6.04
The Biological Pump

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NOMENCLATURE

b_1 and b_2	D/W (m^{-1})
C_e	extracellular CO_2 concentration (μM)
C_{export}	export production (mmol C $m^{-2} d^{-1}$ or mg C $m^{-2} d^{-1}$)
C_{flux}	sinking flux of POC (mmol C $m^{-2} d^{-1}$ or mg C $m^{-2} d^{-1}$)
C_i	intracellular CO_2 concentration (μM)
C_{prod}	primary production (mmol C $m^{-2} d^{-1}$ or mg C $m^{-2} d^{-1}$)
D	organic matter decomposition rate (d^{-1})
D_{CO_2}	diffusivity of CO_2 in seawater ($m^2 s^{-1}$)
F_{CO_2}	flux of CO_2 to cell surface (μmol s^{-1})
G	acceleration due to gravity ($m s^{-2}$)
$H_2CO_3^*$	dissolved $CO_2 + H_2CO_3$ (μM)
k'	rate constant for $HCO_3^- \rightarrow CO_2$ (s^{-1})
R	radius (m)
W	particle sinking rate ($m d^{-1}$)
z	depth (m)
$\triangle\rho$	density difference ($g m^{-3}$)
μ	dynamic viscosity of seawater (Pa s)
ρ	partition coefficient
$\sum CO_2$	total CO_2 (μM)
τ	residence time (years)

6.04.1 INTRODUCTION

Despite having residence times (τ) that exceed the ~1,000 years mixing time of the ocean, many dissolved constituents of seawater have concentrations that vary with depth and from place to place. Silicic acid ($\tau = 15{,}000$ years), nitrate ($\tau = 3{,}000$), phosphate ($\tau = 10{,}000$–$50{,}000$ years), and dissolved inorganic carbon (DIC; $\tau = 83{,}000$) are generally present in low concentrations in surface waters and at much higher concentrations below the thermocline (Figure 1). Additionally, their concentrations are higher in the older deep waters of the North Pacific than they are in the younger waters of the deep North Atlantic. This is the general distribution exhibited by elements and compounds taking part in biological processes in the ocean and is generally referred to as a "nutrient-type" distribution.

Both the lateral and vertical gradients in the concentrations of nutrients result from "the biological pump" (Figure 2). Dissolved inorganic materials (e.g., CO_2, NO_3^-, PO_4^{2-}, and $Si(OH)_4$) are fixed into particulate organic matter (POM; carbohydrates, lipids, and proteins) and biominerals (silica and calcium carbonate) by phytoplankton in surface waters. These particles are subsequently transported, by sinking, into the deep. The bulk of the organic material and biominerals decomposes in the upper ocean via dissolution, zooplankton grazing, and microbial hydrolysis, but a significant supply of material survives to reach the deep sea and sediments. Thus just as biological uptake removes certain dissolved inorganic materials from surface waters, the decomposition of sinking biogenic particles provides a source of dissolved inorganic material to deeper waters. Because of this, deeper waters contain higher concentrations of biologically utilized materials than surface waters, and older deep waters contain more than deep waters more recently formed from ocean surface waters.

One side effect of the biological pump is that CO_2 is shunted from the surface ocean into the deep sea, lowering the amount present in the atmosphere. For many years it has been recognized that pre-Industrial levels of CO_2 in the atmosphere were a one-third of what they would have been, had there been no biological pump operating in the ocean (Broecker, 1982). It has also long been considered that the biological pump is not operating at its full

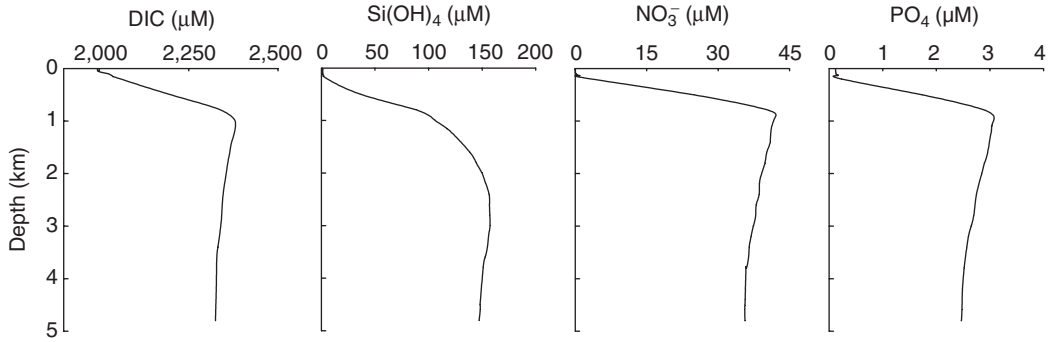

Figure 1 Idealized profiles of dissolved inorganic carbon, silicic acid, nitrate, and phosphate with depth in the ocean.

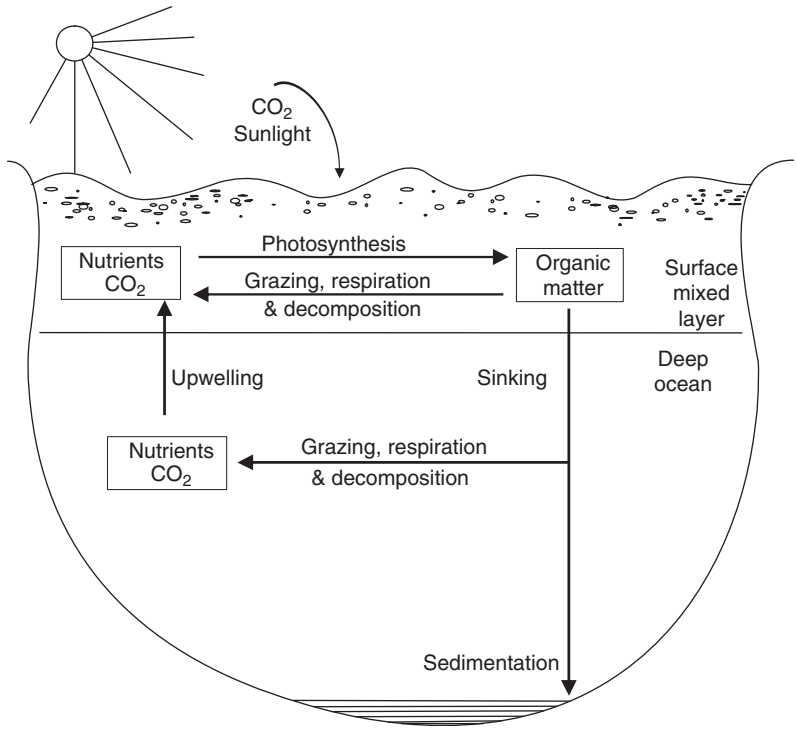

Figure 2 Simplified diagram of the biological pump.

capacity. In the so-called high-nutrient, low-chlorophyll (HNLC) areas of the ocean, a considerable portion of the nutrients supplied to the surface waters is not utilized in support of primary production, most probably due to the limitation of phytoplankton growth by an inadequate supply of trace elements (Martin and Fitzwater, 1988). The possibility that the biological pump in HNLC areas might be stimulated by massive additions of Fe, both artificially as a means of removing anthropogenic CO_2 from the atmosphere and naturally as a cause for the lower glacial atmospheric CO_2 levels (Martin, 1990), is a current focus of research and debate (Watson *et al.*, 1994; Chisholm *et al.*, 2001; de Baar *et al.*, 2005).

Although the biological pump is most popularly known for its impact on the cycling of carbon and major nutrients, it also affects the geochemistry of other elements and compounds. The biological pump influences the cycling, concentrations, and residence times of trace elements such as Cd, Ge, Zn, Ni, Fe, As, and Se, through their incorporation into organic matter and biominerals (Bruland, 1980; Azam and Volcani, 1981; Elderfield and Rickaby, 2000). Scavenging by sinking biogenic particles and precipitation of materials in the microenvironment of organic aggregates and fecal pellets plays a major role in the marine geochemistry of elements such as Ba, Th, Pa, Be, rare earth elements (REEs), and Y (Dehairs *et al.*, 1980; Anderson *et al.*, 1990; Buesseler *et al.*, 1992; Kumar *et al.*, 1993; Zhang and Nozaki, 1996; Azetsu-Scott and Niven, 2005). Even major elements in seawater such as Ca^{2+} and Sr^{2+} display slight surface depletions (Broecker and Peng, 1982; de Villiers, 1999) as a result of the biological pump, despite their long respective oceanic residence times of 1 and 5 Myr (Broecker and Peng, 1982; Elderfield and Schultz, 1996).

6.04.2 DESCRIPTION OF THE BIOLOGICAL PUMP

The biological pump can be sectioned into several major steps: the production of organic matter and biominerals in surface waters, the sinking of these particles into the deep, and the decomposition of the settling (or settled) particles. In general, phytoplankton in surface waters take up DIC and nutrients. Carbon is fixed into organic matter via photosynthesis and, together with N, P, and trace elements, forms the carbohydrates, lipids, and proteins that comprise the bulk organic matter. Once formed, this organic matter faces the immediate prospect of decomposition back to CO_2, phosphate, ammonia, and other dissolved nutrients through consumption by herbivorous

zooplankton and degradation by bacteria; most of the primary products formed will be recycled within a few hundred meters of the surface (Martin *et al.*, 1987). Some portion of the primary production will, however, be exported to deeper waters or even to the sediments before decomposition and may even escape remineralization entirely and remain in the sedimentary reservoir.

It is worth taking a closer look at the various steps in the biological pump (Figure 2). By what processes does organic matter make it from surface to deep? What factors define the proportion of surface primary production that survives transport to the seabed?

6.04.2.1 Photosynthesis and Nutrient Uptake

In the initial step of the biological pump, phytoplankton in sunlit surface waters converts CO_2 into organic matter via photosynthesis:

$$CO_2 + H_2O + \text{light} \rightarrow CH_2O + O_2 \qquad (1)$$

The first stable product of carbon fixation by the enzyme, ribulose bisphosphate carboxylase (Rubisco), is glyceraldehyde 3-phosphate, a 3-C sugar. This 3-C sugar is fed into biosynthetic pathways and forms the basis for all organic compounds produced by photosynthetic organisms. Fixed carbon and major trace elements such as H, N, P, Ca, Si, Fe, Zn, Cd, Mg, I, Se, and Mo are used for the synthesis of carbohydrates, lipids, proteins, biominerals, amino acids, enzymes, DNA, and other essential compounds.

Besides C, the two main components of phytoplankton organic matter are N and P, in the roughly average molar proportion of 106:16:1 (C:N:P) (Redfield, 1934, 1958) known as the Redfield ratio. In addition, diatoms, by virtue of depositing opal (amorphous, hydrated silica) in their cell wall, have an average C/Si ratio of 8 (Brzezinski, 1985), although this ratio may vary from at least 3–40 depending on the conditions of light, temperature, and nutrient availability (Harrison *et al.*, 1977; Brzezinski, 1985; De La Rocha *et al.*, 2000; Franck *et al.*, 2005). Coccolithophorids produce scales (coccoliths) made of $CaCO_3$ and contain 20–100 μmol of $CaCO_3$ per mol of organic C (Paasche, 1999).

POM and biominerals produced by phytoplankton contain many trace elements. The most abundant are Mg, Cd, Fe, Ca, Ba, Cu, Ni, Zn, and Al (Table 1), which are important constituents of enzymes, pigments, and structural materials. Carbonic anhydrase requires Zn or Cd (Price and Morel, 1990; Lane and Morel, 2000), nitrate reductase requires Fe (Geider and LaRoche, 1994), and chlorophyll contains Mg. Additionally, elements such as Na, Mg, P, Cl, K, and Ca are present as ions within cells and are important for osmoregulation and the maintenance of charge balance (e.g., Fagerbakke *et al.*, 1999).

A wide variety of ions may also be adsorbed onto the surfaces of biogenic particles. The removal from the water column and deposition

Table 1 Elemental composition of marine phytoplankton from cultures and plankton tows.

Element	*Element/C ratio* (mol mol^{-1})	*References*
N	0.15	Redfield (1958)
Si (diatoms)	0.13	Brzezinski (1985)
P	0.009	Redfield (1958)
Ca	0.03	Martin and Knauer (1973), Collier and Edmond (1984)
Fe	2.3×10^{-6}–1.8×10^{-3}	Martin and Knauer (1973), Collier and Edmond (1984), Sunda and Huntsman (1995a)
Zn	6×10^{-5}	Martin and Knauer (1973), Collier and Edmond (1984)
Al	1×10^{-4}	Martin and Knauer (1973), Collier and Edmond (1984)
Cu	3×10^{-6}–0.006[a]	Martin and Knauer (1973), Collier and Edmond (1984)
Ni	2×10^{-5}–0.006[a]	Collier and Edmond (1984)
Cd	5×10^{-7}–0.005[a]	Martin and Knauer (1973), Collier and Edmond (1984)
Mn	4×10^{-6}–0.004[a]	Martin and Knauer (1973), Collier and Edmond (1984)
Ba	1×10^{-5}–0.01[a]	Martin and Knauer (1973), Collier and Edmond (1984)
Mg	0.02[a]	Martin and Knauer (1973)
Na	0.1[a]	Martin and Knauer (1973)
Sr	8×10^{-5}[a]	Martin and Knauer (1973)
Ti	1×10^{-5}[a]	Martin and Knauer (1973)
Cr	2×10^{-6}[a]	Martin and Knauer (1973)

[a] Calculated from dry weight data using an average phytoplankton C content on a dry weight basis of 50%.

in the sediments of particle-reactive elements such as Th (Buesseler *et al.*, 1992) and Pa (Kumar *et al.*, 1993) have been shown to correlate with the primary production of particles in the ocean. Additionally, Th has been shown to complex with colloidal, surface-reactive polysaccharides (Quigley *et al.*, 2002; Azetsu-Scott and Niven, 2005).

