

# NITROGEN CYCLE

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doi:10.1006/rwos.2001.0275

## Introduction

The continued production of organic matter in the sea requires the availability of the many building blocks of life, including essential major elements such as carbon (C), nitrogen (N), and phosphorus (P); essential minor elements such as iron, zinc, and cobalt; and, for many marine organisms, essential trace organic nutrients that they cannot manufacture themselves (e.g., amino acids and vitamins). These required nutrients have diverse structural and metabolic function and, by definition, marine organisms cannot survive in their absence.

The marine nitrogen cycle is part of the much larger and interconnected hydrosphere–lithosphere–atmosphere–biosphere nitrogen cycle of the Earth. Furthermore, the oceanic cycles of carbon, nitrogen, and phosphorus are inextricably linked together through the production and remineralization of organic matter, especially near surface ocean phytoplankton production. This coordinated web of major bioelements can be viewed as the nutrient ‘super-cycle.’

The dominant form of nitrogen in the sea is dissolved gaseous dinitrogen ( $N_2$ ) which accounts for more than 95% of the total nitrogen inventory. However, the relative stability of the triple bond of  $N_2$  renders this form nearly inert. Although  $N_2$  can serve as a biologically-available nitrogen source for specialized  $N_2$ -fixing microorganisms, these organisms are relatively rare in most marine ecosystems. Consequently, chemically ‘fixed’ or ‘reactive’ nitrogen compounds such as nitrate ( $NO_3^-$ ), nitrite ( $NO_2^-$ ), ammonium ( $NH_4^+$ ), and dissolved and particulate organic nitrogen (DON/PON) serve as the principal sources of nitrogen to sustain biological processes.

For more than a century, oceanographers have been concerned with the identification of growth- and production-rate limiting factors. This has stimulated investigations of the marine nitrogen cycle including both inventory determinations and path-

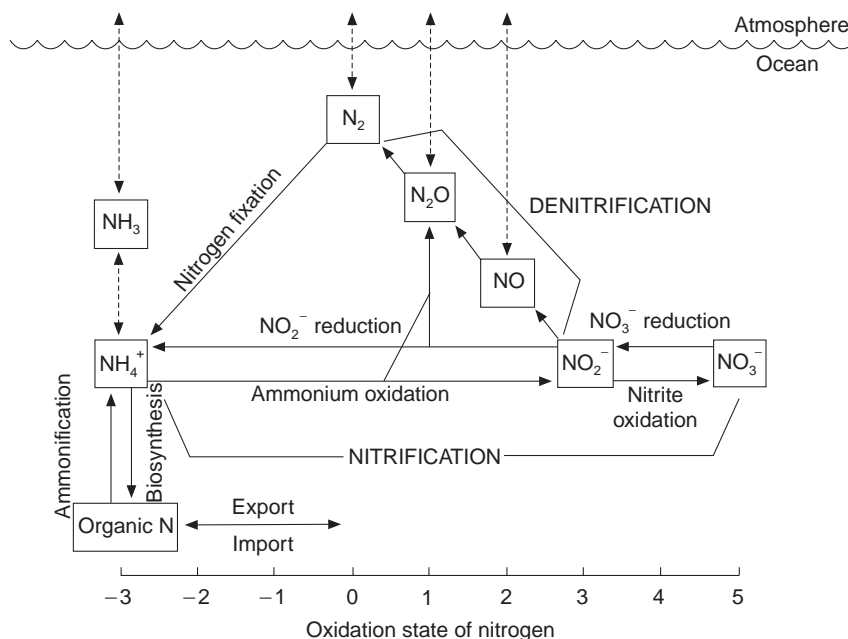
ways and controls of nitrogen transformations from one form to another. Contemporaneous ocean investigations have documented an inextricable link between nitrogen and phosphorus cycles, as well as the importance of trace inorganic nutrients. It now appears almost certain that nitrogen is only one of several key elements for life in the sea, neither more nor less important than the others. Although the basic features of the marine nitrogen cycle were established nearly 50 years ago, new pathways and novel microorganisms continue to be discovered. Consequently, our conceptual view of the nitrogen cycle is a flexible framework, always poised for readjustment.

## Methods and Units

The analytical determinations of the various dissolved and particulate forms of nitrogen in the sea rely largely on methods that have been in routine use for several decades. Determinations of  $NO_3^-$ ,  $NO_2^-$ , and  $NH_4^+$  generally employ automated shipboard, colorimetric assays, although surface waters of open ocean ecosystems demand the use of modern high-sensitivity chemiluminescence and fluorometric detection systems. PON is measured by high-temperature combustion followed by chromatographic detection of the by-product ( $N_2$ ), usually with a commercial C–N analyzer. Total dissolved nitrogen (TDN) determination employs sample oxidation, by chemical or photolytic means, followed by measurement of  $NO_3^-$ . DON is calculated as the difference between TDN and the measured dissolved, reactive inorganic forms of N ( $NO_3^-$ ,  $NO_2^-$ ,  $NH_4^+$ ) present in the original sample. Gaseous forms of nitrogen, including  $N_2$ , nitrous oxide ( $N_2O$ ), and nitric oxide (NO) are generally measured by gas chromatography.

Nitrogen exists naturally as two stable isotopes,  $^{14}N$  (99.6% by atoms) and  $^{15}N$  (0.4% by atoms). These isotopes can be used to study the marine nitrogen cycle by examination of natural variations in the  $^{14}N/^{15}N$  ratio, or by the addition of specific tracers that are artificially enriched in  $^{15}N$ .

