PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY B BIOLOGICAL SCIENCES

Nitrogen Cycling in Sea Waters

G. E. Fogg

Phil. Trans. R. Soc. Lond. B 1982 **296**, 511-520
doi: 10.1098/rstb.1982.0023

Phil. Trans. R. Soc. Lond. B **296**, 511–520 (1982)
Printed in Great Britain

Nitrogen cycling in sea waters

By G. E. Fogg, F.R.S.

Department of Marine Biology, University College of North Wales, Marine Science Laboratories,
Menai Bridge, Anglesey, Gwynedd LL59 5EH, U.K.

An attempt to quantify the cycling of N in the oceans suggests that losses of combined N greatly exceed gains, a discrepancy that points to the inadequacy of our knowledge of the processes involved. Combined N in particulate matter sedimenting into deep water is partly returned to the euphotic zone in the form of nitrate, the rate of this upward flux of new nitrogen being the main determinant of the upper limit of biomass in any given area. Within the euphotic zone combined N is rapidly recycled by bacteria and animals and in oligotrophic areas the ammonium, urea, and perhaps organic, N that they make available is the main source maintaining phytoplankton growth.

1. Introduction

The biochemical transformations of N in sea waters are presumably similar to those that take place in terrestrial situations, but the pattern in which they occur is a characteristic one imposed by the marine environment. Since combined N often seems to be a major factor limiting organic production in the sea, understanding of its cycling is of basic importance to marine biologists. In considering our present rather incomplete knowledge, it is convenient to distinguish processes at three different levels: the oceanic cycle and cycling between the euphotic zone and deep water, both of which have turnover times of the order of 1000 years, and cycling within the euphotic zone, with a turnover time of days. The general oceanic cycle has been discussed by Söderland & Svensson (1976) and Fogg (1978), whereas Spencer (1975), Dugdale (1976) and McCarthy (1980) have reviewed chemical aspects and N nutrition of phytoplankton.

2. The oceanic cycle

(*a*) *Inputs*

(i) *Biological N_2 fixation*

The greatest contribution in N_2 fixation seems to come from photosynthetic blue-green algae (Cyanobacteria) of the genus *Trichodesmium* (*Oscillatoria*), fixation by heterotrophic bacteria, either in the water column or sediments, being negligible (Fogg 1978). Fixation by *Trichodesmium*, assuming it to be widespread between 30° N and 30° S, may amount to 10.6 Mt N annually (Fogg 1981). Even in sea areas where it is abundant, *Trichodesmium* and another occasionally abundant blue-green alga, the symbiotic *Richelia*, appear usually to contribute only a small percentage of the total N requirement of the phytoplankton (Mague *et al.* 1974, 1977; Gundersen *et al.* 1976; Dunstan & Atkinson 1976). Although high rates of N_2 fixation are achieved locally in brackish water by heterocystous blue-green algae such as Nodularia spp. (Hübel & Hübel 1980) the total fixation in the Baltic seems only to be about 0.1 Mt N annually (Horstmann *et al.* 1978).

Rau (1981) reported that $^{15}N:^{14}N$ ratios in animals from hydrothermal vents are lower than those for organic, ammonium and nitrate nitrogen in deep Pacific Ocean water and resemble those of marine biota dependent on N_2 fixation. If N_2 fixation occurs in these areas – and the conditions would seem to favour it – then this might be an appreciable source of combined N in the oceans. Taking the length of the mid-ocean ridges as 64000 km and the average width as 1000 km, and guessing that hydrothermal vents occupy 1% of the area and that the annual fixation rate is 30 kg N ha^{-1}, as on a reef flat (Burris 1976), then the total would be about 2 Mt N annually. Fixation in deep-sea sediments seems otherwise negligible (Hartwig & Stanley 1978).

High rates of fixation have been recorded for intertidal and sublittoral habitats. Gotto *et al.* (1981), for example, estimated 40 kg N ha^{-1} annually for fixation in algal mats on the Texas Gulf coast. Such areas are comparatively limited in extent, however, and on most rocky coasts N_2-fixing organisms are not abundant and inshore sediments show only low rates of fixation (Maruyama 1975) unless they are anoxic (Hartwig & Stanley 1978). Although of local importance for productivity, it does not seem likely that N_2 fixation in coastal habitats can make any great contribution to the oceans as a whole.

The estimate of 30–130 Mt of combined N contributed annually to the oceans by biological fixation put forward by Söderlund & Svensson (1976) was based on somewhat arbitrary assumptions about the distribution and activity of *Trichodesmium* and what seem to be overestimates of fixation in the sediments of the continental shelves. From the information given above it seems unlikely that biological N_2 fixation in the oceans can be much in excess of 15 Mt N annually.

