PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B

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**Cite this article:** Voss M, Bange HW, Dippner JW, Middelburg JJ, Montoya JP, Ward B. 2013 The marine nitrogen cycle: recent discoveries, uncertainties and the potential relevance of climate change. Phil Trans R Soc B 368: 20130121.
http://dx.doi.org/10.1098/rstb.2013.0121

One contribution of 15 to a Discussion Meeting Issue 'The global nitrogen cycle in the twenty-first century'.

**Subject Areas:**
environmental science

**Keywords:**
ocean, nitrogen, budget

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# The marine nitrogen cycle: recent discoveries, uncertainties and the potential relevance of climate change

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The ocean's nitrogen cycle is driven by complex microbial transformations, including nitrogen fixation, assimilation, nitrification, anammox and denitrification. Dinitrogen is the most abundant form of nitrogen in sea water but only accessible by nitrogen-fixing microbes. Denitrification and nitrification are both regulated by oxygen concentrations and potentially produce nitrous oxide ($N_2O$), a climate-relevant atmospheric trace gas. The world's oceans, including the coastal areas and upwelling areas, contribute about 30 per cent to the atmospheric $N_2O$ budget and are, therefore, a major source of this gas to the atmosphere. Human activities now add more nitrogen to the environment than is naturally fixed. More than half of the nitrogen reaches the coastal ocean via river input and atmospheric deposition, of which the latter affects even remote oceanic regions. A nitrogen budget for the coastal and open ocean, where inputs and outputs match rather well, is presented. Furthermore, predicted climate change will impact the expansion of the oceans' oxygen minimum zones, the productivity of surface waters and presumably other microbial processes, with unpredictable consequences for the cycling of nitrogen. Nitrogen cycling is closely intertwined with that of carbon, phosphorous and other biologically important elements via biological stoichiometric requirements. This linkage implies that human alterations of nitrogen cycling are likely to have major consequences for other biogeochemical processes and ecosystem functions and services.

## 1. Introduction

The nitrogen cycle on the Earth has evolved over three billion years through biogeochemical and microbial processes coupled via natural feedbacks that keep the nitrogen cycle of the oceans in approximate balance [1]. However, recent findings strongly suggest a significant imbalance of the oceans' nitrogen budget towards higher losses than inputs [2,3]. Moreover, new processes have been identified, such as the anaerobic ammonium oxidation (anammox) process [4], the conversion of ammonia and nitrite to dinitrogen gas or the denitrification by eukaryotic species such as foraminifera [5]. Previously, canonical denitrification by prokaryotes was thought to be the only removal process of reactive nitrogen. Likewise, the single major N source to the ocean was considered to be the nitrogen-fixing photoautotrophic bacteria of the genus *Trichodesmium*, a species that occurs globally in tropical and subtropical waters [6]. However, today, numerous other nitrogen-fixing bacteria have been described which may raise the estimate of the global nitrogen input to the oceans significantly [7]. Moreover, nitrogen fixation seems to be a significant process not only in tropical surface waters and some benthic systems [8], but also in anoxic waters, at the sea floor [9], in estuaries and in river plumes where diatom–diazotroph associations prevail [10,11]. Nitrification, the microbially mediated,



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two-step oxidation of ammonium to nitrite and nitrate, was traditionally attributed to bacteria, but ammonia-oxidizing archaea now seem even more important [12–14].

On top of these recent findings and uncertainties are the perturbation of the nitrogen cycle by fossil fuel combustion and the production of artificial fertilizers, which together exceed the amount produced by natural nitrogen fixation [15,16]. The extra nitrogen disrupts the N balance in marine systems, fuels eutrophication of coastal oceans and supports extension of hypoxic zones [17]. These sites act as an additional, poorly quantified, source of nitrous oxide ($N_2O$). Climate change imposes numerous threats to the functioning of the Earth's elemental cycles. This overview paper will give a brief insight into the functioning of the marine nitrogen cycle, how the major processes are interlinked, what is known and where the critical limits of our understanding are.

## 2. Surface water processes: assimilation of dissolved inorganic nitrogen, dissolved organic nitrogen and nitrogen fixation

### (a) Global patterns in dissolved inorganic nitrogen concentrations

Nitrogen is an essential element for all life forms but, in sea water, nitrogen mostly occurs as inert dissolved $N_2$ gas (more than 95%) that is inaccessible to most species. The rest is reactive nitrogen ($N_r$), such as nitrate, ammonia and dissolved organic compounds. Nitrate concentrations in surface waters vary from almost zero in the tropics and subtropics up to several tens of micromoles per litre in the temperate and Arctic and Antarctic oceans (figure 1*a*).