Most studies of oceanic nitrogen inventories or transformations use either molar or mass units; conversion between the two is straightforward (1 mole N = 14 gN, keeping in mind that the molecular weight of  $N_2$  gas is 28).



**Figure 1** Schematic representation of the various transformations from one form of nitrogen to another that compose the marine nitrogen cycle. Shown at the bottom is the oxidation state of nitrogen for each of the components. Most transformations are microbiological and most involve nitrogen reduction or oxidation. (Adapted from Capone, ch. 14 of Rogers and Whitman (1991).)

### Components of the Marine Nitrogen Cycle

The systematic transformation of one form of nitrogen to another is referred to as the nitrogen cycle (Figure 1). In the sea, the nitrogen cycle revolves around the metabolic activities of selected microorganisms and it is reasonable to refer to it as the microbial nitrogen cycle because it depends on bacteria (Table 1). During most of these nitrogen transformations there is a gain or loss of electrons and, therefore, a change in the oxidation state of nitrogen from the most oxidized form,  $NO_3^-$  (+5), to

the most reduced form,  $NH_4^+$  (-3). Transformations in the nitrogen cycle are generally either energy-requiring (reductions) or energy-yielding (oxidations). The gaseous forms of nitrogen in the surface ocean can freely exchange with the atmosphere, so there is a constant flux of nitrogen between these two pools.

The natural, stepwise process for the regeneration of  $NO_3^-$  from PON can be reproduced in a simple ‘decomposition experiment’ in an enclosed bottle of sea water (Figure 2). During a 3-month incubation period, the nitrogen contained in particulate matter is first released as  $NH_4^+$  (the process of

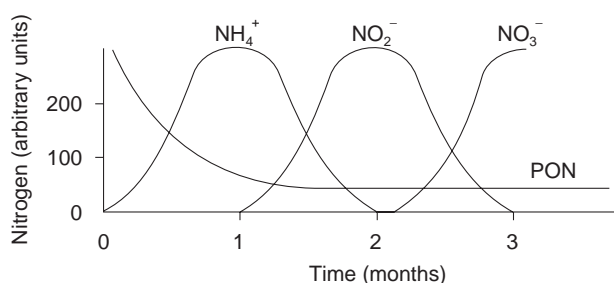
**Table 1** Marine nitrogen cycle

Process	Credits		
	Bacteria	Phytoplankton <sup>a</sup>	Zooplankton/Fish <sup>b</sup>
$NH_4^+$ production from DON/PON (ammonification)	+	+	+
$NH_4^+$ / $NO_2^-$ / $NO_3^-$ /DON assimilation	+	+	-
PON ingestion	-	+	+
$NH_4^+ \rightarrow NO_2^-$ (nitrification, step 1)	+	-	-
$NO_2^- \rightarrow NO_3^-/N_2O$ (nitrification, step 2)	+	-	-
$NO_3^-/NO_2^- \rightarrow N_2/N_2O$ (denitrification)	+	+	-
$N_2 \rightarrow NH_4^+$ /organic N ( $N_2$ fixation)	+	-	-

Abbreviations:  $NH_4^+$ , ammonium;  $NO_2^-$ , nitrite;  $NO_3^-$ , nitrate;  $N_2O$ , nitrous oxide;  $N_2$ , dinitrogen; DON, dissolved organic N; PON, particulate organic N; organic N, DON and PON.

<sup>a</sup>Phytoplankton – eukaryotic phytoplankton.

<sup>b</sup>Zooplankton – including protozoans and metazoans.



**Figure 2** Stepwise decomposition of particulate organic nitrogen (PON) in arbitrary units versus time during a dark incubation. Nitrogen is transformed, first to  $\text{NH}_4^+$  by bacterial ammonification and finally to  $\text{NO}_2^-$  and  $\text{NO}_3^-$  by the two-step process of bacterial nitrification. These same processes are responsible for the global ocean formation of  $\text{NO}_3^-$  in the deep sea. These data are the idealized results of pioneering nitrogen cycle investigators, T. von Brand and N. Rakestraw, who unraveled these processes more than 50 years ago.

ammonification), then transformed to  $\text{NO}_2^-$  (first step of nitrification), and finally, and quantitatively, to  $\text{NO}_3^-$  (the second step of nitrification). These transformations are almost exclusively a result of the metabolic activities of bacteria. This set of regeneration reactions is vital to the nitrogen cycle, and since most deep water nitrogen (excluding  $\text{N}_2$ ) is in the form of  $\text{NO}_3^-$ , bacterial nitrification must be a very important process (see Nitrogen Distributions in the Sea, below).

### Nitrogen Assimilation

Several forms of nitrogen can be directly transported across cell membranes and assimilated into new cellular materials as required for biosynthesis and growth. Most microorganisms readily transport  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ , and selected DON compounds such as amino acids, urea, and nucleic acid bases. By comparison, the ability to utilize  $\text{N}_2$  as a nitrogen source for biosynthesis is restricted to a very few species of specialized microbes. Many protozoans, including both photosynthetic and heterotrophic species, and all metazoans obtain nitrogen primarily by ingestion of PON.

