

in number. If, as we think, the frequency of disturbances may be increasing, then more sophisticated programs are needed to achieve better understanding of how harvested populations or entire ecosystems respond to climate variations.

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Nutrient Biogeochemistry of the Coastal Zone

T. D. Jickells

The coastal seas are one of the most valuable and vulnerable of Earth's habitats. Significant inputs of nutrients to the coastal zone arrive via rivers, groundwater, and the atmosphere. Nutrient fluxes through these routes have been increased by human activity. In addition, the N:P:Si ratios of these inputs have been perturbed, and many coastal management practices exacerbate these perturbations. There is evidence of impacts arising from these changes (in phytoplankton numbers and relative species abundance, and deep-water oxygen declines) in areas of restricted water exchange. Elsewhere, the nutrient fluxes through the coastal zone appear to be still dominated by large inputs from the open ocean, and there is little evidence of anthropogenic perturbations.

The coastal seas are one of the most important areas of the world oceans from a human perspective. We use these areas for food supplies via fishing, with almost all the world's fish catch coming from coastal waters and adjacent upwellings (1); as a source of nonrenewable (such as hydrocarbons and sand and gravel extraction) and renewable resources; and for power and transportation (2), as well as for waste disposal and for recreation. In a recent attempt to value the world's ecosystems (3), coastal seas were assigned a higher value than the whole terrestrial or open ocean system, despite their much smaller area. Almost all this value is associated with the storage and cycling of the nutrients N and P. The approach and conclusions of this study (3) are open to criticism, because it is not possible to value an

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ecosystem when its structure and functioning is not fully understood (4), but the coastal seas are clearly a very valuable resource. Half of the world's population now lives within 60 km of the coast (1). As populations grow [a growth that will be predominantly in coastal areas (5)], uses of the coastal zone will increasingly come into conflict.

The pressures on the coastal zone are multifaceted and interact to a large extent and at many levels. They broadly fall into four categories: (i) overexploitation of fisheries resources, (ii) direct deleterious effects of contaminants, (iii) eutrophication, and (iv) habitat loss. Fisheries issues were discussed in an earlier special *Science* issue (6), and I shall simply note that most commercial fisheries are very heavily overexploited.

Direct deleterious contaminant effects on the marine ecosystem from waste discharges have occurred many times in the past and, in some cases, continue. Some potential pollutants are now recognized and regulated, and if these regulations can be policed effectively, many problems can be managed (7-9). However, there are hundreds of new chemicals introduced into the coastal environment every year, and vigilance is required to ensure they do not cause unacceptable deleterious effects. The serious damage to the reproductive systems of

some invertebrates due to the use of tributyl tin (TBT) (10) in the recent past demonstrates that regulation and testing systems are far from perfect. Furthermore, the regulatory schemes are based largely on individual chemicals and cannot address possible synergistic effects.

However, I will concentrate on the more insidious problems arising from the inevitability of increasing human population, the resultant habitat destruction and waste disposal/eutrophication, and the interaction of these pressures on the coastal seas. These pressures will inevitably grow in the future and are already fundamentally challenging the biogeochemical cycles in coastal waters in many areas. Therefore, I will focus on the primary potentially limiting inorganic plant nutrients N, P, and Si (11) and particularly the effect of changes in these nutrient inputs on the coastal zone.

It is relatively straightforward to show schematically the processes regulating the behavior of the key inorganic nutrients in coastal areas (Fig. 1). However, the overall impact of these processes is strongly dependent on the physical characteristics of the system in question [for example, (12)], primarily because of the very large dilution capacity available in the open-ocean waters adjacent to the coastal systems. Hence, it is the extent of exchange between the two systems

Fig. 1. Schematic representation of major nutrient cycling processes in coastal systems. The relative importance of suspended solids and phytoplankton are shown in terms of the intensity of brown and green shading, respectively.

