microorganisms crucial to the marine nitrogen cycle may react to decadal-scale changes in ocean temperature and pH. These laboratory culture adaptation experiments have evaluated how nitrogen cycling by marine phytoplankton and cyanobacteria responds to selection by warming and high CO_2 levels over hundreds or thousands of generations. One study demonstrated permanent, constitutive upregulation of nitrogen fixation and growth rates in *Trichodesmium erythraeum* cell lines following several years of selection under high CO_2 levels[143,144], and these adaptive responses to simulated ocean acidification were linked to epigenetic DNA methylation changes[145]. A long-term study using a tropical diatom showed that N-replete cell lines evolved tolerance to stressful high temperatures, whereas N-limited cultures failed to adapt successfully[146]. Extended thermal selection experiments show that, to some extent, diatoms can adapt genetically and phenotypically to maintain fitness under projected future supra-optimal temperatures. This evolutionary self-rescue involves upward shifts in the thermal optimum and maximum temperature limits for growth[147].

Box 1 | **The marine nitrogen cycle in the service of humankind**

Nitrogen biogeochemistry is a crucial component of natural ocean ecosystems, but aspects of the marine nitrogen cycle can also be harnessed in various services to humankind.

Mariculture

With declining natural marine fisheries and the surging human demand for protein, marine aquaculture is undergoing considerable growth worldwide[186]. Mariculture can contribute to biomass, chemical feedstock[187] and fuel production. In nutrient-poor tropical areas of the ocean, microbial nitrogen fixation associated with farmed macroscopic protists (macroalgae or seaweed) and multi-trophic systems (macroalgae and shellfish) may provide an important nutrient subsidy to improve yields[20,23].

Biotechnology

Thermostable enzymes derived from marine sources are already used to power polymerase chain reaction (PCR) chemistry such as Deep Vent Taq (New England Biolabs). Similarly, a nitrogenase enzyme from a thermophilic, diazotrophic archaeon isolated from a deep sea hydrothermal vent[188] may provide a more efficient and lower temperature route for fertilizer synthesis[189] than the energy-intensive, high temperature and pressure Haber–Bosch process[13]. Other nitrogen cycle enzymes of marine microorganisms may also have potential biotechnological uses (for example, proteases and nitrate reductases).

Bioremediation and geoengineering

Human perturbation of the nitrogen cycle is substantial, and qualitatively different to that of the carbon cycle[12]. Properly deployed seaweed aquaculture can improve coastal water quality through the uptake and sequestration of excess nitrogenous nutrients[190]. Seaweed farmed for cattle feed can also reduce agricultural greenhouse gas emissions[191], including N_2O.

Recent research shows that marine diazotrophs are enriched in oil-contaminated sediments[192]. A hydrocarbon-degrading gammaproteobacterial diazotroph was isolated and found to be cosmopolitan in shallow, petroleum-exposed marine sediments[193]. Petroleum hydrocarbons have very high C to N ratios, and inorganic nitrogen enrichment has been required to stimulate hydrocarbon breakdown during previous bioremediation efforts[194]. Hydrocarbon-degrading diazotrophic bacteria may thus provide a useful tool for remediating accidental oil spills.

Ocean fertilization has been proposed as a potential strategy to mitigate increasing atmospheric and upper ocean CO_2 and decreasing surface ocean pH. Phytoplankton growth in many areas of the ocean is constrained by iron availability. Whereas high nutrient, low chlorophyll regions have residual unused nitrate and other macronutrients, other zones, termed low chlorophyll, low nutrient areas, do not[171]. Low chlorophyll, low nutrient regions have been suggested as a potential site for carbon sequestration through iron enrichment of nitrogen fixation[195]. However, strong concerns about the possible unintended environmental consequences of this approach have been voiced[196–198].

Notably missing, though, are published studies that address adaptation in microorganisms that carry out other vital nitrogen biogeochemical functions. For instance, long-term evolutionary responses to ocean environmental change by the bacterial and archaeal taxa that carry out denitrification, nitrification and diazotrophy (other than the cyanobacterium *Trichodesmium*) remain virtually unknown.

