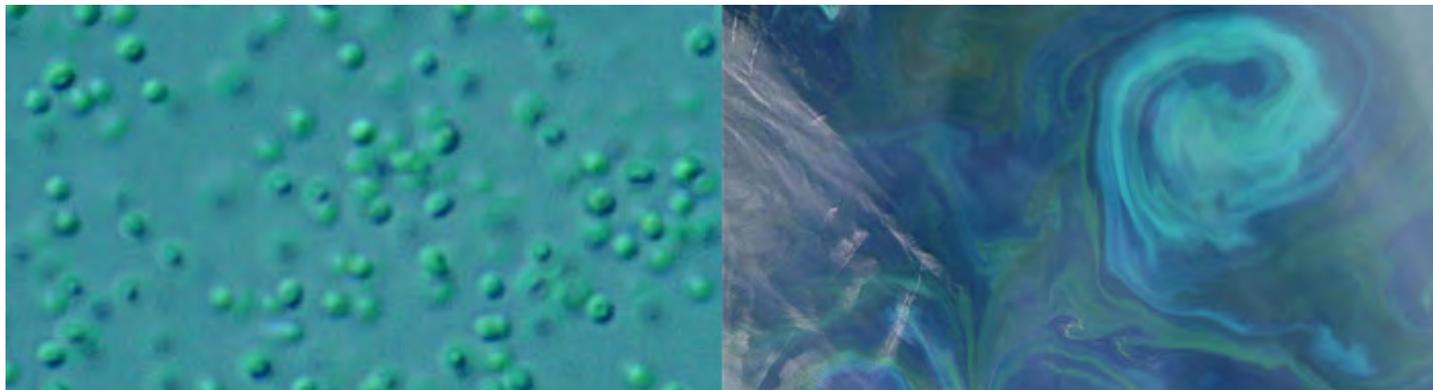


# The Biological Productivity of the Ocean

Daniel M. Sigman<sup>1</sup> & Mathis P. Hain<sup>1,2</sup> © 2012 Nature Education

Productivity fuels life in the ocean, drives its chemical cycles, and lowers atmospheric carbon dioxide. Nutrient uptake and export interact with circulation to yield distinct ocean regimes.



## What is Ocean Productivity?

Ocean productivity largely refers to the production of organic matter by “phytoplankton,” plants suspended in the ocean, most of which are single-celled. Phytoplankton are “photoautotrophs,” harvesting light to convert inorganic to organic carbon, and they supply this organic carbon to diverse “heterotrophs,” organisms that obtain their energy solely from the respiration of organic matter. Open ocean heterotrophs include bacteria as well as more complex single- and multi-celled “zooplankton” (floating animals), “nekton” (swimming organisms, including fish and marine mammals), and the “benthos” (the seafloor community of organisms).

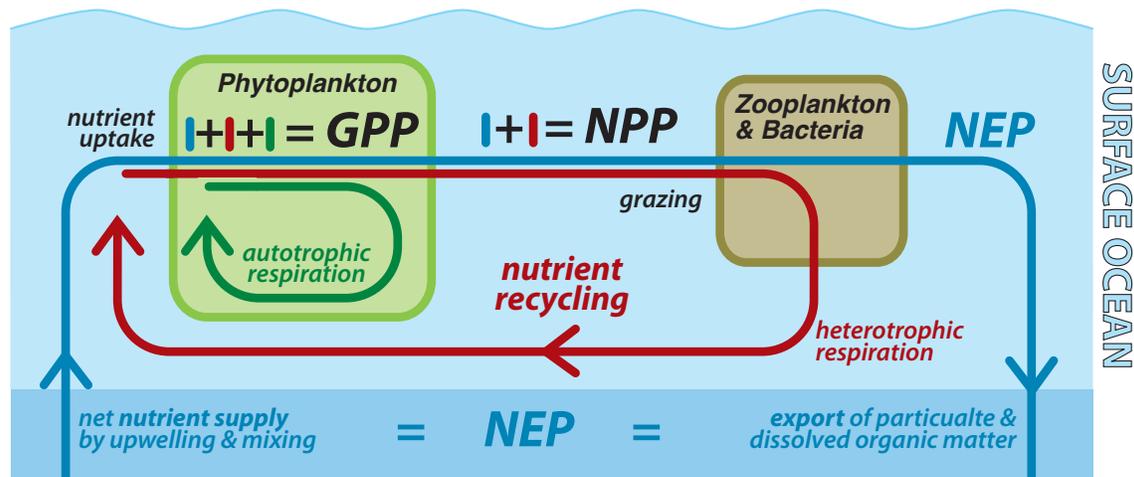
The many nested cycles of carbon associated with ocean productivity are revealed by the following definitions (Bender et al. 1987) (Figure 1). “Gross primary production” (GPP) refers to the total rate of organic carbon production by autotrophs, while “respiration” refers to the energy-yielding oxidation of organic carbon back to carbon dioxide. “Net primary production” (NPP) is GPP minus the autotrophs’ own rate of respiration; it is thus the rate at which the full metabolism of phytoplankton produces biomass. “Secondary production” (SP) typically refers to the growth rate of heterotrophic biomass. Only a small fraction of the organic matter ingested by heterotrophic organisms is used to grow, the majority being respired back to dissolved inorganic carbon and nutrients that can be reused by autotrophs. Therefore, SP in the ocean is small in comparison to NPP. Fisheries rely on SP; thus they depend on both NPP and the efficiency with which organic matter is transferred up the foodweb (i.e., the SP/NPP ratio). “Net ecosystem production” (NEP) is

GPP minus the respiration by all organisms in the ecosystem. The value of NEP depends on the boundaries defined for the ecosystem. If one considers the sunlit surface ocean down to the 1% light level (the “euphotic zone”) over the course of an entire year, then NEP is equivalent to the particulate organic carbon sinking into the dark ocean interior plus the dissolved organic carbon being circulated out of the euphotic zone. In this case, NEP is also often referred to as “export production” (or “new production” (Dugdale & Goering 1967), as discussed below). In contrast, the NEP for the entire ocean, including its shallow sediments, is roughly equivalent to the slow burial of organic matter in the sediments minus the rate of organic matter entering from the continents.

There are no accumulations of living biomass in the marine environment that compare with the forests and grasslands on land (Sarmiento & Bender 1994). Nevertheless, ocean biology is responsible for the storage of more carbon away from the atmosphere than is the terrestrial biosphere (Broecker 1982). This is achieved by the sinking of organic matter out of the surface ocean and into the ocean interior before it is returned to dissolved inorganic carbon and dissolved nutrients by bacterial decomposition. Oceanographers often refer to this process as the “biological pump,” as it pumps carbon dioxide (CO<sub>2</sub>) out of the surface ocean and atmosphere and into the voluminous deep ocean (Volk & Hoffert 1985).

Only a fraction of the organic matter produced in the surface ocean has the fate of being exported to the deep ocean. Of the organic matter produced by phytoplankton (NPP), most is respired back to dissolved inorganic forms within the surface ocean and thus recycled for use by phytoplankton (Eppley & Pe-

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**Figure 1.** Productivity in the surface ocean, the definitions used to describe it, and its connections to nutrient cycling. The blue cycle for “net ecosystem production” (NEP) (i.e. “new” or “export” production) encompasses the “new” nutrient supply from the ocean interior, its uptake by autotrophic phytoplankton growth, packaging into large particles by heterotrophic grazing organisms, and sinking of organic matter out of the surface ocean. The red cycle illustrates the fate of the majority of organic matter produced in the surface ocean, which is to be respired by heterotrophic organisms to meet their energy requirements, thereby releasing the nutrients back into the surface water where they can be taken up by phytoplankton once again to fuel “regenerated production.” The green cycle represents the internal respiration of phytoplankton themselves, that is, their own use of the products of photosynthesis for purposes other than growth. These nested cycles combine to yield (1) “gross primary production” (GPP) representing the gross photosynthesis and (2) “net primary production” (NPP) that represents phytoplankton biomass production that forms the basis of the food web plus a much smaller rate of organic matter export from the surface. While the new nutrient supply and export production are ultimately linked by mass balance, there may be imbalances on small scales of space and time, allowing for brief accumulations of biomass.

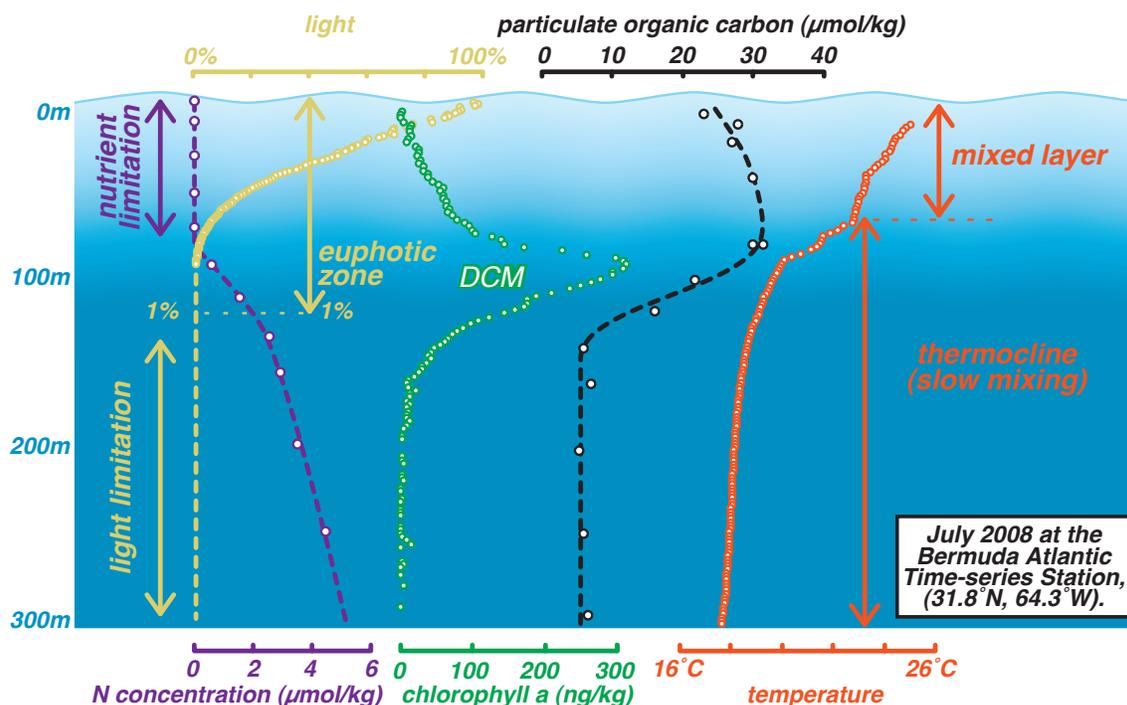
terson 1979) (Figure 1). Most phytoplankton cells are too small to sink individually, so sinking occurs only once they aggregate into larger particles or are packaged into “fecal pellets” by zooplankton. The remains of zooplankton are also adequately large to sink. While sinking is a relatively rare fate for any given particle in the surface ocean, biomass and organic matter do not accumulate in the surface ocean, so export of organic matter by sinking is the ultimate fate for all of the nutrients that enter into the surface ocean in dissolved form — with the exceptions that (1) dissolved nutrients can be returned unused to the interior by the circulation in some polar regions (see below), and (2) circulation also carries dissolved organic matter from the surface ocean into the interior, a significant process (Hansell et al. 2009) that we will not address further. As organic matter settles through the ocean interior and onto the seafloor, it is nearly entirely decomposed back to dissolved chemicals (Emerson & Hedges 2003, Martin et al. 1987). This high efficiency of decomposition is due to the fact that the organisms carrying out the decomposition rely upon it as their sole source of chemical energy; in most of the open ocean, the heterotrophs only leave behind the organic matter that is too chemically resistant for it to be worth the investment to decompose. On the whole, only a tiny fraction (typically much less than 1%) of the organic carbon from NPP in the euphotic zone survives to be buried in deep sea sediments.