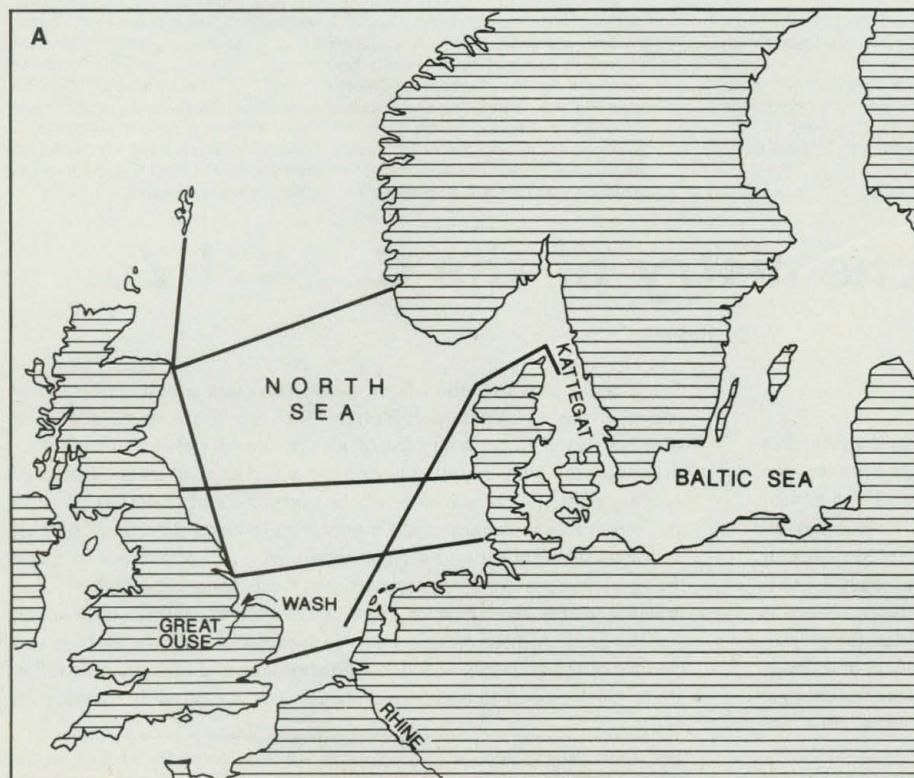
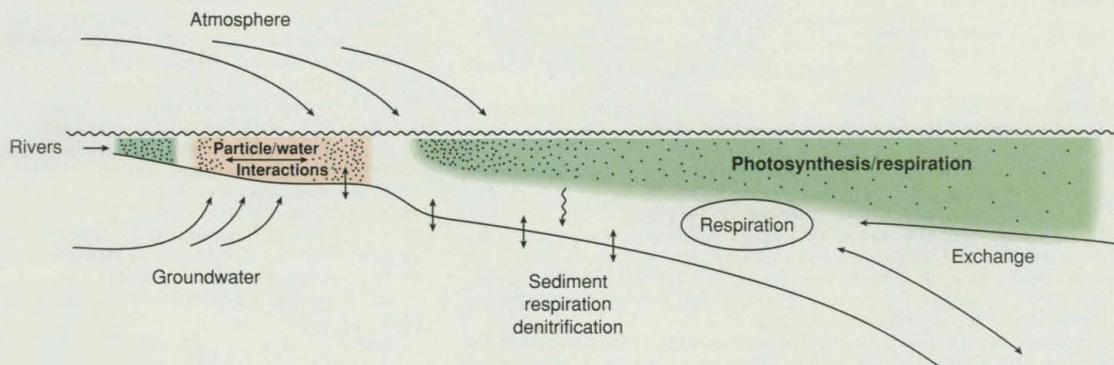


Fig. 2. (A) Map of the North Sea and the Baltic. Lines represent routes for the continuous plankton recorder (CPR). (B) Abundances of mesozooplankton (top graph) and phytoplankton (bottom graph) from 1948-91 in the North Sea as measured by the CPR standardized to zero mean and unit variance (phytoplankton measurements began later than zooplankton). Similar trends are seen in the central North Atlantic but not the northeast North Atlantic (15, 65). The scale and timing of these changes are much more likely the result of climatic factors than a response to nutrient inputs, which have risen steadily from about 1945.

that is such a strong influence. In recent years, there have been a number of attempts to try to synthesize the knowledge of coastal zones into a more generalized understanding, notably in a series of articles addressing the N and P budgets for the North Atlantic (13). This approach is now gathering momentum under the International Geosphere-Biosphere Programme (IGBP) on Land Ocean Interactions in the Coastal Zone (LOICZ) (14). Nevertheless, it is still true that study of the coastal system in general must be done by looking at individual coastal systems and then extrapolating from them. Here, I shall consider predominantly examples from the North Sea and the Baltic (Fig. 2).