Nitrification and environmental change. How nitrifiers might react to a warmer and more acidic ocean has been tested using short-term acclimation time-scale field experiments with natural plankton assemblages. Shipboard incubations show that ammonia oxidation by planktonic nitrifiers in the ocean is frequently inhibited by experimental acidification, probably because unprotonated NH_3 (rather than NH_4^+, which is relatively more abundant at low pH) is the substrate for ammonia oxidation[148,149]. However, this seems inconsistent with the fact that cultured marine AOA typically have quite low optimum pH values for growth in the laboratory[150]. Incubations also demonstrate that ammonia oxidation by open ocean AOA communities can be strongly inhibited by warming, although additional ammonia inputs from sources such as atmospheric deposition may help to provide them with a degree of thermal resiliency[151].

N_2O production and consumption. N_2O is a greenhouse gas that is ~300 times more potent than CO_2 and also damages the ozone layer[152]. N_2O dynamics have been and remain an area of active research, particularly the relative contributions of nitrifiers[153] and denitrifiers to production, whether through nitrifier denitrification or incomplete denitrification[154,155]. Recent results indicate that otherwise aerobic microorganisms that experience transient anoxia (for example, at the edge of ODZs) may be more efficient at consuming N_2O than their neighbours in chronically anoxic zones[154,156].

Field experiments with natural AOA communities show that ocean acidification sometimes enhances incidental production of N_2O (REF.[157]) (FIG. 4). This study estimated that the declining ocean pH could increase N_2O released by nitrifiers in the Subarctic North Pacific by up to 491% at the end of this century. Another N_2O model predicted decreases of up to 7.7% in the upcoming century due to increasing stratification but, with a long-term expansion of ocean deoxygenation, N_2O flux would increase by ~21% over the next two millennia and result in a small positive feedback to climate change[158].

Nitrogen cycling and iron limitation. In general, nitrogen stress usually aggravates the damaging effects of both warming and acidification on phytoplankton[159–161]. This may be a function of the biochemical uses of nitrogen, which, as a major nutrient, is incorporated through covalent bonds into biomolecules. By contrast, rather than a structural element, iron is a micronutrient that is incorporated into enzymes and electron carriers, where it performs a catalytic role. Perhaps for these reasons, iron in marine microorganisms appears to interact quite differently with temperature than do major nutrients. For instance, in diazotrophic cyanobacteria, iron limitation is relieved rather than intensified as temperatures rise[162,163]. This may be because the substrate turnover rates of the enzymes for which iron serves as the catalytic co-factor tend to accelerate with temperature[13]. For N_2 fixers, this includes the exceptionally iron-rich nitrogenase enzyme complex[21]. The result is thus an overall increase in cellular iron use efficiencies (mols of N_2 fixed per mol of cellular Fe per day) with higher temperatures. This positive effect of warming on iron use efficiencies could allow future diazotrophs to thrive in iron-poor regimes such as the South Pacific, where they are currently largely excluded due to intense iron limitation[162,163].

Similarly, as temperatures rise, Antarctic diatoms of the genus *Pseudo-nitzschia* can use the very limited iron supplies available to them much more efficiently to grow. This suggests that they may deplete some of the currently unused nitrate in the warmer future Southern Ocean, regardless of whether or not iron supplies increase[22,164]. It thus seems likely that the consequences of sea surface warming for microbially driven biogeochemical

cycles may be very different in nitrogen-limited and iron-limited parts of the ocean.

Anthropogenic nitrogen enrichment. Ocean warming and acidification are accompanied by other anthropogenic stressors that can be equally disruptive to the marine nitrogen cycle. One example is the immense load of mostly agriculturally derived fixed nitrogen that is discharged directly into coastal ecosystems, particularly from the major rivers of Asia, Europe and North America, but also from other sources such as groundwater outflow[165] (FIG. 4). For instance, NO_3^- concentrations in the Changjiang (Yangtze) River estuary in China can exceed 100 µmol l^{-1} (REF.[166]), similar to levels found in nutrient-rich laboratory algal culture medium. Such artificial fertilization results in a proliferation of dense algal biomass, depleting the water of O_2 when the blooms inevitably senesce and decay[55]. This is the cause of the notorious hypoxic 'dead zone' that recurs annually outside the mouth of the Mississippi River, and which now often covers an area of up to ~20,000 km^2 or more in the northern Gulf of Mexico each year[167]. In fact, it has been estimated that ~75% of such fluvial nitrogen inputs ultimately reach the open sea[165].