6.04.2.1.1 Levels of primary production

The amount of primary production carried out in the oceans each year has been estimated from ocean color satellite data and shipboard ^{14}C incubations to be 140 g C m^{-2}, for a total of 50–60 Pg C (4–5 Pmol C) fixed in the surface ocean each year (Shushkina, 1985; Martin *et al.*, 1987; Field *et al.*, 1998). This represents roughly half of the global annual 105 P g C fixed each year (Field *et al.*, 1998), despite the fact that marine phytoplankton comprise $<1\%$ of the total photosynthetic biomass on Earth. Extrapolation from Redfield ratios suggests the incorporation of 0.6–0.8 Pmol N and 40–50 Tmol P into biogenic particles each year in association with marine primary production. From the proportion of primary production carried out by diatoms and the average Si/C ratio of diatoms of silica, production rates of 200–280 Tmol Si yr^{-1} may be calculated (Nelson *et al.*, 1995; Tréguer *et al.*, 1995).

6.04.2.1.2 Patterns in time and space

Rates of primary production in upwelling regions of the ocean outpace those of nonupwelling coastal regions, which in turn are greater than rates in the oligotrophic open ocean (Figure 3; Ryther, 1969; Martin *et al.*, 1987). Open-ocean primary production levels are of the order of 130 g C m^{-2} yr^{-1}, whereas in nonupwelling coastal areas and upwelling zones they are 250 and 420 g C m^{-2} yr^{-1}, respectively (Martin *et al.*, 1987). However, because the open ocean constitutes 90% of the area of the ocean, the bulk (80%) of the ocean's annual carbon fixation occurs there rather than in coastal and upwelling regions.

Different types of phytoplankton dominate primary production in the different marine regimes. Diatoms perform $\sim 75\%$ of the primary production that occurs in upwelling and coastal regions of the ocean but $<35\%$ of that taking place in the open ocean (Nelson *et al.*, 1995). Phytoplankton biomass and primary production in the open ocean are dominated instead by prokaryotic picoplankton (Chisholm *et al.*, 1988; Liu *et al.*, 1999; Steinberg *et al.*, 2001).

Outside the tropics, levels of marine primary productivity vary systematically throughout the year (Heinrich, 1962). Standing stocks of phytoplankton and levels of primary production peak in the spring following the onset of water

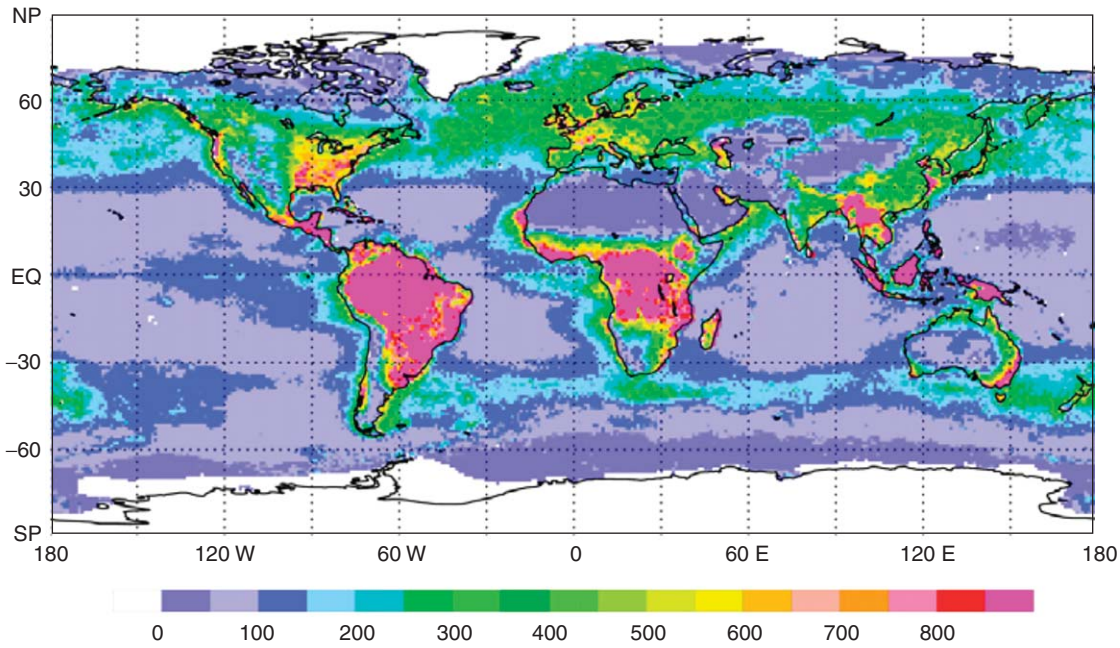

Figure 3 Distribution of primary production in the ocean and terrestrial biosphere. Net primary production levels are given in g C m^{-2} yr^{-1}. Reproduced by permission of American Association for the Advancement of Science from Field *et al.* (1998).

column stratification and the increase in available light. Depletion of nutrients in the stratified water column in summer inhibits phytoplankton growth and grazing by zooplankton reduces standing stocks. Some areas may experience a small bloom of phytoplankton in the autumn when light levels are still adequate and the onset of winter convection and overturning injects nutrients into the euphotic zone.

6.04.2.1.3 Nutrient limitation

The upper limit of primary production is set by the supply of nutrients (N, P, Si, and Fe) into the euphotic zone. N inputs into the surface ocean may limit the primary productivity of the whole ocean over short timescales. Over timescales approaching and exceeding the 10,000–50,000 years residence time of P (Ruttenberg, 1993; Filippelli and Delaney, 1996), P inputs limit global ocean primary production (Tyrrell, 1999).

Regionally and for different types of phytoplankton, the limitation of both the rate and overall amount of primary production is more varied. Major nutrients in HNLC areas of the ocean (such as the Southern Ocean, the Equatorial Pacific, and the North Pacific subarctic) are never completely consumed in support of primary production, because low levels of Fe limit phytoplankton growth (Martin and Fitzwater, 1988; Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000). Diatoms, which require Si for growth, are often limited by low concentrations of silicic acid in surface waters (Brzezinski and Nelson, 1996; Nelson and Dortch, 1996). Growth of diazotrophic (N_2 fixing) phytoplankton such as the cyanobacterium, *Trichodesmium*, will be more susceptible to P and Fe limitation than to N limitation. Even the concentration of dissolved CO_2 in seawater (especially in the midst of a phytoplankton bloom) may limit instantaneous rates, although not ultimate levels, of primary production (Riebesell *et al.*, 1993; Wolf-Gladrow *et al.*, 1999).

6.04.2.2 Flocculation and Sinking

6.04.2.2.1 Marine snow

Material that reaches the deep ocean and seafloor does so not as individual phytoplankton cells slowly meandering down, but as larger, rapidly sinking particles (McCave, 1975; Suess, 1980; Billett *et al.*, 1983; Fowler and Knauer, 1986; Alldredge and Gotschalk, 1989), which have traversed the distance between surface and deep in a space of days (Billett *et al.*, 1983; Asper *et al.*, 1992). These larger particles, known collectively as "marine snow," are largely aggregates (Alldredge and Silver, 1988) formed either by zooplankton, which produce mucous feeding structures and fecal pellets, or by the physical coagulation of smaller particles (McCave, 1984; Alldredge *et al.*, 1993). Coagulation is the more important of the two formation pathways; the bulk of the organic material reaching the deep sea does so as aggregated phytoplankton that have not been ingested by zooplankton (Billett *et al.*, 1983; Turner, 2002).

Sinking rates of marine snow are orders of magnitude greater than those of unaggregated phytoplankton cells (Smayda, 1970; Shanks and Trent, 1980; Alldredge and Gotschalk, 1989). The shorter transit time from surface to bottom for aggregated particles results in the enhanced transport of C, N, P, Si, and other materials to the deep, despite the fact that marine snow particles are sites of elevated rates of decomposition and nutrient regeneration. Intense colonization and hydrolysis of the particles by bacteria (Smith *et al.*, 1992; Bidle and Azam, 1999, 2001) and fragmentation and consumption of the particles by zooplankton (Steinberg, 1995; Dilling *et al.*, 1998; Dilling and Alldredge, 2000; Goldthwait *et al.*, 2004) reduce the vertical flux of materials to the seafloor.

6.04.2.2.2 Aggregation and exopolymers

Coagulation requires the success of two activities, the collision of particles and their subsequent joining to form an aggregate. In the ocean, particles collide due to processes such as shear, Brownian motion, and differential settling. The probability of particles attaching following a collision is controlled by the physical and chemical properties of the particles' surfaces (Alldredge and Jackson, 1995). The probability of sticking is greatly enhanced by exopolymers produced by phytoplankton and bacteria (Alldredge and McGillivary, 1991; Alldredge *et al.*, 1993).

These exopolymers turn out to be important for the transport of material to the deep. In a coastal system, it was observed that transparent exopolymer particles (TEPs), which are colloidal polysaccharides exuded by phytoplankton, were required for the aggregation and sedimentation of diatoms out of the water column (Passow *et al.*, 2001). The formation of rapidly sinking aggregates has also been shown to be controlled more by TEP abundance than by phytoplankton concentrations (Logan *et al.*, 1995).

Little is known about the composition of the polymers responsible for particle aggregation in marine systems. They are generally composed of polysaccharides (Alldredge *et al.*, 1993) and proteins (Long and Azam, 1996). The carbohydrate

component of TEP contains glucose, mannose, arabinose, xylose, galactose, rhamnose, glucuronate, and O-methylated sugars (Janse *et al.*, 1996; Holloway and Cowen, 1997), and is generally rich in deoxysugars (Mopper *et al.*, 1995). Very little is known about the specific composition of TEP, and virtually nothing is known of its structural characteristics (Holloway and Cowen, 1997; Schumann and Rentsch, 1998; Engel and Passow, 2001).

Exopolymer particles may scavenge dissolved organic matter (DOM) as they form, providing a mechanism for the biological pumping of DOM into the deep sea (Engel and Passow, 2001). TEP also contains C and N in proportions exceeding Redfield ratios (Mari *et al.*, 2001; Engel *et al.*, 2002), providing a mechanism for pumping of carbon in excess of what would be predicted from the availability of nitrogen.

6.04.2.2.3 *Sinking and transport of POM to depth*

The flux (C_{flux}) of particulate organic carbon (POC) to depth (z) reflects the balance between the rate of decomposition (D) of the POC and the velocity at which it sinks (W) (Banse, 1990):

$$C_{\text{flux}} = C_{\text{flux}(z_0)} e^{-(D/W)z} \qquad (2)$$

The faster the particles sink into the deep, the larger the fraction of their organic matter that arrives with them. According to Stokes' law, the key players in particle sinking velocities are the size and density of the particle, with sinking velocities increasing with the square of the radius (r) of a particle or with the density difference between the particle and seawater ($\Delta\rho$):

$$W = \frac{2gr^2(\Delta\rho)}{9 \quad \mu} \qquad (3)$$

where g is the acceleration due to gravity and μ the dynamic viscosity of seawater.

Because of their small size (generally not more than a few micrometers), sinking velocities of solitary phytoplankton cells are only about a meter per day (Smayda, 1970). Particles sinking so slowly require more than a year to reach the benthos of even a relatively shallow continental shelf, and 10 years to reach the abyssal ocean floor. Given the rapid rates of microbial decomposition of organic material in the ocean and the abundance of zooplankton grazers, it is virtually impossible for such a slowly sinking particle to reach the seabed.

Sinking velocities of large (>0.5 mm) particles, in contrast, are $>100\,\text{m day}^{-1}$ (Shanks and Trent, 1980; Alldredge and Gotschalk, 1989). Transit time to the deep in this case is days to weeks, which agrees with observations of a close temporal coupling between surface production and seafloor sedimentation (e.g., Billett *et al.*, 1983; Asper *et al.*, 1992).

It might be argued that particle flux is controlled by rates of particle aggregation and sinking more than it is controlled by overall levels of primary production. Year to year variability in carbon export to deep waters correlates more strongly with the size of the dominant primary producer, for example, than with year to year variations in levels of carbon fixation (Boyd and Newton, 1995).