The increase in deep-water nutrient concentration from the northern Atlantic towards the Indian and Pacific oceans (figure 1*b*) is a result of a global circulation pattern, called the oceanic 'conveyor belt' [19]. The circulation is driven by the excess salt in the northern Atlantic Ocean where surface waters sink to the bottom and travel southwards. This southward current partly supplies water to the Antarctic Circumpolar Current, and continues to the Indian and the Pacific Oceans [19] from whence the flow returns to the surface to travel back through the Indonesian Islands the Tasman Sea [20], and further into the Indian and Atlantic Oceans. The residence time of the Atlantic water is around 180 years, whereas the complete overturning of ocean deep waters takes approximately 1000 years [19].

Four major processes deliver nutrient-rich waters to the surface: upwelling, winter mixing, eddies and diffusion from below a permanent or seasonal thermocline (table 1). Coastal upwelling is especially strongly developed in eastern boundary currents along the west coasts off North and South America and Africa, where nutrient-rich water from approximately 200 m is brought to the surface (figure 1*a*). The upwelled water stimulates primary production and the export of organic material, with the consequence of oxygen deficiency in subsurface waters owing to remineralization. The recycling of organic matter at depth leads to accumulation of nutrients with nitrate concentrations between 20 and 50 $\mu mol\ l^{-1}$ (figure 1*b*). At high latitudes, deep wintertime convection mixes the waters down to a depth of several hundred metres so that seasonal interfaces are destroyed. Thus, nutrients from greater depth are redistributed into the surface layer to provide the nutrient reservoir for the spring bloom in the following year. In the open ocean, eddy fields are generated by baroclinic or barotropic instabilities and large-scale gyres by the divergence of the horizontal wind field. Within these, structure nutrients are supplied to the surface by Ekman pumping, stimulating blooms of phytoplankton [21,22]. To what extent these sites contribute to global primary production is difficult to estimate, because the occurrence of eddies is transient and varies greatly in time and location. For the Atlantic Ocean, roughly one-third of the total N flux may be delivered by eddy transport [23]. Phytoplankton living in surface waters drives the N cycle and often consumes all inorganic nutrients down to a depth where ambient light level is 1–0.1% of the surface irradiation. At these depths, turbulent diffusion is another important source for primary production [24].

Our understanding of ocean productivity regulation was significantly advanced when the concept of new and regenerated production was introduced by Dugdale & Goering [25]. They defined new production as that based on the input of nitrate from outside the euphotic zone (including nitrogen fixation), whereas regenerated production (based on ammonium) fuels a 'microbial loop' first introduced by Azam *et al.* [26] within a defined surface layer of the ocean. Based on Dugdale and Goerings's concept, only the amount of newly produced biomass can be quantitatively exported to the deep ocean without running down the primary production system [27]. However, this concept assumes that sources of new nitrogen are small, and that the ocean is in steady state, which often seems not to be the case [3,6,28]. Other potential problems with the Dugdale and Goering concept are bacterial uptake of dissolved inorganic nitrogen (DIN), assimilation of dissolved organic nitrogen (DON) and nitrification in the euphotic zone [29,30]. Of the global net primary production in the oceans of 1900 Tg C $yr^{-1}$ [31], 320 Tg $yr^{-1}$ should be N, using a C : N ratio of 6. To these, about 140 Tg N $yr^{-1}$ are added by nitrogen fixation [32], whereas global losses may be around 400 Tg N $yr^{-1}$ [33]. A global nitrogen budget considering all natural and human sources and incorporating recent discoveries has not yet been put together, but qualitative attempts have been made [3,6,32,34].

Nitrogen in atmospheric deposition develops into a significant N source in the open ocean, where usually very little combined nitrogen occurs in surface waters [15]. To what extent these atmospheric nutrients support oceanic productivity, and decrease oxygen concentrations, remains unclear, but Dentener *et al.* [35] estimate a total nitrogen deposition of 46.2 Tg N $yr^{-1}$, whereas Duce *et al.* [15] derive a global estimate of 67 Tg N $yr^{-1}$.

### (b) Nitrogen fixation

Nitrogen-fixing organisms are independent of combined N sources and able to use the dissolved $N_2$ gas, which has concentrations of over 400 $\mu mol\ l^{-1}$ in sea water. In order to be used as a source of nitrogen, dinitrogen has to be reduced to ammonium for which specific enzymes are required [36]. Moreover, nitrogen-fixing species rely on phosphate and require iron in much larger quantities than other phytoplankton [37]. Therefore, co-limitation of Fe and P occurs [38] and may even regulate the global occurrence of nitrogen-fixing species. Because the Fe input from land is lower in the Pacific than the Atlantic Ocean