Inputs

In general, the attempt to manage contaminant problems in the environment is undertaken via controls on inputs; hence, it is logical to consider the nature and magnitude of these inputs. There is a large input to the coastal seas associated with the exchanges with the offshore environment. The other inputs derive from the land and can, potentially at least, be regulated by humans. River inputs are very important both in terms of the physical structure of the systems and as a source of N, P, and Si (12). Recently, the importance of other inputs, notably groundwater and the atmosphere, has also begun to be realized.

Exchanges with offshore waters. The North Sea has open ocean exchange only along part of its boundary and a residence time of water of the order of 1 to 2 years (15). The Baltic has very restricted water exchange through the Kattegat and a residence time of the order of decades (16). By contrast, the South Atlantic bight off the U.S. East Coast has essentially open exchange with adjacent ocean waters resulting in a water residence time of only a few months (17). Individual small estuaries will have shorter residence times, in general.

A longer water residence time in a restricted coastal area will, potentially, allow an increasing buildup of inputs from land. Similarly, vertical density stratification of the water column also restricts exchange (18) and, therefore, areas like the Baltic, and to a lesser extent Chesapeake Bay, USA, face twin problems of restricted horizontal exchange and stagnation of bottom waters. This leads to seasonal (in the case of Chesapeake Bay) or essentially permanent (in the case of the Baltic) O₂ depletion problems in bottom waters via processes that will be discussed later. The exchanges at the offshore boundary of all coastal systems are influenced both by ocean currents and meteorological forcing, both of which may be very episodic. Climate changes may alter these forcings to an extent that cannot be predicted, via changes in ocean circulation and storminess (19).

Rivers. Riverine inputs of N and P to the coastal zone have been increased considerably by human activity, possibly by factors of 2 to 3 globally (20, 21) and by much more in many regions, particularly in Northern Europe and parts of North America (22). Inputs of N to rivers arise primarily from fertilizers, atmospheric deposition to the catchment, and to a lesser extent, direct discharges. Direct discharges of P to rivers are more important because of efficient retention in soils and sediments (23).

Following discharge to a river system, denitrification, photosynthesis, and particle water interactions can modify N and P fluxes. The

Table 1. Changes in dissolved atomic Si:N ratios for three rivers. The Po and Mississippi are based on 24 and the Rhine on 25 and 61. The coastal seas into which the rivers empty are given in parentheses.

Time period	Po (Adriatic Sea)	Rhine (North Sea)	Mississippi (Gulf of Mexico)
1960–62	1.1	0.3	4.3
1981–87	0.7	0.2	0.9

balance of inputs and river processing of nutrients is such that river fluxes have not only increased in absolute magnitude, but the N:P ratio of those inputs has increased to greater than the value required for optimal plant growth [16:1 on an atomic basis, (22–24)]. This has led to pressure to reduce inputs, which has met with some success for P but less for N. The dissolved N:P ratio in the Rhine has increased from about 30 before 1950 to 30 to 50 in the period 1960–85, along with a threefold increase in N flux. More recently, P fluxes have been reduced significantly, with a much smaller decrease in N, leading to dissolved N:P ratios >100 (25). Riverine Si fluxes (predominantly from mineral weathering) have been altered little by human activity. Thus, the ratio of N+P:Si has also changed considerably (Table 1).

A further point of concern is the increasing damming of major rivers. Particulate P is the dominant P species carried by rivers (22, 26, 27), and the ongoing damming of rivers substantially reduces sediment (and hence P) inputs to the oceans (28). Damming also produces large lake systems that promote diatom (siliceous phytoplankton) blooms (23, 29), which reduce Si fluxes particularly and hence further increase N+P:Si ratios. For example, the damming of the Danube has resulted in a >50% decrease in dissolved Si concentrations (29). Such diatom blooms can also be seen in some rivers when their flow rate drops as they move onto the coastal plane (23, 30).