It has been recently suggested that minerals such as calcium carbonate, opal, and clays may drive the sedimentation of POM in the ocean by adding density, or "ballast" to organic aggregates (Armstrong *et al.*, 2002; François *et al.*, 2002; Klaas and Archer, 2002). This hypothesis is based on several observations. Below 3,000 m, sinking particles contain a fairly constant 5 wt.% of organic carbon (Armstrong *et al.*, 2002; Passow, 2004), as if they are saturated with mineral particles. The fluxes of calcium carbonate and POC into sediment traps below 3,000 m also appear correlated (r^2 values ~ 0.7) (François *et al.*, 2002; Klaas and Archer, 2002). There is also a significant correlation between opal and POC fluxes (François *et al.*, 2002; Klaas and Archer, 2002) that is not as strong in large part due (Passow and De La Rocha, 2006) to high variability in the Si/C ratio of primary production in various regions of the ocean (e.g., Ragueneau *et al.*, 2000).

There are two points against the mineral "ballast" controlling the flux of POC to depth. The first is that correlation does not imply causation; from the regression data (François *et al.*, 2002; Klaas and Archer, 2002), there is no way to tell if it is the mineral fluxes that are responsible for the POC fluxes or vice versa (Passow, 2004; Passow and De La Rocha, 2006). The second is that the accumulation of minerals on organic aggregates causes aggregates to fragment into smaller particles (Passow and De La Rocha, 2006). The competing processes of density addition and size reduction mean that the relationship between sinking rates and the accumulation of minerals on aggregates is not a straightforward, linear one (Hamm, 2002). This points toward sinking of POC fluxes being important to the settling of suspended mineral fragments rather than minerals being critical to the sedimentation of POC (Passow and De La Rocha, 2006).

6.04.2.3 Particle Decomposition and Repackaging

Less than half of the particles produced during primary production survive zooplankton grazing and microbial attack to be exported from the euphotic zone and only about 1% endure to settle into the deep ocean and sediments (Suess, 1980; Martin *et al.*, 1987; Lutz *et al.*, 2002; Andersson *et al.*, 2004). This leaves the efficiency of the biological pump largely in the hands of processes taking place during the sinking of particles to the deep. The processes influencing the balance between particle sinking and decomposition rates are only poorly known.

Following its formation, organic matter in the ocean rapidly decomposes and there is intense recycling of elements even within the euphotic zone. The flux of POC in the ocean decreases more or less exponentially with depth below the euphotic zone (Figure 4; Suess, 1980; Martin *et al.*, 1987; Lutz *et al.*, 2002; Andersson *et al.*, 2004). The amount of organic matter exported to the deep ocean (C_{flux}) has been classically described as a function of primary production in the euphotic zone (C_{prod}) (Suess, 1980):

$$C_{\text{flux}}(z) = \frac{C_{\text{prod}}}{(0.0238z + 0.212)} \quad (4)$$

where z is the depth in the water column, or as a function of export from the euphotic zone (C_{export}) (Martin *et al.*, 1987):

$$C_{\text{flux}}(z) = C_{\text{export}}\left(\frac{z}{z_0}\right)^{-0.858} \quad (5)$$

These curves were derived from POC flux measured via sediment traps and are widely used to describe carbon flux in global circulation models. Other curves have been proposed, based on sediment traps or sediment oxygen consumption, that take into account the increase in the refractory nature of particles with depth (Lutz *et al.*, 2002; Andersson *et al.*, 2004):

$$C_{\text{flux}}(z) = C_{\text{flux}_0}\left[(1-p)\mathrm{e}^{-b_1 z} + p\mathrm{e}^{-b_2 z}\right] \quad (6)$$

In this approach, C_{flux_0} is partitioned (p) into a pool of fresh, labile POC degrading rapidly relative to its sinking rate and a pool too rapidly sinking or too refractory for significant decomposition to take place en route to the seabed. The two relationships for D/W are b_1 and b_2.

The simplicity of these curves belies the complexity of the processes causing the decrease in POC flux with depth. Mediating the decomposition and recycling of organic matter in the ocean are zooplankton and heterotrophic bacteria (Cho and Azam, 1988; Smith *et al.*, 1992; Steinberg, 1995; Dilling *et al.*, 1998; Dilling and Alldredge, 2000). Bacteria and zooplankton diminish the sinking particulate flux by consuming particles and converting them back into CO_2 and dissolved materials, and by converting large, sinking particles into smaller particles with reduced or nonexistent sinking rates.

Although most particles are broken down in the surface ocean, processes occurring in the mesopelagic and bathypelagic zones are significant enough to wipe out the regional variability in POC fluxes seen in the surface ocean (Antia *et al.*, 2001). At 125 m in the Atlantic, for example, POC flux ranges regionally from 0.5 to 12 g C m^{-2} yr^{-1}. By 3,000 m, the variability has been compressed by 85% to 0.5–2.4 g C m^{-2} yr^{-1}.

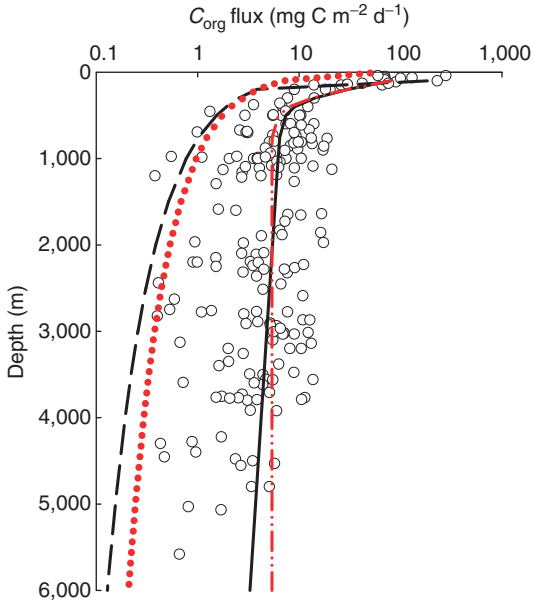

Figure 4 Sinking fluxes of organic C in the ocean as estimated from sediment traps and regional estimates of export production. Data are from tables 1 and 2 in Lutz *et al.*, 2002. The fitted curves are equation (4), the Suess curve (Suess, 1980) (black dashed line), equation (5), the Martin curve (Martin *et al.*, 1987) (dotted red line), equation (6), following Lutz *et al.* (2002) (red dashed and dotted line), and equation (7), following Andersson *et al.* (2004) (black solid line).

6.04.2.3.1 *Zooplankton grazing*

Zooplankton may reduce the sinking flux of biogenic particles in the ocean in two ways. The first is by grazing upon particles which reduces

the total amount of POM in the water column and shifts its occurrence from large, fast-sinking aggregates to smaller fecal pellets, which constitute only a minor portion of the sinking organic flux (Turner, 2002). In the second way the particle flux is reduced by actively breaking up aggregates into smaller particles (Dilling and Alldredge, 2001; Goldthwait *et al.*, 2004). At stations off of southern California, for instance, the average overnight increase in the number of aggregates per liter by 15% was attributable to the fragmentation of larger particles by swimming euphausiids (Dilling and Alldredge, 2001).

The relative impact of zooplankton grazing on primary production decreases with increasing production levels; the proportion of primary production that is consumed by zooplankton decreases exponentially as productivity levels increase (Calbet, 2001). This supports the observation that the ratio of export production to total production is higher in areas of high productivity. Globally, about 12% of marine primary production, or 5.5 Pg C (0.5 Pmol C), is consumed by mesozooplankton each year (Calbet, 2001).

6.04.2.3.2 Bacterial hydrolysis

Bacterial hydrolysis plays a major role in the decomposition of sinking and suspended matter in the ocean. Bacterial organic carbon has been observed to make up over 40% of the total POC in the water column, and the proportion of the sinking flux of carbon utilized by bacteria may be equal to 40–80% of the surface primary production in nearshore areas (Cho and Azam, 1988). Marine aggregates have been shown to contain high concentrations of hydrolytic enzymes, such as proteases, polysaccharidases, and glucosidases (Smith *et al.*, 1992). Turnover times of organic components of marine aggregates due to hydrolysis may be short, on the order of fractions of days to days (Smith *et al.*, 1992). Bacterial proteases have also been shown to enhance the dissolution rates of biogenic silica in diatom aggregates (Bidle and Azam, 2001). Much of the hydrolyzed material is not taken up by the bacteria attached to the particles but instead joins the pool of DOM present in the water (Smith *et al.*, 1992).

6.04.2.3.3 Geochemistry of decomposition

Ingestion of POM by zooplankton results in the respiration and excretion of a portion of that POM as CO_2, NH_4, dissolved organic nitrogen (DON), phosphate, and dissolved organic phosphorus (DOP). Assimilation efficiencies for organic matter for zooplankton grazing on phytoplankton range from 10% to 40% (Ryther, 1969; Michaels and Silver, 1988). Zooplankton do not assimilate significant quantities of silicon from diatoms consumed, leaving regeneration of silicic acid to be mediated strictly by opal dissolution rates.

6.04.2.4 Sedimentation and Burial

Of the net 50–60 Pg C (4–5 Pmol C) fixed into organic matter in the surface ocean each year (Shuskina, 1985; Martin *et al.*, 1987; Field *et al.*, 1998), only ~10% is exported from the euphotic zone (Buesseler, 1998). Each year roughly 0.16 Pg C (13 Tmol C) are preserved in ocean sediments (Hedges and Keil, 1995), an accumulation rate representing 0.3% of that of carbon fixation in the surface ocean.

The accumulation of sedimentary organic carbon in the ocean varies greatly from place to place, with continental margin sediments accounting for the bulk of the organic carbon buildup (Hedges and Keil, 1995; de Haas *et al.*, 2002). About 94% of the sedimentary organic carbon that is preserved in the oceans is buried on continental shelves and slopes (Hedges and Keil, 1995). This leaves only 6% of the total sedimentary organic carbon to accumulate in the open ocean. Since the open ocean, due to its vast area, plays host to 80% of the annual primary production, the accumulation of only 6% of the organic carbon suggests an overall preservation efficiency of 0.02% here. Preservation efficiency on continental shelves and slopes is, at 1.4%, much greater.

Many reasons have been given for the regional differences in the accumulation and preservation of organic carbon in the sediments. Differences in the flux of organic particles to the seafloor due to differences in primary production levels, rates of aggregation and sinking, and depth of the water column may contribute to a higher preservation efficiency. The oxygen content of bottom waters may also be important, although a correlation between burial Qefficiency and bottom water oxygen concentration is not seen (Hedges and Keil, 1995) and rates of hydrolysis of organic matter by bacteria may be high even under anoxic conditions (e.g., Arnosti *et al.*, 1994). The long-term preservation of organic material in sediments may be tied to the sorption of the organic molecules to mineral surfaces (Hedges and Keil, 1995), although the nature of the associations and the rates at which they occur have not been closely detailed.

6.04.2.5 Dissolved Organic Matter

DOM has not been as intensively studied as other aspects of the biological pump perhaps

because DOM does not sink. However, DOM does play an active role in the biological pump in at least three ways. Much of the DOM is biologically utilizable and may directly provide P and N for primary production (Clark *et al.*, 1998; Zehr and Ward, 2002). DOM may assemble into colloidal and particulate material that can sink as well as scavenge other material to form marine snow (Alldredge *et al.*, 1993; Kepkay, 1994; Chin *et al.*, 1998). DOM is also a large reservoir of carbon in the ocean, containing at least an order of magnitude more carbon than the other marine organic carbon reservoirs (Kepkay, 1994).

Although the origins of DOM have not been fully detailed, phytoplankton are thought to serve as the dominant source of DOM to the ocean. Actively growing phytoplankton secrete DOM (Biddanda and Benner, 1997; Soendergaard *et al.*, 2000; Teira *et al.*, 2001) and the polysaccharide composition of phytoplankton exudates resembles that of the high-molecular-weight fraction of DOM (Aluwihare and Repeta, 1999). Phytoplankton DOM is also released during grazing by zooplankton (Strom *et al.*, 1997). Organic matter, such as mucus, on phytoplankton cell surfaces may also be hydrolyzed by bacteria and released as DOM (Smith *et al.*, 1995).

The exact composition of marine DOM is not known. It has so far been shown to contain neutral sugars (such as glucose, fucose, mannose, and arabinose), polysaccharides, amino acids, amides (such as chitin), phosphorus esters, and phosphonates (Benner *et al.*, 1992; McCarthy *et al.*, 1997; Clark *et al.*, 1998; Amon *et al.*, 2001). Microbial degradation is thought to play a role in setting the composition of DOM in the ocean (Amon *et al.*, 2001).

One interesting feature of DOM, at least with respect to the carbon cycle, is its enrichment in C over the Redfield ratio. The C:N:P ratios of high-molecular-weight DOM are roughly 350:20:1 (Kolowith *et al.*, 2001). C-enrichment is also observed for bulk DOM (Kaehler and Koeve, 2001). Part of this enrichment in C may be due to the enhanced remineralization of P and N from DOM (Clark *et al.*, 1998; Kolowith *et al.*, 2001), as suggested by an increase in the C/P ratio of DOM with depth (Kolowith *et al.*, 2001). DOM may also just simply be produced with high C/N and C/P ratios. TEP, for example, which forms from DOM precursors (Alldredge *et al.*, 1993; Chin *et al.*, 1998) has high C/N ratios (Engel and Passow, 2001; Mari *et al.*, 2001). The polysaccharides that eventually form TEP are exuded by phytoplankton and may represent excess photosynthate, which is carbohydrates, and lipids formed in the absence of nutrients like N, that are needed for the synthesis of compounds, like proteins (Morris, 1981).

