Other Nutrients and Dissolved Oxygen and Climate Change

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Definition

Primary and secondary production in the ocean depends on the supply of a few key elements. A combination of physical, chemical, and microbial processes mediates the cycling of these elements through the environment and determines their supply. Anthropogenic perturbations to the cycles of these elements, either directly or through global warming, could result in severe alterations of patterns of primary production and a reorganization of marine ecosystems.

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Cycling of Essential Elements in the Ocean

The distribution and cycling of several key elements determines primary and secondary production and biogeochemical processes in the ocean; of particular interest are nitrogen (N), phosphorus (P), silicon (Si), oxygen (O), and the trace metal iron (Fe). All marine organisms require N and P as essential building blocks of their lipids, proteins, and carbohydrates. Si is only required by diatoms, a major group of unicellular marine algae that plays an important role in the biological carbon cycle. Diatom growth is typically limited by silicic acid. Fe is required only in trace amounts but necessary for the synthesis of a range of essential enzymes including those used in the photosynthetic apparatus. Free oxygen (O_2), a by-product of photosynthesis, is essential for all multicellular heterotrophs and for many microbes as electron acceptor in the respiratory oxidation of organic matter. While there are other elements required for the synthesis of organic matter, cell walls, enzymes, etc. (first and foremost carbon but also sulfur, calcium, molybdenum, and others), these elements are typically available in sufficient amounts, thus their supply does not affect patterns of productivity in the modern ocean. Consequently anthropogenic perturbations in their cycling are not thought to be of first-order importance.

The N cycle essentially consists of a number of redox reactions that transform a variety of N species, ranging in oxidation state from −3 to 5, from one form to another. The important inorganic species are the gaseous forms nitrogen gas (N_2) and nitrous oxide (N_2O) and the dissolved forms nitrate (NO_3^-) and ammonium (NH_4^+). While N_2 gas is extremely abundant, making up about 80 % of the Earth's atmosphere and representing 99 % of all N in the ocean and atmosphere combined, it is biologically unavailable to most microorganisms. Only a specialized group, referred to as N_2 fixers or diazotrophs, is able to split the stable triple bond in the N_2 molecule and reduce it to bioavailable ammonium, which is readily incorporated in the synthesis of organic matter (ammonium and organic matter represent the most reduced forms of N with an oxidation state of −3). This process is referred to as N_2 fixation. In the presence of free oxygen, ammonium is oxidized to nitrate (the most oxidized form of N with an oxidation state of 5; nitrate is also bioavailable to most microorganisms) by chemoautotrophic bacteria in a process referred to as nitrification. In the present, well-oxygenated ocean, the overwhelming majority of bioavailable N is present in its oxidized form as nitrate. In the absence of oxygen, certain heterotrophic bacteria can use nitrate as electron acceptor instead of oxygen for the respiration of organic matter. This process is referred to as denitrification and one of its end products is N_2. Denitrification thus represents a sink for bioavailable nitrogen. N_2O is an intermediate product during nitrification and denitrification and only present in small quantities but is of interest because it is a potent greenhouse gas. In summary, the N cycle in the modern ocean is mediated by three key processes – N_2 fixation, nitrification, and denitrification – and is thus completely dependent on microbial activity. The balance of N_2 fixation (source) and denitrification (sink) determines the oceanic reservoir of bioavailable nitrogen.

The cycling of P differs from that of N in the following two major aspects. There is no P in the atmosphere, and P is found in only one oxidation state, as phosphate (PO_4^-). The oceanic reservoir of phosphate is determined by the balance of river inputs from rock weathering (source) and removal due to permanent burial of organic matter in sediments (sink). Both of these processes are slow, leading to a much larger turnover time for phosphate in the ocean than for nitrate.

The oceanic distributions of nitrate and phosphate are highly correlated, and their relative proportion of about 16 atoms of N per 1 atom of P matches the average composition of marine organic matter ($C_{106}N_{16}P_1$) – an observation that was first articulated by Redfield in 1934 (the average relative ratios of elements in organic matter have since been referred to as Redfield ratios). This remarkable correspondence can be explained by the interplay of N_2 fixation and denitrification, which, in an oxygenated ocean and over sufficiently long time scales, will regulate the oceanic inventory of bioavailable N to match the P inventory in terms of the Redfield ratio (Lenton and Watson 2000). In the modern ocean, there is only a slight deficit in nitrate with respect to phosphate, so N is typically the element limiting marine primary production.

Si is required only by diatoms for their characteristic silica cell walls or frustules. Diatoms are very abundant and an important contributor to export of organic matter from the sunlit surface ocean to depth by sinking. Model-based estimates suggest that diatoms make up 40 % of the global export of particulate organic carbon (Jin et al. 2006).