(ii) *Combined nitrogen from river inflow, precipitation and dry deposition*

The estimates of Söderlund & Svensson (1976) and of Fogg (1978) of the annual input of total combined N to the oceans from rivers and from precipitation are of the same orders, 13–24 Mt and 31 Mt respectively for rivers and 13–41 Mt and 59 Mt respectively from precipitation. Walsh *et al.* (1981) point out that the nitrate content of rivers draining developed areas has doubled over the last 25–50 years, so that the figure for input of total combined N by rivers should be increased to 35 Mt. The poles may be regions of especially high input of N fixed by auroral or cosmic ray activity in the upper atmosphere (Parker *et al.* 1978; Bauer 1978). From analyses of ice samples from the South Pole, Parker *et al.* (1978) estimated that this contributed 0.046 Mt of combined N annually to the Southern Ocean. Although this is less than 1% of the amount of inorganic combined N in the mixed surface layer of this ocean (Biggs 1978), the relatively high concentrations of nitrate around melting icebergs may be of local importance for phytoplankton growth (Parker *et al.* 1978).

Annual dry deposition into the oceans, either from the gaseous phase or from particles, is estimated by Söderlund & Svensson (1976) as between 11 and 25 Mt N for ammonia and between 5 and 16 Mt N for oxides of N. The extent of dry deposition of organic N is unknown.

(*b*) *Losses*

(i) *Denitrification*

Denitrification, which occurs when nitrate or nitrite are used as terminal electron acceptors in respiration with the production of N_2, is the thermodynamically favoured means for the oxidation of organic matter when the free oxygen content of seawater is low. Nitrous oxide is an intermediate in this process and may be an accumulating product under acid conditions (Fenchel & Blackburn 1979), but it seems that there is no significant production of nitrous oxide by denitrification in seawater (Goering & Cline 1970), it being consumed, rather than otherwise, in regions of denitrification (Cohen & Gordon 1978; Pierotti & Rasmussen 1980). In this discussion, therefore, denitrification will be regarded as implying reduction to N_2.

Denitrification does not occur when the oxygen content of seawater is above about 10 µM, evidently because formation of the enzymes concerned is repressed. The finding of Benson & Parker (1961) that N_2:Ar ratios in aerobic seawater are within $\pm 1\,\%$ of those calculated from a purely physical model supports the expectation that denitrification is negligible in the bulk of the oceans. Denitrification can, however, occur at low oxygen concentrations and in environments with fluctuating oxygen concentration (Fenchel & Blackburn 1979) or low oxygen microhabitats such as faecal pellets (Svensson & Söderlund 1976).

Production of N_2 in seawater is difficult to measure directly. Denitrification may be estimated indirectly from the difference between expected nitrate and observed nitrate plus nitrite concentrations or from respiration or electron transport activity on the assumption that it is the dominant respiratory process in oxygen-deficient waters with more than 0.5 µg at. NO_3^--N l^{-1} (Codispoti & Packard 1980). Using the former method, Codispoti & Richards (1976) estimated denitrification as liberating 20 Mt N annually in the tropical North Pacific east of 112° W, in good agreement with another estimate made from respiration measurements. Deuser *et al.* (1978) used the nitrate deficit method to estimate a loss of between 0.1 and 1.0 Mt N annually from the Arabian Sea. Codispoti & Packard (1980) used electron transport activity to estimate annual denitrification in the oxygen-deficient waters of the eastern tropical South Pacific as about 25 Mt N in 1976–7 but gave reasons for thinking that it was distinctly lower in 1972. The estimate from nitrate deficiency was less certain but in reasonable agreement, namely 19 Mt N for 1976–7. Being consistent among themselves and with what would be expected from primary production in the areas examined, these estimates appear to be reasonably reliable.

Denitrification also occurs in sediments. Barnes *et al.* (1975) found N_2:Ar ratios indicative of denitrification as well as actual increases in dissolved N_2, in pore waters from southern California borderland basin sediments. From determinations of pore-water nitrate concentrations in cores from 4000 to 5000 m in the eastern equatorial Atlantic, Bender *et al.* (1977) obtained an estimate of the benthic flux of nitrate much less than the average flux of nitrate to deep waters, suggesting an annual rate of denitrification of about 0.13 µM N cm^{-2}. A more direct method, using $^{15}NO_3^-$, was employed to estimate denitrification rates at *in situ* nitrate concentration in sediments from a Danish fiord by Oren & Blackburn (1979). The rates found were some 45 times those reported by Bender *et al.* (1977), but this is to be expected since inshore sediments are richer in organic substrates than oceanic ones. If the estimate of Bender *et al.* (1977) is representative of pelagic sediments there would be a total annual loss of 5 Mt N.

In the light of these results the estimate quoted by Piper & Codispoti (1975) of an annual denitrification rate of 100 Mt N in the oceans seems reasonable. Söderlund & Svensson (1976) arrived at a figure of 91 Mt N annually for the global rate (including loss of both N_2 and nitrous oxide), or, taking it as the difference between the annual gain of combined N to the oceans (including an estimate for N_2 fixation which seems too high, see §2*a*(i)) and the losses from causes other than denitrification, considered that it might be as high as 179 Mt N (but see §2*a*(i)).