The importance of the carbon-enriched DOM pool in the carbon cycle hinges on the size and turnover time of the reservoir. A recent estimate of dissolved organic carbon (DOC) in the ocean is 200 Pg C (Kepkay, 1994), which is more comparable to the 750 Pg of carbon present in the atmosphere than it is to the 36,000 Pg C deep sea reservoir of DIC (Sundquist, 1993). The average age of marine DOM is ~6,000 years (Williams and Druffel, 1987), although the turnover time of different fractions of the DOM pool varies from decades to nearly 20,000 years (Loh *et al.*, 2004). The bulk (~70%) of DOM is low molecular weight (Benner *et al.*, 1992) and relatively resistant to microbial degradation (Bauer *et al.*, 1992; Amon and Benner, 1994). High-molecular-weight compounds that are quickly turned over by bacterial decomposition (Amon and Benner, 1994) make up the remaining 30% of the DOM pool.

6.04.2.6 New, Export, and Regenerated Production

Not all of the primary production in the ocean feeds carbon into the biological pump. Most of the carbon fixed each year is converted straight back into CO_2 and dissolved nutrients by zooplankton and bacteria in the euphotic zone. These recycled nutrients may then be used to fuel further carbon fixation.

It has long been recognized (Dugdale and Goering, 1967) that a portion of the primary production (regenerated production) is supported by nutrients regenerated in the euphotic zone and another portion (new production) is supported by nutrients imported in the euphotic zone through upwelling, river inputs, nitrogen fixation, or atmospheric deposition. The ratio of new to total primary production in the ocean, known as the f ratio (Eppley and Peterson, 1979), is generally higher in upwelling environments than it is in oligotrophic regions of the ocean (Harrison, 1990; Laws *et al.*, 2000). On average, ~20% of the total global marine primary production is new production, ranging from 7% to 70% from region to region (Laws *et al.*, 2000).

6.04.3 IMPACT OF THE BIOLOGICAL PUMP ON GEOCHEMICAL CYCLING

6.04.3.1 Macronutrients

6.04.3.1.1 Carbon

The influence of the biological pump on the distribution of DIC in the ocean illustrates the influence it has on the distribution of many

other elements. Low concentrations of DIC are observed in surface waters (Figure 1) due to the uptake of dissolved CO_2 (and perhaps HCO_3^-; Raven, 1997) by phytoplankton. Concentrations of dissolved CO_2 increase most rapidly just below the euphotic zone, associated with the bulk of the decomposition of POC (Martin *et al.*, 1987; Antia *et al.*, 2001). Deepwater concentrations of dissolved CO_2 are higher than surface water concentrations, and older deep waters contain more dissolved CO_2 than younger ones (Broecker and Peng, 1982).

Much of the current scientific interest in the biological pump revolves around the impact it has on levels of CO_2 in the atmosphere and, subsequently, on climate. The photosynthetic fixation of carbon into organic matter lowers the concentration of dissolved CO_2 in surface waters, allowing influx of CO_2 from the atmosphere. This fixed carbon may then be exported to deeper waters or the sediments before it decomposes back to CO_2, maintaining the observed gradient in dissolved CO_2 concentrations between waters of the surface and deep (Figure 1).

Atmospheric concentrations of CO_2 are thus lower for the given size of the oceanic DIC reservoir than they would be in the absence of this biological transport of carbon to the deep. If all life in the ocean were to die off and the ocean and atmosphere came to equilibrium with respect to CO_2, concentrations of CO_2 in the atmosphere would rise by $\sim$140 µatm (Broecker, 1982), which is a remarkable 50% of the preindustrial interglacial value of 280 µatm.

Details of the influence of the biological pump on the distribution and cycling of carbon in the ocean and the controlling factors are discussed later in this chapter. The next few pages are devoted to the relationship of the biological pump to the cycling of other elements. This is by no means an exhaustive overview of the biological shuffling of elements throughout the ocean, but instead a highlight of several elements of particular biogeochemical interest.

6.04.3.1.2 Nitrogen

Of all the elements playing an important role in the regulation of the biological pump, nitrogen is the one with the most complex biologically mediated cycling. Nitrogenous species taking part in productivity range from N_2, which may be fixed into a more universally biologically available form by nitrogen-fixing bacteria, to NO_3^-, which follows from the production of NO_2^- from NH_4^+ through nitrification (Figure 5). The denitrification pathway sequentially results in the transformation of NO_2^- to N_2O and N_2. NH_4^+ can also be directly

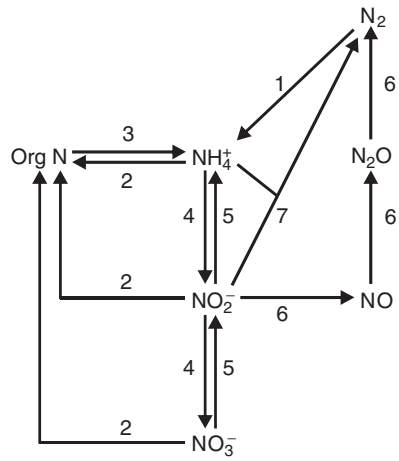

Figure 5 Microbial transformations of the nitrogen cycle. Pathways depicted are (1) N_2 fixation, (2) DIN assimilation, (3) ammonium regeneration, (4) nitrification, (5) nitrate/nitrite reduction, (6) denitrification, and (7) anaerobic ammonium oxidation (anammox).

oxidized into N_2 with NO_2^- as the oxidant, via anaerobic ammonium oxidation (anammox) (Mulder *et al.*, 1995; Thamdrup and Dalsgaard, 2002; Dalsgaard *et al.*, 2003). There are also dissolved organic forms of nitrogen, such as amides, urea, free amino acids, amines (McCarthy *et al.*, 1997), which are also biologically utilizable to varying degrees.

The average marine *f*-ratio of 0.2 (Laws *et al.*, 2000) suggests that most of the primary production in the ocean is supported by dissolved inorganic nitrogen (DIN) that has been recycled in the euphotic zone. This further suggests that the bulk of the primary production in the ocean relies on NH_4^+, since that is the predominant recycled form of nitrogen. Extrapolating from the Redfield C/N ratio of 6.6 and the average *f* ratio of 0.2 and the overall estimate of primary production of 4–5 Pmol C in the ocean each year (Shushkina, 1985; Martin *et al.*, 1987; Field *et al.*, 1998) yields 0.7 Pmol of particulate organic nitrogen (PON) produced each year, 0.1 Pmol of which is exported out of the euphotic zone.

6.04.3.1.2.1 Nitrogen fixation. The two aspects of the nitrogen cycle having the greatest impact on the biological pump are nitrogen fixation and denitrification. The first provides a mechanism for drawing on the extensive atmospheric pool of N_2 gas in support of primary production. The second provides a pathway for DIN to be converted back into N_2 gas and removed from the ocean system.

Approximately 28 Tg N (2 Tmol N) are added to the marine nitrogen inventory

through nitrogen fixation each year (Gruber and Sarmiento, 1997; Capone *et al.*, 2005), although the overall amount of nitrogen fixed each year is considerably higher than this. Nitrogen fixation accounts for about half of the new nitrogen used in primary production (Karl *et al.*, 1997). Only prokaryotic organisms can fix nitrogen, leaving this, at least in the ocean, in the hands of the cyanobacteria and out of the hands of eukaryotic algae such as diatoms, dinoflagellates, and coccolithophorids (unless they are hosting diazotrophic symbionts). Until recently it was believed that the filamentous, colony-forming cyanobacterium *Trichodesmium,* and cyanobacterial symbionts in diatoms were responsible for the bulk of the nitrogen fixation occurring in the ocean (Capone *et al.*, 1997). However, direct measurements of the rates of nitrogen fixation by *Trichodesmium*, coupled with knowledge of their distribution and abundance, fell significantly short of nitrogen fixation rates calculated from geochemical budgets (Gruber and Sarmiento, 1997). It has now been discovered that free-living, unicellular cyanobacteria are expressing the genes for the nitrogen-fixing enzyme, nitrogenase (Zehr *et al.*, 2001), and contribute considerably to fixed nitrogen budgets in the ocean (Montoya *et al.*, 2004).

It has been suggested that rates of nitrogen fixation are currently limited by the availability of Fe. The Fe-requirement of *Trichodesmium*, however, turns out to be much lower than previously estimated. Instead it is the availability of P that controls the upper limit of nitrogen fixation in the modern ocean (Sañudo-Wilhelmy *et al.*, 2001).

The demonstration of the P limitation of nitrogen fixation by cyanobacteria supports the notion that over geologic time phosphorus ultimately limits productivity (Tyrrell, 1999). When cyanobacteria face a shortfall of nitrogen, they fix nitrogen to meet their demands. This influx of new nitrogen to N-limited systems allows for the drawdown of phosphate until the system is P-limited. Under P limitation, nitrogen fixation is curtailed (Sañudo-Wilhelmy *et al.*, 2001). Thus while nitrogen may at times limit instantaneous rates of carbon fixation, as is frequently the case in the modern ocean, over long time periods the input of phosphorus to the oceans sets the upper limit of net primary production (Tyrrell, 1999).

6.04.3.1.3 Phosphorus

Although there is a tendency to consider dissolved inorganic phosphorus (DIP, measured as soluble-reactive phosphate; Strickland and Parsons, 1968) as being simply PO_4^{3-}, DIP exists as a considerable number of species. At seawater pH, DIP is predominantly H_2PO_4 (87%) and only 12% PO_4^{3-} and 1% $H_2PO_4^-$ (Greenwood and Earnshaw, 1984). There are also numerous dissolved organic forms of phosphorus that are taken up by phytoplankton and used to fuel primary production in the ocean.

One interesting aspect of the phosphorus cycle is that, unlike the cases for the other major nutrient elements in the ocean, the phosphorus cycle contains sinks that are not mediated by biological activities. Dissolved phosphate may be scavenged onto iron or manganese oxyhydroxide particles associated with hydrothermal activity or reacted with basalt during the circulation of water through mid-ocean ridge hydrothermal systems (Föllmi, 1996). Although the exact values are poorly known, it is estimated that the scavenging of phosphate by the hydrothermal oxyhydroxides constitutes up to 50% of the removal flux of phosphorus from the ocean (e.g., Froelich *et al.*, 1982; Berner *et al.*, 1993). Another large inorganic sink for dissolved phosphorus is the precipitation of authigenic phosphate, which accounts for 10–40% of the removal flux. Removal of phosphorus as sedimenting POC by comparison is thought to be 20–50% of the output of phosphorus from the ocean.

Roughly, 5 Tg P (0.2 Tmol P) are removed from the ocean each year as both organic and inorganic phases. This is in reasonable balance with the roughly 5 Tg of reactive P being brought into the system each year naturally. However these natural sources constitute only half of the modern-day input of phosphorus to the ocean (Froelich *et al.*, 1982), anthropogenic inputs having doubled the annual phosphate flux. A doubling of phosphorus inputs to the ocean could have a significant impact on the biological pump, although it should be noted that the ocean is already nitrogen limited and further inputs of phosphorus will only exacerbate this. Shifts in N/P ratios of surface waters may alter the structure of the phytoplankton community. Phaeocystis, for example, grows poorly under high phosphate conditions and may see its numbers decline.

6.04.3.1.4 Silicon

Dissolved silicic acid is required for the growth of diatoms, which deposit opal (amorphous, hydrated silica) in their cell wall and dominate the production of opal in the modern-day ocean (Lisitzin, 1972). About 240 Tmol of silica are produced by diatoms in the surface

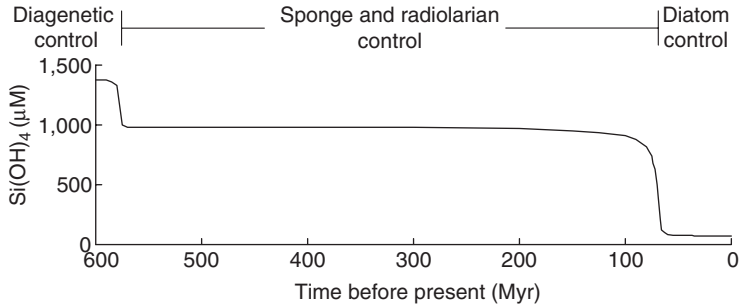

Figure 6 Estimated average marine concentrations of silicic acid over the Phanerozoic. Adapted from Siever (1991).

ocean each year (Nelson *et al.*, 1995; Tréguer *et al.*, 1995). Total inputs of dissolved silicic acid to the euphotic zone are 120 Tmol Si, mostly from rivers (6 Tmol Si) and upwelling (115 Tmol Si; Tréguer *et al.*, 1995).