Productivity in coastal ecosystems is often distinct from that of the open ocean. Along the coasts,

the seafloor is shallow, and sunlight can sometimes penetrate all the way through the water column to the bottom, thus enabling bottom-dwelling (“benthic”) organisms to photosynthesize. Furthermore, sinking organic matter is intercepted by the seabed, where it supports thriving benthic faunal communities, in the process being recycled back to dissolved nutrients that are then immediately available for primary production. The proximity to land and its nutrient sources, the interception of sinking organic matter by the shallow seafloor, and the propensity for coastal upwelling all result in highly productive ecosystems. Here, we mainly address the productivity of the vast open ocean; nevertheless, many of the same concepts, albeit in modified form, apply to coastal systems.

## What Does Ocean Productivity Need?

Phytoplankton require a suite of chemicals, and those with the potential to be scarce in surface waters are typically identified as “nutrients.” Calcium is an example of an element that is rapidly assimilated by some plankton (for production of calcium carbonate “hard parts”) but is not typically considered a nutrient because of its uniformly high concentration in seawater. Dissolved inorganic carbon, which is the feedstock for organic carbon production by photosynthesis, is also abundant and so is not typically listed among the nutrients. However, its acidic form dissolved  $CO_2$  is often at adequately low concentrations to affect the growth of at least some phytoplankton.



**Figure 2.** Typical conditions in the subtropical ocean, as indicated by data collected at the Bermuda Atlantic Time-series Station in July, 2008. The thermocline (vertical temperature gradient) stratifies the upper water column. During this particular station occupation, the shallow wind-mixed surface layer is not well defined, presumably because of strong insolation and a lack of wind that allowed continuous stratification all the way to the surface. Very little sunlight penetrates deeper than ~100 m. New supply of the major nutrients N and P is limited by the slow mixing across the upper thermocline (showing here only the N nutrient nitrate,  $\text{NO}_3^-$ ). Within the upper euphotic zone, the slow nutrient supply is completely consumed by phytoplankton in their growth. This growth leads to the accumulation of particulate organic carbon in the surface ocean, some of which is respired by bacteria, zooplankton, and other heterotrophs, and some of which is exported as sinking material. The deep chlorophyll maximum (DCM) occurs at the contact where there is adequate light for photosynthesis and yet significant nutrient supply from below. The DCM should not be strictly interpreted as a depth maximum in phytoplankton biomass, as the phytoplankton at the DCM have a particularly high internal chlorophyll concentration. The data shown here is made available by the Bermuda Institute of Ocean Sciences (<http://bats.bios.edu>) and the Bermuda Bio Optics Project (<http://www.ices.ucsb.edu/bbop/>).

Broadly important nutrients include nitrogen (N), phosphorus (P), iron (Fe), and silicon (Si). There appear to be relatively uniform requirements for N and P among phytoplankton. In the early 1900s, oceanographer Alfred Redfield found that plankton build their biomass with C:N:P stoichiometric ratios of ~106:16:1, to which we now refer as the Redfield ratios (Redfield 1958). As Redfield noted, the dissolved N:P in the deep ocean is close to the 16:1 ratio of plankton biomass, and we will argue below that plankton impose this ratio on the deep, not vice versa. Iron is found in biomass only in trace amounts, but it is used for diverse essential purposes in organisms, and it has become clear over the last 25 years that iron's scarcity often limits or affects productivity in the open ocean, especially those regions where high-N and -P deep water is brought rapidly to the surface (Martin & Fitzwater 1988). Research is ongoing to understand the role of other trace elements in productivity (Morel et al. 2003). Silicon is a nutrient only for specific plankton taxa—diatoms (autotrophic phytoplankton), silicoflagellates, and radiolaria (heterotrophic zooplankton)—which use it to make opal hard parts. However, the typical dominance of diatoms in Si-bearing waters, and the tendency of diatom-associated organic matter to sink out of the

surface ocean, make Si availability a major factor in the broader ecology and biogeochemistry of surface waters.

Sunlight is the ultimate energy source — directly or indirectly — for almost all life on Earth, including in the deep ocean. However, light is absorbed and scattered such that very little of it penetrates below a depth of ~80 m (as deep as 150 m in the least productive subtropical regions, but as shallow as 10 m in highly productive and coastal regions) (Figure 2). Thus, photosynthesis is largely restricted to the upper light-penetrated skin of the ocean. Moreover, across most of the ocean's area, including the tropics, subtropics, and the temperate zone, the absorption of sunlight causes surface water to be much warmer than the underlying deep ocean, the latter being filled with water that sank from the surface in the high latitudes. Warm water is more buoyant than cold, which causes the upper sunlit layer to float on the denser deep ocean, with the transition between the two known as the "pycnocline" (for "density gradient") or "thermocline" (the vertical temperature gradient that drives density stratification across most of the ocean, Figure 2). Wind or another source of energy is required to drive mixing across the

pycnocline, and so the transport of water with its dissolved chemicals between the sunlit surface and the dark interior is sluggish. This dual effect of light on photosynthesis and seawater buoyancy is critical for the success of ocean phytoplankton. If the ocean did not have a thin buoyant surface layer, mixing would carry algae out of the light and thus away from their energy source for most of the time. Instead of nearly neutrally buoyant single celled algae, larger, positively buoyant photosynthetic organisms (e.g., pelagic seaweeds) might dominate the open ocean. This hypothetical case aside, although viable phytoplankton cells are found (albeit at low concentrations) in deeper waters, photosynthesis limits active phytoplankton growth to the upper skin of the ocean, while upper ocean density stratification prevents them from being mixed down into the dark abyss. Thus, most open ocean biomass, including phytoplankton, zooplankton, and nekton, is found within ~200 m of the ocean surface.

At the same time, the existence of a thin buoyant surface layer conspires with other processes to impose nutrient limitation on ocean productivity. The export of organic matter to depth depletes the surface ocean of nutrients, causing the nutrients to accumulate in deep waters where there is no light available for photosynthesis (Figure 2). Because of the density difference between surface water and the deep sea across most of the ocean, ocean circulation can only very slowly reintroduce dissolved nutrients to the euphotic zone. By driving nutrients out of the sunlit, buoyant surface waters, ocean productivity effectively limits itself.

Phytoplankton growth limitation has traditionally been interpreted in the context of Liebig's Law of the Minimum, which states that plant growth will be as great as allowed by the least available resource, the "limiting nutrient" that sets the productivity of the system (de Baar 1994). While this view is powerful, interactions among nutrients and between nutrients and light can also control productivity. A simple but important example of this potential for "co-limitation" comes from polar regions, where oblique solar insolation combines with deep mixing of surface waters to yield low light availability. In such environments, higher iron supply can increase the efficiency with which phytoplankton capture light energy (Maldonado et al. 1999, Sunda & Huntsman 1997). More broadly, it has been argued that phytoplankton should generally seek a state of co-limitation by all the chemicals they require, including the many trace metal nutrients (Morel 2008).

## Who Are the Major Players in Ocean Productivity?

### Photoautotrophs

In contrast to the terrestrial biosphere, most marine photosynthesis is conducted by single-celled organisms, and the more abundant of the multicellular forms are structurally much simpler than the vascular

plants on land. During much of the twentieth century, it was thought that cells in the range of ~5 to ~100 microns diameter account for most phytoplankton biomass and productivity. This size range is composed mostly of eukaryotes, organisms whose cells contain complex membrane-bound structures ("organelles"), including the cell's nucleus and chloroplasts. Well-studied forms of eukaryotic phytoplankton include the opal-secreting diatoms, prymnesiophytes (including the CaCO<sub>3</sub>-secreting coccolithophorids), and the organic wall-forming dinoflagellates. The centrality of these organisms in early oceanographic thought was due to their accessibility by standard light microscopy.

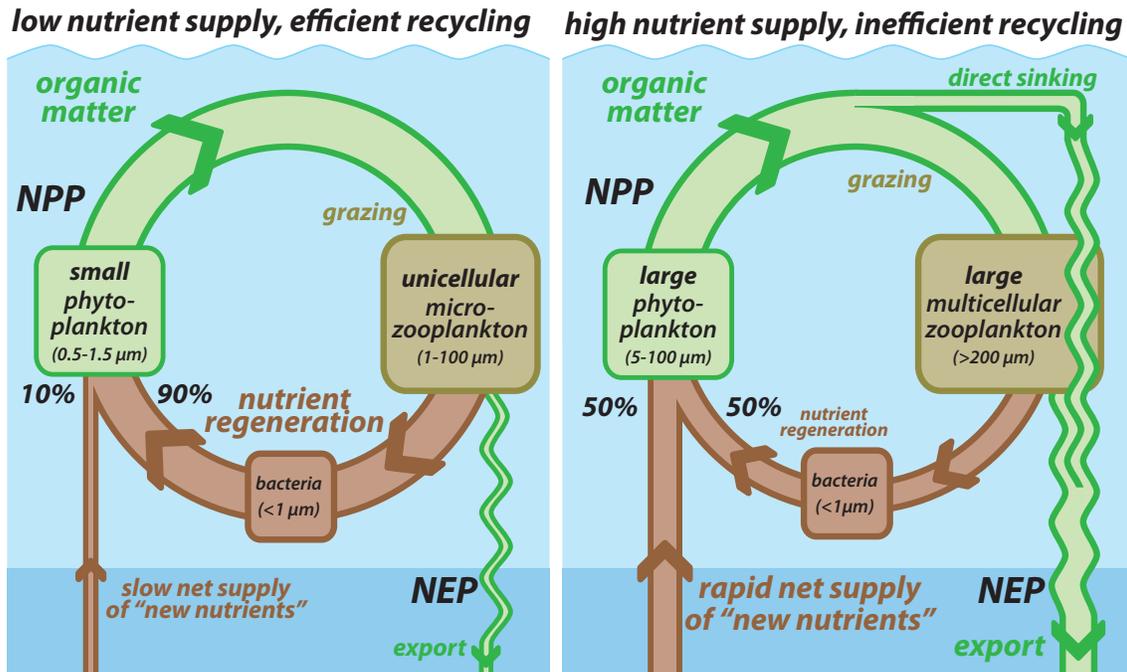
Only with recent technological advances have smaller organisms become readily observable, revolutionizing our view of the plankton. In particular, the cyanobacteria, which are prokaryotes (lacking a nucleus and most other organelles found in eukaryotes), are now known to be important among the phytoplankton. Initially, the cyanobacteria were identified largely with colonial forms such as *Trichodesmium* that play the critical role of "fixing" nitrogen (see below). However, major discoveries over the last thirty years have revealed the prevalence across the global ocean of unicellular cyanobacteria of ~0.5 to ~1.5 microns diameter. It is now recognized that two cyanobacterial genera — *Synechococcus* and *Prochlorococcus* — dominate phytoplankton numbers and biomass in the nutrient-poor tropical and subtropical ocean (Waterbury et al. 1979, Chisholm et al. 1988). In addition, new methods, both microscopic and genetic, are revealing a previously unappreciated diversity of smaller eukaryotes in the open ocean.

Mapping ecological and biogeochemical functions onto the genetic diversity of the phytoplankton is an active area in biological and chemical oceanography. Based on observations as well as theory, the smaller phytoplankton such as the unicellular cyanobacteria are thought to dominate regenerated production in many systems, whereas the larger eukaryotes appear to play a more important role in new production (i.e., NEP, Figure 1; see below).