(ii) *Loss of nitrous oxide to the atmosphere*

Nitrous oxide is generally present in seawater at about twice the concentration expected if there were equilibrium with its atmospheric partial pressure (Kester 1975). The supposition that it is biogenic in origin is supported by McElroy *et al.* (1978), who found a release of 1 t N_2O

daily into the atmosphere from the Potomac Estuary, as a result of conversion of between 1 and 5% of the total N input from sewage. Cohen & Gordon (1978) considered that nitrous oxide in seawater is a product of nitrification and its formation is associated with microbial oxidation of ammonia in Atlantic seawater (McElroy *et al.* 1978). Supersaturation with nitrous oxide was found to increase from about 110% at the surface to a maximum of between 224 and 600% in shallow waters above the base of the pycnocline in the eastern tropical North Pacific (Cohen & Gordon 1978). Singh *et al.* (1979) and Pierotti & Rasmussen (1980) consider the oceans to be a significant source of nitrous oxide for the atmosphere and the latter authors estimated the upper limit for the annual loss from the whole ocean as 60 Mt N.

3. Cycling between the euphotic zone and deep water

Primary production in the euphotic zone results in the incorporation of dissolved combined N into particulate matter liable to sedimentation. The mineralization of this particulate matter takes place largely in sediments in shallow seas. Billen (1978) found fluxes of ammonium and nitrate from sediments to water column accounting for 105–62% and 52–30% of the requirements of the phytoplankton in the coastal and offshore zones, respectively, of the North Sea. In deeper waters most of the organic N becomes converted to nitrate, presumably by the activity of nitrifying bacteria, although these seem to be infrequent in the water column (Billen 1978).

Nitrate in deep water may be returned to the surface by turbulent mixing or upwelling. Dugdale & Goering (1967) introduced the concept of 'new nitrogen', including nitrate returned to the euphotic zone as well as lesser amounts of N brought in by fixation or other means, as opposed to 'regenerated nitrogen' produced within the euphotic zone itself. Estimates of the ratio of primary production based on new N to the total (f) are based on measurements of the assimilation of $^{15}NO_3^-$ and $^{15}NH_4^+$. It should be noted that difficulties may arise in the use of ^{15}N-labelled nutrients when the ambient concentrations of the substances concerned are low (McCarthy 1980; Fisher *et al.* 1981), that accurate estimations of ammonium concentration are essential and that it is assumed that assimilation of organic N is negligible. Olson (1980), who found values between 0.40 and 0.54 even in nitrate-rich Antarctic water, summarized estimates of f, which range from 0.06 for the oligotrophic waters of the North Pacific central gyre to 0.66 for the Peru upwelling. In the New York Bight, Conway & Whitledge (1979) found f values around 0.59 inshore rising offshore to 0.70 at the shelf break.

Variations of productivity from one sea area to another are related to the input of new N (Conover 1975; Eppley *et al.* 1979), which itself is related to the amount of auxiliary energy available to bring it to the surface, as Margalef (1978) has pointed out. The flux of nitrate into shelf areas is balanced by export of detrital N to continental slopes (Walsh *et al.* 1981). For the oceans as a whole, Eppley & Peterson (1979) estimated that annual primary production based on new N amounts to between 3400 and 4700 Mt C, about 10% of the total. This would correspond to an input of new N of between 500 and 710 Mt and imply a turnover time for nitrate N in the oceans of about 1200 years, an estimate that seems reasonable on other grounds.

4. Cycling within the euphotic zone

Various lines of evidence show that combined N is cycled rapidly within the euphotic zone. For most algae, other conditions being equal, ammonium is the most readily asimilated source of N (Morris 1974; Dugdale 1976; McCarthy 1980; Syrett 1982). The ambient concentration in seawater is usually sufficient to suppress uptake of nitrate and nitrite (McCarthy 1980), and uptake of ammonium is less dependent on light than is that of nitrate (Morris 1974; Dugdale 1976; MacIsaac 1978; Nelson & Conway 1979; Olson 1980). As we have seen, *f* values show that ammonium normally exceeds nitrate as a source of N for natural populations and becomes almost the sole source under oligotrophic conditions. Despite its usually low concentration it seems that the flux of ammonium is sufficient to maintain high growth rates. Morris *et al.* (1971) showed that supply of ammonium did not enhance carbon dioxide fixation in the dark in phytoplankton from the nitrate poor waters of the Florida Strait, as would be expected if the cells were physiologically N-deficient. Goldman *et al.* (1979) pointed out that the typical composition of oceanic phytoplankton as expressed in the 'Redfield ratio', $C_{106}\,N_{16}\,P$, is only achieved in laboratory cultures at high growth rates with minimal nutrient limitation. In oligotrophic waters we thus appear to be dealing with a balanced dynamic state in which nutrients are regenerated as rapidly as they are assimilated.