Half of the biogenic silica produced each year dissolves in the upper 100 m of the water column (Nelson *et al.*, 1995), and a further 47% dissolves in the deep ocean and seafloor, for a net deposition of ~6 Tmol (3% of surface production) each year (Tréguer *et al.*, 1995; DeMaster, 2002). Opal preservation efficiencies are generally highest in productive environments (e.g., 6% in the permanently open ocean zone of the Southern Ocean versus 0.4% in the oligotrophic North Atlantic). The traditional view of opal accumulation in the sediments is that it is closely linked to opal production in overlying waters (e.g., Broecker and Peng, 1982), but many factors besides opal production govern opal preservation. Opal dissolution rates more than double for every 10 °C rise in temperature (Kamitani, 1982). Aggregation has been shown to reduce rates of Si regeneration from diatoms (Bidle and Azam, 2001). Additionally, the fraction of produced silica that reaches the seabed correlates with high seasonality and high ratios of carbon export to production (Pondaven *et al.*, 2000), which also tend to be in areas where organic matter is formed in blooms and is transported quickly to the sediments as large aggregates.

6.04.3.1.4.1 The impact of the appearance of the diatoms on the marine silica cycle. The silica cycle is an excellent example of how much the biological pump can impact the concentration and distribution of elements in seawater. Presently, surface concentrations of silicic acid are low: the overall average silicic acid content of ocean waters is only 70 μM (Tréguer *et al.*, 1995). Prior to the appearance of the diatoms in the early Tertiary (Tappan and Loeblich, 1973), oceanic concentrations of silicic acid were ~1,000 μM (Siever, 1991). The sponges and radiolarians controlling the oceanic inventory of silicic acid at that time possessed neither the numbers nor demand for Si needed to draw down silicic acid concentrations. The increased output of biogenic silica from the ocean associated with the ascension of diatoms, with their high affinity for silicic acid and high cellular requirements for silicon, resulted in a precipitous drop in the silicic acid content of ocean waters over the late Cretaceous and Paleocene (Figure 6), stabilizing in the Eocene to the <100 μM values that have held ever since (Siever, 1991).

Since sponges and radiolarians are not great players in particle flux, the rise of the diatoms must have profoundly altered the partitioning of silicic acid between surface and deep. The familiar nutrient-type distribution may have only existed for the last 50–100 Myr. The approximate 14-fold drop in silicic acid concentration also suggests that the residence time of Si in the ocean dropped from 200,000 years to today's 15,000.

6.04.3.1.4.2 Excessive pumping of silicon. Silicic acid, by virtue of being regenerated from silica instead of from relatively labile POM, is regenerated more deeply than the other major nutrients (Figure 1; Dugdale *et al.*, 1995). This decoupling between silicic acid and the other nutrients and the fact that not all phytoplankton utilize Si means that there is no Redfield relationship between Si and C, N, or P. On average across the ocean, water upwelled into the euphotic zone, with an Si/N of roughly 0.6, contains a slight excess of nitrate over silicic acid relative to the 1:1 utilization ratio of nutrient replete diatoms (Figure 7). Below ~500 m, however, there is more silicic acid than nitrate, with deep ocean Si/N ratios being near 3 (Figure 7).

Fe limitation of diatoms increases the pumping of Si (relative to N and C) to deeper waters. Fe-limited diatoms are inhibited in their utilization of N as a result of the Fe

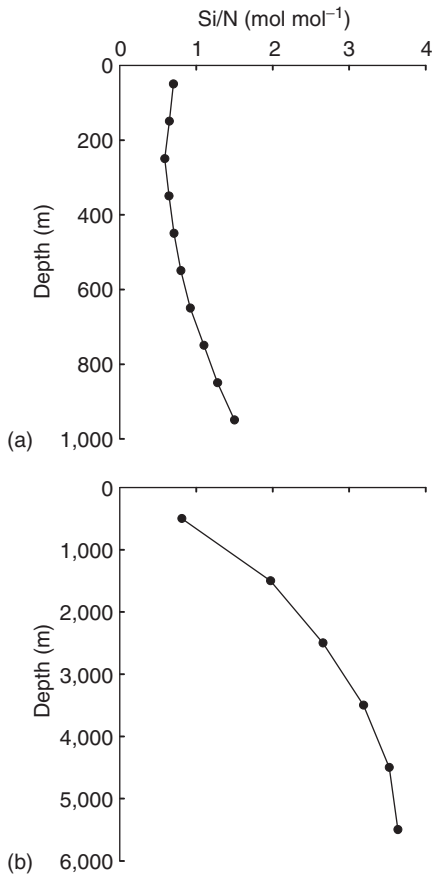

Figure 7 Ratio of silicic acid to nitrate with depth in the ocean between (a) 0 and 1000 m and (b) between 0 and 6,000 m. Profiles have been constructed from volume-weighted averages of average silicic acid and nitrate concentrations in the Southern Ocean, North Atlantic, South Atlantic, North Pacific, South Pacific, and Indian Ocean from the WOCE dataset.

requirement of nitrate reductase (Geider and LaRoche, 1994). However, Fe-limited diatoms continue to take up silicic acid, although at lowered rates (De La Rocha *et al.*, 2000). As a result, the Si/N ratios of Fe-limited diatoms may be as high as 2 or 3 (Takeda, 1998; Hutchins and Bruland, 1998), much higher than 1 of nutrient replete diatoms (Brzezinski, 1985).

6.04.3.2 Trace Elements

The biological pump influences the distribution of many elements in seawater besides C and the major nutrients. Ba, Cd, Ge, Zn, Ni, Fe, As, Se, Y, and many of the REEs show depth distributions that closely resemble profiles of the major nutrients. Additionally, Be, Sc, Ti, Cu, Zr, and Ra have profiles where concentrations increase with depth, although the correspondence of these profiles with nutrient profiles is not very tight (Nozaki, 1997).

6.04.3.2.1 Barium

Vertical profiles of dissolved barium (Ba^{2+}) in the ocean resemble profiles of silicic acid and alkalinity (Figure 8; Lea and Boyle, 1989; Jeandel *et al.*, 1996), suggesting that biological processes strongly influence Ba distributions throughout the ocean. However, the strict incorporation of Ba into biogenic materials is not the dominant means of Ba^{2+} removal from ocean waters. Although the similarity between the profiles of Ba^{2+} and $Si(OH)_4$ suggests a common removal phase, the amount of barium incorporated into diatom opal ($<9\times10^{-6}$ mol Ba mol^{-1} Si; Shemesh *et al.*, 1988) cannot account for the 2×10^{-4} mol Ba^{2+} mol^{-1} $Si(OH)_4$ slope (Jeandel *et al.*, 1996) in the ocean. Ba^{2+} appears instead to be mainly removed from seawater as barite ($BaSO_4$) formed in association with opal and decaying organic material (Dehairs *et al.*, 1980; Bishop, 1988). The exact mechanism for barite precipitation is unknown, but it is thought that it forms in the SO_4^{2-}-enriched microenvironments of decaying particles that may be thus supersaturated with respect to barite (Dehairs *et al.*, 1980; Ganeshram *et al.*, 2003).

Although the marine budget of barium is only approximately known, it appears to be both balanced and controlled by biogenic particle formation. Approximately 35 Gmol of Ba^{2+} are removed from surface waters every year (Dehairs *et al.*, 1980). Of this 35 Gmol, 60% settles as barite and the rest is incorporated into or adsorbed onto phases such as $CaCO_3$ or SiO_2 (Dehairs *et al.*, 1980; Dymond *et al.*, 1992). About 10–25 Gmol of Ba are buried on the seafloor each year (Dehairs *et al.*, 1980).

Because barite forms in association with organic material, there is a tight correlation ($r^2=0.93$) between the sedimentary fluxes of carbon and barite (Dymond *et al.*, 1992). Thus, barite accumulation rates have been used to infer past levels of export production in the ocean (e.g., Dymond *et al.*, 1992; Paytan *et al.*, 1996).

6.04.3.2.2 Zinc

The profiles of dissolved Zn in the ocean are also similar to those of $Si(OH)_4$ (Figure 9; Bruland, 1980), but as with Ba, the main removal phase for Zn is not opal. Less than 3% of the Zn taken up by diatoms is deposited in their opaline cell wall (Ellwood and Hunter, 2000) and the Zn/Si ratio of acid-leached opal is much lower than the ratio of dissolved Zn

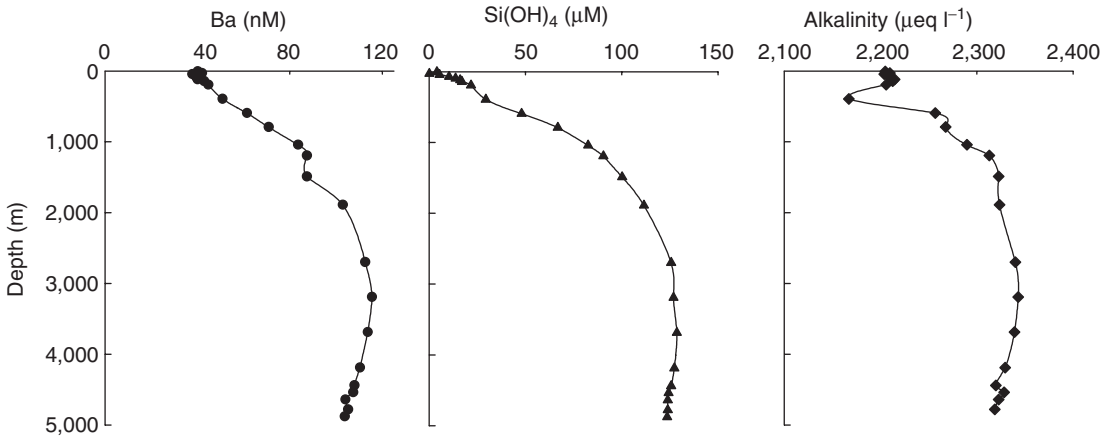

Figure 8 Profiles of Ba^{2+}, $Si(OH)_4$, and alkalinity in the Indian Ocean (06° 09′ S, 50° 55′ E). Data are from Station 36 of Jeandel *et al.* (1996).

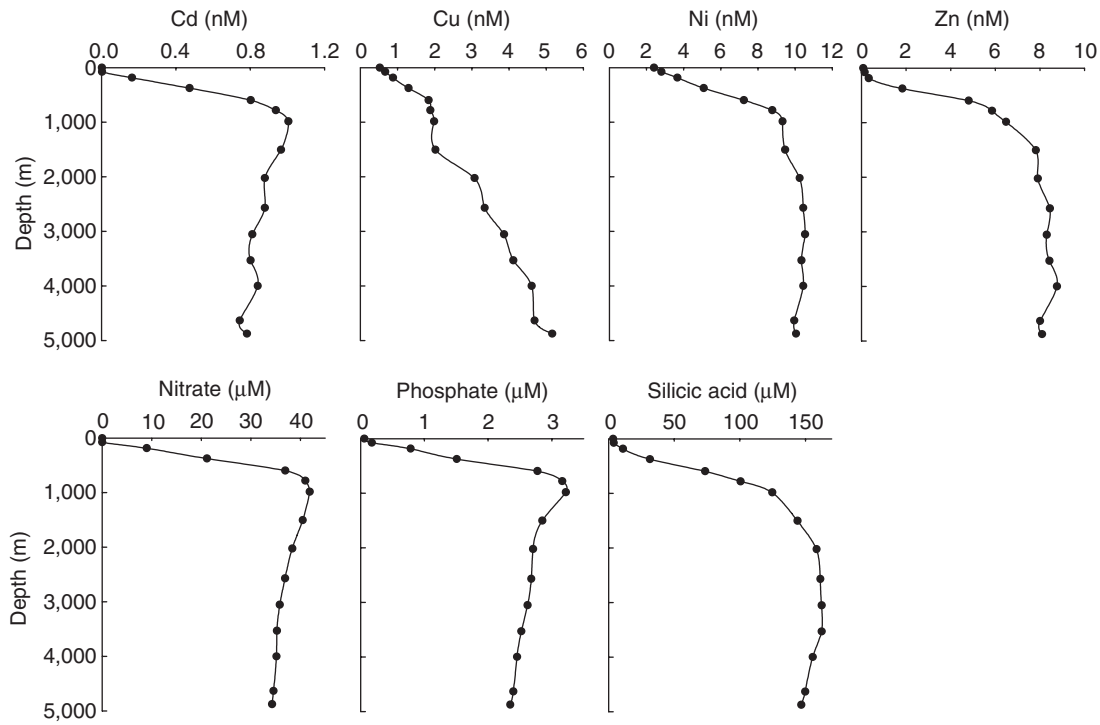

Figure 9 Profiles of Cd, Cu, Ni, Zn, nitrate, phosphate, and silicic acid in the north Pacific (32° 41.0′ N, 144° 59.4′ W). Plots have been redrawn from Bruland (1980).

and $Si(OH)_4$ in the water column (Bruland, 1980; Collier and Edmond, 1984). Instead most of the Zn removed from the surface ocean is bound up in POM.