Atmospheric deposition of anthropogenic nitrogen is perhaps even more consequential than coastal eutrophication due to the vast expanses of open ocean affected[165] (FIG. 4). Fossil fuel combustion and agricultural activities produce both oxidized (NO_2^- and NO) and reduced (NH_3) forms of nitrogen, and industrialization has increased these atmospheric emissions by up to 250%[168]. Downwind of major population centres in the north-western Pacific, deposition of pollution-derived aerosols is strongly correlated with increased surface ocean fixed nitrogen concentrations[169] and phytoplankton biomass and productivity[170]. However, these anthropogenic aerosols are highly enriched in nitrogen relative to phosphorus (molar N to P ratios of ~110, compared to ratios of ~16 required by phytoplankton), so formerly N-limited oligotrophic regions may be driven instead towards P-limitation[168]. Another potential impact is that high concentrations of toxic metals in air pollution particles can have direct inhibitory effects on the growth of marine microorganisms[170].

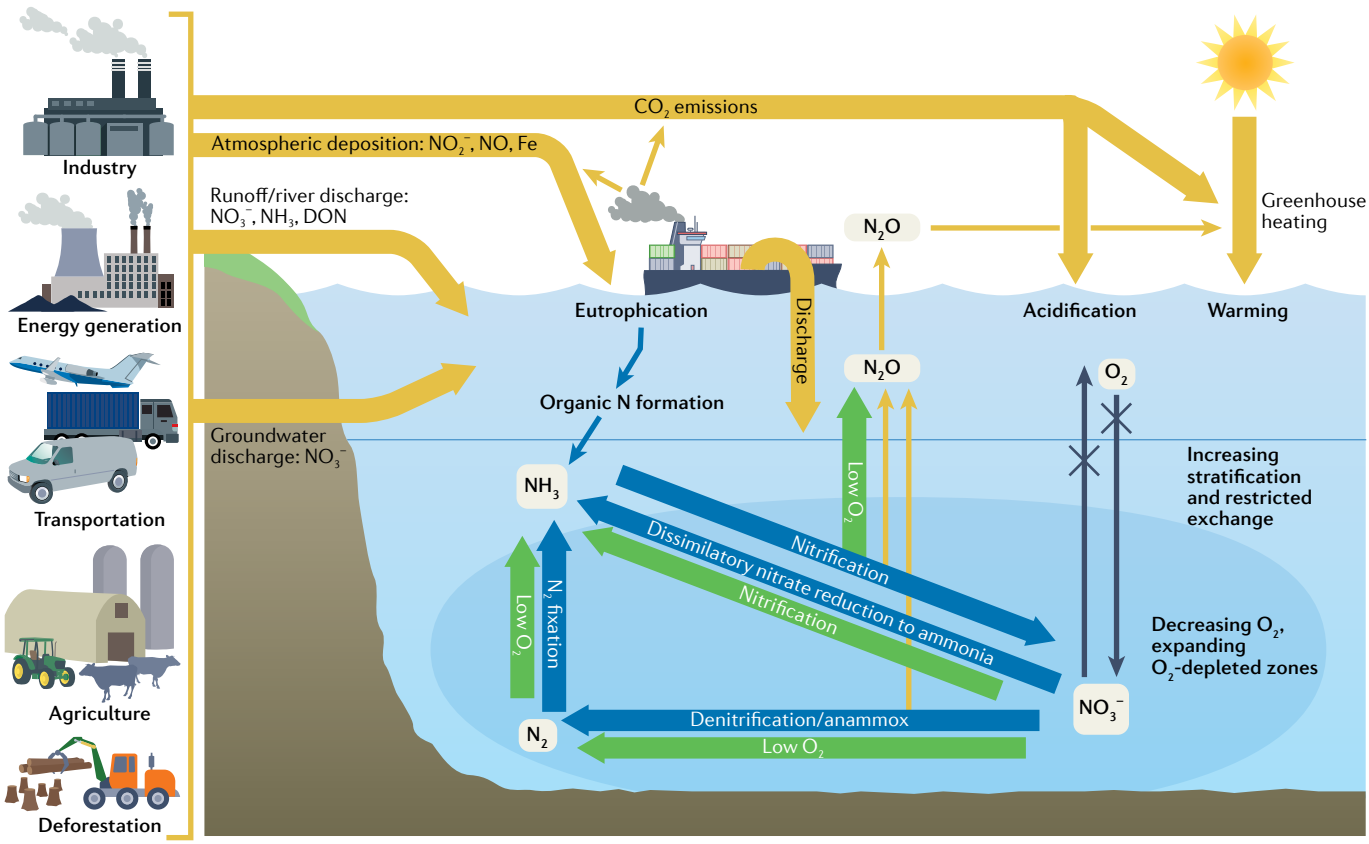

Fig. 4 | **Human impacts on the marine nitrogen cycle, including deoxygenation.** Yellow arrows show fluxes of oxidized and reduced nitrogen compounds including nitrate (NO_3^-), nitrite (NO_2^-), nitric oxide (NO), ammonia (NH_3), and dissolved organic nitrogen (DON) as well as iron (Fe), carbon dioxide (CO_2), and heat entering the ocean because of a range of human industrial, energy production, transportation, agricultural and deforestation activities. Also shown in yellow is nitrous oxide (N_2O) leaving the ocean as an indirect effect of anthropogenic deoxygenation. Effects on marine ecosystems with important consequences for the ocean nitrogen cycle include nutrient-driven eutrophication, followed by increased organic nitrogen production and subsequent subsurface deoxygenation (darker blue shading denotes these O_2-depleted zones). Other anthropogenic impacts affecting nitrogen biogeochemistry include ocean acidification and sea surface warming, with resulting intensified water column stratification (horizontal blue line). The latter process inhibits the vertically advected supply of nitrate to surface plankton communities (upward black arrow with X) and exacerbates subsurface deoxygenation by preventing downward mixing of O_2 (downward black arrow with X). Blue arrows represent key nitrogen cycle reactions; green arrows show which of these reactions or fluxes (for N_2O) are enhanced by lowered O_2 concentrations.