### Heterotrophs

Just as large eukaryotes were once thought to dominate the phytoplankton, it was long believed that multicellular zooplankton of ≥200 microns dominate heterotrophy — the small crustaceans known as copepods are the prototypical example. We now know that heterotrophy is often dominated by single-celled eukaryotes ("microzooplankton," of ~1 to ~200 microns) and by bacteria (of ~0.3 to ~1 microns), the latter carrying out most of the organic carbon decomposition in the ocean.

The food source of a given form of zooplankton is typically driven by its own size, with microzooplankton grazing on the prokaryotes and smaller eukaryotes and multicellular zooplankton grazing on larger eukaryotes, both phytoplankton and microzooplankton. Because of their relative physiological simplicity, micro-



**Figure 3.** The most broadly accepted paradigm for the controls on surface nutrient recycling efficiency. NPP is supported by both new nutrient supply from the deep ocean and nutrients regenerated within the surface ocean. The fraction of NEP:NPP ratio appears to vary with the nutrient supply, because links to the ecology of the plankton. In the nutrient-poor tropical and subtropical ocean (a), the (small) cyanobacteria tend to be numerically dominant. The microzooplankton that graze these small cells do so effectively, preventing phytoplankton from sinking directly. Moreover, these single-celled microzooplankton do not produce sinking fecal pellets. Instead, any residual organic matter remains to be degraded by bacteria. This increases recycling relative to organic matter export, yielding a low NEP:NPP ratio ( $\sim 0.1$ ). In nutrient-rich regions (b), large phytoplankton are more important, and these can be grazed directly by multicellular zooplankton. By growing adequately rapidly to outstrip the grazing rates of zooplankton, the large phytoplankton can sometimes accumulate to high concentrations and produce abundant sinking material. In addition, the zooplankton export organic matter as fecal pellets. In these productive systems, the less intensive upper ocean recycling causes NEP and NPP to be more similar, with an NEP:NPP ratio often near 0.5. The relationships between nutrient supply, phytoplankton size, and sinking thus dominate this view of upper ocean nutrient cycling.

zooplankton are thought to be highly efficient grazers that strongly limit the biomass accumulation of their prey. In contrast, the multicellular zooplankton, because they typically have more complex life histories, can lag behind the proliferation of their prey, allowing them to bloom and sometimes avoid predation altogether and sink directly. The multicellular zooplankton also often facilitate the production of sinking organic matter, for example, through the production of fecal pellets by copepods.

#### Effect of diversity on productivity

The diversity of the plankton interacts with open ocean environmental conditions to affect the productivity of the larger ecosystem (Michaels & Silver 1988, Morel et al. 1991, Buesseler 1998) (Figure 3). In the nutrient-poor tropical and subtropical ocean, the (small) cyanobacteria tend to be numerically dominant, perhaps because they specialize in taking up nutrients at low concentrations. Small phytoplankton have a greater surface area-to-volume ratio than do large phytoplankton. A greater proportional surface area promotes the uptake of nutrients across the cell boundary, a critical process when nutrients are scarce, likely explaining why small phytoplankton dominate the biomass in the nutrient-poor ocean. The micro-

zooplankton effectively graze these small cells, preventing their biomass from accumulating and sinking directly. Moreover, these single-celled microzooplankton lack a digestive tract, so they do not produce the fecal pellets that represent a major mechanism of export. Instead, any residual organic matter remains in the upper ocean, to be degraded by bacteria. All told, microzooplankton grazing of phytoplankton biomass leads to the remineralization of most of its contained nutrients and carbon in the surface ocean, and thus increases recycling relative to organic matter export. This very efficient recycling elevates NPP relative to NEP, yielding a low NEP:NPP ratio ( $\sim 0.05$ – $0.3$ ) in nutrient-poor systems (Figure 3a). In contrast, larger phytoplankton, such as diatoms, often dominate the nutrient-rich polar ocean, and these can be grazed directly by multicellular zooplankton. By growing adequately rapidly to outstrip the grazing rates of these zooplankton, the diatoms can sometimes accumulate to high concentrations and produce abundant sinking material. In addition, the zooplankton export organic matter as fecal pellets. In these productive systems, the less intensive upper ocean recycling causes NEP and NPP to be more similar, with an NEP:NPP ratio often near 0.5 (Figure 3b).

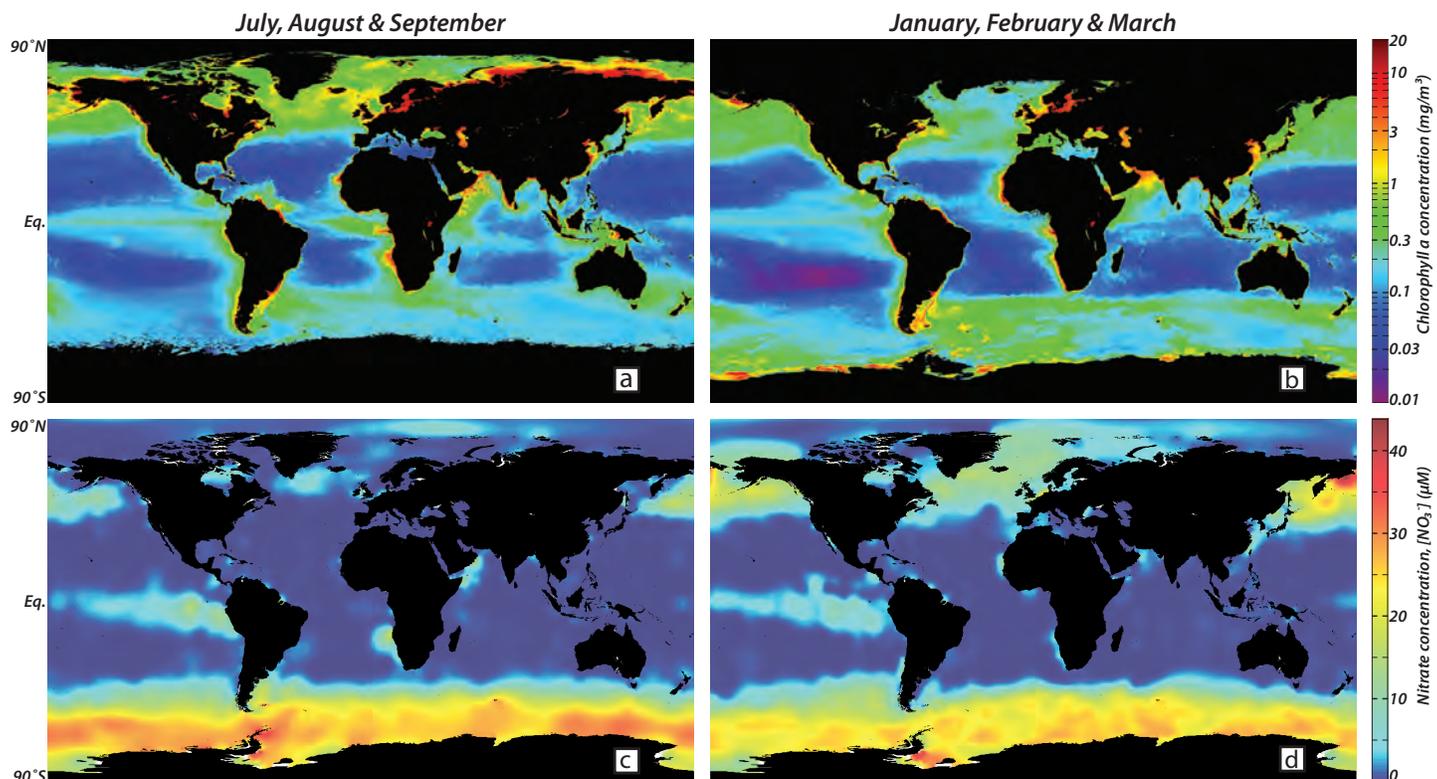
## How Does Ocean Productivity Vary in the Modern Ocean?

### Geographic variation

Satellites can measure the color of the surface ocean in order to track the concentration of the green pigment chlorophyll that is used to harvest light in photosynthesis (Figure 4). Higher chlorophyll concentrations and in general higher productivity are observed on the equator, along the coasts (especially eastern margins), and in the high latitude ocean (Figure 4a and b). A major driver of these patterns is the upwelling and/or mixing of high nutrient subsurface water into the euphotic zone, as is evident from surface nutrient measurements (Figure 4c and d).

There are caveats regarding the use of satellite-derived chlorophyll maps to deduce productivity, phytoplankton abundance, and their variation. First, the relationship between chlorophyll and biomass is changeable, depending on the physiology of phy-

toplankton; for example, phytoplankton adapted to lower light and/or higher nutrients (e.g., iron) tend to have a higher cellular concentration of chlorophyll (Geider et al. 1997). Second, chlorophyll concentration speaks more directly to the rate of photosynthesis (i.e., GPP) than to NPP, the latter representing the growth of phytoplankton biomass plus the transfer of organic matter-bound energy to higher trophic levels. Third, for a given NPP, small variations in grazing can lead to large proportional changes in phytoplankton biomass (Landry & Hassett 1982). Fourth, the depth range sensed by the satellite ocean color measurements extends only to the uppermost ten's of meters, much shallower than the base of the euphotic zone (Figure 2). Compared to nutrient-bearing regions, nutrient-deplete regions (e.g., the subtropical gyres) have a larger fraction of chlorophyll below the depth that can be sensed by the satellite (Smith 1981). Thus, satellite chlorophyll observations tend to over-accentuate the productivity differences between nutrient-bearing and -depleted regions. Despite these caveats, satellite-derived ocean color observations have transformed our



**Figure 4.** Composite global ocean maps of concentrations of satellite-derived chlorophyll and ship-sampled nitrate ( $\text{NO}_3^-$ ; the dominant N-containing nutrient). Northern hemisphere summer is shown in the left panels and southern hemisphere summer on the right. In the vast unproductive low- and mid-latitude ocean, warm and sunlit surface water is separated from cold, nutrient-rich interior water by a strong density difference that restricts mixing of water and thereby reduces nutrient supply, which becomes the limiting factor for productivity. These “ocean deserts” are dissected by areas, mainly at the equator and the eastern margins of ocean basins, where the wind pushes aside the buoyant, warm surface lid and allows nutrient-rich deeper water to be upwelled. In the high latitude ocean, surface water is cold and therefore the vertical density gradient is weak, which allows for vertical mixing of water to depths much greater than the sunlit “euphotic zone” as a result, the nutrient supply is greater than the phytoplankton can consume, given the available light (and iron, see text). The data shown here are available through the NASA’s OceanColor (<http://oceancolor.gsfc.nasa.gov/>) and NOAA’s National Oceanographic Data Center (<http://www.nodc.noaa.gov/>) websites. Sea ice cover impedes measurement of ocean color from space, reducing the apparent areas of the polar oceans in the winter hemisphere (upper panels).

view of ocean productivity.

### Depth variation

Due to the impoverishment of low latitude surface waters in N and P, the productivity of the low latitude ocean is typically described as nutrient limited. However, limitation by light is also at work (Figure 2). As one descends from sunlit but nutrient-deplete surface waters, the nutrient concentrations of the water rise, but light drops off. The cross-over from sunlit and nutrient-poor to dark and nutrient-rich typically occurs at roughly 80 m depth and is demarcated by the “deep chlorophyll maximum” (DCM; Figure 2) (Cullen 1982), a depth zone of elevated chlorophyll concentration due to higher phytoplankton biomass and/or a higher chlorophyll-to-bulk carbon ratio in the biomass. Phytoplankton at the DCM are compromising between limitation by light and by nutrients. Phytoplankton growth at the DCM intercepts the nutrient supply from below, reducing its transport into the shallower euphotic zone. Thus, the DCM is not only a response to the depth structure of nutrients and light but indeed helps to set these conditions (Figure 2). Conversely, in highly productive regions of the ocean, high phytoplankton density near the surface limits the depth to which light penetrates, reducing productivity in deeper waters. Such self-limitation of primary productivity is a common dynamic in the ocean biosphere.