Once inside the cell or organism, nitrogen is digested and, if necessary, reduced to  $\text{NH}_4^+$ . If oxidized compounds such as  $\text{NO}_3^-$  or  $\text{NO}_2^-$  are utilized, cellular energy must be invested to reduce these substrates to ammonium for incorporation into organic matter. The process of reduction of  $\text{NO}_3^-$  (or  $\text{NO}_2^-$ ) for the purpose of cell growth is referred to as assimilatory nitrogen ( $\text{NO}_3^-/\text{NO}_2^-$ ) reduction and most microorganisms, both bacteria and phytoplankton, possess this metabolic capability (Table 1). In theory, there should be a metabolic

preference for  $\text{NH}_4^+$  over either  $\text{NO}_3^-$  or  $\text{NO}_2^-$ , based strictly on energetic considerations. However, it should be emphasized that preferential utilization of  $\text{NH}_4^+$  does not always occur. For example, two closely related and abundant planktonic cyanobacteria that coexist in tropical and subtropical marine habitats have devised alternate metabolic strategies: *Synechococcus* prefers  $\text{NO}_3^-$  and *Prochlorococcus* prefers  $\text{NH}_4^+$ . In fact, *Prochlorococcus* cannot reduce  $\text{NO}_3^-$  to  $\text{NH}_4^+$ , presumably because the critical enzyme systems are absent.

### Nitrification

As nitrogen is oxidized from  $\text{NH}_4^+$  through  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , energy is released (Figure 1), a portion of which can be coupled to the reduction of carbon dioxide ( $\text{CO}_2$ ) to organic matter ( $\text{CH}_2\text{O}$ ) by nitrifying bacteria. These specialized bacteria, one group capable only of the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  and the second capable only of the oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , are termed 'chemolithoautotrophic' because they can fix  $\text{CO}_2$  in the dark at the expense of chemical energy. Other related chemolithoautotrophs can oxidize reduced sulfur compounds, and this pathway of organic matter production has been hypothesized as the basis for life at deep-sea hydrothermal vents.

It is essential to emphasize an important ecological aspect of  $\text{NH}_4^+/\text{NO}_2^-$  chemolithoautotrophy. First, the oxidation of  $\text{NH}_4^+$  to  $\text{NO}_2^-$  and of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  usually requires oxygen and these processes are ultimately coupled to the photosynthetic production of oxygen in the surface water. Second, the continued formation of reduced nitrogen, in the form of  $\text{NH}_4^+$  or organic nitrogen, is also dependent, ultimately, on photosynthesis. In this regard the  $\text{CO}_2$  reduced via this 'autotrophic' pathway must be considered secondary, not primary, production from an ecological energetics perspective.

Marine nitrifying bacteria, especially the  $\text{NO}_2^-$  oxidizers are ubiquitous in the world ocean and key to the regeneration of  $\text{NO}_3^-$ , which dominates waters below the well-illuminated, euphotic zone. However they are never very abundant and, at least for those species in culture, grow very slowly. Certain heterotrophic bacteria can also oxidize  $\text{NH}_4^+$  to both  $\text{NO}_2^-$  and  $\text{NO}_3^-$  during metabolism of preformed organic matter. However, very little is known about the potential for 'heterotrophic nitrification' in the sea.

### Denitrification

Under conditions of reduced oxygen ( $\text{O}_2$ ) availability, selected species of marine bacteria can use

$\text{NO}_3^-$  as a terminal acceptor for electrons during metabolism, a process termed  $\text{NO}_3^-$  respiration or dissimilatory  $\text{NO}_3^-$  reduction. This process allows microorganisms to utilize organic matter in low- $\text{O}_2$  or anoxic habitats with only a slight loss of efficiency relative to  $\text{O}_2$ -based metabolism. A majority of marine bacteria have the ability for  $\text{NO}_3^-$  respiration under the appropriate environmental conditions (Table 1). Potential by-products of  $\text{NO}_3^-$  respiration are  $\text{NO}_2^-$ ,  $\text{N}_2$ , and  $\text{N}_2\text{O}$ ; if a gas is formed ( $\text{N}_2/\text{N}_2\text{O}$ ) then the process is termed denitrification because the net effect is to remove bioavailable nitrogen from the local environment. The total rate of denitrification is generally limited by the availability of  $\text{NO}_3^-$ , and a continued supply of  $\text{NO}_3^-$  via nitrification is dependent upon the availability of  $\text{NH}_4^+$  and free  $\text{O}_2$ . Consequently denitrification typically occurs at boundaries between low- $\text{O}_2$  and anoxic conditions where the supply of  $\text{NH}_4^+$  from the anoxic zone sustains a high rate of  $\text{NO}_3^-$  production via nitrification to fuel-sustained  $\text{NO}_3^-$  respiration and denitrification. Recently a new group of microorganisms has been isolated that are capable of simultaneously using both  $\text{O}_2$  and  $\text{NO}_3^-/\text{NO}_2^-$  as terminal electron acceptors. This process is termed 'aerobic denitrification.' Likewise, there are exceptional microorganisms that are able to carry out anaerobic nitrification (oxidation of  $\text{NH}_4^+$  in the absence of  $\text{O}_2$ ). It appears difficult to establish any hard-and-fast rules regarding marine nitrogen cycle processes.

### **$\text{N}_2$ Fixation**

The ability to use  $\text{N}_2$  as a growth substrate is restricted to a relatively small group of microorganisms. Open ocean ecosystems that are chronically depleted in fixed nitrogen would appear to be ideal habitats for the proliferation of  $\text{N}_2$ -fixing microorganisms. However, the enzyme that is required for reduction of  $\text{N}_2$  to  $\text{NH}_4^+$  is also inhibited by  $\text{O}_2$ , so specialized structural, molecular, and behavioral adaptations have evolved to promote oceanic  $\text{N}_2$  fixation.