Bacteria and most aquatic animals produce ammonia as a major end-product of metabolism. In shallow seas this does not undergo nitrification in the water column (Billen 1978) but, as Harris (1959) pointed out, is directly an important source of N for the phytoplankton. The contribution of regenerated N from larger zooplankton and benthic fauna in the natural environment may be computed from observed numbers and laboratory determinations of excretion rates. Thus Furnas *et al.* (1976) concluded that during a summer bloom in Narragansett Bay it took the zooplankton and benthos 2–5 days to supply one day's requirement of the phytoplankton. Preliminary results from a study in Carmarthen Bay (R. F. C. Mantoura, P. H. Burkill & N. J. P. Owens, personal communication), in which regeneration by zooplankton was computed from standing stocks and excretion rates determined experimentally at sea, show that the smallest size class (100–280 μm) contributed 77 % of the total ammonium excreted and that in August the maximum turnover time by zooplankton for NH_4^+-N varied between 70 and 90 days, compared with a minimum figure for uptake of all forms of N by phytoplankton of between 1 and 20 days. The bacterial contribution, for which the maximum turnover time in the previous year varied between 1 and 16 days, thus seemed more important. More direct measurements of NH_4^+-N flux have been carried out with the use of a ^{15}N isotope dilution technique by Harrison (1978). His samples, from the Cepax enclosure in Saanich Inlet, British Columbia, and from the southern Californian Bight gave median assimilation: regeneration ratios of 0.65 and 0.77 respectively. The median turnover time for regeneration was 2 days in Saanich Inlet and 7 days in the southern Californian Bight. Regeneration was associated to the extent of 10 % with particles greater than 35 μm, 50 % with particles between 1 and 35 μm and 40 % with particles of less than 1 μm size. Thus microplankton (bacteria and microzooplankton) appeared to be the main agent in regeneration. Regenerative fluxes were to some extent light-dependent, possibly because of dependence on extracellular products of photosynthesis, and decreased with depth and distance offshore. Caperon *et al.* (1979) used a similar method to determine ammonium ion uptake and production in Kaneoke Bay, Hawaii, and found that, on the average, they were roughly in balance. High excretion rates appeared to be associated with high standing crops of microzooplankton (less than 333 μm), but the actual regeneration was again due primarily to organisms less than 35 μm in size. Bacterial biomass in seawater may be as much as or more than that of any other category of organism and bacterial activity is correspondingly high (Sorokin 1973; Watson 1978) even in some Antarctic waters

(Hodson *et al.* 1981). Hollibaugh *et al.* (1980) determined concentration and flux of dissolved free amino acids in the CEPAX enclosures in Saanich Inlet and concluded that amino acid degradation accounted for 60% of the flux into the ammonium pool and for an average of 78% of the primary production. Their results thus confirm that a large part of the regenerated N flux passes through the bacterioplankton.

Some organic N compounds, under which heading urea may be included for present purposes, can be assimilated directly by phytoplankton (Morris 1974; Syrett 1982). Most of the total dissolved N in seawater, which has probably been underestimated in the past (Solórzano & Sharp 1980) seems to be in the form of refactory organic compounds of large molecular mass. Gardner & Stephens (1978) found that terrestrially derived dissolved organic N was stable for at least 2–3 months in seawater and that the measured amino N accounted for about 20% of the total leaving the remainder undefined. However, urea, which is often present in seawater in concentrations up to 5 μM, appears to be the preferred N source for phytoplankton after ammonium and before nitrate, and often constitutes a major part of the total N that it assimilates (Dugdale 1976; Webb & Haas 1976; McCarthy 1980; Turley 1980). Urea utilization is mainly effected by phytoplankton when light is available, heterotrophic utilization in the dark being usually less (Webb & Haas 1976; Mitamura & Saijo 1980; Turley 1980). Turnover times of between 5 and 80 or more days were found by Turley (1980) in the Elbe Estuary and southern German Bight, and of between 12 and 113 days in the Pacific by Mitamura & Saijo (1980). Uptake of amino N by natural phytoplankton populations seems slight (Dugdale 1976), the bacterioplankton appearing to be the main utilizer of this form of combined N (Hollibaugh *et al.* 1980). Antia *et al.* (1980) suggested that purines excreted by ciliates may be directly utilized by a large proportion of marine phytoplankton. The importance of the dissolved organic N fraction for phytoplankton nutrition was studied by Butler *et al.* (1979) in observations over 11 years in the English Channel. As nitrate disappeared, the concentration of dissolved organic N increased so that the total N concentration in the seawater showed less variation than either fraction. Butler *et al.* (1979) suggest that in the seasonal succession, nitrate-preferring algae of the spring bloom are replaced in the summer by species able to utilize organic forms of N. This is an attractive hypothesis but there is nothing in their results to show that the summer phytoplankton was not dependent on ammonium N regenerated by bacteria, rather than utilizing organic forms directly.

Steady-state conditions of N nutrition do not exist in natural waters. Apart from variations related to fluctuating light intensity, phytoplankton cells may be affected by transient local concentrations of animal excretion or bacterial breakdown products. An extreme situation was described by Porter (1976) who found that colonies of the planktonic freshwater alga *Sphaerocystis schroeteri* were only partly disrupted and digested by *Daphnia magna* and that cells that remained intact took up nutrients during gut passage from digested cells of other species, showing enhanced growth afterwards. Similar situations may well occur in the marine plankton. Rapid uptake of ammonium may enable phytoplankton cells to benefit if they find themselves in the wake of an excreting animal. A herbivorous oceanic copepod such as *Octhona* or *Clausocalanus* may excrete sufficient in 5 s to increase the concentration of ammonium by about 5 μM in a volume approximating the displacement volume of the animal (McCarthy & Goldman 1979). Experiments with both laboratory cultures and natural populations show that phytoplankton algae are capable of high rates of uptake of ammonium over short periods, the more so the more N-deficient the cells are, and are thus able to benefit from pulses of ammonium lasting 30 min or so (McCarthy & Goldman 1979; Glibert & Goldman 1981). Turpin & Harrison (1979) found that pulsed, as opposed to uniform, supply of ammonium in mixed N-limited chemostat cultures altered the outcome of competition between *Chaetoceros* and *Skeletonema*.

