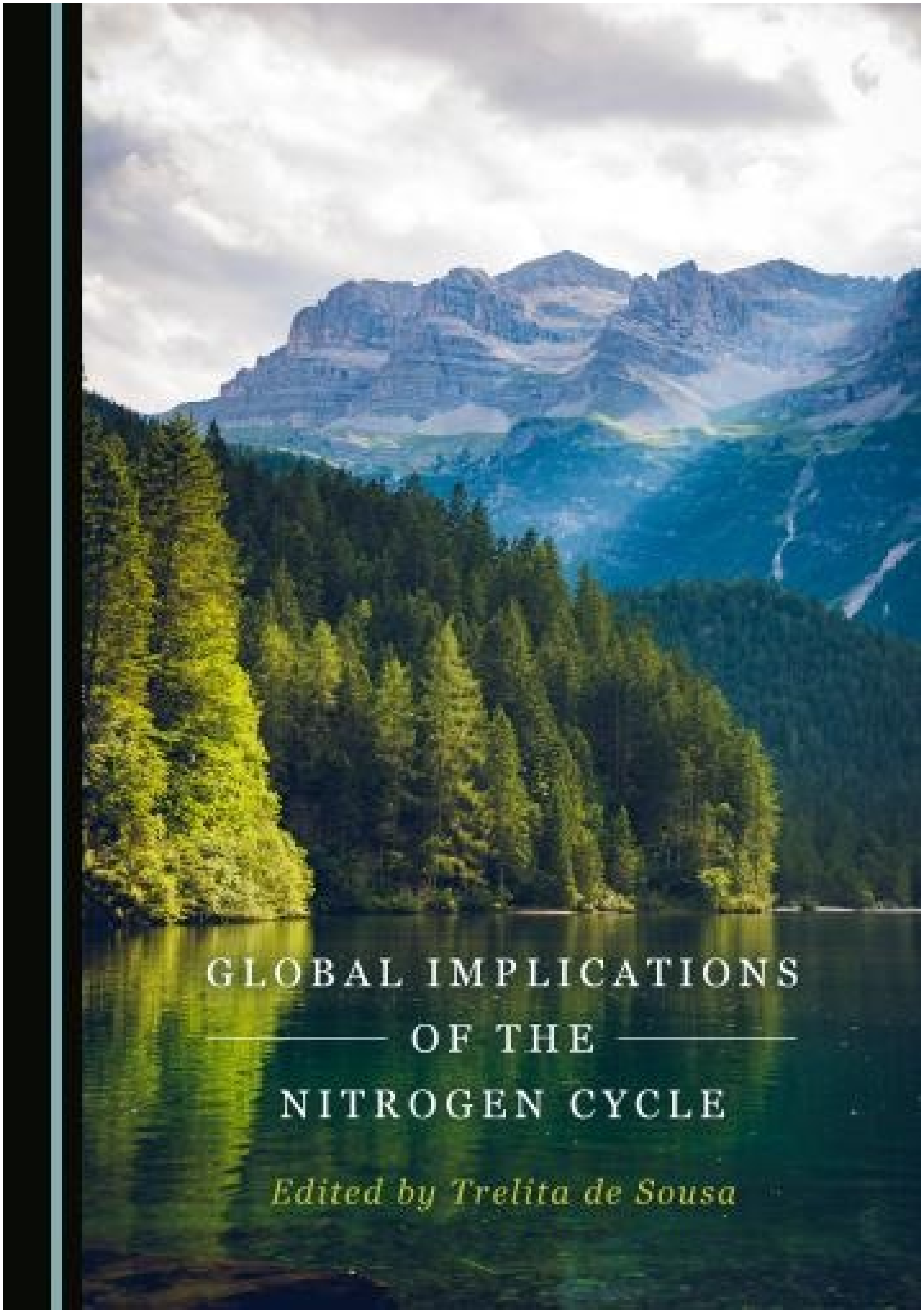

GLOBAL IMPLICATIONS OF THE NITROGEN CYCLE

Edited by Trelita de Sousa

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CHAPTER 15

THE IMPLICATIONS OF THE ALTERED NITROGEN CYCLE ON COASTAL ECOSYSTEMS: EMPHASIS ON PRIMARY PRODUCERS

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Abstract

Nitrogen plays a central role in the oceanic biogeochemical cycles. The marine nitrogen cycle is considered very complex and has hence attracted considerable research interest. The availability of nitrogen is an important factor controlling the primary productivity and species diversity of both aquatic and terrestrial ecosystems. Given that nitrogen in its elemental form is inert and, therefore, unavailable for biological use, various biologically-driven processes including nitrogen fixation, ammonification, nitrification, and denitrification are responsible for deciding the fate of nitrogen transformation and thus, its bioavailability. However, human activities linked to global climate change, such as the combustion of fossil fuels, the indiscriminate use of artificial fertilisers, and the consequent release of nitrogenous compounds through the runoff into aquatic systems, have tremendously altered the nitrogen cycle. The positive correlation between human population density and nitrogen fluxes has resulted in a 10-15 fold increase in nitrogen input in many coastal areas. This has catastrophic effects, such as eutrophication, harmful algal blooms, hypoxia/anoxia, and alterations in community structure and food web dynamics, and ultimately affects the structure and functioning of the coastal ecosystems. This chapter focuses on the response of primary

producers to these changes and explores the concerns related to the altered nitrogen cycle, links with ocean acidification, and emerging paradigms.

Introduction

In general, the oceanic nitrogen (N) cycle sustains itself on an approximately balanced budget (Canfield, Glazer, and Falkowski 2010, 193) governed by microbial and biogeochemical processes together with natural feedback mechanisms (Voss et al. 2013, 1). However, recent findings indicate an altered ocean N budget with elevated losses rather than gains (Codispoti et al. 2001, 86; Gruber and Galloway 2008, 293).