Fixation of molecular nitrogen in the open ocean may also be limited by the availability of iron, which is an essential cofactor for the  $\text{N}_2$  reduction enzyme system. Changes in iron loading are caused by climate variations, in particular the areal extent of global deserts, by the intensity of atmospheric circulation, and more recently by changes in land use practices. Conversion of deserts into irrigated croplands may cause a change in the pattern and intensity of dust production and, therefore, of iron transport to the sea. Humanity is also altering the

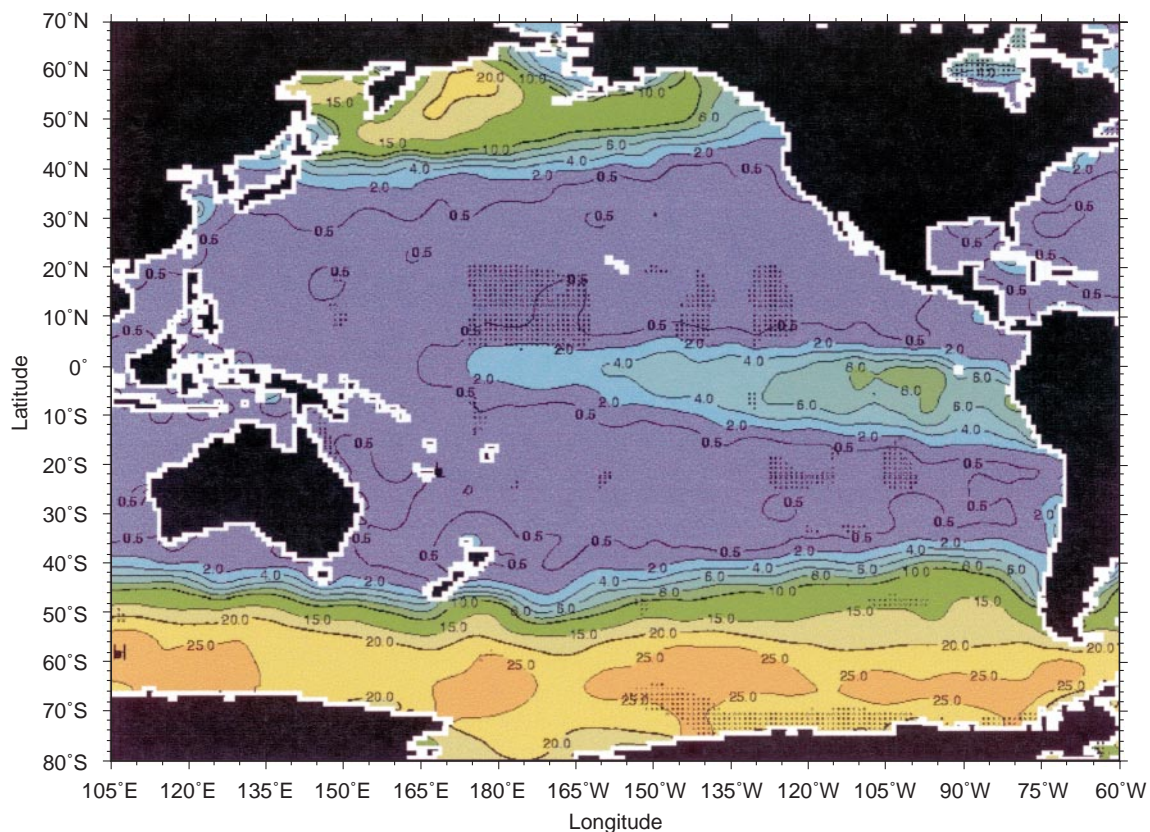
global nitrogen cycle by enhancing the fixation of  $\text{N}_2$  by the manufacturing of fertilizer. At the present time, the industrial fixation of  $\text{N}_2$  is approximately equivalent to the pre-industrial, natural  $\text{N}_2$  fixation rate. Eventually some of this artificially fixed  $\text{N}_2$  will make its way to the sea, and this may lead to a perturbation in the natural nitrogen cycle.

On a global scale and over relatively long timescales, the total rate of  $\text{N}_2$  fixation is more or less in balance with total denitrification, so that the nitrogen cycle is mass-balanced. However, significant net deficits or excesses can be observed locally or even on ocean basin space scales and on decade to century timescales. These nitrogen imbalances may impact the global carbon and phosphorus cycles as well, including the net balance of  $\text{CO}_2$  between the ocean and the atmosphere.

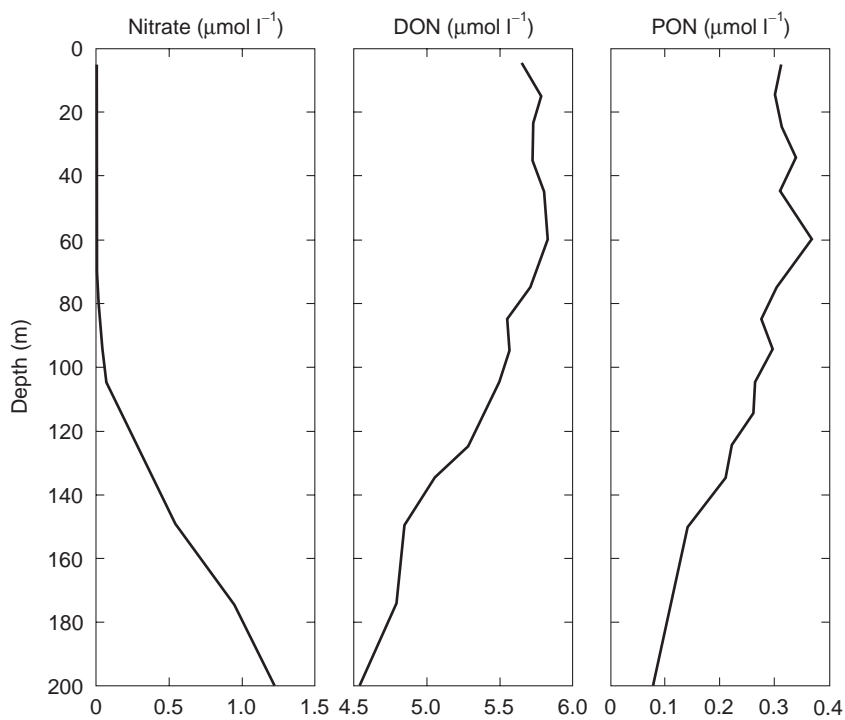
### **Nitrogen Distributions in the Sea**