Larger-scale and more persistent patchiness in the distribution of N sources may arise through concentration of particulate matter at fronts. Floodgate *et al.* (1981) showed that concentrations of bacteria, phytoplankton and zooplankton are maximum at a front in Liverpool Bay. Corresponding with the peak in zooplankton numbers, urea concentration and utilization were higher than elsewhere. Redfield & Keys (1938) and Butler *et al.* (1979) noted high concentrations of ammonium N associated with dense patches of zooplankton. Floodgate *et al.* (1981) found indications of increased bacterial activity at the front studied and suggested that cycling of nutrients is enhanced in this situation. It should be noted that once higher concentrations of plankton are established as a result of purely physical processes, fish and other nekton may migrate into the front and by their excretion increase the N available to phytoplankton.

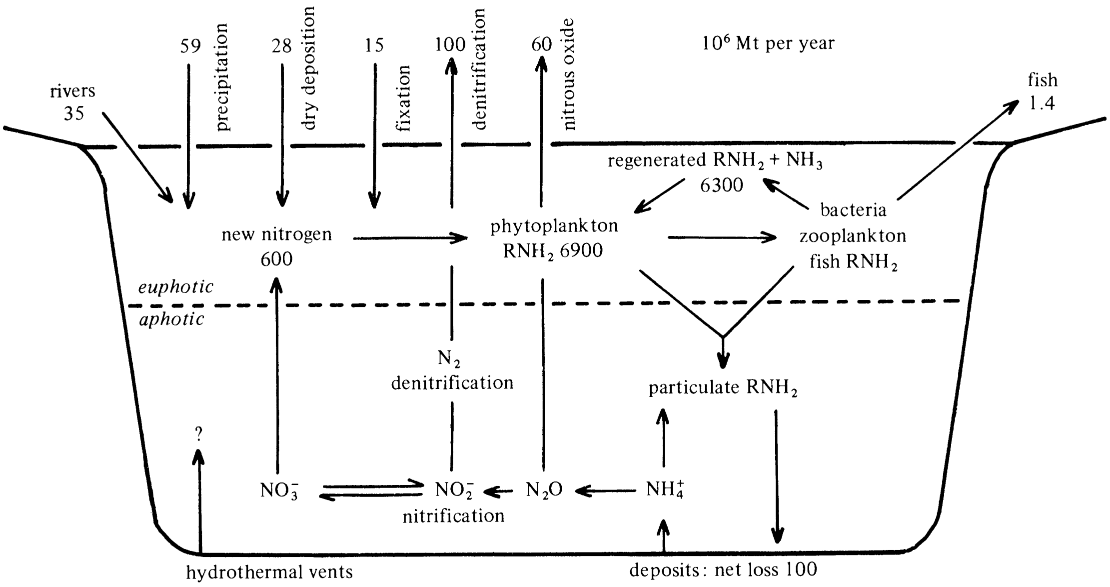

FIGURE 1. The oceanic nitrogen cycle. Estimates of the amounts of nitrogen passing through the various compartments are given in megatonnes per year. Estimates not in the text are from Fogg (1978).

5. DISCUSSION

The information discussed above is summarized in figure 1. Recent investigations give more confidence in estimates of the magnitudes of two of the major sources of loss of combined N from the oceans, denitrification and partition of nitrous oxide to the atmosphere, and of one of the major inputs, N_2 fixation. Calculations of other losses and gains seem dependable but the estimated total of gains is still less than that of losses by some 124 Mt N annually. There seems to be no compelling reason for exact balance and, indeed, Piper & Codispoti (1975) have argued that over geological time there have been oscillations, with denitrification and N_2 fixation predominating alternately. Denitrification, being controlled by oxygenation of the water, is extremely sensitive to hydrographical conditions and hence to changes in climate and, on the other hand, N_2 fixation becomes of greater biological advantage and is promoted when combined N is in short supply, so that such oscillation seems plausible. Nevertheless, it seems improbable that there could be quite such imbalance as is suggested by the available estimates. If continued, this imbalance would imply exhaustion of the present combined N reserves of the oceans in about 10000 years. It seems more likely that some important factor has been overlooked.

The flux of combined N into the euphotic zone from deeper water, a process of first importance in determining the level of productivity of the seas, has long been a preoccupation of oceanographers and much is known about its hydrographical aspects. The major biochemical transformations involved are well established but many microbiological details remain obscure.

The extent of cycling within the euphotic zone itself has only recently been fully realized. Forgetting that the measure of the importance of a substance in an ecosystem is rate of turnover rather than concentration, oceanographers have been preoccupied with nitrate concentrations and have tended to think of plankton growth coming to a virtual standstill when nitrate is exhausted. The evidence now available shows that even in the most oligotrophic waters the growth of phytoplankton continues rapidly, the cycle being maintained by grazing and rapid regeneration of the N as ammonia and urea. It remains true that the amount of harvestable production depends mainly on the input of new N – by upwelling of nitrate-rich water, inflow of river water or intense local N_2 fixation. In regions where production depends almost entirely on regenerated N, combined N may become concentrated in large carnivores or by shoaling of fish, and harvesting of these by man may lead to rapid depletion of local reserves of combined N and loss of productivity.