Groundwater. Groundwater inputs to the coastal seas are also believed to be important, but it has been hard to demonstrate this (31). However, Moore recently (32) has provided evidence that such sources are important, at least on parts of the U.S. East Coast. Moore's approach (based on ²²⁶Ra) should allow the significance of groundwater to be assessed elsewhere. Nitrate concentrations in groundwaters have increased substantially over natural levels (22), while particle-water interactions have limited the rise in dissolved inorganic phosphorus (DIP).

Atmospheric Inputs. Atmospheric inputs are now recognized as an important input to the coastal ocean (21), although delivered as a diffuse flux in contrast to localized river inputs. This input can be episodic (33), and occasional high-deposition events may have significant effects on the phytoplankton community.

Both oxidized (predominantly HNO₃/NO₃⁻) and reduced (predominantly NH₃/NH₄⁺) N species contribute, although they have very different terrestrial sources (34) whose relative importance varies with location. In the North Sea, about a third of the land-derived N input is atmospheric, mainly as oxidized N (Table 2) (35). Nitrate deposition over the United Kingdom has more than doubled since 1950 (36), and it seems likely that this is also the case for the North Sea. In the Kattegat, 20 to 30% of N inputs are from the atmosphere, predominantly as reduced N (37). The contribution of atmospheric N inputs to some U.S. coastal areas may be >50% of the phytoplankton requirement (38). For a smaller estuarine system with relatively large riverine inputs such as the Chesapeake Bay, the importance of atmospheric inputs is less (39).

In coastal areas, polluted air containing nitric acid can mix and react with clean marine air rich in sea salt (NaCl), which is associated with relatively large aerosol particles (40).

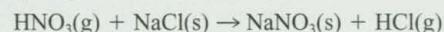


Table 2. Nitrogen inputs to the North Sea (34).

Source	Nitrogen (1000 tons/year)
North Atlantic inflow	7000
English Channel inflow	705
River inputs	1073
Atmospheric inputs	412
Direct discharges and dumping	129

This interaction alters the size distribution of aerosol nitrate (41) and thereby increases the efficiency of atmospheric nitrate deposition of nitrate, by a factor of 3 in the case of the North Sea (42). The halogen released by this reaction may play an important role in atmospheric chemistry in the marine atmosphere. (43).

This discussion of atmospheric inputs has focused on N because the atmospheric inputs of P and Si are relatively small compared to N. For example, the N:Si:P ratio for wet deposition over the North Sea is 503:2:1 (35).

Coastal and Estuarine Processing

Nutrient fluxes entering the coastal zone are further modified within estuaries. Parts of such areas are usually turbid as a result of the trapping and resuspension of both marine and freshwater sediments (44), and hence, primary productivity is limited by light availability. Particle-water interactions are particularly important in such turbid areas, and sediments in these regions can be a significant sink for contaminants. Moving seaward, water-column light levels improve as the turbidity declines, making primary production a major process in modifying biogeochemical cycles. Modeling of such primary production in coastal waters has now progressed to the point where it is possible to integrate primary production and nutrient cycling into water transport models (45).

Bacterial denitrification as a mechanism of organic C degradation is an important process throughout the coastal zone. This process occurs primarily in muddy sediments, since it requires large amounts of organic matter and a restricted supply of O₂, as well as a nitrate source (46, 47). Denitrification can be a major sink for nitrate. A recent study (48) suggests that the large intertidal mud flats of the Wash can remove 1 to 56% (depending on season) of the nitrate flux from the Great Ouse estuary, a river where nitrate concentrations are particularly high. Within estuaries and coastal waters, as in rivers (23), the elimination of habitats that favor denitrification has taken place and continues apace. For example, the United Kingdom has lost 50% of its salt marshes (47), and in the countries of Central Africa, 50 to 70% of mangrove stands have been lost (49). The loss of these habitats brings with it the loss of fish nursery areas, habitat for wading birds, coastal defense, and reservoirs for C storage, in addition to the capacity to regulate nitrate fluxes (47).