Required growth nutrients, like nitrogen, typically have uneven distributions in the open sea, with deficits in areas where net organic matter is produced and exported, and excesses in areas where organic matter is decomposed. For example, surface ocean  $\text{NO}_3^-$  distributions in the Pacific basin reveal a coherent pattern with excess  $\text{NO}_3^-$  in high latitudes, especially in the Southern Ocean (south of  $60^\circ\text{S}$ ), and along the Equator (especially east of the dateline), and generally depleted  $\text{NO}_3^-$  concentrations in the middle latitudes of both hemispheres (Figure 3). These distributions are a result of the balance between  $\text{NO}_3^-$  supply mostly by ocean mixing and  $\text{NO}_3^-$  demand or net photosynthesis. The very large  $\text{NO}_3^-$  inventory in the surface waters of the Southern Ocean implies that factors other than fixed nitrogen availability control photosynthesis in these regions. It has been hypothesized that the availability of iron is key in this and perhaps other regions of the open ocean. The much smaller but very distinctive band of elevated  $\text{NO}_3^-$  along the Equator is the result of upwelling of  $\text{NO}_3^-$ -enriched waters from depth to the surface. This process has a large seasonal and, especially, interannual variability, and it is almost absent during El Niño conditions.

Excluding these high-latitude and equatorial regions, the remainder of the surface waters of the North and South Pacific Oceans from about  $40^\circ\text{N}$  to  $40^\circ\text{S}$  are relatively depleted in  $\text{NO}_3^-$ . In fact surface (0–50 m)  $\text{NO}_3^-$  concentrations in the North Pacific subtropical gyre near Hawaii are typically below  $0.01\ \mu\text{mol l}^{-1}$  (Figure 4). Within the upper 200 m, the major pools of fixed nitrogen (e.g.,  $\text{NO}_3^-$ , DON, and PON) have different depth



**Figure 3** Mean annual  $\text{NO}_3^-$  concentration ( $\mu\text{mol l}^{-1}$ ) at the sea surface for samples collected in the Pacific Ocean basin and Pacific sector of the Southern Ocean. (From Conkright *et al.* 1998.)



**Figure 4** Average concentrations ( $\mu\text{mol l}^{-1}$ ) of  $\text{NO}_3^-$ , DON, and PON versus water depth for samples collected in the upper 200 m of the water column at Sta. ALOHA (22.75°N, 158.0°W). These field data are from the Hawaii Ocean Time-series program and are available at <http://hahana.soest.edu/hotLjgofs.html>.

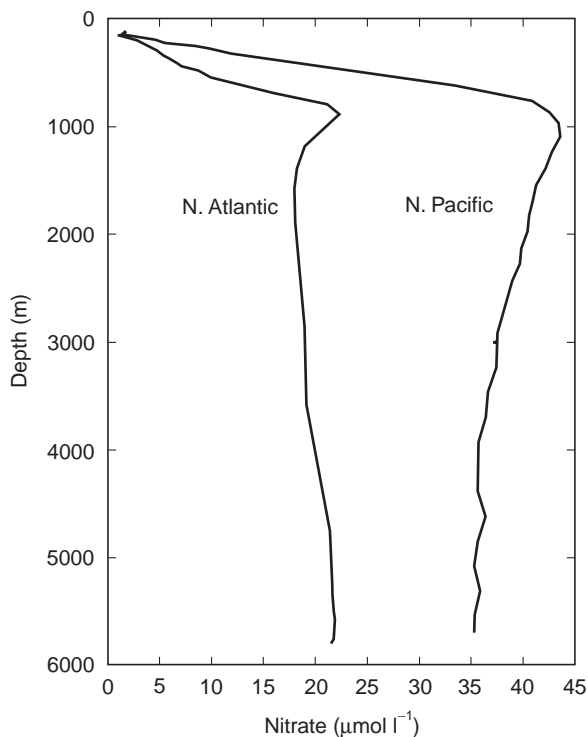
distributions. In the sunlit surface zone,  $\text{NO}_3^-$  is removed to sustain organic matter production and export. Beneath 100 m, there is a steep concentration versus depth gradient (referred to as the nutricline), which reaches a maximum of about  $40\text{--}45\ \mu\text{mol l}^{-1}$  at about 1000 m in the North Pacific Ocean. PON concentration is greatest in the near-surface waters where the production of organic matter via photosynthesis is highest (Figure 4). PON includes both living (biomass) and nonliving (detrital) components; usually biomass nitrogen is less than 50% of the total PON in near-surface waters, and less than 10% beneath the euphotic zone ( $>150\text{ m}$ ). DON concentration is also highest in the euphotic zone ( $\sim 5\text{--}6\ \mu\text{mol l}^{-1}$ ) and decreases systematically with depth to a minimum of  $2\text{--}3\ \mu\text{mol l}^{-1}$  at 800–1000 m. The main sources for DON in the surface ocean are the combined processes of excretion, grazing, death, and cell lysis. Consequently, DON is a complex mixture of cell-derived biochemicals; at present, less than 20% of the total DON has been chemically characterized. Dissolved  $\text{N}_2$  (not shown) is always high ( $\sim 800\ \mu\text{mol l}^{-1}$ ) and increases systematically with depth. The major controls of  $\text{N}_2$  concentration are

temperature and salinity, which together determine gas solubility. Marine life has little impact on  $\text{N}_2$  distributions in the open sea even though some microorganisms can utilize  $\text{N}_2$  as a growth substrate and others can produce  $\text{N}_2$  as a metabolic by-product. These transformations are simply too small to significantly impact the large  $\text{N}_2$  inventories in most regions of the world ocean.