The N cycle is largely impacted by anthropogenic activities, ranging from the burning of fossil fuels and the indiscriminate use of synthetic fertilisers in crops, to the selective cultivation of crops harbouring N-fixing bacteria. Human intervention in the N cycle has been known since the 20th century and has risen simultaneously over the decades with the unprecedented increase in the combustion of fuels and development of practices to improve food production using synthetic fertilisers (Galloway et al. 2008, 889; Canfield, Glazer, and Falkowski 2010, 195). Consequently, human activities have had the following wide-ranging effects on the N cycle: (1) Increase in the amount of N cycling between the biota, soil, water, and atmosphere; (2) Increase in the amount of reactive nitrogen (N_r) in the terrestrial phase of the cycle, a phenomenon often termed human-driven N fixation; and (3) Increase in the mobility of various forms of N through air and water. Concerns about these changes have been voiced by several researchers over the last few decades. Delwiche (1970, 137) had already noticed that anthropogenic influences had increased the amount of N_r to a much higher concentration compared to naturally fixed N. He highlighted the fact that the fate of the new N_r was uncertain. Vitousek et al. (1997, 739) also emphasised the accelerated discharge of N from long-term storage in organic matter and soils due to anthropogenic activities. Galloway (2004, 156) reported that the amount of N_r produced due to anthropogenic activities had increased by a factor of 10 compared to the late 19th century values. Additionally, changes in land usage patterns have led to a decrease in biological N fixation (Galloway 2004, 156). Considering the burgeoning human population and the huge expected demand for food and fuel in the future, the effects of the altered N cycle on the environment are bound to be on a much larger scale than previously imagined. Additionally, because of the increased mobility of N from the huge unavailable atmospheric pool to the biosphere (as fixed N), human activities, though local in scale, will have profound and long-term consequences on the environment on a global scale.

In a seminal paper on the anthropogenic effects on the N cycle and its consequences on the environment, Vitousek et al. (1997, 737) highlighted the following impacts: (1) increased global concentrations of nitrous oxide (N_2O), a potent greenhouse gas, in the atmosphere, as well as increased regional concentrations of other oxides of nitrogen which drive the formation of photochemical smog; (2) losses of soil nutrients, such as calcium and potassium which are crucial for soil fertility; (3) substantial acidification of soils, streams, and lakes in several regions; and (4) increased transport of N by rivers into estuaries and coastal waters.