### Seasonality

Seasonality in productivity is greatest at high latitudes, driven by the availability of light (Figure 4a and b). The areal intensity and daily duration of sunlight are much greater in summer, an obvious direct benefit for photosynthesis. In addition, the wind-mixed layer (or “mixed layer”) of the upper ocean shoals such that it does not mix phytoplankton into darkness during their growth (Siegel et al. 2002). The mixed layer shoals in the spring partly because increased sunlight causes warming and freshening (the latter by the melting of ice), both of which increase the buoyancy of surface waters. Mixed layer shoaling is sometimes also encouraged by generally calmer spring and summer weather, which reduces wind-driven turbulence. During the “spring bloom,” NPP exceeds the loss of phytoplankton biomass to grazing and mortality, leading to transient net biomass accumulation and a peak in export production. The population of grazing organisms also rises in response to the increase of their feedstock, transferring the organic carbon from NPP to higher trophic levels. In regions such as the North Atlantic, the preceding deep winter mixed layers may be important in initiating the spring bloom by briefly releasing growing phytoplankton from grazing pressure (Boss & Behrenfeld 2009). However, the robust connection of the spring bloom with mixed layer shoaling across many environments argues strongly for the general importance of the mixed layer/light availability dynamic described above (Siegel et al. 2002).

In some temperate and subpolar regions, productivity reaches a maximum during the spring as the phy-

toplankton transition from light to nutrient limitation. In the highest latitude settings, while the “major nutrients” N and P remain at substantial concentrations, the trace metal iron can become limiting into the summer (Boyd et al. 2007, Martin & Fitzwater 1988). In at least some of these polar systems, it appears that light and iron can “co-limit” summertime photosynthesis (Maldonado et al. 1999, Mitchell et al. 1991).

## What Controls Ocean Productivity on Long Time Scales?

Reconstructions of ocean productivity using sediment records typically involve the accumulation of biogenic matter (organics or mineral hard parts) in the sediment; therefore, these studies speak to export production rather than NPP. However, if export production is reconstructed, it is at least a fair assumption that NPP would have changed in the same direction. Moreover, as described below, the export of organic matter out of the surface ocean can have broad biogeochemical and climate implications, so reconstructing export production is valuable in itself. One of the greatest challenges for reconstructing ocean productivity is the potential for changes in the fraction of export production that reaches the seabed and is preserved into the sediments, which could be misinterpreted as changes in productivity. The development and improvement of such reconstructions is an active area of research.

### Circulation

There is evidence from the geologic record that ocean productivity has changed in response to ocean circulation. As a prominent example, over the course of the last 35 million years, the Southern Ocean has developed into a cold, highly productive region (Kennett 1977). These changes suggest the development of circulation (upwelling and other processes) that today imports new nutrients into the euphotic zone. In contrast, during the last ice age, export production was reduced relative to interglacial levels in the Antarctic Zone of the Southern Ocean and in the similar environment of the subarctic North Pacific (Jaccard et al. 2005, Mortlock et al. 1991). While explanations have been proposed for these changes (Sigman et al. 2010), it is nevertheless counter-intuitive that productivity in the Southern Ocean should have increased over tens of millions of years as global climate cooled, only to decrease upon further cooling into the periodic ice ages of the last three million years. Deep water is upwelled into the Southern Ocean surface, from which this nutrient-bearing water is pumped by the winds into the mid-depth ocean interior that supplies nutrients to the low latitude surface ocean (Palter et al. 2010) (Figure 6). As a result, Southern Ocean circulation changes can affect ocean productivity on a global basis.

### Nutrients

Much of the ongoing discussion regarding the stability or variability of ocean productivity through Earth history focuses on the potential for changes in the

ocean's concentrations of different nutrients, with a higher mean ocean concentration of a common limiting nutrient possibly leading to higher productivity. Central to this question is the concept of "residence time." The residence time of a chemical in the ocean is the average time that the chemical spends in the ocean between entering it and being removed from it. When the input/output budget of the chemical is at steady state, the residence time is calculated as the reservoir size of that chemical (e.g., in moles) divided by the rate at which the chemical enters or leaves the ocean (e.g., in moles per year). The shorter the residence time of a chemical, the faster its reservoir size can change because of an imbalance between inputs and outputs.

Approaches are lacking to directly reconstruct the past reservoir sizes of different ocean nutrients. Nevertheless, a framework for considering the potential for such changes has been developed, and this is our focus below.

**Phosphorus:** The ocean's P budget is largely controlled by geological and geochemical processes. P enters the ocean by weathering, and it is removed through the sedimentary burial of organic P, P adsorbed onto iron oxides, phosphatic fossil material such as fish debris and shark teeth, and authigenic P minerals (Froelich et al. 1982). The residence time of P in the ocean has been estimated as 20–40 thousand years (Ruttenberg 1993), which indicates that the ocean P reservoir could change greatly over millions of years. Given the potential for changes in the P reservoir, it is a mystery why there aren't more clear signs of dramatic variation in global ocean productivity over Earth's history. This has driven a search for feedbacks within the Earth system that might work to stabilize the size of the ocean's P reservoir (Van Cappellen & Ingall 1996). Changes in the P reservoir have been hypothesized to cause ocean productivity changes that might explain glacial/interglacial CO<sub>2</sub> change (Broecker 1982), but this hypothesis has now been all but ruled out (Sigman & Boyle 2000). While a residence time of P in the ocean of order 20–40 thousand years is short in the context of geologic history, it makes it difficult to change the ocean P reservoir over the ~5 thousand years that characterize the rapid increases in atmospheric CO<sub>2</sub> upon the transitions from ice ages to warm interglacials.

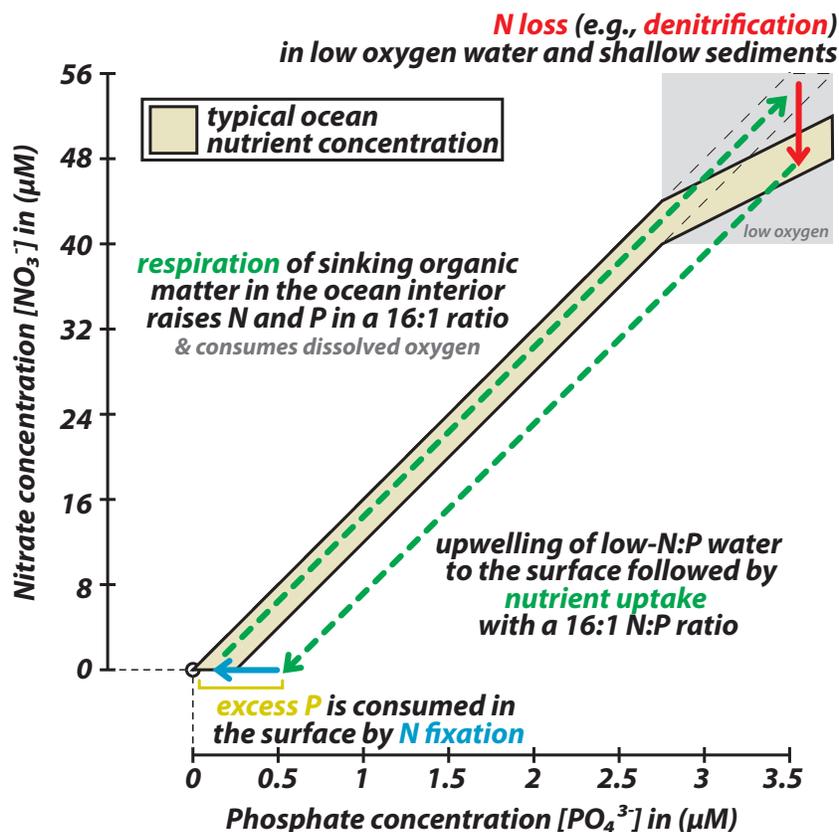
**Nitrogen:** The input/output budget of ocean N is largely biologically driven. Biologically available (or "fixed") N is brought into the ocean mostly by oceanic N "fixers," a set of cyanobacterial phytoplankton that cleave the strong triple bond between the N atoms of N<sub>2</sub> to produce ammonium (NH<sub>4</sub><sup>+</sup>) and then organic N. Once fixed, the N is incorporated into the global ocean N cycle, which is dominated by the large reservoir of nitrate (NO<sub>3</sub><sup>-</sup>) stored in deep water. The upwelling or mixing of this nitrate into the euphotic zone (which along with the slower processes of N fixation and atmospheric N deposition represents the "new" N supply to the euphotic zone) drives the export production across the global ocean (Figure 1). Fixed N is domi-

nantly lost from the ocean by "denitrification," the use of nitrate as an oxidant to decompose organic matter by bacteria that grow in low-oxygen environments. Just as the ocean's fixed N is derived from the huge atmospheric reservoir of N<sub>2</sub> by N fixation, denitrification converts the fixed N back to N<sub>2</sub>. A second widespread reaction removing fixed N in low-oxygen settings is known as "anammox" (for anaerobic ammonium oxidation), which combines ammonium with nitrite (NO<sub>2</sub><sup>-</sup>) to produce N<sub>2</sub> (Dalsgaard et al. 2005). The quantitative importance of this process is not yet clear.

Recent decades have seen a number of hypotheses regarding past ocean productivity centered around N reservoir changes. During recent ice ages, there is strong evidence that denitrification slowed (Altabet et al. 1995, Christensen 1994, Ganeshram et al. 1995). It has been proposed that this increased the size of the ocean N reservoir, leading to higher ocean productivity and explaining the observed drop in atmospheric CO<sub>2</sub> during ice ages. Since the residence time of N in the ocean is ~3 thousand years (Brandes & Devol 2002) — more than 5-fold shorter than that of P—N could have changed substantially across glacial-to-interglacial transitions and over longer time scales in Earth history. However, a potent argument involving P has been made against such changes in the ocean N budget, as described below.

Dissolved N (dominantly nitrate) is tightly correlated with dissolved P (phosphate, PO<sub>4</sub><sup>3-</sup>) in open ocean waters, with an N:P ratio of 16:1 (Figure 5). As this is also the N:P observed in plankton, Redfield (1958) explained the dissolved nitrate-to-phosphate correlation as the result of internal nutrient cycling in the ocean, with N and P consumed from water in a 16:1 ratio by phytoplankton growth and then put back into solution with the same ratio upon "remineralization" (decomposition by heterotrophs) of marine organic matter (Figure 5, green dashed lines). Biological assays tend to indicate that N limits oceanic phytoplankton more often than does phosphorus (Kilham & Hecky 1988), consistent with the observation that there is a positive x-intercept in Figure 5 (nitrate tends to be depleted "before" phosphate).