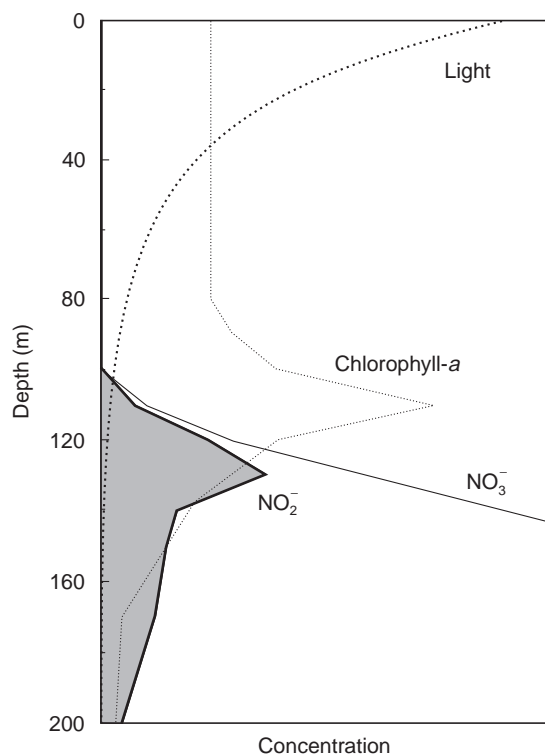
Another important feature of the global distribution of  $\text{NO}_3^-$  is the regional variability in the deep water inventory (Figure 5). Deep ocean circulation can be viewed as a conveyor-belt-like flow, with the youngest waters in the North Atlantic and the oldest in the North Pacific. The transit time is in excess of 1000 y, during which time  $\text{NO}_3^-$  is continuously regenerated from exported particulate and dissolved organic matter via coupled ammonification and nitrification (Figure 2). Consequently, the deep Pacific Ocean has nearly twice as much  $\text{NO}_3^-$  as comparable depths in the North Atlantic (Figure 5).

#### Nitrous Oxide Production

Nitrous oxide ( $\text{N}_2\text{O}$ ) is a potent greenhouse gas that has also been implicated in stratospheric ozone depletion. The atmospheric inventory of  $\text{N}_2\text{O}$  is presently increasing, so there is a renewed interest in the marine ecosystem as a potential source of  $\text{N}_2\text{O}$ . Nitrous oxide is a trace gas in sea water, with typical concentrations ranging from 5 to  $50\ \text{nmol l}^{-1}$ . Concentrations of  $\text{N}_2\text{O}$  in oceanic surface waters are generally in slight excess of air saturation, implying both a local source and a sustained ocean-to-atmosphere flux. Typically there is a mid-water (500–1000 m) peak in  $\text{N}_2\text{O}$  concentration that coincides with the dissolved oxygen minimum. At these intermediate water depths,  $\text{N}_2\text{O}$  can exceed 300% saturation relative to atmospheric equilibrium. The two most probable sources of  $\text{N}_2\text{O}$  in the ocean are bacterial nitrification and bacterial denitrification, although to date it has been difficult to quantify the relative contribution of each pathway for a given habitat. Isotopic measurements of nitrogen and oxygen could prove invaluable in this regard. Because the various nitrogen cycle reactions are interconnected, changes in the rate of any one process will likely have an impact on the others. For example, selection for  $\text{N}_2$ -fixing organisms as a consequence of dust deposition or deliberate iron fertilization would increase the local  $\text{NH}_4^+$  inventory and lead to accelerated rates of nitrification and, hence, enhanced  $\text{N}_2\text{O}$  production in the surface ocean and flux to the atmosphere.



**Figure 5** Nitrate concentrations ( $\mu\text{mol l}^{-1}$ ) versus water depth at two contrasting stations located in the North Atlantic ( $31.8^\circ\text{N}$ ,  $50.9^\circ\text{W}$ ) and North Pacific ( $30^\circ\text{N}$ ,  $160.3^\circ\text{W}$ ) Oceans. These data were collected in the 1970s during the worldwide GEOSECS expedition, stations #119 and #212, respectively.



**Figure 6** Schematic representation of the depth distributions of sunlight, chlorophyll-*a*,  $\text{NO}_2^-$ , and  $\text{NO}_3^-$  for a representative station in the subtropical North Pacific Ocean showing the relationship of the primary  $\text{NO}_2^-$  maximum (PNM) zone (shaded) to the other environmental variables. (Modified from J. E. Dore, Microbial nitrification in the marine euphotic zone, Ph.D. Dissertation, University of Hawaii, redrawn with permission of the author.)