Coastal ecosystems are particularly vulnerable to changes in the N cycle. They have unique characteristics that distinguish them from other aquatic ecosystems. These shallow systems receive relatively large amounts of N from land, rivers, and groundwater, and exchange matter with the Open Ocean and atmosphere. Nitrogen input and output occur through several processes (N fixation, nitrification, denitrification, ammonification, and anammox). The interlinking of such processes plays a major role in the N budget of coastal ecosystems.

Nitrogen transformation processes

The processes involved in N transformation have received considerable attention due to the obvious significance of the N cycle in both terrestrial and aquatic ecosystems and the impact of human activities on the N budget.

Nitrogen Fixation

The process of transforming the stable triple bonded dinitrogen (N_2) into bioavailable N is called N fixation. Oceanic N fixation was formerly largely linked to bloom-forming *Trichodesmium* (Capone et al. 2005, 1). However, subsequent studies have identified and demonstrated the N-fixing potential of smaller unicellular species (Zehr, Mellon, and Zani 1998, 3445; Zehr et al. 2001, 636; Montoya et al. 2004, 1028) and also the occurrence of N fixation through diatom-cyanobacterial symbioses (Foster et al. 2011, 1485). Direct measurements of N fixation rates are few. The variability in such measurements is also very high (Capone et al. 2005, 2). Hence, the global estimates of N fixation are calculated based on the N* method (unbalanced N/P ratios). Presently, the available global N fixation rates vary between 100-200 Tg N yr $^{-1}$ (Moore, Doney, and Lindsay 2004, 17; Capone et al. 2005, 1; Deutsch et al. 2007, 165; Gruber and Galloway 2008, 293; Monteiro, Dutkiewicz, and Follows 2011, 6). The model-derived lower estimates were attributed to the limiting factors for N fixation (Moore, Doney, and Lindsay 2004, 17; Monteiro, Dutkiewicz, and Follows 2011, 6). It is observed that phosphorus and iron play a significant role in N-fixing species. Furthermore, the iron requirement of such species is higher compared to that of other phytoplankton (Berman-Frank et al. 2007, 2267). Possibly, phosphorus and iron limitation may regulate global N fixation rates. Presently, the global N fixation rate is 140 Tg N yr $^{-1}$ (Gruber and Galloway 2008, 293).

Nitrification

Nitrification is a very important part of the N cycle, reflecting the transformation of ammonia (NH_3) to nitrite (NO_2^-) and then to nitrate (NO_3^-). It is a two-step oxidation process and occurs usually in the presence of oxygen in prokaryotes. The NH_3-oxidising microbes convert NH_3 to NO_2^- using different enzymes (ammonia monooxygenase and hydroxylamine oxidoreductase). The second step of converting NO_2^- to NO_3^- is mediated by a different set of prokaryotes (nitrite oxidisers). *Nitrosomonas* spp. and *Nitrobacter* spp. are the key organisms responsible for nitrification in coastal ecosystems (Herbert 1999, 570).

Denitrification

This process contributes to the loss of N from the ecosystem by converting bioavailable N (NO_3^-) to N_2. Unlike nitrification, this process occurs under anaerobic conditions and is carried out by bacteria *(Alcaligenes, Paracoccus, Bacillus*, and *Pseudomonas),* archaea *(Haloarcula, Halovibrio, Halospina, Pyrobaculum,* and *Ferroglobus),* and certain fungi (*Fusarium, Cylindrocarpon, Giberella, Trichoderma, Penicillium, Aspergillus, Chaetomium,* and *Hansenula)* (De Sousa and Bhosle 2012, 688, 689). Recent findings also point to the capability of benthic foraminifera (unicellular eukaryotes) to perform denitrification (Risgaard-Peterson et al. 2006, 93). Denitrification has been observed in the foraminifer, *Globobulamina pseudospinescens*. The rate of N flux through denitrification in the modern oceanic N cycle is $17x10^{12}$ mol yr^{-1} (Canfield, Glazer, and Falkowski 2010, 195).

Anammox

Anaerobic ammonium oxidation (anammox) is another important process of the N cycle, carried out by prokaryotes belonging to the bacterial order *Planctomycetes*. It is an oxidation process of NH_3 occurring under anoxic conditions and plays a significant role in the removal of N from the oxygen minimum zones (OMZ) (Devol 2003, 575; Kuypers et al. 2005, 6478). However, denitrification is the more predominant pathway responsible for the removal of N in the Arabian Sea OMZ (Ward et al. 2009, 78). Yet, anammox performs a pivotal function in the global N cycle (Benhard 2010, 5).