Changing iron supplies and the nitrogen cycle. Continental dust aerosols are the main natural source of bio-limiting iron for much of the open ocean. Across ~30–40% of the ocean in areas where dust supplies are scarce, nitrate and other nutrients accumulate unused in surface waters due to severe phytoplankton iron limitation (high-nutrient, low chlorophyll (HNLC) regimes)[171]. Ocean nitrogen biogeochemistry is therefore also very sensitive to accelerating atmospheric iron supplies from human activities. Climate change-driven drought and desertification along with suboptimal agricultural practices are predicted to substantially increase inputs of continental dust to much of the future ocean[22,168] (FIG. 4).

Coal, oil and biomass burning also release large amounts of iron-containing aerosols, and this iron can be far more soluble and bioavailable to marine microorganisms than iron bound within natural mineral dust[172]. Iron and lead isotopic evidence show that fossil fuel emissions now contribute 21–59% of the dissolved iron in North Pacific surface waters, suggesting that natural iron inputs to this region may have been increased by 27–143% owing to anthropogenic pollutants. This iron not only fertilizes the nearby oligotrophic ocean, but also likely allows iron-limited phytoplankton to draw down excess nitrate in the more distant Subarctic Pacific HNLC region[173] (FIG. 5). This raises the question of how much higher the standing stock of HNLC nutrients would have been in the north-western Pacific prior to industrialization.

Pyrogenic iron from forest and agricultural burning is particularly biologically labile, and may be a prominent remotely transported source to the Southern Ocean[174]. In this strongly iron-limited HNLC area where natural dust inputs are very sparse[175], these additional supplies from intensifying Southern Hemisphere deforestation could be substantial. In fact, new evidence suggests that pyrogenic iron deposited from the 2019–2020 Australian bush fires fertilized a massive phytoplankton bloom that covered a vast stretch of the usually unproductive South Pacific Ocean, and which fixed roughly the same amount of carbon dioxide released by the fires[176].