Because Zn is required for the growth of phytoplankton, Zn availability affects the biological pump. Although Zn limitation of an entire phytoplankton community has never been demonstrated (e.g., Leblanc *et al.*, 2005), levels of dissolved Zn are often low enough to limit many taxa (Morel *et al.*, 1994; Sunda and Huntsman, 1995b; Timmermans *et al.*, 2001). Zn is an integral part of the enzyme, carbonic anhydrase (Morel *et al.*, 1994), which helps maintain an efficient supply of CO_2 to Rubisco (Sunda and Huntsman, 2005). Zn may also be involved in the acquisition or use of organic forms of P (Shi *et al.*, 2004).

The impact of low concentrations of Zn on phytoplankton growth varies. Some phytoplankton substitute cobalt for zinc in many enzymes (Price and Morel, 1990; Sunda and Huntsman, 1995b; Timmermans *et al.*, 2001) and can maintain maximal growth rates at low

levels of Zn. Calcification aids with the acquisition of DIC, so calcareous phytoplankton such as the coccolithophorids are not as dependent on carbonic anhydrase (and therefore Zn) to maintain high rates of C fixation (Sunda and Huntsman, 1995b). Thus while low levels of Zn may not curtail overall levels of primary production, they may shift the phytoplankton community structure away from diatoms and toward coccolithophorids (Morel *et al.*, 1994; Sunda and Huntsman, 1995b; Timmermans *et al.*, 2001), which will shift the ratio of organic C to $CaCO_3$ of particles sinking to the deep.

6.04.3.2.3 Cadmium

Like Ba and Zn, Cd shows a nutrient-like distribution in the ocean (Figure 9; Bruland, 1980; Löscher *et al.*, 1998), more closely mirroring those of the labile nutrients, nitrate and phosphate than those of silicic acid and alkalinity. Cd is taken up by phytoplankton and incorporated into organic material, accounting for the similarity of its profile to that of nitrate and phosphate. Cadmium may also be adsorbed onto the surfaces of phytoplankton (Collier and Edmond, 1984).

Cd is taken up by phytoplankton slightly preferentially to phosphate (Löscher *et al.*, 1998; Elderfield and Rickaby, 2000) In general, waters with low phosphate concentrations have lower Cd/P ratios ($0.1\,\text{nmol Cd}\,(\mu\text{mol P})^{-1}$) than waters with higher phosphate concentrations where Cd/P may approach $0.4\,\text{nmol Cd}\,(\mu\text{mol P})^{-1}$ (Elderfield and Rickaby, 2000). Additionally, surface water Cd/P ratios drop over the development of the spring bloom in the Southern Ocean (Löscher *et al.*, 1998). This may be tied to variations in the Cd/P utilization ratio of phytoplankton with dissolved CO_2, Mn, and Zn concentrations as well as physiological state of the phytoplankton community (Cullen and Sherrell, 2005).

Cd also regenerates preferentially from decomposing particles (Knauer and Martin, 1981; Collier and Edmond, 1984). More labile components of decaying particles have higher Cd/P ratios than bulk decaying particles (Knauer and Martin, 1981). Box models of Cd and P cycling also require enhanced regeneration of Cd from particles for the replication of observed Cd distributions in the ocean (Collier and Edmond, 1984).

Cadmium is generally toxic to organisms and the how the marine phytoplankton utilize their cadmium is unknown. Cd may substitute for Zn in carbonic anhydrase at times when Zn is limiting (Price and Morel, 1990; Lane and Morel, 2000). It is possible that Cd may play a role in polyphosphate bodies, a form of cellular storage of P that have been shown to contain significant quantities of elements such as Ca, Zn, and Mg (Ruiz *et al.*, 2001).

Because of the similarity between Cd profiles and nutrient profiles, attempts have been made to reconstruct past phosphate concentrations from the Cd/Ca ratio of foraminifera (Boyle, 1988; Elderfield and Rickaby, 2000). Foraminifera substitute Cd^{2+} for Ca^{2+} in the lattice of their calcite tests, and the ratio of Cd/Ca incorporation varies with the Cd/Ca ratio of seawater (Boyle, 1988). The Cd/Ca ratio of foraminifera in the Southern Ocean suggests that P in surface waters was not as heavily utilized by phytoplankton during the last glacial maximum (LGM), suggesting lower levels of primary production relative to nutrient flux into the euphotic zone at that time (Elderfield and Rickaby, 2000).

6.04.3.2.4 Iron

Of all the trace elements whose distributions are affected by the biological pump, Fe is the one that has the most profound impact on the workings of the biological pump. Fe plays a key role in many of the crucial enzymes in biological systems, such as superoxide dismutase, ferredoxin, and nitrate reductase (Geider and LaRoche, 1994), which evolved at a time when the oceans were low in oxygen and therefore high in dissolved Fe. As a result, marine phytoplankton have a heavy demand for Fe relative to the present-day availability of dissolved Fe in the ocean. Growth of phytoplankton and rates of photosynthesis are frequently limited by the lack of Fe in surface waters (Martin and Fitzwater, 1988).

One of the major inputs of iron to the ocean comes from the dissolution of Fe(II) from windborne continental dust deposited on the surface of the ocean (Zhuang *et al.*, 1990). In oxygenic environments, such as surface ocean waters, Fe(II) will quickly be oxidized to the insoluble form Fe(III) and removed from seawater. Fe(II) is also taken up by phytoplankton as well as complexed by ligands exuded into the water by marine organisms to prevent its precipitation as Fe(III).

Profiles of dissolved Fe in seawater show the influence of both biotic and abiotic processes. At stations in the Northeast Pacific, dissolved Fe concentrations are low in surface waters reflecting biological uptake. Fe concentrations also show peak values at depth, corresponding to the oxygen minimum zone (Martin and Gordon, 1988), suggesting the abiotic reduction of Fe(III) back to the soluble Fe(II).

Vast tracks of the ocean, such as the Equatorial Pacific, the Northeast Pacific subarctic,

the Southern Ocean, and even parts of the California upwelling zone do not have sufficient supplies of Fe to fully support phytoplankton growth (Martin and Fitzwater, 1988; Martin *et al.*, 1994; Coale *et al.*, 1996; Hutchins and Bruland, 1998; Boyd *et al.*, 2000). In these areas, macronutrients such as N and P are rarely depleted. Attention has turned to these HNLC areas as sites where further primary production (and the associated drawdown of atmospheric CO_2) could occur. Increased supplies of dust stimulating the biological pump in HNLC regions may be responsible for low atmospheric CO_2 concentrations during glacial times (Martin and Gordon, 1988; Watson *et al.*, 2000). Artificially stimulating the biological pump by seeding HNLC areas with chelated Fe has been proposed as a means of pumping into the deep sea the 90 µatm of CO_2 in the atmosphere put there by human hands, although there is not much consensus as to the effectiveness of such an endeavor (Chisholm *et al.*, 2001; de Baar *et al.*, 2005).

6.04.4 QUANTIFYING THE BIOLOGICAL PUMP

There are many different ways to quantify the biological pump. Total levels of carbon fixation in surface waters may be estimated in bottle incubations from the uptake of $^{14}CO_2$ by phytoplankton (Steemann Nielsen, 1952) or from the deviation of oxygen isotopes from their terrestrial mass fractionation line (Luz and Barkan, 2000). At the other end of the biological pump, the rate of organic C accumulation or oxygen consumption in the sediments may be measured. And in between, the impact of the feeding and vertical migration activities of midwater organisms on the flux of particles may be investigated (e.g., Steinberg, 1995; Dilling *et al.*, 1998). The next few pages will concentrate on the methods used to estimate export production and particle flux from the euphotic zone.

Particle flux is frequently extrapolated from the measurement of new production in surface waters (Dugdale and Goering, 1967). Export of POM out of surface waters or into the deep sea may also be estimated directly through its collection in sediment traps (e.g., Martin *et al.*, 1987; Antia *et al.*, 2001). Export or sedimentation of POM may also be estimated from disequilibria between two nuclides (such as ^{238}U and ^{234}Th, and ^{230}Th and ^{231}Pa) that are scavenged by particles of different degrees (Buesseler *et al.*, 1992; Kumar *et al.*, 1993).

Some methods for quantifying the biological pump focus on the relationship between the biological pump and CO_2. POC flux measurements or estimates of nutrient removal from surface waters may be used in conjunction with various ocean models to estimate the impact of the biological pump on atmospheric concentrations of CO_2 (Sarmiento and Toggweiler, 1984; Sarmiento and Orr, 1991). Others have focused on the importance of the ratio of POC to $CaCO_3$ to the sequestering of CO_2 in the ocean (Antia *et al.*, 2001; Buitenhuis *et al.*, 2001).

6.04.4.1 Measurement of New Production

The method in most widespread use for quantifying the biological pump hinges on the ideas that the surface ocean is at steady state on annual timescales with respect to the nitrogen budget and that nitrogen predominantly limits phytoplankton growth in the ocean. In such a system, the amount of productivity that is exported from the euphotic zone must be equal to the amount of productivity that is fueled by the input of allocthonous or "new" nitrogen to the euphotic zone (Dugdale and Goering, 1967). New production by this definition is that which is supported from dissolved nitrogen upwelled into the euphotic zone or fixed from N_2 into PON, and export production is taken to be equal to new production. For the sake of measurement, the above definition of new production has been simplified even further. Experimentally, new production is taken to be equal to the production that uses nitrate (and nitrite) as its nitrogen source, as opposed to ammonium or any of the organic forms of nitrogen.

It should be pointed out that measurement of new production is the measurement of the maximum amount of productivity that can be exported without running the system down with respect to the annual supply of nutrients to the euphotic zone. It may not be always appropriate to assume that new production and export production are equal; the fluxes will be equal only in systems that are not evolving. The validity of the assumption that new production equals export production depends on to what degree and over what timescale the nitrogen cycle in surface waters is at steady state.

At the moment the nitrogen cycle in the ocean is not at steady state on the decadal timescale. In the last few decades the N/P ratio of many oceanic waters has changed (Pahlow and Riebesell, 2000; Emerson *et al.*, 2001) and nearshore waters have shifted toward Si limitation from N limitation (Conley *et al.*, 1993) due to anthropogenic inputs of DIN to these systems and an increase in the extent of nitrogen fixation. On very long timescales, the N

cycle is not at steady state either, but responds to changes in the oceanic inventory of P, which ultimately governs the rate of nitrogen fixation (Tyrrell, 1999).

Another assumption open to question is that the rate of nitrate uptake adequately represents the rate of uptake of new forms of nitrogen. This simplification has come about for two reasons. The first is that the uptake rate of nitrate by phytoplankton can be measured with reasonable ease by tracking the uptake of ^{15}N-labelled nitrate (Dugdale and Goering, 1967). The second is that nitrate is not produced in the euphotic zone to any significant degree and so its presence there can only be as a result of upwelling or atmospheric deposition.

The form of DIN released during the death, decay, and grazing of phytoplankton is ammonium which is also the most easily utilizable form of DIN to phytoplankton. Oxidized forms of DIN, such as nitrate and nitrite must be reduced to ammonium by nitrifying bacteria such as *Nitrosomonas*, *Nitrobacter*, *Nitrospira*, and *Proteobacteria* (Zehr and Ward, 2002) prior to assimilation by phytoplankton. The classical view is that nitrification does not occur in the euphotic zone due to the inhibition of nitrifying bacteria by light (Zehr and Ward, 2002). Eukaryotic phytoplankton are also thought to outcompete nitrifying bacteria for the supplies of ammonium in surface waters. Thus, nitrate found in the euphotic zone must have had its origins outside of the euphotic zone, in deeper waters, in rivers or agricultural runoff, or from atmospheric deposition and is taken as the sole representative of new nitrogen in the euphotic zone (Dugdale and Goering, 1967).

Of course, nitrate is not likely to be the only form of allocthonous nitrogen in the euphotic zone. Concentrations of ammonium in upwelled water are not zero, although they are significantly lower than those of nitrate. DON may also serve as a significant source of new nitrogen to the euphotic zone.

There is one last word of caution concerning the use of nitrate uptake to estimate the transport of CO_2 to depth via the biological pump. Measurement of new production divulges no information concerning the depth of decomposition of the POM formed or the ratio of POC to $CaCO_3$ of the exported particles (Antia *et al.*, 2001). For instance, CO_2 from material decomposed beneath the euphotic zone, but above the maximum depth of winter mixing will be ventilated straight back out of the atmosphere. $CaCO_3$ formation, a feature that is not common to all phytoplankton, diminishes the efficiency of CO_2 drawdown with primary production (see below; Buitenhuis *et al.*, 2001).

6.04.4.2 Measurement of Particle Flux

Means more direct than the measurement of new production exist for the estimation of particle fluxes into the deep. Moored or free-floating traps may be used to collect sinking particles (e.g., Martin *et al.*, 1987). Alternatively, particle flux may be estimated from particle-reactive nuclides (e.g., Buesseler *et al.*, 1992). Particle flux may also be estimated from the consumption of oxygen (associated with the decomposition of sinking POM) in waters below the surface layer (e.g., Jenkins, 1982).