Denitrification is not confined to intertidal sediments but occurs in sediments throughout the oceans (50). It is difficult to accurately measure the denitrification rate in sediments, particularly that associated with coupled nitrification/denitrification, in which organic matter breaks down to ammonium and is subsequently oxidized to nitrate, which is then denitrified. Scaling up individual measurements to wider geographic areas is also problematic. Recently, Seitzinger and Giblin (50) derived a relationship between primary productivity and the rates of O₂ consumption and denitrification in the underlying sediments. They used this to demonstrate that denitrification in the shelf sediments of the whole North Atlantic is a major sink for nitrate. Nixon *et al.* (51) attempted to estimate the efficiency of N transmission through the fluvial and estuarine system. They propose a relationship between residence time and N retention (largely via denitrification) which suggests that large-scale N losses will only occur in estuaries with residence times in excess of 1 month. In smaller estuaries with shorter water residence times, N transmission is relatively efficient, consistent with the conservative nitrate behavior seen in such estuaries (52).

A similar but weaker relationship between P retention and residence time has been proposed (51). Such a relationship is perhaps not surprising if, on longer time scales, P is removed via photosynthesis along with deposition of organic matter to the sediments. In an alternative approach, we rationalized the short-term behavior of DIP in estuaries in terms of suspended sediment concentrations and riverine DIP concentrations via adsorption/desorption reactions (53). Such

an approach can explain the release of DIP from suspended sediments seen in some relatively pristine estuaries and the extensive DIP removal to particles seen in other estuaries with much higher riverine DIP levels. This implies a feedback system that can prevent increases in riverine DIP inputs reaching coastal waters. If most estuaries are a net sink for sediments, as generally accepted (12, 51), then the adsorbed P will be retained in the estuaries, though this will not be the case for the very large rivers that discharge directly onto the continental shelf, or indeed, beyond it (51, 54). The sediment balance of estuaries is subject to very large-scale human disturbance. As noted earlier, the damming of rivers is reducing the supply of sediment to estuaries. The dredging of estuaries can obviously promote the export of particulate P to coastal waters. The reclamation of intertidal systems such as mud flats and salt marshes removes estuarine sediment sinks and promotes the export of particulate P to offshore water, where it can desorb to supply DIP to sustain phytoplankton activity (53).

Impacts of Changing Nutrient Inputs

Increased riverine nutrient concentrations and the loss of intertidal habitats have altered both the fluxes of nutrients into the coastal seas and the ratio of the key nutrients to one another. This enrichment process has gone on for some time. Large-scale increases in nitrate and DIP in U.K. and European rivers have been documented since 1950 (25, 55), and Narragansett Bay, USA, may have been impacted from 1870 onward (56). The question now arises of what has been the effect of these changes.

Coastal zones are, in general, more productive than offshore waters (57) so we must look for changes in phytoplankton numbers and relative species abundance with increasing nutrient inputs, rather than for higher productivity alone. Detailed scientific measurements only go back a few decades, and therefore, researchers have used a variety of techniques to reconstruct histories of change. Nutrient enrichment can be expected to yield a succession of effects, depending on the scale of the enrichment and the hydrodynamics of the area. Assuming that the phytoplankton production in the system is limited by nutrient supply rather than physical mixing or light supply, an increase in nutrient input can be expected to increase the phytoplankton activity. Given that the marine environment is traditionally viewed as being N limited in the short term, in contrast to the freshwater P-limited system [for example, (58)], an increase in N:P ratios can potentially have profound impacts on the phytoplankton community, not only in terms of increasing algal abundance but also by altering the relative abundance of species present. Justic *et al.* (24) argued that in pristine river systems, Si:N input ratios are such that Si supply is in excess of requirements, and hence, that increasing fluxes of N and P relative to Si will increase productivity without affecting diatom abundance, until eventually Si limitation becomes an important factor.

In the Chesapeake Bay, it has been possible to separate out the large interannual variability in phytoplankton abundance associated with variations in river flow from long-term changes in nutrient inputs, and hence, show a significant increase in phytoplankton abundance arising from increases in nutrient inputs since 1945 (59). In the Mississippi delta, an increase in diatom remains in sediments is seen from 1960 onward, paralleling increasing N fluxes in the Mississippi itself, and despite a decline in riverine Si inputs (60). Thus, the diatoms in this system can clearly obtain enough Si to respond to the increased N and P inputs.