Ammonia-oxidising archaea

Archaea, one of the most abundant and widespread groups of microorganisms, have been recently found to contribute to the N cycle (Francis, Beman, and Kuypers 2007, 22). Metagenomic studies of marine samples have revealed the presence of the ammonia monooxygenase (*amoA*) gene in uncultivated archaea (Treusch et al. 2005, 1985), suggesting their genetic potential for NH_3 oxidation. Further findings indicated the wide distribution of *amoA* in the oceanic realm, particularly in the euphotic zone, suboxic zones, and coastal estuarine area, which are critical to the global N cycle (Francis et al. 2005, 14683). Since these findings highlighted the potential of many archaea to oxidise ammonia, the archaea involved were termed ammonia-oxidising archaea (AOA) (Francis et al. 2005, 14686).

Ammonification

Once the bioavailable N is utilised by organisms, it remains inside the organism in the form of amino acids and DNA. Such organic N gets released via excretion, death, and decomposition. The conversion of such organic N to inorganic N is carried out by decomposing prokaryotes and fungi. The formation of NH_3 is called ammonification. The rate of mineralisation depends on the quality of the deposited organic matter (labile or refractory) and the origin of the matter (Buchsbaum et al. 1991, 141; Enriquez, Duarte, and Sand-Jensen 1993, 457). The structural complexity of the organic matter will decide whether ammonification can take place by simple deamination reactions or via a complex metabolic series through hydrolytic enzymes (Herbert 1999, 564).

Effects of the altered nitrogen cycling on aquatic systems

The increase in the amount of biologically available N_r in the atmosphere has cascading effects on both aquatic and terrestrial ecosystems. It contributes to the greenhouse effect, smog formation, ozone depletion, acid rain, altered productivity of terrestrial and marine systems, development of hypoxic zones, and eutrophication of coastal waters. The combustion of fossil fuels leads to the input of N to the atmosphere whereas fertiliser overuse leads to runoffs into adjacent water bodies. Ultimately, the marine N cycle gets affected.

Concerns raised for terrestrial environments include accelerated losses of biological diversity, especially among plants adapted to low N soils. The aspects of the marine environment that tend to be affected are numerous and include eutrophication, harmful algal blooms, hypoxia/anoxia, acidification, community alteration, and foodweb dynamics. In the subsequent sections, the different aspects of the altered N cycle in marine environments will be elaborated with due consideration to the effects on phytoplankton, including diatoms, dinoflagellates, cyanobacteria, and other algal groups in the size range of 0.2-2 µm (termed picophytoplankton, for example, *Prochlorococcus* and *Synechococcus)*. These single-celled organisms function as primary producers in the food web and, therefore, form the base of the food web in the open sea. Being ubiquitous in aquatic systems, they contribute significantly to climatic processes (Jeffrey and Vesk 1997).

Links between altered nitrogen cycle and eutrophication

Eutrophication of estuaries and coastal seas resulting from the anthropogenic alteration of the N cycle is widely investigated. Globally, it is one of the most widespread pollution problems (Howarth 2008, 14). Based on Nixon (1995, 200-202), eutrophication is defined as the process of increased nutrient enrichment of an ecosystem. It can be classified into 2 types: natural eutrophication and cultural (anthropogenic) eutrophication. In natural eutrophication, the nutrients responsible for enrichment are of natural origin whereas cultural eutrophication is attributed to human population growth, food production (agriculture, animal operations, and aquaculture), and energy (Smil 2001; Glibert et al. 2005a, 199).

Another contributory factor is the soaring use of chemical fertiliser right from the time they were introduced in the 1950s (Smil 2001; Glibert et al.