6.04.4.2.1 Sediment traps

The collection of particles in sediment traps, while perhaps the most direct way of measuring the sinking flux of POM, is a method not free from controversy. Sediment traps both over- and under-collect particles. Comparison of ^{234}Th accumulating in a suite of sediment traps with ^{234}Th fluxes expected from U–Th disequilibria in the upper 300 m of the ocean suggests that the particle collection efficiency of these traps ranged from 10% to 1,000% (Buesseler, 1991). Traps deployed in the deep ocean also show a considerable variability in trapping efficiencies (e.g., Scholten *et al.*, 2001). Despite the magnitude of these biases, there is no generally applied method for correcting fluxes using particle-reactive isotopes (Antia *et al.*, 2001).

Zooplankton actively swimming into sediment traps also serve as a source of error in flux measurements. It is impossible to differentiate these "swimmers" from zooplankton that have settled passively into the cup as part of the sinking POM flux. Swimmers may constitute as much as a quarter of the POC collected by the trap (Steinberg *et al.*, 1998) and are generally removed from trap material prior to analysis. This introduces minimal error into the trap estimates of POC flux, as detrital zooplankton likely only comprise ~2% of the total organic matter sinking into the traps (Steinberg *et al.*, 1998).

6.04.4.2.2 Particle-reactive nuclides

Radionuclides in the uranium decay series serve as useful tracers of particle flux. One type of these tracers consists of a soluble parent nuclide and a particle-reactive daughter. These soluble–particle-reactive pairs include ^{238}U–^{234}Th, ^{234}U–^{230}Th, and ^{235}U–^{231}Pa. The half-life of the parent exceeds the mixing time of the ocean and its distribution throughout the ocean is

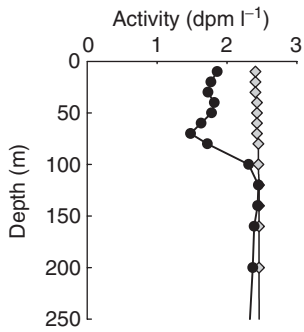

Figure 10 Profiles of ^{234}Th (black circles) and ^{238}U (gray diamonds) in the upper ocean. Redrawn from Buesseler (1991).

uniform. Once the soluble parent isotope decays to the particle-reactive daughter, the daughter is scavenged onto particulate material.

In systems with no particle scavenging, the activities of the parent and daughter nuclide will be in secular equilibrium. What is seen instead is that the activities of ^{234}Th, ^{230}Th, and ^{231}Pa are lower in surface waters than those of their parents (Figure 10). The difference in the activities of parent and daughter is a measure of the uptake of the daughter onto particles (Buesseler *et al.*, 1992). With the help of a model of particle scavenging, fluxes of the particle-reactive daughter may be estimated from its vertical distribution (e.g., Coale and Bruland, 1985; Buesseler *et al.*, 1992). If the ratio of the particle-reactive nuclide to POC or PON is known, then the calculated flux of nuclide can be converted into an estimate of particle flux (Buesseler *et al.*, 1992).

Relative estimates of particle flux may also be made from the ratio of two particle-reactive nuclides, such as ^{230}Th and ^{231}Pa, which are scavenged onto particles to different degrees. The half-lives of these isotopes are much larger than their residences times in the ocean (on the order of 10^4 years versus tens to hundreds of years) and thus there is no significant radioactive decay that occurs in the water column. The extent of the scavenging of ^{231}Pa, which is not as particle-reactive as ^{230}Th, is highest in areas of high particle flux (Anderson *et al.*, 1990). Thus sediments in high flux areas exhibit ^{231}Pa/^{230}Th ratios in excess of the initial production ratio of 0.093, and sediments accumulating slowly exhibit ratios <0.093 (Anderson *et al.*, 1990). ^{231}Pa/^{230}Th ratios have been used to infer changes in productivity and sediment accumulation rates between the present-day interglacial and the LGM, roughly 20,000 years ago (Kumar *et al.*, 1993).

6.04.4.2.3 *Oxygen utilization rates*

The distribution of oxygen in ocean waters contains information about primary production. The amount of excess oxygen present in the seasonal thermocline in the Pacific, for example, was long ago used to suggest that ^{14}C-based estimates of primary production were severely underestimating levels of primary production in the ocean (Shulenberger and Reid, 1981). Oxygen deficiencies in deeper waters have been used to estimate levels of export production (Jenkins, 1982).

The supplies of oxygen to waters below the euphotic zone are primarily physical: advection and mixing. The removal of oxygen from these waters takes place through the oxidation of organic matter:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138O_2 \rightarrow 106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ \quad (7)$$

By measuring rates of ventilation and the degree of oxygen undersaturation in deeper waters an estimate of the rates of oxygen utilization (OUR) may be made and integrated to yield the total amount of oxygen consumed beneath the euphotic zone each year (Jenkins, 1982). From this number a flux of POC and PON may be calculated. Estimates of export production based on OURs are reasonably in line with the amount of new production that could be supported from measured fluxes of NO_3^- into surface waters (Jenkins, 1988).

One advantage of using the OUR method for estimating export fluxes is that it integrates over larger spatial and temporal scales than estimates based on sediment traps and nuclide fluxes. Also, unlike the estimates of new production based on NO_3^- uptake, OURs are directly coupled to the recycling of CO_2 via particle decomposition and are thus a more direct measure of the impact of the biological pump on atmospheric CO_2. In practice, however, the measurement of NO_3^- uptake is less technically challenging and is carried out much more frequently than are estimates from nuclides and OURs.

6.04.5 THE EFFICIENCY OF THE BIOLOGICAL PUMP

6.04.5.1 Altering the Efficiency of the Biological Pump

There is much talk concerning the "efficiency" of the biological pump. Is it pumping as much carbon to the deep sea as it could be? The general consensus is that it is not operating at its full capacity, and this is generally meant

to imply that globally, the nitrate flux into the euphotic zone is not fully consumed in support of marine primary production. Broecker (1982) has estimated, for example, that if all of the nutrients supplied to present-day ocean surface waters were consumed by phytoplankton in support of primary production the atmospheric CO_2 content would drop by $\sim$130 ppmv.

6.04.5.1.1 In HNLC areas

The biological pump in HNLC areas is not operating at full efficiency on at least 2 counts. Phytoplankton growth is curtailed by the lack of availability of trace metals and so the major nutrients N and P are not completely utilized and carbon fixation does not occur to its maximum possible extent (Martin and Fitzwater, 1988). Fe limitation also heavily impacts the larger phytoplankton, like diatoms, that are important to particle flux. When a phytoplankton community is released from Fe limitation, diatom growth is stimulated more strongly than is the growth of the other phytoplankton (Cavender-Bares *et al.*, 1999; Lam *et al.*, 2001).

Given all of this, the addition of Fe to HNLC waters should result in higher levels of carbon fixation, increased growth of diatoms, local drawdown of CO_2, and enhanced export of carbon to the deep sea. Fe-addition experiments in bottles and *in situ* on the mesoscale unequivocally support the first two points. Addition of Fe to HNLC waters results in phytoplankton blooms (Martin and Fitzwater, 1988; Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000; de Baar *et al.*, 2005). Chlorophyll concentrations may quadruple and carbon-fixation rates may triple (e.g., Coale *et al.*, 1996) over the first few days after Fe addition (Figure 11).

In contrast, support for the drawdown of CO_2 following Fe addition has been mixed. In IronEx I, the first mesoscale Fe experiment, Fe addition did not result in a marked drop of CO_2 concentrations in surface waters of the Equatorial Pacific (Watson *et al.*, 1994). Some CO_2 was drawn down during IronEx II, also in the Equatorial Pacific, but the amount removed from surface waters was not enough to prevent these recently upwelled, high CO_2 waters from outgassing CO_2 to the atmosphere (Coale *et al.*, 1996). Large-scale Fe-addition experiments in the Southern Ocean have produced a significant lowering (25–30 µatm) of the CO_2 content of surface waters (Boyd *et al.*, 2000; Watson *et al.*, 2000; Bozec *et al.*, 2005; Hiscock and Millero, 2005).

The one key critical point that the Fe-enrichment experiments have largely failed to show is an increase in the export of carbon to the deep sea (de Baar *et al.*, 2005). Even the Southern Ocean experiments, where a CO_2 drawdown occurred, did not result in substantial increases in export flux. Sediment traps set out at a depth of 100 m (below the fertilized patch) in the SOIREE experiment collected a similar amount of POC to traps stationed outside of the patch (Boyd *et al.*, 2000). Likewise particle flux in the SOFeX-South experiment was similar to that seen normally in the Southern Ocean (de Baar *et al.*, 2005).

There are many possible reasons for the lack of an observed increase in export flux in the mesoscale Fe-addition experiments. The additional carbon fixed might not become export flux, but instead flow through the microbial loop (microzooplankton and bacteria), which would result in the regeneration of CO_2 and nutrients in the euphotic zone. Microzooplankton biomass and bacterial activities were

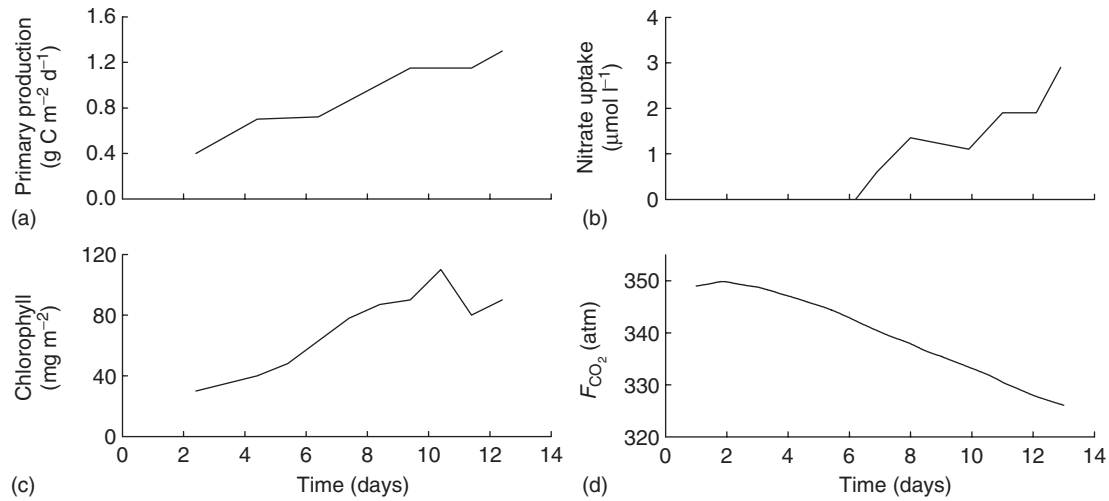

Figure 11 Responses to Fe addition to HNLC waters: chlorophyll, carbon fixation, NO_3^-, and PCO_2. Redrawn from Boyd *et al.* (2000) and Watson *et al.* (2000).

seen to increase in many of the mesoscale Fe-addition experiments (e.g., Boyd *et al.*, 2000), suggesting that some fraction of the carbon fixed through Fe addition was being shunted into the microbial loop instead of being pumped into deeper waters. Alternatively, the sediment traps used may simply have not been deployed for long enough or in the right location to catch the carbon sinking out as a result of the Fe-induced bloom.

6.04.5.1.2 *Through changes in community composition*

Changes in community composition should profoundly affect the efficiency of the biological pump. Shifting productivity from small cells, like photosynthetic picoplankton, which do not efficiently sink, to large cells, such as diatoms, capable of aggregating into particles that sink at hundreds of meters a day will result in the pumping of more carbon to the deep. However, there is finite amount of productivity that may be exported without running the nutrients in the system down to zero. In a steady-state system, shifting the community structure cannot increase the total amount of export production above the level of new production. But a shift in community structure may export carbon deeper into the water column before it decomposes, thus delaying the return of that carbon to the surface ocean by a significant number of years.

A shift in community composition may also be important to the biological pump if the shift is from a calcareous to a noncalcareous phytoplankton, as precipitation of $CaCO_3$ diminishes the ocean's ability to hold dissolved CO_2. DIC ($\sum CO_2$) is present in seawater as several species, dissolved CO_2, carbonic acid, and the dissociated forms, bicarbonate ion and carbonate ion:

$$\sum CO_2 \rightleftharpoons H_2CO_3^* + HCO_3^- + CO_3^{2-} \quad (8)$$

where $H_2CO_3^*$ represents the sum of dissolved CO_2 and carbonic acid. The ratio of the three species varies with pH, with the undissociated forms dominating only at low pH and HCO_3^- favored at the typical seawater pH of 8.3 (Zeebe and Wolf-Gladrow, 2001). The saturation concentration of $H_2CO_3^*$ is controlled in large part by the amount of HCO_3^- and CO_3^{2-} present in solution. Removal of HCO_3^- or CO_3^{2-} during $CaCO_3$ formation results in a lowering of the saturation concentration of dissolved CO_2, and therefore the outgassing of CO_2 from solution to the atmosphere.