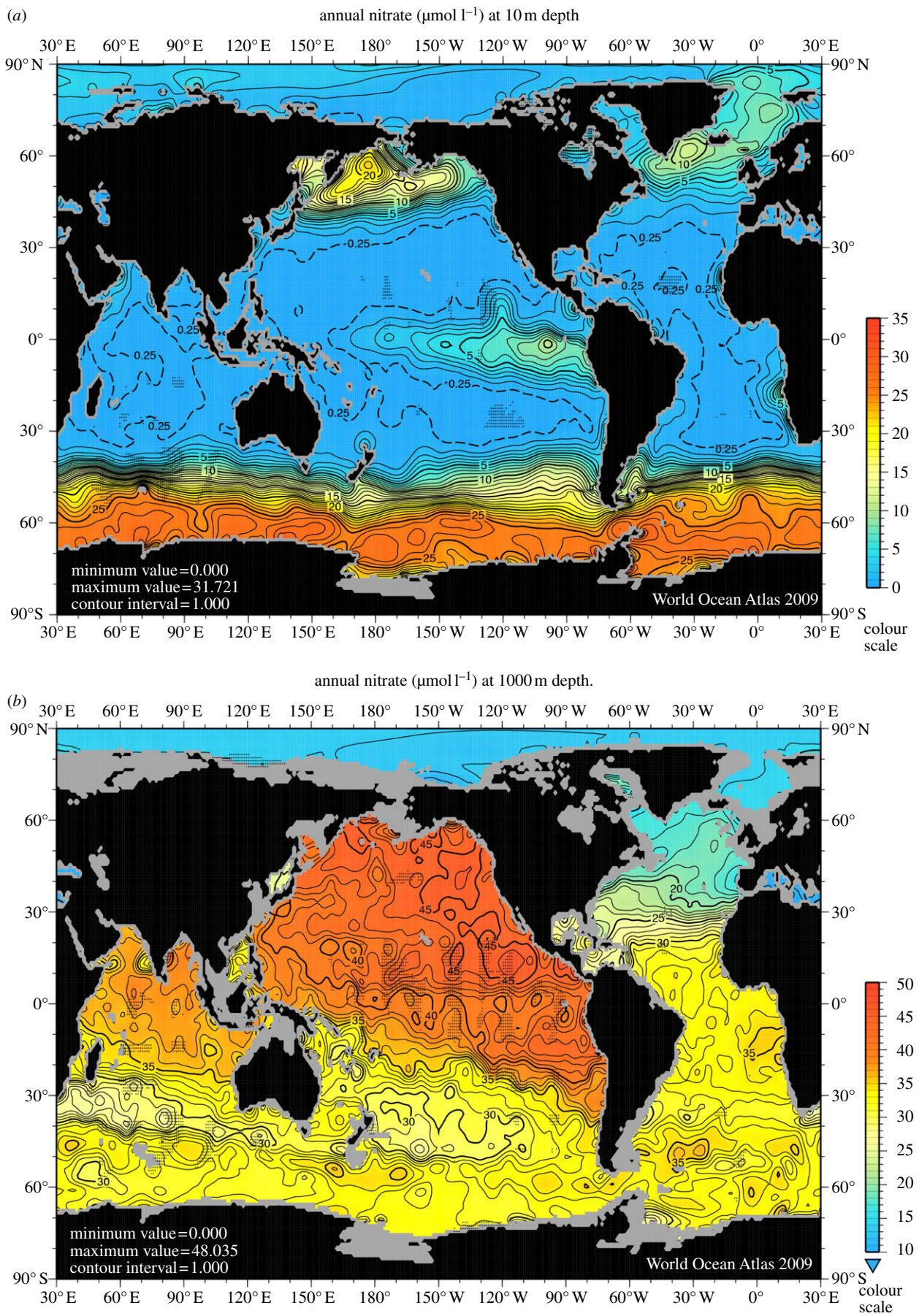



**Figure 1.** Nitrate concentrations in (*a*) surface waters of the ocean and (*b*) at 1000 m depth. Adapted from Boyer *et al.* [18].

[39], the tropical Atlantic Ocean may experience higher overall N fixation than the Pacific [40]. But recent evidence suggests higher rates in the Pacific Ocean than previously assumed, possibly higher than in the Atlantic Ocean [28,41].

Nitrogen fixation in the ocean has long been focused on the large bloom-forming genus *Trichodesmium* [6], until smaller unicellular species were discovered and their potential fixation activity demonstrated [7,42,43]. These are heterotrophic

**Table 1.** Summary of major nitrogen nutrient sources to the ocean.

| source of nutrient | major sites of occurrence | example of sites where process is of significance | type of nutrient | timing |
|---|---|---|---|---|
| convective overturning | high latitudes | North Atlantic, Greenland and Norwegian Seas | $NO_3^-$ | autumn, winter |
| wind induced and Ekman upwelling | eastern boundary upwelling systems | off Oregon/California/Mexico, Peru/Chile, Iberian Peninsula/Mauretania, Namibia, NW Indian Ocean (Arabian Sea) | $NO_3^-$, DON | during upwelling season (depending on the direction of the wind fields) |
| eddy activity/gyres | everywhere | frontal systems; Gulf stream, Kuroshio, Polar front | $NO_3^-$ | sporadically/permanent |
| diffusion | thermoclines | oligotrophic ocean | $NO_3^-$, $NH_4^+$ | permanent, depending on the gradient |
| rivers | continental shelves | Amazon, Mississippi, Yangtze, Mekong | $NO_3^-$, DON | permanent |
| atmospheric deposition | coastal, but globally relevant | oligotrophic tropical ocean | $NH_4^+$, $NO_3^-$, DON | sporadically |
| shelf processes | on continental shelves | European shelf, Patagonian shelf | $NO_3^-$, DON | permanent |
| regeneration of particles | everywhere in the water column and in sediments | high latitude surface waters in summer, low latitude surface waters, benthic boundary layers | $NH_4^+$, $NO_3^-$, $NO_2^-$, DON | permanent |