Simultaneous fertilization of the ocean by anthropogenic sources of nitrogen and iron pollution will thus have a profound influence on the marine nitrogen cycle. Additional iron supplies to oligotrophic regions should stimulate nitrogen-fixing cyanobacteria[22,172]. However, any concurrent anthropogenic fixed-nitrogen additions are likely to instead inhibit diazotrophy, thus cancelling out some of the net increase in community productivity expected from aerosol iron and nitrogen fertilization[165,168,177].

Ocean stratification. Future intensified ocean stratification due to surface warming and freshening is likely to reduce nutrient supplies to the euphotic zone[178]. The lowered availability of limiting nutrients will lead to diminished primary production and, consequently, to decreased nitrification rates and associated N_2O releases. As long as phosphorus and iron are not limiting, stratification and warming may also allow more nitrogen fixation, and may thus partially offset reductions in advective nitrogen inputs.

Ocean deoxygenation. Anthropogenic iron-containing and nitrogen-containing aerosol inputs are having a major impact on the overall O_2 balance of the ocean. Models predict a resultant increase in open ocean primary productivity, and thus enhanced deoxygenation and denitrification in the underlying waters where much of this carbon is respired[165,172,177] (FIG. 4). Along with warming-driven decreases in O_2 solubility, this ocean fertilization process may contribute to the steady decline in global ocean O_2 content that has been observed over the past half century[107,179].

The expansion of ODZs can also have strong feedbacks on global change processes. N_2O derived from both denitrification and nitrification is extremely elevated in and around oceanic ODZs[180,181], and N_2O production is inversely related to O_2 concentrations in cultured AOA[182]. In the ocean, any vertical fluxes of this greenhouse gas not consumed by microorganisms living in and above the ODZ vent into the atmosphere[156] (FIG. 4). The proclivity of AOA for living in the margins of ODZs means that they are likely to benefit from anthropogenic deoxygenation. Indeed, a specific AOA oligotype has been identified as a hypoxia specialist within the Gulf of Mexico dead zone[183].

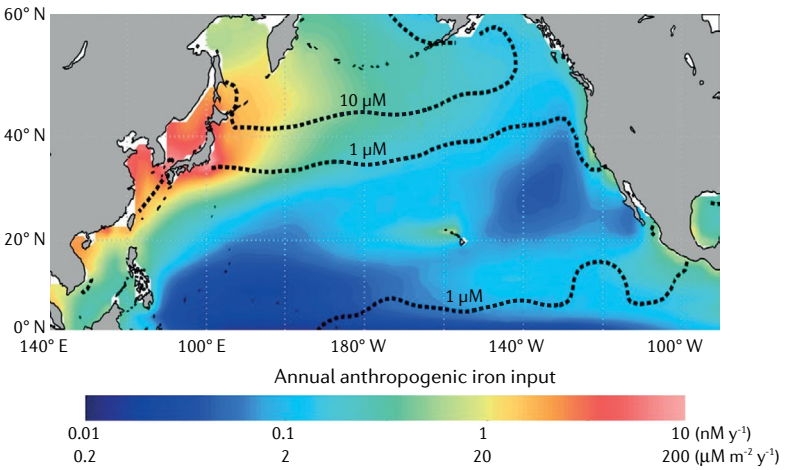

Fig. 5 | **Modelled annual anthropogenic iron supply and surface nitrate concentrations in the North Pacific Ocean.** Pollution-derived iron aerosol fluxes (warm colours) provide a major fraction (~one-quarter to one-half) of the dissolved concentrations of this biologically limiting micronutrient in this region. This artificially fertilizes iron-limited nitrogen fixers in southerly low-nutrient gyre waters as well as allowing iron-limited diatoms to deplete some of the otherwise unused nitrate present in the northerly Subarctic Pacific high nutrient, low chlorophyll area. Black contour lines show surface nitrate concentrations, illustrating the approximate boundaries of the iron-limited high nutrient, low chlorophyll region (>10 μM nitrate) and the oligotrophic North Pacific Central Gyre (<1 μM nitrate). Adapted with permission from REF.[173], PNAS.

Conclusions

The future of marine ecosystems is under threat as humans increasingly come to dominate the planet, and virtually every aspect of our industrial civilization has impacts on the ocean nitrogen cycle (FIG. 4). Biological cycling of this primary oceanic limiting nutrient is intimately linked to the cycles of carbon, iron, phosphorus and other nutrients; therefore, our many interferences with the Earth's other elemental cycles will

also inevitably affect how nitrogen moves through the marine biosphere. The breath-taking current pace of new discoveries in ocean nitrogen biogeochemistry comes at an opportune time as we face an urgent need to predict, mitigate and adapt to the consequences of these global anthropogenic perturbations.