I am grateful to Dr R. F. C. Mantoura, Dr P. H. Burkill and Mr N. J. P. Owens of the Institute for Marine Environmental Research, Plymouth, for permission to quote unpublished results and to Mr C. Lumb for helpful discussion of nitrification in marine habitats.

REFERENCES (Fogg)

Antia, N. J., Berland, B. R. & Bonin, D. J. 1980 Proposal for an abridged nitrogen turnover cycle in certain marine planktonic systems involving hypoxanthine–guanine excretion by ciliates and their reutilization by phytoplankton. *Mar. Ecol. Prog. Ser.* **2**, 97–103.

Barnes, R. O., Bertine, K. K. & Goldberg, E. D. 1975 N_2/Ar, nitrification and denitrification in southern California borderland basin sediments. *Limnol. Oceanogr.* **20**, 962–970.

Bauer, E. 1978 Non-biogenic fixed nitrogen in Antarctic surface waters. *Nature, Lond.* **276**, 96.

Bender, M. L., Fanning, K. A., Froelich, P. N., Heath, G. R. & Maynard, V. 1977 Interstitial nitrate profiles and oxidation of sedimentary organic matter in the eastern equatorial Atlantic. *Science, N.Y.* **198**, 605–609.

Benson, B. B. & Parker, P. D. M. 1961 Nitrogen/argon and nitrogen isotope ratios in aerobic sea water. *Deep Sea Res.* **7**, 237–253.

Biggs, D. C. 1978 Non-biogenic fixed nitrogen in Antarctic surface waters. *Nature, Lond.* **276**, 96–97.

Billen, G. 1978 A budget of nitrogen recycling in North Sea sediments off the Belgian coast. *Estuar. coast. mar. Sci.* **7**, 127–146.

Burris, R. H. 1976 Nitrogen fixation by blue-green algae of the Lizard Island area of the Great Barrier Reef. *Aust. J. Pl. Physiol.* **3**, 41–51.

Butler, E. I., Knox, S. & Liddicoat, M. I. 1979 The relationship between inorganic and organic nutrients in sea water. *J. mar. biol. Ass. U.K.* **59**, 239–250.

Caperon, J., Schell, D., Hirota, J. & Laws, E. 1979 Ammonium excretion rates in Kaneoke Bay, Hawaii, measured by a ^{15}N isotope dilution technique. *Mar. Biol.* **54**, 33–40.

Codispoti, L. A. & Packard, T. T. 1980 Denitrification rates in the eastern tropical South Pacific. *J. mar. Res.* **38**, 453–477.

Codispoti, L. A. & Richards, F. A. 1976 An analysis of the horizontal regime of denitrification in the eastern tropical North Atlantic. *Limnol. Oceanogr.* **21**, 379–388.

Cohen, Y. & Gordon, L. I. 1978 Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: evidence for its consumption during denitrification and possible mechanisms for its production. *Deep Sea Res.* **25**, 509–524.

Conover, S. A. M. 1975 Nitrogen utilization during spring blooms of marine phytoplankton in Bedford Basin, Nova Scotia, Canada. *Mar. Biol.* **32**, 247–261.

Conway, H. L. & Whitledge, T. E. 1979 Distribution, fluxes and biological utilization of inorganic nitrogen during a spring bloom in the New York Bight. *J. mar. Res.* **37**, 657–668.

Deuser, W. G., Ross, E. H. & Mlodzinska, S. J. 1978 Evidence for and rate of denitrification in the Arabian Sea. *Deep Sea Res.* **25**, 431–445.

Dugdale, R. C. 1976 Nutrient cycles. In *The ecology of the seas* (ed. D. H. Cushing & J. J. Walsh), pp. 141–172. Oxford: Blackwell Scientific Publications.

Dugdale, R. C. & Goering, J. J. 1967 Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnol. Oceanogr.* **12**, 196–206.

Dunstan, W. M. & Atkinson, L. P. 1976 Sources of new nitrogen for the South Atlantic Bight. In *Estuarine processes*, vol. 1 (*Uses, stresses and adaptation to the estuary*) (ed. M. Wiley), pp. 69–78. New York: Academic Press.

Eppley, R. W. & Peterson, B. J. 1979 Particulate organic matter flux and planktonic new production in the deep ocean. *Nature, Lond.* **282**, 677–680.

Eppley, R. W., Renger, E. H. & Harrison, W. G. 1979 Nitrate and phytoplankton production in southern California coastal waters. *Limnol. Oceanogr.* **24**, 483–494.

Fenchel, T. & Blackburn, T. H. 1979 *Bacteria and mineral cycling.* (225 pages.) London and New York: Academic Press.

Fisher, T. R., Carlson, P. R. & Barber, R. T. 1981 Some problems in the interpretation of ammonium uptake kinetics. *Mar. Biol. Lett.* **2**, 33–44.

Floodgate, G. D., Fogg, G. E., Jones, D. A., Lochte, K. & Turley, C. M. 1981 Microbiological and zooplankton activity at a front in Liverpool Bay. *Nature, Lond.* **290**, 133–136.