Assuming that the N:P ratio of most phytoplankton is conserved (i.e., cannot vary so as to compensate for changes in the N:P of the nutrient supply from deep water), then a negative feedback develops between the N:P of the ocean and the rate of N fixation. This feedback has been proposed to stabilize the ocean N budget as follows (Figure 5). Denitrification removes nitrate from the ocean interior. This leads waters upwelled into the surface to have a deficit in N relative to the N and P demands of phytoplankton growth (or, more precisely, the N and P supply required to balance the N and P exported in sinking organic matter). This leads to N depleted surface waters with "excess P," conditions under which N fixers are surmised to compete successfully. The N fixers then fix the N that compensates for the N deficit in upwelled waters and that



**Figure 5.** The surface-to-deep ocean cycle of the major nutrients N and P and the regulation of the ocean's budget of fixed (i.e. bio-available) N. The decomposition of sinking organic matter in the deep ocean remineralizes the nutrients N (nitrate; [NO<sub>3</sub><sup>-</sup>]) and P (phosphate; [PO<sub>4</sub><sup>3-</sup>]) in the stoichiometric ratio of 16:1 that characterizes plankton biomass (dashed diagonal-upward arrow that follows the observed ocean nutrient trend). This decomposition consumes dissolved oxygen (O<sub>2</sub>), which leads to oxygen depletion in sediment pore waters and in the water column of certain stagnant regions of the ocean. In these low-oxygen waters, microbes that decompose organic matter using nitrate instead of oxygen cause the removal of fixed N from the ocean, which depresses the N:P nutrient ratio below 16:1, thereby producing a "N deficit" or "excess P" (red downward arrow). When a water parcel that has experienced N loss in the ocean interior is brought to the surface, phytoplankton take up nutrients in a ~16:1 N:P ratio until productivity becomes limited due to the N deficit (dashed downward-diagonal arrow), leaving behind excess P. This is thought to encourage "N fixing" organisms that produce new bio-available N from the large inventory of otherwise unavailable dissolved N<sub>2</sub>, consuming the excess P in the process (blue horizontal arrow indicates the uptake of excess P by N fixation, not the conversion of N fixation itself). The addition of the newly fixed N to the water occurs when the N fixer biomass is decomposed, in the surface ocean or after export to depth.

balances the N loss due to denitrification. This feedback has been recognized in lake studies, in which the addition of excess P caused blooms of cyanobacteria, which fixed N and thus shifted the lake back toward its pre-amendment N:P ratio (Schindler 1977), and apparent spatial coupling between denitrification and N fixation support its applicability to the ocean (Deutsch et al. 2007). If the negative feedback is strong in the ocean and the N:P of sinking organic matter is conserved through time, then the ocean N:P cannot stray far from the modern 16:1 ratio, and the P reservoir determines the nutrient reservoir sizes and their effect on ocean productivity (Tyrrell 1999).

In this context, at the end of the last ice age, the increase in denitrification would have lowered the ocean's N reservoir and reduced the ocean's N:P ratio. This appears to have led to an increase in the rate of N fixation (Ren et al. 2009), which worked to stabilize the N reservoir and bring the ocean N budget to a new

(interglacial) steady state (Deutsch et al. 2004). This feedback has also been inferred for other events in Earth history, such as the "ocean anoxic events" of the Cretaceous Period, when an acceleration in the denitrification rate apparently led to a compensatory increase in N fixation rate (Rau et al. 1987).

The coupling between N and P in the ocean might be weakened by variation in the N:P stoichiometry of phytoplankton. In recent years, researchers have begun to investigate apparent particulate and dissolved N:P deviations from the modern oceanic mean of 16:1 (Arrigo et al. 1999, Weber & Deutsch 2010). Of particular importance is the question of whether the N:P of organic matter exported out of the surface ocean could vary on a global basis over time. In addition, N fixation requires two metals — iron and molybdenum — that could potentially limit the rate of this process and thus interfere with the N fixation feedback. It has been argued that the scarcity of iron in the modern ocean (see

below) contributes to the widespread tendency toward N deficit in the global ocean by suppressing N fixation rates (Falkowski 1997). More dramatically, it has been hypothesized that the long spell of slow evolution in life from 2.0 to 0.6 billion years ago was due to molybdenum limitation of N fixers, which slowed ocean productivity, organic carbon burial, and the build-up of oxygen in the atmosphere (Anbar & Knoll 2002).

**Iron:** Iron is required for many phytoplankton functions, perhaps most importantly in the electron transport chain of photosynthesis. However, iron was not suspected as a limiting nutrient until the advent of trace metal clean techniques allowed for uncontaminated iron addition experiments and demonstrated that iron has nutrient-like structure in the ocean, with extreme depletion in the surface waters of many regions, especially in polar surface waters with high concentrations of the “major nutrients,” N and P (Martin et al. 1989) (Figure 4c and d). In regions with high surface concentrations of the major nutrients, iron addition experiments on diverse scales have consistently yielded large enhancements of NPP, increases in biomass, and changes in phytoplankton assemblage; in several cases, an increase in export production has also been observed (Boyd et al. 2007).

Iron enters the ocean mostly through dust deposition on the ocean surface, although ocean margins and hydrothermal vents are also substantial sources (Figure 6). The nutrient-like depth structure of iron indicates that it is consumed in surface water by phytoplankton and then put back into solution when sinking organic matter is remineralized at depth (Martin et al. 1989). Iron is also known to have an active internal cycle in the euphotic zone, involving both biological processes and reactions with light (Barbeau et al. 2001, Morel et al. 1991). However — unlike CO<sub>2</sub>, N, P, or Si — iron in the ocean water column precipitates and is scavenged by settling particles that transport it to the seabed, thus removing it from the ocean (Boyd & Ellwood 2010) (Figure 6). As a result, in comparison to the major nutrients, iron is cycled fewer times within the ocean between the times of its input and its removal (Johnson et al. 1997). This difference derives fundamentally from the high O<sub>2</sub> of the modern atmosphere and ocean, which ensures that iron is largely present in the low solubility oxidation state of +III. The oxidized nature of the global environment is itself a consequence of past photosynthesis followed by organic carbon burial. Thus, the scarcity of iron in the modern ocean is an example of the ability of Earth's biosphere to affect its own fertility.

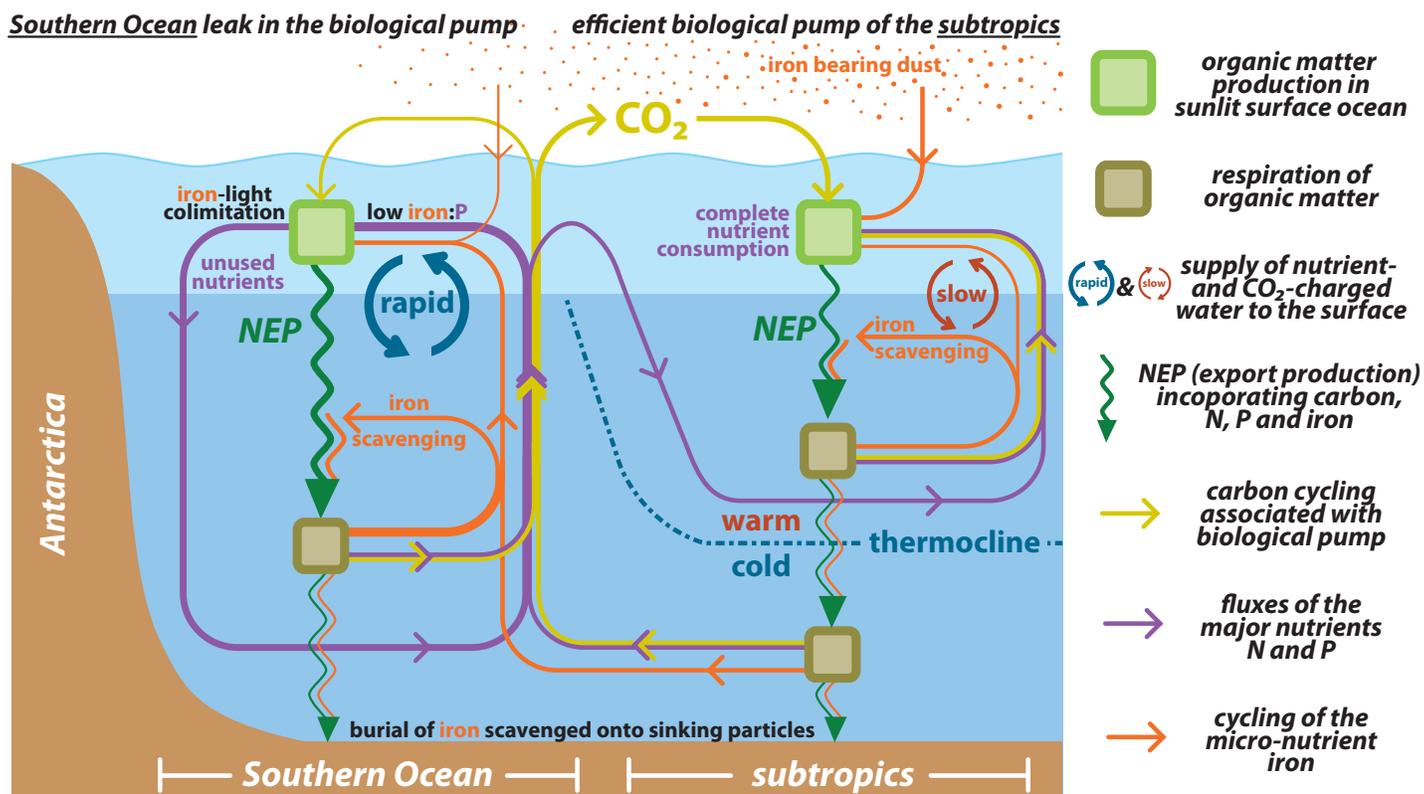
The lower cycling-to-throughput ratio for iron in the ocean helps to explain its tendency to limit productivity in polar waters and in upwellings. Because iron is constantly being scavenged out of ocean water, deep water has a lower iron-to-major nutrient ratio than phytoplankton require. When deep water is brought to the surface, phytoplankton thus run out of iron first, leaving a large fraction of the major nutrients unused

(Figure 6, left side). The iron supply from dust and other shallow sources can augment the iron supply in these settings, mitigating but not erasing the inherent iron deficit. In contrast, in the permanently stratified tropical and subtropical ocean where the input of deep water to the surface is very slow, the dust flux from above typically compensates for any iron deficit in the nutrients supplied from below, such that the total iron supply is adequate for the phytoplankton to completely consume the slow supply of major nutrient from below (Figure 6, right side). Thus, these low latitude regions are largely limited by the major nutrients rather than iron.

Because the deep ocean is ventilated largely by the polar ocean regions, the incomplete consumption of nutrients in these regions introduces substantial inefficiency to the global ocean's biological pump (Sarmiento & Toggweiler 1984) (Figure 6, left side). Fertilization with iron represents a potential mechanism for reducing this inefficiency and thus lowering atmospheric CO<sub>2</sub>. Indeed, John Martin hypothesized that the lower CO<sub>2</sub> concentrations observed during ice ages were driven by increased dust flux to the Southern Ocean, which fertilized the region with iron (Martin 1990). This process alone cannot explain all of the data from the ice age Southern Ocean; for example, the apparent ice age decrease in productivity in Antarctic waters requires an alternative or additional change, such as reduced upwelling (Francois et al. 1997, Sigman & Boyle 2000). Nevertheless, iron fertilization does appear to have been important in the ice age Southern Ocean, most clearly the Subantarctic Zone under the westerly wind belt (Kohfeld et al. 2005), and it probably played a part in lowering atmospheric CO<sub>2</sub> during ice ages (Watson et al. 2000, Martinez-Garcia et al. 2011).

**Silicon:** Silicon — as Si(OH)<sub>4</sub> — is required by a number of phytoplankton and zooplankton groups for the construction of opal hard parts, all of which are well represented in the sedimentary record. Most important among these are the diatoms, a phytoplankton group that is pervasive throughout the global ocean and often dominant in temperate to polar waters. The ocean's input/output budget of dissolved Si is likely important for variations in the characteristics and spatial variation of ocean productivity over Earth history. However, the longer-term dynamics of the ocean's Si reservoir and its impacts is too uncertain to safely summarize here. Instead, we focus on the dynamics of this nutrient in the modern ocean, which gives some insight into its possible changes through time.