In contrast, in the southern North Sea and in the Black Sea, it appears that the increasing relative abundance of N and P compared to Si has resulted in displacement of diatoms by other phytoplankton species, including coccoliths and flagellates in the case of the Black Sea (29) and by flagellates in the southern North Sea. In the southern North Sea, the nuisance algae *Phaeocystis* now blooms regularly (61). Such blooms have been reported in this area since the end of the last century, but over the period 1974–85, the duration and cell numbers

in these blooms increased at least fivefold. Such blooms continue into the 1990s, despite declines in Rhine P fluxes (62). This algae appears to be inefficiently grazed by zooplankton, leading to beach foams and increased organic carbon deposition to sediments. Indeed, nuisance blooms along the North Sea, Baltic, and Adriatic coasts are now reasonably common, and toxic algal blooms may be becoming more common generally (61).

The decomposition of dead phytoplankton material that has sunk into deeper waters produces a large O₂ demand that can exceed supply if there is inefficient vertical exchange. There is evidence for decreasing O₂ concentrations in the Baltic and Kattegat, which appear to be well correlated with increasing nutrient inputs and presumably phytoplankton abundance in surface waters (63). In the Northern Adriatic, O₂ levels in the surface waters have increased over the last 70 years, presumably as a result of increased photosynthesis, and deep-water O₂ levels have fallen (55). Similarly, areas of low O₂ concentrations in the Gulf of Mexico appear to have increased in response to increased nutrient inputs (60). Increases in chlorophyll levels in the Chesapeake Bay (58) are probably associated with the increasing incidences of anoxia in the deeper waters (64).

The picture painted so far is one of serious environmental impacts associated with increasing nutrient inputs to coastal waters. However, this impression can be misleading. For example, the southern North Sea region around the coasts of Holland, Belgium, and Germany is clearly being impacted by increasing *Phaeocystis* blooms. In the rest of the North Sea, there is little evidence of such impacts, with phytoplankton appearing to respond instead to large-scale climate changes (Fig. 1). This observation is consistent with the estimates of N inputs to the North Sea, which suggest that the bulk of the N arises from offshore transport rather than from terrestrial sources (Table 2), although the exact magnitude of this offshore flux is uncertain. Similarly, in the recent assessment of inputs to the North Atlantic as a whole (13, 51), it is estimated that the major source of N for the shelf region is associated with inputs from the open ocean. These results again emphasize the critical importance of physical water exchange in understanding the coastal system. Areas of restricted water exchange are seriously impacted, while other areas with similarly large nutrient inputs from terrestrial sources show little response.

Climate change may alter exchange processes between the coastal waters and the open ocean and also affect phytoplankton abundance as a result of changes in bloom timing and magnitude related to climatic factors (65). Coastal systems will show considerable variability in their responses to such changes in external forcing. This natural variability makes it difficult to detect changes arising from specific effects. Thus, for example, there appears to have been no detectable effect of reduced P inputs to Dutch coastal waters (25). Richardson (66) has estimated that it will take up to 11 years to detect changes in the Kattegat arising from reductions in nutrient inputs over the natural variability. If climate change should increase the frequency of extreme events (19), then variability will increase and it will become even more difficult to detect change.

The margins themselves are not passive in response to climatic forcing. The release of gases such as N₂O [a byproduct of denitrification (67)] and dimethyl sulfide (68) from marine waters can impact the climate system. The ocean margins are also important sites of C burial, though the magnitude of this is uncertain (51) and it is not clear if the coastal oceans are a net source or sink of C [for example, (69)].