2005a, 199). Nitrogen and phosphorus are the main nutrients implicated in eutrophication (Howarth and Marino 2006, 364). The main source of N pollutants is runoff from fields (in the form of NO_3^-) whereas phosphorus pollution originates from household and industrial waste, including phosphorus-based detergents. However, N has received far more attention because firstly, it often limits primary production in estuaries and coastal waters, in contrast to phosphorus which is the limiting nutrient in temperate zone lakes (Vitousek et al. 1997, 11). Secondly, the global application of N from synthetic fertilisers is far greater than that of phosphorus (Wassman and Olli 2005). Up to the 1960s, most of the N fertilisers used worldwide were NH_3-based. Subsequently, urea-based fertilisers began increasing in popularity. From constituting approximately 5% of the fertilisers used globally in the late 1960s, the use of urea-based fertilisers showed a dramatic spurt. In the 1990s, it represented approximately 40% of the total N fertilisers used worldwide (Smil 2001) and had already taken over ammonium nitrate as the preferred N fertiliser (Overdahl, Rehm, and Meredith 1991).

Nitrifying bacteria can convert ammonium nitrate to highly mobile NO_3^-, which, ultimately enters rivers and nearshore coastal systems (Bernhard 2010), resulting in eutrophication. It has been observed that with the increase in the human population, there has been a drastic increase in the amount of NO_3^- in surface waters, thereby compounding the eutrophication problem. The increase in the use of urea-based fertilisers has also further aggravated the problem of coastal eutrophication (Glibert et al. 2006, 443). This is especially relevant because urea-based fertilisers can leach into coastal waters and be utilised by some species of phytoplankton (Glibert et al. 2006, 442). Aquaculture is also a cause of coastal eutrophication, mainly through the discharge of nutrient-rich effluents in the coastal waters. These nutrients reach aquatic environments via surface water, groundwater, and even air. This ultimately leads to the nutrient enrichment of water bodies from oligotrophic (low nutrient concentrations), mesotrophic (intermediate), eutrophic (high) and finally, hypertrophic stages (excessive nutrient enrichment).

Consequences of eutrophication

Reduced diversity of biotic communities

A pivotal consequence associated with eutrophication is the loss of diversity of biotic communities both planktonic and benthic. The changes in communities of macroscopic groups, such as seaweeds, seagrasses, and corals are evident. Comparatively, the changes in phytoplankton are not immediately noticeable. Also, given that phytoplankton form the base of food webs in aquatic systems, any change in the phytoplankton community structure will have cascading effects on organisms belonging to all trophic levels.

Effects on phytoplankton

Several changes are evident in phytoplankton communities in response to eutrophication. Firstly, phytoplankton communities under eutrophication conditions generally exhibit an increase in biomass, productivity, and chlorophyll a (Riegman 1995, 63; Ramaiah, Ramaiah, and Nair 1998, 281). This may be beneficial to coastal productivity and may even sustain high levels of fisheries until they exceed the assimilative capacity of the system, after which hypoxia and other adverse effects occur. Secondly, a shift in phytoplankton size classes may also be observed. Small-sized nanoplankton (microflagellates and coccoids) tend to dominate in eutrophic water bodies (Kimor 1992, 871). Thirdly, a reduction in the diversity and complexity of the phytoplankton community has also been noted (Taslakian and Hardy 1976, 315), with a single or few species dominating the phytoplankton assemblages. For example, a comparison of the Visakhapatnam harbour, along the East Coast of India, and the Mormugao Port Trust, Goa, along the West Coast of India, indicated several differences in the phytoplankton community both in the water column (planktonic) and the sediment (cyst forms) (unpublished data). Visakhapatnam has several eutrophic stations, which are dominated by *Skeletonema costatum*, a bloom-forming diatom (Naik 2010). Also, the dinoflagellate cyst assemblages in the inner eutrophic stations of the harbour were markedly different and had lower species diversity compared to the outer stations, which had comparatively lower nutrient concentrations (D’Silva, Anil, and Sawant 2013, 59).

The phytoplankton community may also shift from diatom dominance to flagellate dominance, in response to eutrophication conditions, especially when silica is depleted. Diatoms, the major phytoplankton group in coastal waters, require silica for the synthesis of their frustules or shells. Shifts from the dominance of diatoms to flagellates in algal communities have been detected in response to alterations in the composition of the nutrient load (Smayda 1990, 29).