Si is available in the same regions where N and P supply is rapid (e.g., in coastal upwellings and around Antarctica). However, Si is typically depleted “before” N and P; for example, in the Subantarctic Zone of the Southern Ocean, N and P are at relatively high concentrations in the euphotic zone, but Si concentrations frequently fall below the detection limit of standard analysis methods. While Si is consumed in the construction of diatom shells (“frustules”), the sinking and



**Figure 6.** Illustration of the coupled biogeochemical cycles of the “major” nutrients N and P, the trace nutrient iron and CO<sub>2</sub> sequestered by the biological pump. Mixing and overturning between the ocean interior and the surface waters supply N and P in close to the 16:1 stoichiometric ratio required for production of organic matter (see Fig. 6). Iron, however, is continuously scavenged from ocean water onto sinking particles such that the iron-to-major nutrient ratio of the water that comes to the ocean surface is less than that required by phytoplankton to fully consume the major nutrients. In the low latitude surface ocean, the input of iron dust from above is sufficient to compensate for the “iron deficit” of deep water that comes to the surface; therefore, major nutrient consumption can proceed to completion. In the polar ocean, where mixing and overturning are vigorous, atmospheric iron supply is overwhelmed by the deep ocean iron deficit, iron is consumed to completion, productivity becomes iron–light co-limited, and the major nutrients go unused at the surface (see Fig. 4). Since a fraction of the nutrients in deep water had been emplaced along with CO<sub>2</sub> by the decomposition of sinking organic matter, the incompleteness of nutrient consumption in polar waters allows this once-sequestered CO<sub>2</sub> to escape back to the atmosphere. Given the inefficiency of the biological pump in the Southern Ocean, the amount of biological CO<sub>2</sub> sequestration in the ocean interior depends in part on how much of the ocean water last circulated through this region. Currently, much of the ocean is filled with water that derives from the Southern Ocean surface, and thus the global biological pump is operating only at ~50% efficiency.

subsequent dissolution of frustules returns the Si to deep waters, analogous to the uptake/sinking/remineralization cycle of the nutrients held within organic matter. However, in comparison to N and P, it appears that biogenic opal on average sinks to greater depth. A substantial fraction (~25% on average) reaches the abyssal seabed before it is dissolved (Treguer et al. 1995), and a significant fraction of this is buried. Indeed, below the Southern Ocean, sediments can be nearly completely composed of biogenic opal. The “deeper remineralization” of biogenic opal probably contributes to the generally greater scarcity of Si relative to N and P in surface and shallow subsurface waters. Regional variation in the Si-to-N and Si-to-P ratio of diatom biomass also appears important in maintaining this Si scarcity (Sarmiento et al. 2004).

While Si availability is much lower in the tropical and subtropical ocean than in polar and temperate waters, diatoms are still present in these regions, where they are common in traditional microscopic examinations.

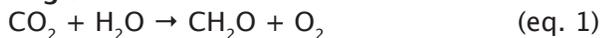
It appears that the pervasive occurrence of diatoms even in the low latitudes is at least partly due to lower Si requirements (thinner frustules) in low latitude species and the vigorous recycling of Si within warm low latitude surface waters, where biogenic opal is more soluble. Despite such upper ocean Si recycling, diatoms are thought to contribute more to the sinking flux of organic matter (i.e., NEP) than they do to NPP (Buesseler 1998). At the simplest level, this may be due to their large size and opal frustules, which protect them from small zooplankton and help them to sink. In correspondence with their role in export production, diatoms appear to specialize on new nutrients imported from below, rather than nutrients recycled in the surface ocean.

## How Does Ocean Productivity Affect Atmospheric Carbon Dioxide?

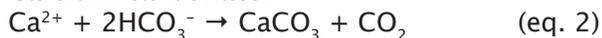
On the time scale of thousands of years, the chem-

istry of the ocean essentially sets the concentration of  $\text{CO}_2$  in the atmosphere (Broecker 1982). Ocean productivity affects atmospheric  $\text{CO}_2$  by the export of both organic carbon and calcium carbonate ( $\text{CaCO}_3$ ) from the surface ocean to depth; the former lowers atmospheric  $\text{CO}_2$ , while the latter raises it more modestly (Archer 2003, Sarmiento & Gruber 2006). These opposing effects on  $\text{CO}_2$  are evident at a simplistic level from the reactions associated with (1) the formation of organic carbon (as  $\text{CH}_2\text{O}$ , sugar) that consumes dissolved  $\text{CO}_2$  and (2) the precipitation of  $\text{CaCO}_3$  that releases it:

**Organic carbon:**



**Calcium carbonate:**



The downward transport of organic carbon extracts dissolved inorganic carbon from the surface ocean and atmosphere, sequestering it in the deep sea. This “biological pump” for carbon is coupled to the removal of nutrients (e.g., N and P) from surface waters and their accumulation in the deep ocean, as described above. However, in the case of dissolved inorganic carbon — the sum of three inorganic carbon species: dissolved  $\text{CO}_2$ , bicarbonate ( $\text{HCO}_3^-$ ), and carbonate ( $\text{CO}_3^{2-}$ ) — only ~10% of it is consumed from surface waters, while N and P consumption is often effectively complete. The term “biological pump” is sometimes replaced with the term “soft tissue pump” to explicitly specify the impact of organic carbon rain out of the surface ocean and its subsequent degradation in deep waters, to be distinguished from the “carbonate pump,” in which  $\text{CaCO}_3$  is precipitated in surface waters and exported to depth.

The soft-tissue pump of carbon from the surface to the interior lowers atmospheric  $\text{CO}_2$  directly by simply shuttling carbon out of surface waters, which causes  $\text{CO}_2$  from the atmosphere to invade the surface ocean. In addition, the soft tissue pump, by pumping the weak acid  $\text{CO}_2$  into deep water, works to lower the pH of the deep ocean. This forces the whole ocean to become more alkaline to bury the requisite amount of  $\text{CaCO}_3$  to balance river inputs from rock weathering on land (see below). Since alkaline solutions can hold more dissolved inorganic carbon by deprotonating carbonic acid ( $\text{H}_2\text{CO}_3$ , or  $\text{CO}_2 + \text{H}_2\text{O}$ ) to bicarbonate and carbonate, this causes a further decline in atmospheric  $\text{CO}_2$ .

The overall strength the soft tissue pump is determined by (1) the major nutrient content of the ocean, (2) the degree to which the major nutrients are consumed in surface waters, and (3) the carbon-to-major nutrient ratio of sinking organic matter. Calculations suggest that, in the context of the modern carbon cycle, if the soft tissue pump were to stop, atmospheric  $\text{CO}_2$  concentration would more than double over the course of roughly a thousand years (the time scale over which deep waters pass through the surface ocean). Conversely, a fully efficient soft tissue pump (one in which all N and P supplied to surface waters is con-

sumed and converted into exported organic matter) would lower  $\text{CO}_2$  by more than half of its current concentration. Given this potential for further  $\text{CO}_2$  draw-down, an increase in the efficiency of the soft-tissue pump (from about ~50% efficiency today to ~75% efficiency) may explain the reduction in atmospheric  $\text{CO}_2$  concentrations that is observed to have occurred during past ice ages. The above estimates are simplifications in that a change in ocean productivity would likely also affect  $\text{CaCO}_3$  cycling. For example, without ocean productivity,  $\text{CaCO}_3$  would not be produced by organisms in the surface ocean, and this  $\text{CaCO}_3$  production raises  $\text{CO}_2$  (see below).

Marine plankton such as coccolithophores (phytoplankton) and foraminifera (zooplankton) produce  $\text{CaCO}_3$  hard parts. Dissolved  $\text{CaCO}_3$  is a base; therefore, its precipitation from solution removes alkalinity and lowers the pH of seawater. The lower pH, in turn, converts more of seawater’s dissolved inorganic carbon into the (acidic)  $\text{CO}_2$  form. Thus, when  $\text{CaCO}_3$  is precipitated in surface waters and exported from them, it raises the  $\text{CO}_2$  concentration of the surface ocean (eq. 2) and drives a  $\text{CO}_2$  flux into the atmosphere.

Carbonates are much denser than seawater and sink rapidly into the deep ocean, where, under the pressure of the water column and the lower pH caused by the breakdown of organic C from the soft-tissue pump, they become chemically unstable and some of the  $\text{CaCO}_3$  dissolves. The  $\text{CaCO}_3$  that is preserved and buried on the seafloor represents the single biggest continuous loss of alkalinity from ocean water, balancing the input of alkalinity from the weathering of carbonate and silicate rocks on land. If it were not for biological precipitation of  $\text{CaCO}_3$ , the ocean would need to have a higher pH in order to spontaneously precipitate  $\text{CaCO}_3$  and balance the input of alkalinity from weathering; the higher pH would lower atmospheric  $\text{CO}_2$ . Thus, both with regard to the internal cycling of  $\text{CaCO}_3$  in the ocean and the whole ocean’s input/output budget of alkalinity, biological  $\text{CaCO}_3$  production works to raise atmospheric  $\text{CO}_2$ . However, the soft-tissue pump can manipulate the  $\text{CaCO}_3$  cycle: strengthening the soft-tissue pump lowers the pH of the deep ocean and reduces deep sea  $\text{CaCO}_3$  burial, forcing the whole ocean to gain alkalinity, which works to lower atmospheric  $\text{CO}_2$ . Finally, there is no fundamental need for ocean productivity to produce  $\text{CaCO}_3$ , so the relative proportions of  $\text{CaCO}_3$  and organic carbon rain generated by ocean productivity may vary greatly, with potential consequences for  $\text{CO}_2$ . A full exposition of this complex system is provided by Archer (2003) and Sarmiento & Gruber (2006).

To address a common misconception, the capacity of ocean productivity to lower atmospheric  $\text{CO}_2$  is not typically made stronger by simply increasing ocean upwelling rates. Increased upwelling increases the nutrient supply for productivity, but also exposes to the atmosphere the  $\text{CO}_2$  previously sequestered by the soft tissue pump. In the low latitude ocean, these effects

roughly offset one another. Productivity is highest in the polar regions (Figure 4), and yet the incompleteness of nutrient consumption in these regions causes them to release biologically sequestered CO<sub>2</sub> back to the atmosphere (Figure 6). For a given concentration of the ocean's major nutrients, it is the completeness of nutrient consumption rather than the rate of organic matter export that matters for CO<sub>2</sub> sequestration. This is true up to the time scale of 100 thousand years or more, at which point the rate of organic matter export does become important because the slow burial of organic carbon is a significant mechanism of carbon removal.

### Are Humans Changing Ocean Productivity?

Human activities can directly add significant quantities of major and trace nutrients to some regions of the coastal ocean, unambiguously impacting local productivity. While this enhanced productivity could theoretically benefit the upper trophic levels—including fisheries—a host of effects lead to habitat disturbance. As an example, in the waters surrounding the Mississippi Delta and the Chesapeake Bay, the decomposition of the sedimented organic matter produced by nutrient-enhanced phytoplankton blooms lowers the oxygen content of subsurface waters, driving away fish and other complex organisms that require oxygenated water. Anthropogenically enhanced nutrient inputs to the open ocean occur mostly through the atmosphere. In some regions (e.g., the North Atlantic), atmospheric N and Fe deposition on the open ocean has already been measurably enhanced by human activities (Duce et al. 2008), but this enhancement is not yet sufficient to have a clear impact beyond coastal regions and inland seas.

The human impacts on open ocean productivity are likely to be complex. Global warming associated with the anthropogenic increase in greenhouse gases appears to be strengthening upper ocean stratification, reducing the nutrient supply from below and thus decreasing global ocean productivity (Behrenfeld et al. 2006). At the same time, elevated CO<sub>2</sub> concentrations may have a fertilizing effect on some phytoplankton (CO<sub>2</sub> scarcity can restrict the rate of phytoplankton photosynthesis), while negatively impacting some organisms that produce CaCO<sub>3</sub> hard parts (seawater CO<sub>3</sub><sup>2-</sup> concentration largely sets the saturation state of CaCO<sub>3</sub> and decreases under higher CO<sub>2</sub>) (Morel et al. 2010). Such changes may alter fisheries substantially, but they are currently much less important than the effects of overfishing.