Precipitation of $CaCO_3$ both produces CO_2:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 \quad (9)$$

and lowers the alkalinity (approximately equal to $2[CO_3^{2-}] + [HCO_3^-]$) of surface waters (Zeebe and Wolf-Gladrow, 2001). Loss of alkalinity decreases the capacity of surface waters to play host to dissolved CO_2. In the surface ocean, under an atmosphere with a CO_2 partial pressure of 350 µatm (19 µatm less than the 2001 values; Keeling and Whorf, 2001) the precipitation of 1 mol of $CaCO_3$ results in the release of 0.6 mol of CO_2 (Ware *et al.*, 1992; Frankignoulle *et al.*, 1994).

The coccolithophorid, *Emiliania huxleyi*, contains on average 0.433 mol of $CaCO_3$ (present as scales covering the cell) for every mole of organic C (Buitenhuis *et al.*, 2001). Thus for every mole of CO_2 fixed into organic matter by coccolithophorids such as *E. huxleyi*, ~0.26 mol of CO_2 will be released due to the formation of $CaCO_3$. A shift from export production being carried out by coccolithophorids to a noncalcareous phytoplankton such as diatoms will result in an increased drawdown of CO_2 for the same amount of primary production. The fact that carbon fixation by phytoplankton that calcify is only 75% as effective at removing CO_2 as carbon fixation done by phytoplankton that do not precipitate $CaCO_3$ complicates estimates of CO_2 drawdown from the surface ocean POC export flux (Antia *et al.*, 2001).

6.04.5.1.3 *By varying the C:N:P ratios of sinking material*

The C:N:P ratios of sinking POM are not fixed; P and N are preferentially regenerated from sinking POM, which allows for the sequestering of more C in the deep ocean per unit N or P than if Redfield ratios remain unaltered during the decomposition of organic matter. It was remineralization ratios calculated from DIC and nutrient concentrations along isopycnals that initially suggested that the C/N of sinking particles might be higher than the value of 6.6 proposed by Redfield (Takahashi *et al.*, 1985). Sediment trap material also showed that the C/N and C/P ratios of sinking particles increases with depth, from near Redfield values of 6.6 and 106 at the base of the euphotic zone to ~180 and 11 by 5,000 m (Martin *et al.*, 1987).

Since these initial observations, evidence has mounted for the preferential remineralization of N and P out of POM relative to C. Ocean models with continuous vertical resolution support the preferential release of N and P from

sinking POM in line with the estimates of Martin *et al.* (Shaffer, 1996). Bacteria have been shown to more rapidly degrade PON than POC (Verity *et al.*, 2000). Increases in the C/N and C/P of sinking particles have also been observed at station ALOHA near Hawaii (Christian *et al.*, 1997). And differences in the C/N ratio of suspended POC (6.4) and less buoyant POC trapped at the pycnocline (8.6) in the Kattegat, just east of the North Sea, further suggest that N is remineralized more rapidly than C at significant levels even in the euphotic zone (Olesen and Lundsgaard, 1995).

6.04.5.1.4 By enhancing particle transport

While sediment trap evidence supports the idea that the flux of organic carbon (e.g., Figure 4), the correlation between POC flux and overlying levels of primary production ($r^2 = 0.53$; Antia *et al.*, 2001) is not strong. The ratio of POC flux (at 125 m) to primary production also shows variability from region to region, ranging from 0.08 to 0.38 in the Atlantic Ocean alone (Antia *et al.*, 2001).

There are many reasons that an increased downward transport of POC out of the euphotic zone does not directly follow from an increase in productivity. Export fluxes are also controlled by the packaging of smaller more numerous particles into larger less numerous aggregates and by the rate at which the resulting aggregates sink. The depth to which POC exported from the euphotic zone is transported must be determined by the balance between the carbon content of the particle, the rate of microbial hydrolysis, and the sinking rate of the particle. Carbon fixed by marine diatoms, which are large and adept at aggregating, stands a better chance at being exported to the deep than carbon fixed by very small, nonsinking phytoplankton.

The mode of productivity is also crucial to the sinking flux of POC. Systems exporting POC in pulses (e.g., following the periodic formation of phytoplankton blooms in temperate and high-latitude areas) export a much higher proportion of their total production than do systems, such as the oligotrophic central gyres, where carbon fixation is a more static, steady process (Lampitt and Antia, 1997). This results partly from the influence of particle concentration on aggregation and partly from zooplankton population dynamics. In temperate areas, zooplankton reproduction cannot begin until after the onset of the spring phytoplankton bloom, leading to a lag in the increase in zooplankton population (and, subsequently, in the grazing pressure exerted by zooplankton) behind that of the increase in phytoplankton numbers (Heinrich, 1962) allowing for the aggregation and sinking of intact phytoplankton from the euphotic zone. In lower latitude, oligotrophic areas, standing stocks of phytoplankton and zooplankton are not as decoupled in time and there is no clear window within which a high density of phytoplankton cells may aggregate, escape predation, and sink to the deep.

6.04.6 THE BIOLOGICAL PUMP IN THE IMMEDIATE FUTURE

What may we expect out of the biological pump in the future? We cannot currently predict how ocean biology will respond to climate warming (Sarmiento *et al.*, 1998), but there are other questions that we may begin to ask. Will, for instance, the biological pump respond to the rise in surface ocean concentrations of DIC tied to the rise in atmospheric CO_2 fueled by anthropogenic emissions? What impact will inputs of agricultural fertilizers have on the biological pump? And what role will artificial stimulation of the biological pump through deliberate ocean fertilization play in the sequestration of excess CO_2?

6.04.6.1 Response to Increased CO_2

Will the biological pump respond to the increase CO_2? Increasing concentrations of CO_2 do not appear to have the significant impact on the C/N or C/P ratios of phytoplankton (Burkhardt *et al.*, 1999) that is necessary if CO_2 is to stimulate productivity in the ocean. It may be possible, however, for CO_2 levels to increase the proportion of carbon diverted into the biological pump at the expense of grazing and microbial food webs. Riebesell *et al.* (1993) suggested that carbon fixation by phytoplankton may be rate limited by the diffusive flux of CO_2 to the cell which delivers CO_2 too slowly relative to nitrate and phosphate to take up C, N, and P in Redfield proportions.

The diffusive flux of CO_2 to the surface of a phytoplankton cell (F_{CO_2}) is controlled not only by the diffusivity of CO_2 (D_{CO_2}) and the radius of the cell (r), but the concentration gradient of CO_2 between the aqueous medium and the interior of the cell ($C_e - C_i$) and the rate constant for the conversion of HCO_3^- into CO_2 (k') as the carbonate system equilibrates following CO_2 removal:

$$F_{CO_2} = -4\pi r D_{CO_2}\left(1 + \frac{r}{\sqrt{D_{CO_2}/k'}}\right)(C_e - C_i) \quad (10)$$

If the diffusive flux of CO_2 is controlling the delivery of CO_2 to the carbon-fixing enzyme,

Rubisco, then an increase in the dissolved CO_2 content of seawater should stimulate phytoplankton growth rates. In particular, an increase in dissolved CO_2 concentrations should stimulate growth rates in the larger (i.e., aggregate forming) size classes and thus should also result in a shunting of carbon out of the mouths of zooplankton and into the biological pump (Riebesell *et al.*, 1993).

At the present time, it is not clear that the acquisition of carbon is the rate-limiting step for photosynthesis even in the larger phytoplankton cells. Phytoplankton are not limited to the passive diffusion of CO_2 to the cell surface for carbon acquisition. HCO_3^- may be taken up directly by phytoplankton and used as a source of CO_2 for photosynthesis (Korb *et al.*, 1997; Nimer *et al.*, 1997; Raven, 1997; Tortell *et al.*, 1997). The considerably greater abundance of HCO_3^- than dissolved CO_2 in seawater would imply that C-fixation rates of marine phytoplankton are not CO_2 limited and increasing concentrations of CO_2 will not have an impact on rates of primary production.

6.04.6.2 Response to Agricultural Runoff

Inputs of agricultural fertilizers are having more than one impact on the biological pump. A shift in the nitrate to phosphate to silicic acid ratio of natural waters is causing a shift in the phytoplankton community structure that should impact the biological cycling of carbon in aquatic systems (Conley *et al.*, 1993). Additionally, a recent shift in the C:N:P ratios of deeper waters and an increase in export production have been observed for the northern hemisphere oceans (Pahlow and Riebesell, 2000).

6.04.6.2.1 Shift toward Si limitation

Over the last 150 years, changes in land use patterns, human population density, and extent of the use of fertilizers have resulted in an increased flux of nitrate and phosphate to rivers, lakes, and the coastal ocean (Conley *et al.*, 1993) and even to the open ocean through atmospheric deposition, for example of anthropogenic nitrous oxides (Pahlow and Riebesell, 2000). At the same time, large freshwater systems, such as the North American Great Lakes, and coastal areas, such as the Adriatic and Baltic Seas and the Mississippi River plume, have been shifting away from N or P limitation and toward Si limitation (Conley *et al.*, 1993; Nelson and Dortch, 1996). The extra productivity fueled on the extra N and P has resulted in the removal of Si from these systems and a shift in the phytoplankton community structure away from diatoms. Given that rivers are significant sources of new nitrate, phosphate, and silicic acid to the global ocean, this effect is expected to spread further throughout the sea.

A shift in community structure associated with silicic acid depletion may sharply reduce the amount of carbon delivered to deep waters and sediments via the biological pump. Diatoms, which are the only major phytoplankton group requiring silicic acid, are relatively large and notable for aggregating and sinking. Diatoms feed a greater portion of the organic matter they produce into the biological pump than do most other classes of phytoplankton. Currently, diatoms perform more than 75% of the primary production that occurs in high nutrient and coastal regions of the ocean (Nelson *et al.*, 1995), the exact areas that will be impacted by this input of additional nitrate and phosphate and the exact areas where carbon tends to make it down into the sediments.

One possible further impact of the decline of the diatoms lies in the identity of their probably successor. If a $CaCO_3$-producing phytoplankter, such as coccolithophorids, step in to utilize the nitrate and phosphate the Si-starved diatoms leave behind, the CO_2 pumping efficiency of the biological pump will decline (Robertson *et al.*, 1994) even if the same amount of organic carbon continues to be removed to the deep sea and sediments each year.

6.04.6.2.2 Shifts in export production and deep ocean C:N:P

There is evidence for anthropogenic perturbations increasing the biological pumping of carbon into deep waters. In both the North Pacific and North Atlantic, for instance, deepwater N/P ratios have increased over the last 50 years (Pahlow and Riebesell, 2000) possibly due to atmospheric deposition of anthropogenic N and a subsequent shift toward P limitation in these areas. Concomitant with the rise in N/P is an increase in the apparent oxygen utilization (AOU) in both the North Atlantic and North Pacific, which suggests that levels of export production have also increased. This is estimated to have resulted in the increased oceanic sequestration of $0.2\,Pg\,C\,yr^{-1}$ (Pahlow and Riebesell, 2000).

6.04.6.3 Carbon Sequestration via Ocean Fertilization and the Biological Pump

There have been many calls to sequester anthropogenic CO_2 in the deep ocean by stimulating primary production through the addition

of literally tons of Fe to HNLC surface waters. Patents have been taken out on the idea (e.g., Markels, 2001) and, counter to the recommendations of the American Society of Limnology and Oceanography (Ocean Fertilization Summary Report, 2001) several companies have been established to dispense carbon credits to industries willing to pay for ocean fertilization (Chisholm *et al.*, 2001). However, it remains unclear whether ocean fertilization will ever successfully transport carbon in the deep sea, how long the transported carbon might remain out of contact with the atmosphere, and what side effect large-scale fertilization will have on marine geochemistry and ecology (Fuhrman and Capone, 1991; Peng and Broecker, 1991a, b; Sarmiento and Orr, 1991; Chisholm *et al.*, 2001; Lenes *et al.*, 2001).

A perusal of the literature suggests that carbon sequestration by Fe fertilization is not a panacea for the anthropogenic carbon emissions that increased atmospheric CO_2 from 280 µatm at the start of the industrial revolution to 369 µatm by December 2000 (Keeling and Whorf, 2001). Ocean models suggest that enhanced ocean uptake of carbon with Fe fertilization of the Antarctic Ocean will at best draw down atmospheric CO_2 by 70 µatm if carried out continuously for a century (Peng and Broecker, 1991a, b) and damp the annual anthropogenic CO_2 input to the atmosphere by $<30\%$ of current annual emission levels (Joos *et al.*, 1991).

Large-scale Fe fertilization will have side effects. If Fe fertilization resulted in a complete drawdown of the nutrients available in the Southern Ocean, for example, the average O_2 content of deep waters would drop by 4–12% (Sarmiento and Orr, 1991), with areas of anoxia cropping up in the Antarctic (Peng and Broecker, 1991b) and Indian Oceans (Sarmiento and Orr, 1991). Even small-scale patches of anoxia would have a profound negative impact on the survival and distribution of metazoan fauna in the ocean and alter the balance of microbial transformations of nitrogen between reduced and oxidized phases (Fuhrman and Capone, 1991).

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