How the various components of the marine nitrogen cycle will vary in the future, and the relationship of these changes to oceanic productivity, remain a challenge for upcoming research. However, specific efforts are currently under way to estimate and constrain these processes. Global fluxes of N_2O have been on the rise and are expected to continue, largely from agriculturally driven terrestrial sources[152]. Variation in the ocean source in the future remains to be resolved. Riverine nitrogen fluxes to the ocean have similarly and steadily increased with intensified fertilizer production and agricultural activity[184]. A study[81] considered an ensemble of models and climate scenarios within those models to predict trends in oceanic nitrogen fixation. Most projections anticipate a decrease in this process, but the variability amongst models was great, leaving a large uncertainty. Changes in oceanic iron deposition can also have direct effects on nitrogen cycling and, in particular, nitrogen fixation, which could be stimulated by increasing iron flux[172].

All of these complex, multivariate effects of environmental change on ocean food webs demand a much better understanding of how all the moving parts of marine microbial assemblages fit together. Recent ocean nitrogen cycling studies have repeatedly revealed the importance of previously unknown microorganisms, novel biogeochemical reactions and unsuspected biogeographic distributions, and we can certainly expect many more paradigm-breaking revelations in the future. For instance, the rapid rate at which new marine diazotrophic groups have been discovered during the past few years has forced a re-evaluation of our basic ideas about how, when and where nitrogen fixation occurs in the ocean. Likewise, the focus of much ongoing marine nitrification research has changed from the oxic to the suboxic ocean, or from dark to sunlit waters. Accurate assimilation of these enigmatic groups and processes into our conceptual models of nitrogen biogeochemistry is a prerequisite to knowing how ocean ecosystem functions and services will change in the decades to come.

Also uncertain is the extent to which evolution may provide nitrogen cycle microorganisms with the ability to adapt to ocean global change. Only a tiny fraction of the microorganisms that drive marine nitrogen biogeochemistry have been tested under sustained selection by warming and acidification. For virtually all microbial functional groups, we know almost nothing about their evolutionary responses to other climate-related stressors such as declining O_2 and changes in supplies of nutrients and electron donors or acceptors. Systematic differences in the capacity of key groups such as phytoplankton, nitrifiers, denitrifiers and diazotrophs to adapt to environmental change could seriously distort the shape and functioning of the future ocean nitrogen cycle.

Despite many impressive recent methodological advances in marine microbial microbiology, important questions remain unanswered. Autonomous observing and sampling platforms, such as drifters, have revolutionized oceanography and yet technological limitations mean they still cannot measure real time, in situ rates of nitrogen fixation, nitrification and denitrification. Another crucial challenge that has not yet been fully met is to specifically and quantitatively tie the taxonomic identities of marine microorganisms with their relative contributions to bulk community nitrogen transformation rates. This is improving, however, partly due to techniques like stable isotope probing, fluorescence in situ hybridization and nanoSIMS (reviewed in REF.[185]), which have provided vital insights into the activity of specific organisms and their contribution to bulk processes[45,46]. New technological developments, which in oceanography have historically often originated from the medical microbiology field, will undoubtedly provide us with further novel insights that we cannot foresee today.

Getting these research priorities right is crucial because the effects of environmental change on the marine nitrogen cycle have implications that extend far beyond the ocean, to the Earth system as a whole[12,13]. Feedbacks from ocean nitrogen biogeochemistry to global climate are plentiful as marine ecosystems have outsized importance for the production and fate of greenhouse gases such as CO_2 and N_2O. Widespread redox potential changes due to advancing ocean deoxygenation will likely be particularly problematic for the nitrogen cycle, which is dominated by a cascade of linked oxidation and reduction reactions. Marine microbiologists who are at the forefront of efforts to understand how the nitrogen cycle works in the present-day ocean will also need to learn how to predict and interpret these changes to come as the biogeochemical cycles of the planet transition into an uncertain future.

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