Purposeful fertilization of N- and P-rich polar surface waters with iron has been proposed as a mechanism for mitigating the anthropogenic rise in atmospheric CO<sub>2</sub> by increasing the biological storage of CO<sub>2</sub> in the deep ocean (Sarmiento et al. 2006). However, fertilizing the modern polar ocean for this purpose appears to yield only modest carbon storage and is likely to have substantial negative impacts, the expenditure

of the effort aside. First, even if iron fertilization were to lead to complete consumption of nutrients, it takes too long for the deep waters to cycle through the polar ocean surface to substantially alter the currently rapid rise in atmospheric CO<sub>2</sub> (Peng & Broecker 1991). Second, humans appear incapable of intentionally fertilizing a significant fraction of the Southern Ocean on a continuous basis; with only sporadic fertilization, a substantial portion of the additional CO<sub>2</sub> sequestered in the deep ocean would upwell back to the surface to be released. Third, any modest increase in carbon storage that such fertilization does cause will come at the expense of lower oxygen concentrations in the ocean interior, one climate consequence of which may be enhanced release of the greenhouse gas nitrous oxide to the atmosphere (Jin & Gruber 2003).

### Glossary

**Alkalinity:** Alkalinity is closely related to pH, both describing the acid-base chemistry of water. While there are more complete definitions, alkalinity is the excess of strong base over strong acid in a solution.

**Autotroph:** As opposed to “heterotroph” and “chemoautotroph”, an organism that has the ability to harvest sunlight as a source of chemical energy.

**Benthos:** The collective group of organisms that share the sea floor as their habitat. This includes organisms that burrow into the sediments, organisms that permanently attach themselves to the seabed substrate, and organisms that simply rest on the seafloor. These benthic lifestyles are distinct from swimming “nekton” and free floating “plankton”.

**Biological pump:** The photosynthetic production, sinking, and deep ocean decomposition of organic matter that cause a vertical gradient of dissolved inorganic carbon in the ocean, in net causing the storage of CO<sub>2</sub> in deep waters and thus lowering atmospheric CO<sub>2</sub>. In some cases, the biological pump is taken to involve two components: (1) the rain of soft-tissue organic carbon from the surface to depth, the “soft-tissue pump”, and (2) the rain of mineral calcium-carbonate from the surface to depth, the “carbonate pump”. The former lowers atmospheric CO<sub>2</sub>, while the latter raises it.

**Euphotic zone:** The upper part of the ocean water column that receives at least 1% of the incident sunlight. The vast majority of photosynthesis in the ocean occurs within this zone.

**Export production:** The export of organic carbon from a given ecosystem (e.g., the surface mixed layer, the euphotic zone) over a specified time interval.

**Fecal pellet:** The particulate excretion of zooplankton. Fecal pellets contain substantial amounts of organic carbon and organically-bound nutrients. The sinking of fecal pellets from the surface ocean to depth is one of the main contributors to export production.

**Heterotroph:** An organism that lives by heterotrophy,

in which the organic carbon produced by other organisms is collected and oxidized (or “respired”) using a chemical oxidant available in the environment, most commonly oxygen ( $O_2$ ).

**GPP:** Gross primary production, the total rate of organic carbon production by autotrophs.

**Inorganic carbon:** Carbon with the oxidation state +IV, including carbon dioxide ( $CO_2$ ), carbonic acid ( $H_2CO_3$ ), bicarbonate ion ( $HCO_3^-$ ), carbonate ion ( $CO_3^{2-}$ ), and carbonate minerals (e.g., calcium carbonate,  $CaCO_3$ ). Dissolved inorganic carbon (DIC) is the sum of  $CO_2$ ,  $H_2CO_3$ ,  $HCO_3^-$  and  $CO_3^{2-}$  that are dissolved in water, thereby excluding gas and mineral solids. The ratio among the species of DIC is controlled by pH, with higher pH (lower activity of protons) converting a greater fraction of the  $CO_2$  to  $HCO_3^-$  and  $CO_3^{2-}$ .

**Microzooplankton:** Zooplankton that are small (~1–100  $\mu m$ ) and thus can only forage the smallest phytoplankton (of their size or smaller). The body of these small grazers is relatively simple, commonly lacking a complex digestive tract, such that they do not excrete solid fecal pellet but instead release metabolic byproducts back into the water column. For this reason, grazing by microzooplankton promotes nutrient recycling in the surface ocean, thereby raising primary productivity relative to new nutrient supply and export productivity (see “NEP:NPP ratio”).

**Mixed layer:** Or wind-mixed layer, the uppermost skin of the ocean where wind-driven turbulence homogenizes chemical properties of surface water down to the mixed layer depth (MLD). The MLD varies both geographically and seasonally, ranging from a few meters to hundreds of meters.

**Nekton:** Organisms that swim or are otherwise self-propelled and not largely reliant on ocean viscosity, turbulence, and circulation; for example, fish, whales, and squid. To be distinguished from more or less passively drifting “plankton” and bottom-dwelling “benthos.”

**NEP:** Net ecosystem production, the amount of photosynthesis minus the amount of respiration within a given ecosystem (e.g., the surface mixed layer, the euphotic zone) over a specified time interval. Depending on the ecosystem and the time interval chosen, NEP may closely track the export of organic carbon from the ecosystem (i.e., export production).

**NEP:NPP ratio:** The ratio between the net ecosystem production and the net production of biomass by phytoplankton (NPP) is a useful measure for nutrient recycling. It has also been named the “f-ratio” (for flux ratio) and represents the fraction of NPP that is supported by new nutrient supply, as opposed to regenerated productivity that is supported by the recycling of nutrients from organic matter within the surface ocean. This ratio is small in the low-nutrient and unproductive subtropical ocean (due to a high degree of recycling) and much greater on the highly productive polar ocean (which has proportionally less recycling).

**NPP:** Net primary production, which is gross primary production (GPP) minus the autotrophs’ own rate of respiration; it is thus the rate at which the full metabolism of phytoplankton produces organic matter.

**Organic carbon:** Carbon that exists in the environment with the oxidation state -IV to +III. Organic carbon is thermodynamically unstable in the presence of the  $O_2$  in the atmosphere and dissolved  $O_2$  in ocean waters (as well as other oxidants, including nitrate and sulfate), such that its biologically mediated oxidation releases energy for life. Organic carbon may exist in particulate or dissolved form.

**Photosynthesis:** The chemical process that uses sunlight as an energy source for the conversion of (oxidized) carbon dioxide to (reduced) organic carbon.

**Phytoplankton:** Planktonic organisms that are autotrophic and thus generate chemical energy from sunlight through photosynthesis.

**Phytoplankton bloom:** When environmental conditions improve, autotrophic phytoplankton may grow and divide rapidly, resulting in an increase in biomass and cell numbers and fuelling higher trophic levels. Thus, increasing light (e.g., winter to summer, shoaling of mixed layer depth), nutrient input and low grazing stress encourage the development of blooms. Overall, if net primary production by a given autotroph exceeds the sum of their mortality and grazing losses this organism is said to bloom. The increase of biomass during a bloom provides the feedstock for secondary production by heterotrophic organisms, which ultimately leads to increased grazing stress on the blooming organism. Over the annual cycle a given ocean region typically experiences a complex succession of blooms by specific autotrophic organisms, closely associated with rises in the population of their respective grazers.

**Plankton:** Organisms that are suspended in and largely drift in ocean water; can be subdivided into (1) (autotrophic) phytoplankton and (2) (heterotrophic) zooplankton and bacteria.

**Remineralization:** The transformation of organic matter to inorganic constituents (e.g., dissolved inorganic carbon, nitrate, and phosphate). Synonymous with “decomposition,” but focusing on the consequence of this process of returning nutrients and other chemical to their dissolved, inorganic form. See also “respiration.”

**Respiration:** The oxidation of organic matter (largely organic carbon being oxidized to carbon dioxide) for the purpose of yielding chemical energy for basic life functions. Often results in the conversion of particulate organic matter back to dissolved inorganic chemicals. Secondary production (SP): The growth rate of heterotrophic biomass.

**Zooplankton:** Planktonic organisms that graze upon organic matter, fulfilling their energy requirements by the respiration of organic carbon.