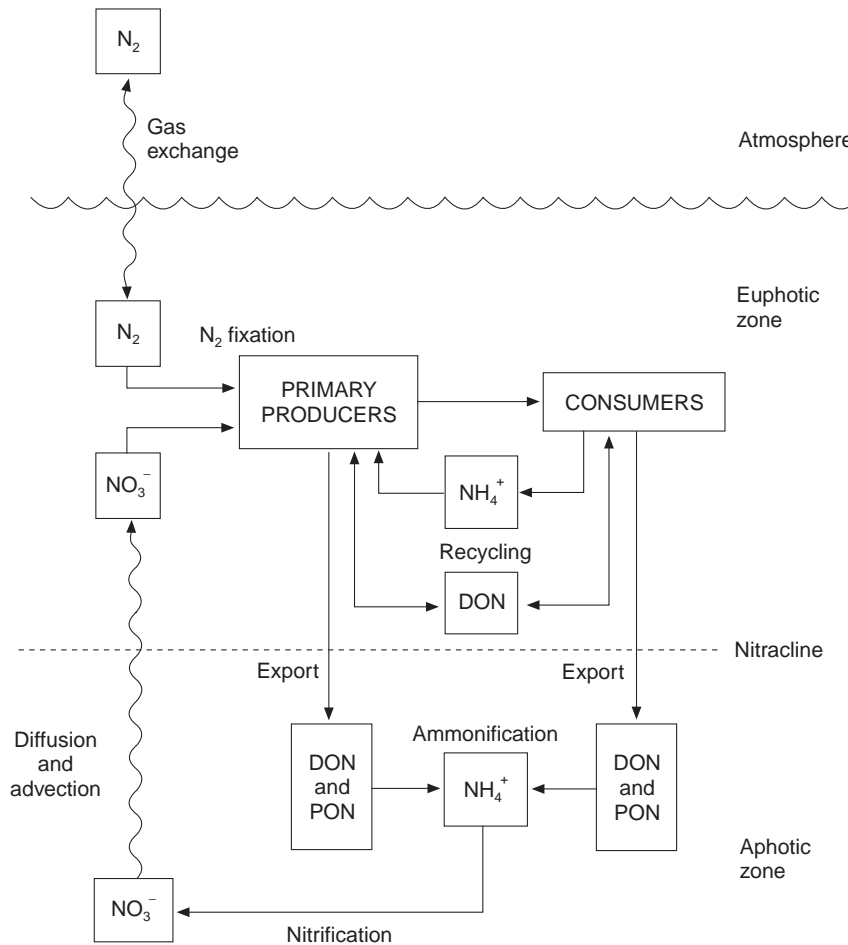
### Primary $\text{NO}_2^-$ Maximum

An interesting, almost cosmopolitan feature of the world ocean is the existence of a primary  $\text{NO}_2^-$  maximum (PNM) near the base of the euphotic zone ( $\sim 100\text{--}150\text{ m}$ ; **Figure 6**). Nitrite is a key intermediate between  $\text{NO}_3^-$  and  $\text{NH}_4^+$ , so there are several potential pathways, both oxidative and reductive, that might lead to its accumulation in sea water. First, phototrophic organisms growing on  $\text{NO}_3^-$  may partially reduce the substrate to  $\text{NO}_2^-$  as the first, and least energy-consuming, step in the assimilatory  $\text{NO}_3^-$  reduction pathway. However, the next step, reduction of  $\text{NO}_2^-$  to  $\text{NH}_4^+$ , requires a substantial amount of energy, so when energy is scarce (e.g., light limitation)  $\text{NO}_2^-$  accumulates inside the cells. Because  $\text{NO}_2^-$  is the salt of a weak acid, nitrous acid ( $\text{HNO}_2$ ) forms in the slightly acidic intracellular environment, diffuses out of the cell and ionizes to form  $\text{NO}_2^-$  in the alkaline sea water. This  $\text{NO}_3^- \rightarrow \text{NO}_2^-$  phytoplankton pump,

under the control of light intensity, could provide a source of  $\text{NO}_2^-$  necessary to create and maintain the PNM. Alternatively, local regeneration of dissolved and particulate organic matter could produce  $\text{NH}_4^+$  (via ammonification) that is partially oxidized in place to produce a relative excess of  $\text{NO}_2^-$  (the first step of nitrification). Kinetic controls on this process would be rates of  $\text{NH}_4^+$  production and  $\text{NO}_2^-$  oxidation to  $\text{NO}_3^-$  (the second and final step in nitrification). Sunlight, even at very low levels, appears to disrupt the normal coupling between  $\text{NO}_2^-$  production and  $\text{NO}_2^-$  oxidation, in favor of  $\text{NO}_2^-$  accumulation. Finally, it is possible, though perhaps less likely, that  $\text{NO}_3^-$  respiration (terminating at  $\text{NO}_2^-$ ), followed by excretion of  $\text{NO}_2^-$  (into the surrounding sea water might also contribute to the accumulation of  $\text{NO}_2^-$ ) near the base of the euphotic zone. Because the global ocean at the depth of the PNM is characteristically well-oxygenated, one would need to invoke micro-environments like animal guts or large particles as the habitats for this nitrogen cycle pathway. The use of  $^{15}\text{N}$ -labeled substrates, selective metabolic inhibitors, and other experimental manipulations provides an opportunity for direct assessment of the role of each of these potential processes. In all likelihood, more than one of these processes contributes to the observed PNM. Whatever the cause, light appears to be an important determinant that might explain the relative position, with regard to depth, of this global feature.