Fogg, G. E. 1978 Nitrogen fixation in the oceans. In *Environmental role of nitrogen-fixing blue-green algae and asymbiotic bacteria* (ed. U. Granhall) (*Ecol. Bull., Stockh.* **26**), pp. 11–19.

Fogg, G. E. 1981 Cyanobacteria in marine plankton. In *The biology of Cyanobacteria* (ed. N. G. Carr & B. A. Whitton). Oxford: Blackwell. (In the press.)

Furnas, M. J., Hitchcock, G. L. & Smayda, T. J. 1976 In *Estuarine processes*, vol. 1 (*Uses, stresses and adaptation to the estuary*) (ed. M. Wiley), pp. 118–133. New York: Academic Press.

Gardner, W. S. & Stephens, J. A. 1978 Stability and compositition of terrestrially derived dissolved organic nitrogen in continental shelf surface waters. *Mar. Chem.* **6**, 335–342.

Glibert, P. M. & Goldman, J. C. 1981 Rapid ammonium uptake by marine phytoplankton. *Mar. Biol. Lett.* **2**, 25–31.

Goering, J. J. & Cline, J. D. 1970 A note on denitrification in sea-water. *Limnol. Oceanogr.* **15**, 306–309.

Goldman, J. C., McCarthy, J. J. & Peavey, D. G. 1979 Growth rate influence on the chemical composition of phytoplankton in oceanic waters. *Nature, Lond.* **279**, 210–215.

Gotto, J. W., Tabita, F. R. & Van Baalan, C. 1981 Nitrogen fixation in intertidal environments of the Texas Gulf coast. *Estuar. coast. Shelf Sci.* **12**, 231–235.

Gundersen, K. R., Corbin, J. S., Hanson, C. L., Hanson, M. L., Hanson, R. B., Russell, D. J., Stoller, A. & Yamada, O. 1976 Structure and biological dynamics of the oligotrophic ocean zone off the Hawaiian Islands. *Pacif. Sci.* **30**, 45–68.

Harris, E. 1959 The nitrogen cycle in Long Island Sound. *Bull. Bingham oceanogr. Coll.* **17**, 31–65.

Harrison, W. G. 1978 Experimental measurements of nitrogen remineralization in coastal waters. *Limnol. Oceanogr.* **23**, 684–694.

Hartwig, E. O. & Stanley, S. O. 1978 Nitrogen fixation in Atlantic deep-sea and coastal sediments. *Deep Sea Res.* **25**, 411–417.

Hodson, R. E., Azam, F., Carlucci, A. F., Fuhrman, J. A., Karl, D. M. & Holm-Hansen, O. 1981 Microbial uptake of dissolved organic matter in McMurdo Sound, Antarctica. *Mar. Biol.* **61**, 89–94.

Hollibaugh, J. T., Carruthers, A. B., Fuhrman, J. A. & Azam, F. 1980 Cycling of organic nitrogen in marine plankton communities studied in enclosed water columns. *Mar. Biol.* **59**, 15–21.

Horstman, U., Ulbricht, K. A. & Schmidt, D. 1978 Detection of eutrophication processes from air and space. In *Proceedings of the 12th International ERIM Symposium on Remote Sensing of the Environment*, Manila, Philippines, pp. 1379–1389.

Hübel, H. & Hübel, M. 1980 Nitrogen fixation during blooms of *Nodularia* in coastal waters and backwaters of the Arkona Sea (Baltic Sea) in 1974. *Int. Revue ges. Hydrobiol. Hydrogr.* **65**, 793–808.

Kester, D. R. 1975 Dissolved gases other than CO_2. In *Chemical oceanography*, 2nd edn, vol. 1 (ed. J. P. Riley & G. Skirrow), pp. 497–556. London: Academic Press.

MacIsaac, J. J. 1978 Diel cycles of inorganic nitrogen uptake in a natural phytoplankton population dominated by *Gonyaulax polyedra*. *Limnol. Oceanogr.* **23**, 1–9.

Mague, T. H., Mague, F. C. & Holm-Hansen, O. 1977 Physiology and chemical composition of nitrogen-fixing phytoplankton in the Central North Pacific Ocean. *Mar. Biol.* **41**, 213–227.

Mague, T. H., Weare, N. M. & Holm-Hansen, O. 1974 Nitrogen fixation in the North Pacific Ocean. *Mar. Biol.* **24**, 109–119.

Margalef, R. 1978 Life-forms of phytoplankton as survival alternatives in an unstable environment. *Oceanologica Acta* **1**, 493–509.

Maruyama, Y. 1975 Nitrogen fixation in the open sea. In *JIBP Synthesis: Nitrogen fixation and nitrogen cycle* (ed. H. Takahashi), pp. 79–84. University of Tokyo Press.

McCarthy, J. J. 1980 Nitrogen. In *The physiological ecology of phytoplankton* (ed. I. Morris), pp. 191–233. Oxford: Blackwell Scientific Publications.

McCarthy, J. J. & Goldman, J. C. 1979 Nitrogenous nutrition of marine phytoplankton in nutrient-depleted waters. *Science*, *N.Y.* **203**, 670–672.