## References and Recommended Reading

- Altabet, M. A. et al. Climate-related variations in denitrification in the Arabian Sea from sediment  $^{15}\text{N}/^{14}\text{N}$  ratios. *Nature* 373, 506–509 (1995). doi:10.1038/373506a0
- Anbar, A. D. & Knoll, A. H. Proterozoic ocean chemistry and evolution: A bioinorganic bridge? *Science* 297, 1137–1142 (2002). doi:10.1126/science.1069651
- Archer, D. “Biological fluxes in the ocean and atmospheric  $\text{pCO}_2$ ,” in *Treatise on Geochemistry*, Vol. 6, eds. H. D. Holland & K. K. Turekian (Elsevier, 2003) 275–291.
- Arrigo, K. R. et al. Phytoplankton community structure and the drawdown of nutrients and  $\text{CO}_2$  in the Southern Ocean. *Science* 283, 365–367 (1999). doi:10.1126/science.283.5400.365
- Barbeau, K. et al. Photochemical cycling of iron in the surface ocean mediated by microbial iron(III)-binding ligands. *Nature* 413, 409–413 (2001). doi:10.1038/35096545
- Behrenfeld, M. J. et al. Climate-driven trends in contemporary ocean productivity. *Nature* 444, 752–755 (2006). doi:10.1038/nature05317
- Bender, M. et al. A comparison of 4 methods for determining planktonic community production. *Limnology and Oceanography* 32, 1085–1098 (1987).
- Boyd, P. W. & Ellwood, M. J. The biogeochemical cycle of iron in the ocean. *Nature Geoscience* 3, 675–682 (2010). doi:10.1038/ngeo964
- Boyd, P. W. et al. Mesoscale iron enrichment experiments 1993–2005: Synthesis and future directions. *Science* 315, 612–617 (2007). doi:10.1126/science.1131669
- Brandes, J. A. & Devol, A. H. A global marine-fixed nitrogen isotopic budget: Implications for Holocene nitrogen cycling. *Global Biogeochemical Cycles* 16, 1120 (2002). doi:10.1029/2001gb001856
- Broecker, W. S. Ocean chemistry during glacial time. *Geochimica et Cosmochimica Acta* 46, 1689–1705 (1982). doi:10.1016/0016-7037(82)90110-7
- Buesseler, K. O. The decoupling of production and particulate export in the surface ocean. *Global Biogeochemical Cycles* 12, 297–310 (1998). doi:10.1029/97gb03366
- Chisholm, S. W. et al. A novel free-living prochlorophyte abundant in the oceanic euphotic zone. *Nature* 334, 340–343 (1988). doi:10.1038/334340a0
- Christensen, J. P. Carbon export from continental shelves, denitrification and atmospheric carbon dioxide. *Continental Shelf Research* 14, 547–576 (1994). doi:10.1016/0278-4343(94)90103-1
- Morel, F. M. M. et al. *Ocean Acidification: A National Strategy to Meet the Challenges of a Changing Ocean*. The National Academic Press, 2010.
- Cullen, J. J. The deep chlorophyll maximum: Comparing vertical profiles of chlorophyll a. *Canadian Journal of Fisheries and Aquatic Sciences* 39, 791–803 (1982). doi:10.1139/f82-108
- Dalsgaard, T., Thamdrup, B. & Canfield, D. E. Anaerobic ammonium oxidation (anammox) in the marine environment. *Research in Microbiology* 156, 457–464 (2005). doi:10.1016/j.resmic.2005.01.011
- de Baar, H. J. W. von Liebig’s Law of the Minimum and plankton ecology (1899–1991). *Progress in Oceanography* 33, 347–386 (1994). doi:10.1016/0079-6611(94)90022-1
- Deutsch, C. et al. Isotopic constraints on glacial/interglacial changes in the oceanic nitrogen budget. *Global Biogeochemical Cycles* 18, GB4012 (2004). doi:10.1029/2003gb002189
- Deutsch, C. et al. Spatial coupling of nitrogen inputs and losses in the ocean. *Nature* 445, 163–167 (2007). doi:10.1038/nature05392
- Duce, R. A. et al. Impacts of atmospheric anthropogenic nitrogen on the open ocean. *Science* 320, 893–897 (2008). doi:10.1126/science.1150369
- Dugdale, R. C. & Goering, J. J. Uptake of new and regenerated forms of nitrogen in primary productivity. *Limnology and Oceanography* 12, 196–206 (1967).
- Emerson, S. & Hedges, J. “Sediment diagenesis and benthic flux,” in *Treatise on Geochemistry*, Vol. 6, eds. H. D. Holland & K. K. Turekian (Elsevier, 2003) 293–319.
- Eppley, R. W. & Peterson, B. J. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* 282, 677–680 (1979). doi:10.1038/282677a0
- Falkowski, P. G. Evolution of the nitrogen cycle and its influence on the biological sequestration of  $\text{CO}_2$  in the ocean. *Nature* 387, 272–275 (1997). doi:10.1038/387272a0
- Francois, R. et al. Contribution of Southern Ocean surface-water stratification to low atmospheric  $\text{CO}_2$  concentrations during the last glacial period. *Nature* 389, 929–935 (1997).
- Froelich, P. N. et al. The marine phosphorus cycle. *American Journal of Science* 282, 474–511 (1982).
- Ganeshram, R. S. et al. Large changes in oceanic nutrient inventories from glacial to interglacial periods. *Nature* 376, 755–758 (1995). doi:10.1038/376755a0
- Geider, R. J., MacIntyre, H. L. & Kana, T. M. Dynamic model of phytoplankton growth and acclimation: Responses of the balanced growth rate and the chlorophyll a:carbon ratio to light, nutrient-limitation and temperature. *Marine Ecology-Progress Series* 148, 187–200 (1997). doi:10.3354/meps148187
- Hansell, D. A. et al. Dissolved organic matter in the ocean: A controversy stimulates new insights. *Oceanography* 22, 202–211 (2009).
- Jaccard, S. L. et al. Glacial/interglacial changes in subarctic North Pacific stratification. *Science* 308, 1003–1006 (2005). doi:10.1126/science.1108696
- Jin, X. & Gruber, N. Offsetting the radiative benefit of ocean iron fertilization by enhancing  $\text{N}_2\text{O}$  emissions. *Geophysical Research Letters* 30, 2249 (2003). doi:10.1029/2003gl018458
- Johnson, K. S., Gordon, R. M. & Coale, K. H. What controls dissolved iron concentrations in the world ocean? *Marine Chemistry* 57, 137–161 (1997). doi:10.1016/s0304-4203(97)00043-1
- Kennett, J. P. Cenozoic evolution of Antarctic glaciation, the circum-Antarctic Ocean, and their impact on global paleoceanography. *Journal of Geophysical Research-Oceans and Atmospheres* 82, 3843–3860 (1977). doi:10.1029/JC082i027p03843
- Kilham, P. & Hecky, R. E. Comparative ecology of marine and fresh-water phytoplankton. *Limnology and Oceanography* 33, 776–795 (1988).
- Kohfeld, K. E. et al. Role of marine biology in glacial-interglacial  $\text{CO}_2$  cycles. *Science* 308, 74–78 (2005). doi:10.1126/science.1105375
- Landry, M. R. & Hassett, R. P. Estimating the grazing impact of marine micro-zooplankton. *Marine Biology* 67, 283–288 (1982). doi:10.1007/bf00397668
- Maldonado, M. T. et al. Co-limitation of phytoplankton growth by light and Fe during winter in the NE subarctic Pacific Ocean. *Deep-Sea Research Part II-Topical Studies in Oceanography* 46, 2475–2485 (1999). doi:10.1016/s0967-0645(99)00072-7
- Martin, J. H. & Fitzwater, S. E. Iron-deficiency limits phytoplankton growth in the Northeast Pacific Subarctic. *Nature* 331, 341–343 (1988). doi:10.1038/331341a0
- Martin, J. H. et al. VERTEX: Phytoplankton/iron studies in the Gulf of Alaska. *Deep-Sea Research Part A: Oceanographic Research Papers* 36, 649–680 (1989). doi:10.1016/0198-0149(89)90144-1
- Martin, J. H. et al. VERTEX: Carbon cycling in the northeast Pacific. *Deep-Sea Research Part A: Oceanographic Research Papers* 34, 267–285 (1987). doi:10.1016/0198-0149(87)90086-0
- Martin, J. H. Glacial-interglacial  $\text{CO}_2$  change: The iron hy-

- pothesis. *Paleoceanography* 5, 1–13 (1990). doi:10.1029/PA005i001p00001
- Martinez-Garcia, A. et al. Southern Ocean dust–climate coupling over the past four million years. *Nature* 476, 312–315 (2011). doi:10.1038/nature10310
- Michaels, A. F. & Silver, M. W. Primary production, sinking fluxes and the microbial food web. *Deep-Sea Research Part A: Oceanographic Research Papers* 35, 473–490 (1988). doi:10.1016/0198-0149(88)90126-4
- Mitchell, B. G. et al. Light limitation of phytoplankton biomass and macronutrient utilization in the Southern Ocean. *Limnology and Oceanography* 36, 1662–1677 (1991).
- Morel, F. M. M. The co-evolution of phytoplankton and trace element cycles in the oceans. *Geobiology* 6, 318–324 (2008).
- Morel, F. M. M., Milligan, A. J. & Saito, M. A. “Marine bioinorganic chemistry: The role of trace metals in the oceanic cycles of major nutrients,” in *Treatise on Geochemistry*, Vol. 6, eds. H. D. Holland & K. K. Turekian (Elsevier, 2003) 113–143.
- Morel, F. M. M., Rueter, J. G. & Price, N. M. Iron nutrition of phytoplankton and its possible importance in the ecology of ocean regions with high nutrient and low biomass. *Oceanography* 4, 56–61 (1991).
- Mortlock, R. A. et al. Evidence for lower productivity in the Antarctic during the last glaciation. *Nature* 351, 220–223 (1991). doi:10.1038/351220a0
- Palter, J. B. et al. Fueling export production: Nutrient return pathways from the deep ocean and their dependence on the Meridional Overturning Circulation. *Biogeosciences* 7, 3549–3568 (1991). doi:10.5194/bg-7-3549-2010
- Peng, T. H. & Broecker, W. S. Dynamic limitations on the Antarctic iron fertilization strategy. *Nature* 349, 227–229 (1991). doi:10.1038/349227a0
- Rau, G. H., Arthur, M. A. & Dean, W. E.  $^{15}\text{N}/^{14}\text{N}$  variations in Cretaceous Atlantic sedimentary sequences: Implication for past changes in marine nitrogen biogeochemistry. *Earth and Planetary Science Letters* 82, 269–279 (1987). doi:10.1016/0012-821x(87)90201-9
- Redfield, A. C. The biological control of chemical factors in the environment. *American Scientist* 46, 205–221 (1958).
- Ren, H. et al. Foraminiferal isotope evidence of reduced nitrogen fixation in the Ice Age Atlantic Ocean. *Science* 323, 244–248 (2009). doi:10.1126/science.1165787
- Ruttenberg, K. C. Reassessment of the oceanic residence time of phosphorus. *Chemical Geology* 107, 405–409 (1993). doi:10.1016/0009-2541(93)90220-d
- Sarmiento, J. L. & Bender, M. Carbon biogeochemistry and climate change. *Photosynthesis Research* 39, 209–234 (1994). doi:10.1007/bf00014585
- Sarmiento, J. L. et al. High-latitude controls of thermocline nutrients and low latitude biological productivity. *Nature* 427, 56–60 (2004). doi:10.1038/nature02127
- Sarmiento, J. L. & Toggweiler, J. R. A new model for the role of the oceans in determining atmospheric  $\text{pCO}_2$ . *Nature* 308, 621–624 (1984).
- Sarmiento, J. L., Gnanadesikan, A. & Gruber, N. Carbon Sequestration by Patch Fertilization: A Comprehensive Assessment Using Coupled Physical–Ecological–Biogeochemical Models. Final Report. Princeton, NJ: DOE Office of Biological and Environmental Research, 2006.
- Sarmiento, J. L. & Gruber, N. *Ocean Biogeochemical Cycles*. Princeton, NJ: Princeton University Press, 2006.
- Schindler, D. W. Evolution of phosphorus limitation in lakes. *Science* 195, 260–262 (1977). doi:10.1126/science.195.4275.260
- Siegel, D. A., Doney, S. C. & Yoder, J. A. The North Atlantic spring phytoplankton bloom and Sverdrup’s critical depth hypothesis. *Science* 296, 730–733 (2002). doi:10.1126/science.1069174
- Sigman, D. M. & Boyle, E. A. Glacial/interglacial variations in atmospheric carbon dioxide. *Nature* 407, 859–869 (2000). doi:10.1038/35038000
- Sigman, D. M., Hain, M. P. & Haug, G. H. The polar ocean and glacial cycles in atmospheric  $\text{CO}_2$  concentration. *Nature* 466, 47–55 (2010). doi:10.1038/nature09149
- Smith, R. C. Remote sensing and depth distribution of ocean chlorophyll. *Marine Ecology–Progress Series* 5, 359–361 (1981). doi:10.3354/meps005359
- Sunda, W. G. & Huntsman, S. A. Interrelated influence of iron, light and cell size on marine phytoplankton growth. *Nature* 390, 389–392 (1997). doi:10.1038/37093
- Treguer, P. et al. The silica balance in the world ocean: A re-estimate. *Science* 268, 375–379 (1995). doi:10.1126/science.268.5209.375
- Tyrrell, T. The relative influences of nitrogen and phosphorus on oceanic primary production. *Nature* 400, 525–531 (1999). doi:10.1038/22941
- VanCappellen, P. & Ingall, E. D. Redox stabilization of the atmosphere and oceans by phosphorus-limited marine productivity. *Science* 271, 493–496 (1996). doi:10.1126/science.271.5248.493
- Volk, T. & Hoffert, M. I. “Ocean carbon pumps: Analysis of relative strengths and efficiencies in ocean-driven atmospheric  $\text{CO}_2$  changes,” in *The Carbon Cycle and Atmospheric  $\text{CO}_2$ : Natural Variations Archaean to Present*, *Geophysical Monograph Series*, Vol. 32, eds. E. T. Sundquist & W. S. Broecker. (American Geophysical Union, 1985) 99–110. ()
- Watson, A. J. et al. Effect of iron supply on Southern Ocean  $\text{CO}_2$  uptake and implications for glacial atmospheric  $\text{CO}_2$ . *Nature* 407, 730–733 (2000). doi:10.1038/35037561
- Waterbury, J. B. et al. Widespread occurrence of a unicellular, marine, planktonic, cyanobacterium. *Nature* 277, 293–294 (1979). doi:10.1038/277293a0
- Weber, T. S. & Deutsch, C. Ocean nutrient ratios governed by plankton biogeography. *Nature* 467, 550–554 (2010). doi:10.1038/nature09403