Fe, although required in much smaller quantities than N, P, and Si, is essential for many enzyme systems, including the photosynthetic apparatus and nitrogenase, the enzyme required for N_2 fixation. Insufficient supply of Fe has been shown to limit primary production in the eastern equatorial Pacific, the subarctic Pacific, and the Southern Ocean. These areas are the so-called high-nutrient, low-chlorophyll (or HNLC) regions, where unused nitrate and phosphate remain present in surface waters at the end of the growing season.

O_2 is produced by photosynthesis and is consumed during aerobic respiration of organic matter (in terms of thermodynamic energy gain, O_2 is the most beneficial electron acceptor). About 20 % of the Earth's atmosphere consists of O_2, which accumulated after the evolution of oxygenic photosynthesis early in the Earth's history because some reduced organic carbon was stored in sedimentary rocks (at the ocean floor and on continental cratons) and thus effectively removed from the reduction-oxidation cycle. The modern ocean is also well-oxygenated, with relatively small oxygen minimum zones and anoxia occurring only in isolated spots with restricted circulation, e.g., the Cariaco Basin, the Black Sea, and the Baltic Sea. However, an oxygenated ocean is not an inevitable consequence of an oxygen-rich atmosphere. There have been extended periods throughout the Earth's history when the ocean was anoxic (Fennel et al. 2005). Below the sunlit surface ocean, the only source that offsets respiratory consumption of oxygen is physical transport of oxygenated water through convective mixing and thermohaline circulation. Since both of these physical processes are highly sensitive to climate, subsurface oxygen will likely be affected by climate change.

The cycles of N, P, and O are linked and are also tightly coupled with the carbon cycle. One example illustrating the close coupling of N, P, and carbon cycling is the fact that oceanic nitrate and phosphate are available almost in Redfield proportions, as mentioned above. This regulation of nitrate availability can however be disrupted by a decrease in the O_2 supply as described below.

Recent and Projected Changes

Humans are massively perturbing the natural N cycle by adding bioavailable N through industrial N_2 fixation for production of synthetic fertilizers, cultivation of leguminous crops, and fossil fuel burning. By 1990, anthropogenic sources of bioavailable N had exceeded the rate of natural N_2 fixation in the terrestrial biosphere as well as the rate of marine N_2 fixation; by 2050, anthropogenic production of bioavailable N is projected to exceed natural terrestrial and oceanic N_2 fixation combined (Galloway et al. 2004). While application of synthetic fertilizers is necessary to feed the growing world population, inequalities in its distribution and inefficiencies in its use are pervasive. Some regions lack sufficient fertilizer to meet even the most basic caloric demands of millions of people, while elsewhere an excess of food leads to unhealthy diets and fertilizers are applied so inefficiently that they lead to eutrophication of aquatic environments (Galloway et al. 2008). Estimates suggest that about 80 % of anthropogenic N is denitrified in soils and freshwater systems and that the bulk of the remainder is denitrified on continental shelves (Fennel et al. 2006; Seitzinger et al. 2006). Hence, river inputs of anthropogenic N are likely not an important nutrient source for the open ocean yet lead to many negative effects in coastal waters including decreased water clarity, harmful algal blooms, and an increasing occurrence of hypoxia and anoxia (Diaz and Rosenberg 2008).

In the open ocean, global warming is expected to lead to stronger vertical density stratification and a slowdown of the thermohaline overturning circulation, both of which would result in a decrease in O_2 supply to waters below the sunlit surface. Evidence of this deoxygenation has already been reported (Stramma et al. 2008). If this trend continues, implications could be severe for deep-sea animals, especially benthic organisms with limited mobility. Ocean deoxygenation would also have biogeochemical consequences. In a hypoxic or anoxic ocean, denitrification would become more important as a pathway for the respiration of organic matter compared to aerobic respiration, which could result in a larger loss of bioavailable N than can be replenished by N_2 fixation. This, consequently, would decrease the inventory of bioavailable N and reduce primary production globally. A massive increase in denitrification could also result in a significant additional source of the greenhouse gas N_2O to the atmosphere, further amplifying global warming.

Direct natural perturbations to the cycling of P, Si, and Fe are possible but would likely be smaller, at least over the next few hundred years. While dissolution and weathering of rocks is affected by climate (faster in warmer and more humid

conditions), weathering rates are comparatively small. An expansion of arid regions and increase in the frequency of storms could accelerate Fe supply to the ocean, but this prediction is speculative. Variations in atmospheric Fe deposition to the ocean are thought to have occurred in concert with glacial/interglacial cycles in the past. In fact, these variations in Fe supply have been suggested to explain the glacial/interglacial changes in partitioning of carbon between the atmosphere and ocean (Martin 1990), which has prompted geo-engineering proposals to apply large-scale fertilization of the ocean with Fe in order to mitigate future warming. Given the tight coupling of elemental cycles and the likelihood for unintended consequences, such proposals should be treated with caution.

Cross-References

► Ecological Carbon Sequestration in the Oceans and Climate Change
► Marine Net Primary Production

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