### Nitrogen Cycle and Ocean Productivity

Because nitrogen transformations include both the formation and decomposition of organic matter, much of the nitrogen used in photosynthesis is locally recycled back to  $\text{NH}_4^+$  or  $\text{NO}_3^-$  to support another pass through the cycle. The net removal of nitrogen in particulate, dissolved, or gaseous form can cause the cycle to slow down or even terminate unless new nitrogen is imported from an external source. A unifying concept in the study of nutrient dynamics in the sea is the 'new' versus 'regenerated' nitrogen dichotomy (**Figure 7**). New nitrogen is imported from surrounding regions (e.g.,  $\text{NO}_3^-$  injection from below) or locally created (e.g.,  $\text{NH}_4^+$ /organic N from  $\text{N}_2$  fixation). Regenerated nitrogen is locally recycled (e.g.,  $\text{NH}_4^+$  from ammonification,  $\text{NO}_2^-/\text{NO}_3^-$  from nitrification, or DON from grazing or cell lysis). Under steady-state conditions, the amount of new nitrogen entering an



**Figure 7** Schematic representation of the major pools and transformations/fluxes of nitrogen in a typical open ocean ecosystem. New sources of bioavailable N ( $\text{NO}_3^-$  and  $\text{N}_2$  in this presentation) continuously resupply nitrogen that is lost via DON and PON export. These interactions and ocean processes form the conceptual framework for the 'new' versus 'regenerated' paradigm for nitrogen dynamics in the sea that was originally proposed by R. Dugdale and J. Goering.

ecosystem will determine the total amount that can be exported without the system running down.

In shallow, coastal regions runoff from land or movement upward from the sediments are potentially major sources of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and DON for water column processes. In certain regions, atmospheric deposition (both wet and dry) may also supply bioavailable nitrogen to the system. However, in most open ocean environments, new sources of nitrogen required to balance the net losses from the euphotic zone are restricted to upward diffusion or mixing of  $\text{NO}_3^-$  from deep water and to local fixation of  $\text{N}_2$  gas. In a balanced steady state, the importation rate of new sources of bioavailable nitrogen will constrain the export of nitrogen (including fisheries production and harvesting). If all other required nutrients are available, export-rich ecosystems are those characterized by high bioavailable nitrogen loading such as coastal and open

ocean upwelling regions. These are also the major regions of fish production in the sea.

## See also

**Atmospheric Input of Pollutants. Nitrogen Isotopes in the Ocean. Phosphorus Cycle. Primary Production Processes.**

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## NITROGEN ISOTOPES IN THE OCEAN

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doi:10.1006/rwos.2001.0172

### Introduction

Nitrogen has two stable isotopes,  $^{14}\text{N}$  and  $^{15}\text{N}$  (atomic masses of 14 and 15, respectively).  $^{14}\text{N}$  is the more abundant of the two, comprising 99.63% of the nitrogen found in nature. Physical, chemical, and biological processes discriminate between the two isotopes. This is known as isotopic fractionation, and it leads to subtle but measurable differences in the ratio of  $^{15}\text{N}$  to  $^{14}\text{N}$  among different forms of nitrogen found in the marine environment.

Nitrogen is a central component of marine biomass and one of the major nutrients required by all phytoplankton. In this sense, biologically available (or 'fixed') N is representative of the fundamental patterns of biogeochemical cycling in the ocean. However, N differs from other nutrients in that its oceanic sources and sinks are dominantly internal and biological, with marine  $\text{N}_2$  fixation supplying much of the fixed N in the ocean and marine denitrification removing it. The N isotopes provide a means of studying both the internal cycling and input/output budget of oceanic fixed N, yielding information on both its representative and unique aspects. This overview outlines the isotope systematics of N cycle processes and their impacts on the isotopic composition of the major N reservoirs in the ocean. This information provides a starting point for considering the wide range of questions in ocean sciences to which the N isotopes can be applied.

### Terms and Units

Mass spectrometry can measure precisely the ratio of the N isotopes relative to a N standard containing a constant isotopic ratio. The universal reference

standard for N isotopes is atmospheric  $\text{N}_2$ , with a  $^{15}\text{N}/^{14}\text{N}$  ratio of  $0.36765\% \pm 0.00081\%$ . Natural samples exhibit small deviations from the standard ratio, which are expressed in  $\delta$ -notation (in units of per mil, ‰):

$$\delta^{15}\text{N}(\text{‰}) = \left( \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} - 1 \right) \times 1000 \quad [1]$$

In this notation, the  $\delta^{15}\text{N}$  of atmospheric  $\text{N}_2$  is 0‰.

Special terms are also used to characterize the amplitude of isotopic fractionation caused by a given process. Isotope fractionation occurs both in equilibrium processes ('equilibrium fractionation') and unidirectional reactions ('kinetic fractionation'). Nitrogen isotope variations in the ocean are dominated by kinetic fractionation associated with the conversions of N from one form to another. The kinetic effect,  $\varepsilon$ , of a given reaction is defined by the difference in rates with which the two N isotopes are converted from reactant into product. For instance, if a reaction has an  $\varepsilon$  of 5‰, then the  $\delta^{15}\text{N}$  of the product N generated at any given time will be  $\sim 5\%$  lower than the  $\delta^{15}\text{N}$  of the reactant N.

$$\varepsilon(\text{‰}) = ({}^{14}k/{}^{15}k - 1) \times 1000, \quad [2]$$

where  ${}^{14}k$  and  ${}^{15}k$  are the rate coefficients of the reaction for  $^{14}\text{N}$ - and  $^{15}\text{N}$ -containing reactant, respectively. For  $\varepsilon \ll 1000\%$ ,  $\varepsilon$  is approximated by the difference in  $\delta^{15}\text{N}$  between the reactant and its instantaneous product.

### Measurements

The isotopic analysis of N relies on the generation of a stable gas, typically  $\text{N}_2$ , as the analyte for isotope ratio mass spectrometry. On-line combustion to  $\text{N}_2$  is the standard method for the preparation of a N sample for isotopic analysis. With current 'off-the-shelf' technology, a typical sample size requirement is 1–4  $\mu\text{mol}$  N per analysis. There are standard methods of collection for most bulk