nitrogen fixers, including the photoheterotroph group-A (UCYN-A), which lacks the photosystem II [44], and *Richelia intracellularis*, a symbiont that fixes nitrogen in diatoms cells and has been found in tropical river plumes [45,46].

Nitrogen fixation may also be an important source of nitrogen to support biological production in deep-sea environments. Mehta *et al*. [47] described a diverse group of organisms possessing *nif*H genes, and therefore potentially capable of fixing $N_2$, from hydrothermal vent sites of the Juan de Fuca Ridge system. Other archaeal *nif*H sequences, many of uncertain phylogeny, have been linked to subsurface circulation through hydrothermal vent systems [48] and to methane cold seeps [9,49–51] and a mud volcano [52]. Further work at a cold seep field has revealed that methanotrophic archaea form syntrophic associations with sulfur-reducing bacteria, and that these consortia actively fix $N_2$ [9,50,51]. The overall contribution of these benthic diazotrophs to the oceanic nitrogen budget remains poorly known, but may be significant.

Nitrogen fixation rates based on direct measurements are sparse, and the variability is extremely high [6]. Therefore, global estimates of total marine nitrogen fixation are often based on geochemical factors such as unbalanced N : P ratios (N* method) which are assumed to support nitrogen fixation. Recently, Groszkopf *et al*. [53] reported a global marine N-fixation rate of 177 Tg N $yr^{-1}$ based on extrapolation of direct measurement, and suggest that $N_2$ fixers other than *Trichodesmium* are quite important outside the tropics. From global nutrient distributions and an ocean circulation model, Deutsch *et al*. [32] calculated a nitrogen fixation rate of 140 Tg N $yr^{-1}$, which agrees well with other estimates in the range of 100–200 Tg N $yr^{-1}$ [6]. It seems that lower estimates mainly result from model exercises where additional factors limiting N fixation such as iron have been implemented [54,55]. The global N-fixation rate of 140 Tg N $yr^{-1}$ has been largely unquestioned and is widely used [3].

## (c) The role of dissolved organic nitrogen in nitrogen cycling

Dissolved organic nitrogen is rather uniformly distributed in the water column of the open ocean, with slightly higher concentrations in the surface than at depth, but with DON increasing considerably towards coastal areas and in estuaries [56]. With a mean concentration of $5.8 \pm 2$ μmol $l^{-1}$, DON may potentially be more important than inorganic forms, because DON concentrations comprise between 18 per cent and 85 per cent of the total nitrogen pool in coastal and open ocean surface water, respectively, with particulate nitrogen being negligible [56]. The DON pool is not as inert as suggested by the relatively high and constant concentrations found in the oceans, but a small part of it is rather dynamic and consumed by phytoplankton and bacteria [57]. Furthermore, DON is mainly of autochthonous origin because it stems from direct release by phytoplankton and bacteria [58,59], egestion and excretion from micro- and meso-zooplankton [60], or viral lysis of bacterioplankton [61].

In coastal waters, rivers are a major source of allochthonous DON, and its composition, bioavailability and quantities may vary with land use [62]. Another allochthonous source relevant also for the open ocean is the DON in atmospheric deposition [63,64]. DON is actively channelled into cells via membrane transport systems [65] and seems to be a quite active component of coastal nitrogen cycling [66,67]. Better understanding

of the dynamic of DON is essential to quantify its role in the nitrogen and carbon cycles and how these will respond to anthropogenic perturbations and global change.

### (d) Stoichiometry of C : N : P in the ocean

The close similarity between nitrogen and phosphorous ratios in plankton and in deep-water nutrients was first noted by Redfield [68], who suggested that life in the ocean adjusts the nutrients according to its requirements. Today, the perception is, rather, vice versa, that life has adjusted to the oceanic ratios. The C : N : P ratio of 106 : 16 : 1 on a molar basis is still a fundamental concept in marine sciences and mirrors the metabolic demands of an average living cell [69]. This 'Redfield ratio' allows linking elemental cycles and has been widely used in ecosystem and element flux models [32]. The cellular stoichiometry is important for the regulation of organic C and N cycling and also for the linkage between single-cell activity and ecosystem function. Heterotrophic organisms maintain low nitrate concentrations in the water when organic C : N ratios match the stoichiometric demands, but as soon as organic carbon becomes limiting, denitrification decreases, and nitrification is enhanced [70]. It may be quite important to focus nutrient management scenarios to maintain balanced elemental ratios because nitrogen supply in excess of the demand leads to significant enrichment of $N_r$ [71].