Breton et al. (2006, 1408) have observed an increase in *Phaeocystis* blooms after a diatom bloom, in the presence of excess NO_3^- during the enrichment of coastal waters with N and phosphate. A similar shift to bloom-forming cyanobacterial dominance in freshwater environments with high phosphorus concentrations has also been reported by Oliver and Ganf (2000). This is because N-fixing cyanobacteria will grow in N-depleted conditions, provided other relevant nutrients like phosphorus and iron are available at sufficient levels.

Development of hypoxic/anoxic zones in water bodies

Eutrophication of water bodies usually results in the development of hypoxic zones around the world (Diaz and Rosenberg 2008, 926). This is reported mainly in stratified waters having a prominent thermocline, which prevents the mixing of cold bottom waters with warm surface waters. Hypoxic (low oxygen) zones are often succeeded by anoxic (no oxygen) zones. According to Diaz and Rosenberg (2008, 926), the number of hypoxic regions in coastal areas has increased dramatically with time; this change has been attributed to anthropogenic activities that increase the amount of bioavailable N that reaches the coastal ocean (Doney et al. 2012, 15).

Harmful Algal Blooms (HABs)

One of the most prominent consequences of nutrient loading is the widespread occurrence of Harmful Algal Blooms (HABs), particularly in response to increased N loading (Howarth 2008, 14). In addition to elevated nutrient levels supporting high biomass HABs, changes in the ratios of N, phosphorus, silica, and other nutrients, and the nature of nutrient input, whether pulsed or sustained, influence the group of HAB species that will dominate over other co-occurring phytoplankton species (Glibert et al. 2005a, 204; Glibert and Burkholder 2006, 348). Nutrient history (nutrient-repleted or nutrient-depleted) also determines the rate of nutrient uptake by the HAB species (Glibert et al. 2005a, 204) and thus, the dominant HAB species. The most common HAB causing organisms are dinoflagellates and cyanobacteria, in marine and freshwater environments, respectively (D'Silva et al. 2012, 1225).

The type of nutrient, whether organic or inorganic, is also significant. In addition to the inorganic N sources (NH_4^+, NO_3^-, and NO_2^-), organic N sources, that often predominate even in regions believed to be N-limited

(Bronk et al. 2007, 283), are also available to HAB species. Bronk et al. (2007, 283) further report that several phytoplankton species, including several HAB species, can utilise organic compounds, and discuss the potential acquisition mechanisms employed for this purpose (Table 15-1, Bronk et al. 2007, Burkholder, Glibert, and Skelton 2008). Moreover, many HAB species display mixo- or heterotrophic modes of nutrition and thus, rely on the organic forms of nutrients (Jones 1994). A case in point is the HAB species, *Aureococcus anophagefferens,* which uses organic N over NO_3^- (Glibert and Burkholder 2006, 347). Many HAB species can utilise urea, an organic compound, as the N substrate. The increase in urea-based fertilisers has been correlated with a documented increase in the worldwide occurrence of Paralytic Shellfish Poisoning (PSP) outbreaks in the period from 1970 to 2000 (Glibert et al. 2006, 441). The enhanced production of domoic acid, a toxin, by Amnesic Shellfish Poisoning (ASP)-causing *Pseudo-nitzschia multiseries* when grown with urea (Martin-Jezequel et al. 2015, 7067) further corroborated this link between urea and toxin production in the HAB species.

The massive proliferation of the HAB species causes deleterious effects on human health, the environment, and the economy. The biomagnification of the HAB toxins across the food web often results in poisoning syndromes in humans (amnesic, diarrhetic, neurotoxic, and paralytic effects, or venerupin shellfish poisoning and ciguatera fish poisoning) (Van Dolah, Roelke, and Greene 2001, 1331; James et al. 2010, 927). The proliferation of HAB species also leads to the overshadowing of benthic organisms, depletion of oxygen, and suffocation of fish, especially when these large amounts of phytoplankton biomass start decaying, leading to hypoxic conditions. The ecological effects also include mechanical interference with filter-feeding by fish and bivalve molluscs and direct toxic effects on fish and shellfish (Glibert et al. 2005b, 138). Various groups of organisms, from producers to secondary consumers are affected and ultimately, the trophic structure of the ecosystem changes.