Despite these caveats, it is clear that in some areas terrestrial inputs of nutrients are having a deleterious effects on coastal systems. The trends in inputs plus the loss of intertidal habitats important for denitrification mean that nutrient fluxes are likely to continue to rise and Si:N ratios will likely fall. It seems very likely that this trend will alter phytoplankton communities in coastal areas. In the past, there have been moves to regulate inputs once a deleterious effect has been documented, as in the case of TBT. In the face of growing concern

over eutrophication problems in freshwater systems, P levels in European and North American rivers have been reduced. In Europe, sewage sludge dumping at sea is being eliminated. The effect of this on nutrient inputs will be trivial when the whole North Sea is considered (Table 1), though of course, the effects on the benthos near the dump sites will be substantial. However, despite these improvements, little progress has been made on the much more politically divisive issues of N inputs from agricultural activity and car emissions, overfishing, and coastal habitat loss. Until these much more difficult issues are confronted, the biogeochemical cycles of the coastal zone will remain under threat.

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- While phytoplankton require a range of chemicals as nutrients to support effective growth, it is generally accepted that, in the presence of adequate light, the most likely nutrients to become limiting are N, P, and Si, plus Fe in certain environments, but not generally in coastal systems. Silicon is only used by certain algal groups for skeleton construction, so its abundance affects species composition rather than the overall abundance of phytoplankton. Nutrients are present in natural waters in dissolved and particulate form. The particulate material, which can include organic forms of N and P and inorganic forms of P and Si, can be solubilized via bacterial degradation and dissolution. Dissolved Si is present exclusively as Si(OH)₄, whereas dissolved P includes DIP, which can exist as a variety of ions formed from the pH-dependent dissociation of phosphoric acid, and dissolved organic P. Dissolved N can exist as nitrate (NO₃⁻), nitrite (NO₂⁻), and ammonium (NH₄⁺), as well as dissolved organic N. Nitrate is the thermodynamically favored form, but the other components are continuously produced via bacterial processes and only oxidize relatively slowly. The composition and bioavailability of dissolved organic N and P is uncertain and is the subject of current research [for example, S. Seitzinger and R. Sanders, *Mar. Ecol. Prog. Ser.* **159**, 1 (1990)]. There are also dissolved nitrogen gases in natural waters, particularly N₂, but this species can only be used by a small number of specialized N-fixing bacteria. Recent research suggests that N fixation may be much more important than previously thought [F. Lipschultz and N. Owens, *Biogeochemistry* **35**, 261 (1996)] and this may be particularly so on intertidal sediments. In the text, references to N and P refer to all the readily bioavailable dissolved and particulate forms of N and P, unless the chemical form is specified.
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The Quantum Event of Oceanic Crustal Accretion: Impacts of Diking at Mid-Ocean Ridges

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REVIEW

Seafloor diking-eruptive events represent the irreducible, quantum events of upper oceanic crustal accretion. They record events by which a large portion of the oceanic crust has formed through geological history. Since 1993, the U.S. Navy's real-time Sound Surveillance System has allowed location of ongoing acoustic signatures of dike emplacement and basalt eruptions at ridge crests in the northeast Pacific. These diking-eruptive events trigger a sequence of related, rapidly evolving physical, chemical, and biological processes. Magmatic volatiles released during these events may provide nutrients for communities of seafloor microorganisms, some of which thrive in high-temperature anaerobic environments. Many of the organisms identified from these systems are Archaea. If microorganisms can thrive in the water-saturated pores and cracks within deep, volcanically active portions of our planet, other hydrothermally active planets may harbor similar life forms.

The ocean basins cover nearly 60% of Earth's surface. They are underlain by 5 to 6 km of oceanic crust formed through solidification

of molten basalt along the global spreading center network (Fig. 1). The basalt is generated by partial melting in the rising mantle beneath mid-ocean ridges. Annually, about 20 km³ (*I*) of basaltic magma is buoyantly emplaced along the spreading centers where it cools to form the trailing edges of large tectonic plates. Rates of plate divergence vary from 10 to nearly 200 mm per year. Upon rising into the young crust bounding the zone of divergence, the melt commonly collects in crustal chambers located 1 to 2 km below the seafloor. A significant fraction of the magma solidifies slowly in the chamber to form coarse-grained gabbros, but the remaining magma episodically breaks through the crystalline roof of the chamber, rises to the seafloor through planar, ridge-parallel conduits, and produces submarine eruptions of basaltic lava flows. The conduits are known as dikes, a term that also applies to the rapidly cooled rock that fills the conduit after magma transfer ceases.

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