The ultimately limiting element for ocean productivity had been debated over decades, and a consensus seems to be that nitrogen is limiting on short time-scales, whereas on geological time scales it seems to be phosphorus [72,73]. Both these views are based on input and loss rates and the turnover of the elements, which all may vary over time [74]. However, human perturbations affecting the input or loss of substances ultimately impact the global elemental cycles and the productivity.

## 3. Biogeochemistry of oxygen deficiency zones

Oxygen controls the distributions of N-cycle processes based on the fact that some microbial reactions require oxygen and others are inhibited by it. Both the microbial pathways that lead to net loss of fixed nitrogen, denitrification and anammox, occur only in the near or total absence of oxygen. These conditions occur in coastal and shelf sediments around the world and in a few locations in the water column where relatively high oxygen utilization rates and low ventilation rates lead to oxygen depleted zones of several hundred metres thickness (e.g. Arabian Sea). Regions where the oxygen concentration is low enough to induce anaerobic metabolism are known as oxygen minimum zones or more precisely oxygen-deficient zones (ODZs) experiencing oxygen concentrations less than 10 $\mu mol\,l^{-1}$, an expression we use throughout this text. Nitrogen cycling in ODZs is fundamentally different from the rest of the open ocean, because only in ODZs can net loss of fixed N occur in the water column.

Denitrification and anammox both lead to the formation of gaseous dinitrogen (and $N_2O$ in the case of the former) and both consume DIN, but have potentially different effects on the carbon cycle. Denitrifying bacteria are mostly heterotrophs, and respire DIN at $O_2$ concentrations below 60 $\mu mol\,l^{-1}$ while oxidizing organic matter. Some denitrifiers, however, are autotrophs, and fix $CO_2$ while oxidizing reduced sulfur compounds with nitrate. Anammox bacteria are also autotrophic, fixing $CO_2$ while oxidizing ammonium plus nitrite to dinitrogen, and oxidizing nitrite to nitrate, all anaerobically. In the open ocean ODZs, denitrification and anammox are both constrained by the stoichiometry of the organic matter supply, and anammox must depend on denitrification for the continuous supply of DIN. The complete utilization of organic matter of average composition (see stoichiometry above) under anaerobic conditions should lead to the loss of fixed N from both denitrification and anammox in the ratio of 71 : 29, i.e. 29 per cent of the fixed N loss is attributed to anammox.

In sediments and coastal systems, however, there are multiple sources of organic matter and DIN, such that the average composition rule does not apply. With an allochthonous supply of ammonium in a stratified basin or sediment, the proportion of anammox can be much higher. It was surprising, therefore, that the first reported direct measurements of anammox and denitrification in the ODZs (where the average rule should apply) failed to detect denitrification. This suggested that all of the fixed N loss was due to anammox. This is apparently a robust result, although the number of measurements is still rather small [75–77]. Only in the Arabian Sea has denitrification been detected at appreciable levels [77,78], whereas another study nearby failed to detect either anammox or denitrification [79]. There are several alternative explanations for the variation in the proportion of anammox and denitrification in the ODZs, but this is an active area of research with no current consensus.

From stoichiometric model studies, Koeve & Kähler [80] conclude that the proportion of anammox and denitrification does not vary widely in the ocean, and direct measurements of excess $N_2$ and DIN concentrations verify that organic matter loss in the ODZs does indeed produce net Redfield stoichiometry [81]. Thus, resolving the question of the relative contribution of anammox and denitrification has small ramifications for the magnitude of the overall fixed N loss. One fundamental difference between the two processes is that denitrification involves $N_2O$ as an intermediate, whereas anammox does not. This issue is explored in §3*a*.

### (a) Nitrous oxide production, consumption and release from the ocean

The marine pathways of $N_2O$ and the quantification of its oceanic emissions have received increased attention during recent decades [82,83]. $N_2O$ acts as a strong greenhouse gas and in the stratosphere it is the precursor of ozone-depleting nitric oxide (NO) radicals [84,85]. Because of the ongoing decline of chlorofluorocarbons and the continuous increase of $N_2O$ in the atmosphere, the contributions of $N_2O$ to both the greenhouse effect and ozone depletion will be even more pronounced in the twenty-first century [84,86]. The oceans, including coastal areas such as continental shelves, estuaries and upwelling areas are a major source of $N_2O$ and contribute about 30 per cent (5.5 $Tg\,N\,yr^{-1}$) to the atmospheric $N_2O$ budget [84]. Oceanic $N_2O$ is produced as a by-product during bacterial as well as archaeal nitrification; however, nitrifying archaea dominate $N_2O$ production [87,88]. $N_2O$ occurs also as an intermediate during denitrification. It is produced by the reduction of $NO_3^-$ and, in turn, can be further reduced to $N_2$. Nitrification is the dominating $N_2O$ production process, whereas denitrification contributes only 7–35% to the overall $N_2O$ water column budget in the

ocean [89,90]. The importance of other microbial processes, such as dissimilatory nitrate reduction to ammonia and anammox, for oceanic, $N_2O$ production is largely unknown [83].