A pivotal concern linked to the development of high biomass algal blooms is the inefficient transfer of energy to higher trophic levels since many bloom species are not the preferred food source for grazers (Mitra and Flynn 2006, 194; Glibert and Burkholder 2011, 725). This results in the reduced transfer of carbon and other nutrients to fish via the trophic web. This occurs through the secretion of bioactive metabolites by the HAB species, which inhibits the growth of co-occurring species (Graneli, Weberg, and Salomon 2008, 94). They also secrete allelochemicals, which serve as a deterrent to grazers due to their insidious effects on the reproductive potential of grazers. Therefore, when the HAB species grow to above a certain threshold value, grazing is suppressed (Mitra and Flynn 2006, 194).

Table 15-1: The strategies adopted by phytoplankton for acquiring dissolved organic compounds based on Bronk et al. (2007) and Burkholder, Glibert, and Skelton (2008)

Sr. No.	Strategy	Salient features
1.	Active transport/ Facilitated diffusion	• Used for small DON molecules like urea and some amino acids
2.	Enzymatic breakdown	• Used for large DON molecules (>1 kDa) such as proteins, polypeptides, and amino acids • Involves proteolytic enzymes (amino acid oxidases and aminopeptidases)
3.	Pinocytosis	• Ingestion by the cell of dissolved organic substrates from the external medium • Also termed 'osmotrophy' • Common strategy reported in HAB dinoflagellates – *Alexandrium catenella, Amphidinium carterae,* and *Prorocentrum micans*
4.	Phagocytosis	• Engulfment by the cell of particulate matter from the external environment • Also termed 'phagotrophy' • Observed in HAB dinoflagellates – *Ceratium furca* and *Heterocapsa triqueta*
5.	Photochemical decomposition	• Photooxidation mechanism through the action of ultraviolet (UV) radiation • Releases inorganic nitrogen and small, labile organic compounds (amino acids, urea) • Efficient strategy for large, humic acid molecules that are labile to UV radiation due to their aromatic nature

It is important to note that the synthesis of allelochemicals by the HAB species is promoted by unbalanced N or phosphorus conditions, that is, by eutrophication (Graneli, Weberg, and Salomon 2008, 94).

It must be remembered that eutrophication promotes HAB formation only along with a suite of favourable environmental factors. Also, the nature of nutrient input (whether pulsed or sustained), the nutritional history of the cell, the growth phase, and the physiological status of the phytoplankton community are some of the relevant factors that must be considered while discerning the effect of eutrophication on HABs (Glibert and Burkholder 2006, 347-349).

The Response of phytoplankton at the physiological level

The effects of eutrophication on phytoplankton communities can also be analysed for their growth strategies and resulting N/P ratios of their cellular machinery. Klausmeier et al. (2004, 171) put forth an optimisation model to study the effects of different growth conditions on the N/P ratios of the cellular machinery, and deviation from the canonical Redfield ratio. He observed that 'bloomers' have a low N/P ratio (<10), contain a significant proportion of growth machinery (for example, ribosomal RNA), and are well suited for exponential growth. They consist mainly of bloom-forming phytoplankton, and are reminiscent of *r*-selected phytoplankton (Kilham and Kilham 1980). The other category, the 'survivalists', have high N/P ratios (>30), possess considerable amounts of resource-acquisition machinery (for example, proteins and chlorophyll), and can sustain growth when resources are scarce. This seems to be analogous to *k*-selected organisms. The N/P ratios of 'survivalists' vary from 36-45, based on which resource is limiting. This indicates that eutrophication could affect even the stoichiometry of the phytoplankton.

Altered Nitrogen cycle and acidification of freshwater ecosystems

The input of N in aquatic systems can result in the acidification of the environments, particularly in those with a low acid neutralising ability (low alkalinity) (Baker and Christensen 1991). The major pollutants implicated in acidification are sulphur dioxide (SO_2), N dioxide (NO_2), and nitric oxide (NO) (Baker and Christensen 1991). Ammonium ions also contribute to acidification, through the process of NH_4^+ nitrification that produces hydrogen ions (Wetzel 2001). Since the regulations enforced in the 1980s in context with the Convention of Long-Range Transport of Air Pollution (CLRTAP), SO_2 emission levels have declined in large parts of Europe and North America. However, the same cannot be said for N oxide inputs in aquatic systems, which is now the major cause of acidification in freshwater systems (Vitousek et al. 2001, 743; Camargo and Alonso 2006, 833).