McElroy, M. B., Elkins, J. W., Wofsy, S. C., Kolb, C. E., Durán, A. P. & Kaplan, W. A. 1978 Production and release of N_2O from the Potomac Estuary. *Limnol. Oceanogr.* **23**, 1168–1182.

Mitamura, O. & Saijo, Y. 1980 *In situ* measurement of the urea decomposition rate and its turnover rate in the Pacific Ocean. *Mar. Biol.* **58**, 147–152.

Morris, I. 1974 Nitrogen assimilation and protein synthesis. In *Algal physiology and biochemistry* (ed. W. D. P. Stewart), pp. 583–609. Oxford: Blackwell Scientific Publications.

Morris, I., Yentsch, C. M. & Yentsch, C. S. 1971 The physiological state with respect to nitrogen of phytoplankton from low-nutrient subtropical water as measured by the effect of ammonium ion on dark carbon dioxide fixation. *Limnol. Oceanogr.* **16**, 859–868.

Nelson, D. M. & Conway, H. L. 1979 Effects of the light regime on nutrient assimilation by phytoplankton in the Baja California and northwest Africa upwelling systems. *J. mar. Res.* **37**, 301–318.

Olson, R. J. 1980 Nitrate and ammonium uptake in Antarctic waters. *Limnol. Oceanogr.* **25**, 1064–1074.

Oren, A. & Blackburn, T. H. 1979 Estimation of sediment denitrification rates at *in situ* nitrate concentrations. *Appl. environ. Microbiol.* **37**, 174–176.

Parker, B. C., Heiskell, L. E. & Thompson, W. J. 1978 Non-biogenic fixed nitrogen in Antarctica and some ecological implications. *Nature*, *Lond.* **271**, 651–652.

Parker, B. C., Heiskell, L. E., Thompson, W. J. & Zeller, E. J. 1978 Non-biogenic fixed nitrogen in Antarctic surface waters. *Nature*, *Lond.* **276**, 97.

Pierotti, D. & Rasmussen, R. A. 1980 Nitrous oxide measurements in the eastern tropical Pacific Ocean. *Tellus* **32**, 56–72.

Piper, D. Z. & Codispoti, L. A. 1975 Marine phosphorite deposits and the nitrogen cycle. *Science*, *N.Y.* **188**, 15–18.

Porter, K. G. 1976 Enhancement of algal growth and productivity by grazing zooplankton. *Science*, *N.Y.* **192**, 1332–1334.

Rau, G. H. 1981 Low $^{15}N/^{14}N$ in hydrothermal vent animals: ecological implication. *Nature*, *Lond.* **289**, 484–485.

Redfield, A. C. & Keys, A. B. 1938 The distribution of ammonia in the waters of the Gulf of Maine. *Biol. Bull. mar. biol. Lab.*, *Woods Hole* **74**, 83–92.

Singh, H. B., Salas, L. J. & Shigeishi, H. 1979 The distribution of nitrous oxide (N_2O) in the global atmosphere and the Pacific Ocean. *Tellus* **31**, 313–320.

Söderlund, R. & Svensson, B. H. 1976 The global nitrogen cycle. In *Nitrogen*, *phosphorus and sulphur – global cycles* (ed. B. H. Svensson & R. Söderlund) (*Ecol. Bull.*, *Stockh.* **22**), pp. 23–73.

Solórzano, L. & Sharp, J. H. 1980 Determination of total dissolved nitrogen in natural waters. *Limnol. Oceanogr.* **25**, 751–754.

Sorokin, Y. I. 1973 Microbiological aspects of the productivity of coral reefs. In *Biology and geology of coral reefs* (ed. O. A. Jones & R. Endean), vol. 2, pp. 17–45. New York: Academic Press.

Spencer, C. P. 1975 The micronutrient elements. In *Chemical oceanography*, 2nd edn, vol. 2 (ed. J. P. Riley & G. Skirrow), pp. 245–300. London: Academic Press.

Syrett, P. J. 1982 Nitrogen metabolism of microalgae. In *Physiological ecology of phytoplankton* (NATO Summer School, October 1981) (ed. T. Platt). (In the press.)

Turley, C. M. 1980 The distribution and biodegradation of urea in coastal water. Ph.D. thesis, University of Wales.

Turpin, D. H. & Harrison, P. J. 1979 Limiting nutrient patchiness and its role in phytoplankton ecology. *J. exp. mar. Biol. Ecol.* **39**, 151–166.

Walsh, J. J., Rowe, G. T., Iverson, R. L. & McRoy, C. P. 1981 Biological export and shelf carbon is a sink of the global CO_2 cycle. *Nature*, *Lond.* **291**, 196–201.

Watson, S. W. 1978 Role of bacteria in an upwelling ecosystem. In *Upwelling ecosystems* (ed. R. Boje & M. Tomczak), pp. 139–154. Berlin: Springer-Verlag.

Webb, K. L. & Haas, L. W. 1976 The significance of urea for phytoplankton nutrition in the York River, Virginia. In *Estuarine processes*, vol. 1 (*Uses*, *stresses*, *and adaptation to the estuary*) (ed. M. Wiley), pp. 90–102. New York: Academic Press.