The amount of $N_2O$ produced during both nitrification and denitrification strongly depends on the prevailing dissolved oxygen ($O_2$) concentrations and is significantly enhanced under low (i.e. suboxic) $O_2$ conditions [2,91]. $N_2O$ is usually not detectable in anoxic waters because of its reduction to $N_2$ during denitrification. Thus, significantly enhanced $N_2O$ concentrations are generally found at oxic/suboxic boundaries in the oceans [2,83]. The strong $O_2$ sensitivity of $N_2O$ production is also observed in coastal systems that are characterized by seasonal shifts in the $O_2$ regime [92]. A biological source of $N_2O$ in the well-oxygenated, mixed layer/euphotic zone seems to be unlikely (see discussion in Freing *et al*. [90]). A recent study of both the $N_2O$ air/sea fluxes and $N_2O$ diapycnal fluxes into the mixed layer in the coastal upwelling off Mauritania, northwest Africa indicated that surfactants may have a dampening effect on air–sea exchanges of $N_2O$ [93]. However, for a reassessment of the global coastal $N_2O$ emissions, further laboratory and field studies of the effect of surfactants on the air/sea flux of $N_2O$ are needed.

Global maps of $N_2O$ in the surface ocean [94,95] show supersaturation of $N_2O$ in coastal and equatorial upwelling regions as well as $N_2O$ anomalies close to zero (i.e. near equilibrium) in large parts of the open ocean. Since the studies of Nevison *et al*. [94] and Suntharalingam & Sarmiento [95], the amount of available $N_2O$ data has been steadily increasing. Therefore, the project 'Marine Methane and Nitrous Oxide' database has been launched with the aim to collect and archive $N_2O$ datasets and to provide actual fields of surface $N_2O$ for emission estimates [96].

The observed ongoing deoxygenation of the open ocean [97] can be translated into an additional $N_2O$ accumulation of less than 6 per cent [83]. In contrast to the open ocean, Naqvi *et al*. [92] cautioned that global $N_2O$ emissions from shallow hypoxic/anoxic coastal systems might increase significantly in the future. It seems realistic to expect that the $N_2O$ emissions from shallow hypoxic/anoxic coastal systems will increase in the near future due to increasing nutrient inputs (caused by the ongoing industrialization and intensification of agricultural activities), whereas future $N_2O$ emissions from the open ocean owing to decreasing oxygen in mid water depths seem to be of minor significance.

## 4. Shelf processes

The coastal ocean is conveniently partitioned into a proximal, i.e. spatially heterogeneous part, including estuaries, lagoons, etc., and a distal compartment, i.e. the continental shelf. The coastal ocean is the eventual sink of most anthropogenic DIN delivered by rivers, groundwater and atmospheric deposition.

### (a) Proximal coastal systems

Each year, rivers transport about 40–66 Tg N $yr^{-1}$ to coastal ecosystems, 40 per cent in the form of DIN (mainly nitrate), 40 per cent in the form of particulate nitrogen and the remaining 20 per cent as dissolved organic nitrogen [62]. The variability in the export is impacted by anthropogenic nitrogen input, whereas DON export varies between 10 and 25 per cent of total N [62]. Submarine groundwater discharge delivers about 4 Tg N $yr^{-1}$ to near-shore ecosystems. Further inputs of nitrogen to the proximate coastal ocean include nitrogen fixation in the water column, sediments and vegetated ecosystems totalling about 15 Tg N $yr^{-1}$ and atmospheric deposition (about 1 Tg N $yr^{-1}$). Losses of fixed nitrogen include export to the continental shelf (38 Tg N $yr^{-1}$), emission of $N_2O$ (0.5 Tg N $yr^{-1}$), denitrification (4–8 Tg N $yr^{-1}$), fish landings (3.7 Tg N $yr^{-1}$) and burial (22 Tg N $yr^{-1}$; figure 2). This burial occurs mainly in vegetated systems such as seagrass meadows and mangroves [98], because of trapping of particulate nitrogen and assimilation of dissolved inorganic and organic nitrogen [67]. The present-day and future nitrogen cycling in proximal coastal systems differs substantially from that before the Anthropocene. Eutrophication has resulted in community shifts such as a loss of submerged vegetation and proliferation of macroalgae and phytoplankton. This will eventually lead to lower rates of nitrogen burial. Denitrification may be higher or lower depending on conditions [99], whereas $N_2O$ emission is higher because of extensive oxic–anoxic interfaces with high rates of nitrification and denitrification.