A pH range of 5.5-6.0 has been held as the threshold below which the aquatic biota will be negatively affected (Doka et al. 2003, 53). The resulting acidification, particularly in freshwater ecosystems, has several detrimental effects on the resident flora and fauna including reduced species diversity, respiratory and metabolic disturbances, arrested embryo development, and delay in egg hatching. The effects on primary producers are mainly observed in terms of the loss of sensitive species and the net reduction in photosynthesis and productivity (detailed in Camargo and Afonso 2006, 834). Additionally, pivotal processes of the N cycle like N fixation and NH_4^+ nitrification, which are significant for nutrient recycling across the various trophic levels, are also impacted.

In a recent study, Weiss et al. (2018, 327) reported the impairment of predator perception in response to acidification in *Daphnia*, a keystone freshwater predator. The authors discussed these effects in terms of ocean acidification. Given that ocean acidification is a widely researched phenomenon, they conceded that comparatively little is known about the impact of anthropogenically caused CO_2 on freshwater systems. This is because while oceans absorb CO_2 from the atmosphere, freshwater ecosystems have numerous sources from which they accumulate CO_2. They also experience N-mediated decreases in pH and thus, changes in biogeochemistry. They analysed the 35-year long-term datasets from four freshwater reservoirs and noticed a continuous pCO_2 increase linked with a decrease in pH, revealing CO_2 accumulation by inland waters. The resulting acidification affected the inducible defences in *Daphnia* caused by increased pCO_2, rather than reduced pH (Weiss et al. 2018, 327).

Concluding remarks

With the increase in studies on N cycling and the different groups of microorganisms involved, our understanding of the marine N cycle and its link to other major processes has been regularly changing. The discovery of anammox in natural systems, the role of AOA, and the recent findings on the significance of benthic foraminifera in N loss by denitrification have upended the previous understanding of the N cycle. Though several uncertainties still exist, the current global N budget indicates a non-linear input-output concentration of N in the oceanic ecosystem. The altered budget is a cause of concern in many ways. The increased loading of N_r in coastal ecosystems is the reason for eutrophication and proliferation of HABs. The consequences of HABs as an emerging threat for maritime countries and human health are globally known. Regular blooms and subsequent bloom decay have increased the number of dead zones or oxygen-deficient zones (ODZ) in coastal ecosystems. Such zones are the reason for sending N_2 back to the atmosphere through processes like denitrification and anammox. Furthermore, processes like nitrification and denitrification produce N_2O as a by-product. This strong greenhouse gas has received substantial interest from researchers concerning the quantification of its marine pathways and oceanic emissions. The production of N_2O is dependent on the oxygen content of the surrounding water column. Its production increases under suboxic conditions. Thus, ODZ formed due to eutrophication-triggered phytoplankton blooms can be ideal zones for the high emissions of N_2O. The oceans including coastal zones (particularly hypoxic/anoxic zones) contribute about 30% of the atmospheric N_2O budget. An increase in sea surface temperature would restrict primary production, reducing the organic matter transport, which would then serve to counteract oxygen depletion in deep waters. Similarly, the rate of nitrification and thus, the production of N_2O, would significantly reduce due to ocean acidification. However, there have been reports of a positive response of nitrification to low pH values. There are many missing gaps to predict anything at large and it opens up new paradigms.

The processes that are involved in the N cycle and their interactions are too complex and the complexity might be region-specific. There is a need of multiple complementary approaches including mesocosm and field experiments (designed based on mathematical models keeping specifically targeted processes), molecular approaches, metagenomics, cultivation, and biogeochemistry of microorganisms, and finally sophisticated computer models to simulate the interaction between these processes and evaluate the net effect on the ocean N cycle. In addition to this, it is also important to understand the critical issue of anthropogenic input that has a bigger share in altering the coastal ocean N budget. It is the root cause of the altered N cycles and the cascading events that follow. A question that urgently needs to be addressed is ‘How can we minimise the amount of N_r that gets released into the coastal ecosystems during food production?’

Such critical issues require a vision encompassing both environmental and resource management.

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