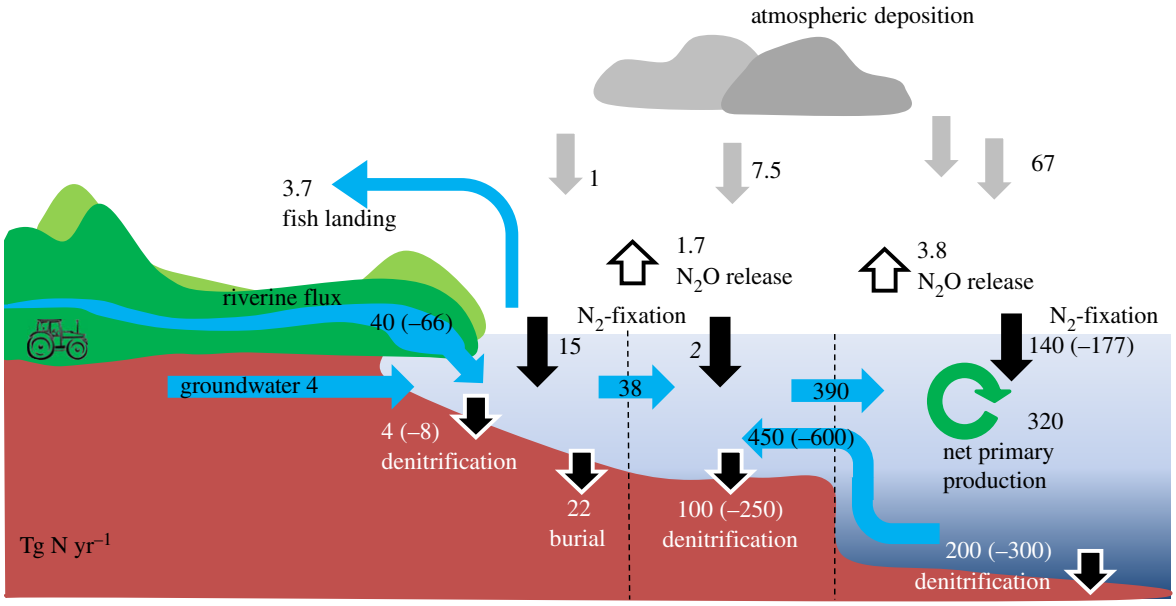
### (b) Distal coastal systems

The fixed nitrogen budget of continental shelf systems is primarily governed by exchanges with the open ocean (figure 2). Globally, continental shelves receive about 38 Tg N $yr^{-1}$ exported from the proximal coastal zone, 7.5 Tg N $yr^{-1}$ from atmospheric deposition (almost all anthropogenic) and a small contribution by nitrogen-fixing organisms (about 2 Tg N $yr^{-1}$). Continental shelf systems lose nitrogen via denitrification (100–250 Tg N $yr^{-1}$); the uncertainty, however, is high [100]. Because the global estimate of 400 Tg N $yr^{-1}$ removal per year exists, about 200–300 Tg N $yr^{-1}$ remain for the open ocean (figure 2). Recent estimates suggested five times higher denitrification rates in permeable sediments [101], so the number may need an upward revision in the future. Most nitrogen entering the continental shelf comes from nitrate exchanges with the open ocean (450–600 Tg N $yr^{-1}$). The majority of the nitrogen imported from subsurface oceanic waters is returned in the form of DON and particulate organic nitrogen (PON) to open ocean surface waters (about 390 Tg N $yr^{-1}$). This organic nitrogen exported from coastal systems supports the reported heterotrophy of oceanic gyre ecosystems and constitutes a source of fixed nitrogen for micro-organisms. A budget of these numbers for the three systems (figure 2) reveals a relatively low uncertainty in the numbers around 10 per cent that supports the reliability of the estimates.

## 5. Model achievements and global budgets considering nitrogen

Ocean biogeochemical and ecosystem models often have $N_r$ as model currency, i.e. nitrogen is modelled as a state variable. The models in use differ in many aspects, in particular regarding complexity in model formulation and spatial coverage. Detailed process models such as nitrogen-fixing models, e.g. Fennel *et al*. [102] and Hood *et al*. [103], and denitrification models, for example [104,105], are designed to investigate single processes (see review by Hood [106]).

Ocean biogeochemical circulation models are often based on the nitrogen–phytoplankton–zooplankton–detritus model of Fasham *et al*. [107], which was the first model to consider DON and bacteria as state variables. This model was coupled




| Tg N yr$^{-1}$ | proximal | distal | open ocean |
|---|---|---|---|
| Σ input | 60 | 497 | 597 |
| Σ output | 69 | 492 | 654 |

**Figure 2.** Nitrogen budget of the ocean. All numbers are given in the text. The table below considers the smaller numbers, therefore the larger numbers are given in parentheses; net primary production is no input/loss term.

to a circulation model and estimated basin-wide nitrate and chlorophyll-a and the relative magnitude of different new N sources [108]. Since then, the complexity of the models has increased by including multiple nutrients, or plankton functional groups. The development of the concept of excess nitrogen N* [109] or excess phosphorous P* [32] was a milestone because it allows coupling of the nitrogen to phosphorous and carbon cycles [3,32]. The imbalance between input and losses and the findings of higher estimates of both terms would result in higher turnover rates of the nitrogen cycle and the question of how other cycles are still linked.

A major uncertainty in global modelling remains meteorological forcing, especially in the tropics. Large differences exist between monthly mean climatologic datasets and reanalysis data of NCEP/NCAR or ECMWF in wind stress forcing [110], as well as in atmospheric temperature of up to 0.8 K in the late 1980s and early 1990s [111]. A further uncertainty is the lack of consensus concerning the question of whether or not it is necessary to include explicit formulations of microbes as state variables [106].

## 6. Impact of climate change

A recent summary explored climate change effects on the future ocean [112] caused by the increase of $CO_2$ in the atmosphere [84,113]. There are direct (warming and acidification) and indirect (oxygen depletion) effects. These factors produce further changes that contribute more or less clearly to the many possible changes in ocean biogeochemistry (figure 3). Warming of the sea water, a direct consequence of the increasing air temperature, enhances stratification of the ocean and microbial activity. This may not develop equally everywhere in the ocean. In the Arctic and in low latitudes (from 20° N to

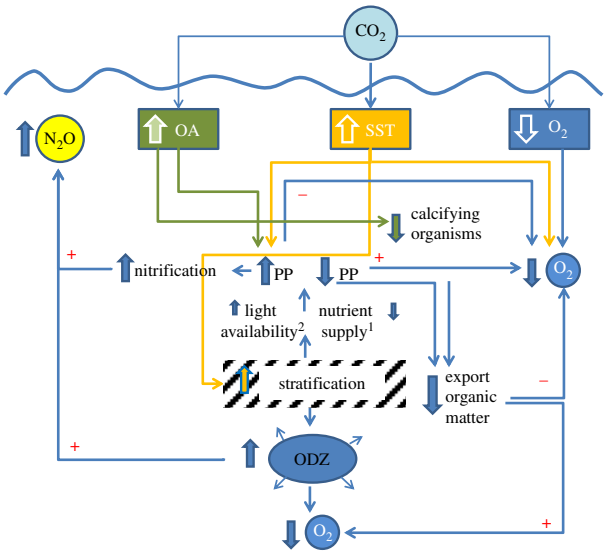



**Figure 3.** Schematic of the major effects of climate change on the ocean biogeochemistry. The graphic does not consider the differences between effects in Arctic and tropical latitudes except for the different effects on primary production (PP); nutrient supply (1) from below the thermocline is restricted due to stronger stratification in low latitudes, but PP is enhanced (2) at high latitudes because of higher light availability. Plus and minus symbols emphasize the positive or negative feedback of a process. OA, ocean acidification; SST, sea surface temperature; PP, primary production; ODZ, oxygen deficiency zone; $O_2$, oxygen concentrations, $N_2O$, nitrous oxide.

20° S) stronger stratification of the water column is expected than in the rest of the ocean, which would, in turn, affect nutrient supply and light availability. Another important impact is the declining solubility of gases, especially of $O_2$ itself, potentially increasing the size of ODZ [97,114]. Ocean acidification

may stimulate $N_2$-fixing cyanobacteria [115]. In areas where primary production increases, more oxygen is consumed at depth during remineralization and potentially more $N_2O$ can escape to the atmosphere when the water masses reach the surface (see section §3*a*). However, increasing temperatures may change the balance between production and respiration so that less export of organic matter may occur counteracting oxygen losses in the deep ocean.

Ocean acidification may directly result in significantly reduced nitrification rates accompanied reduced $N_2O$ production [116]. However, this scenario might be globally counteracted by the generation of more $N_2O$ when the nitrification process itself shows an overall positive response to lower pH values such as some studies suggest [87,117]. Therefore, it seems reasonable to assume only a minor effect of decreasing pH on $N_2O$ production during nitrification, but mesocosm and field experiments to verify the effect of ocean acidification on $N_2O$ production in the ocean are missing. Recently published model results by Suntharalingam *et al*. [118] show that atmospheric deposition of anthropogenic N to the ocean might lead to an enhanced global oceanic $N_2O$ production ($0.06–0.34\ Tg\ N\ y^{-1}$) especially in regions which are sensitive to changes in dissolved oxygen such as coastal zones. At this point, it is difficult to predict which process may dominate, because the interaction of processes is too complex to evaluate the net effect on ocean carbon and nitrogen cycles.

The paper is a contribution to the HYPER Project funded by the BONUS+ programme. J.W.D. has been supported by the BONUS+ Project AMBER. Suggestions to the final text by Mirko Lunau are greatly acknowledged.

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