Chapter 4

Phytoplankton and Their Role in Primary, New, and Export Production

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4.1 Introduction

Phytoplankton have played key roles in shaping Earth's biogeochemistry and contemporary human economy, yet because the human experience is so closely tied to higher plants as sources of food, fiber, and fuel, the role of phytoplankton in our everyday lives is often overlooked. The most familiar phytoplankton products we consume are petroleum and natural gas. Their uses as fuels, and in its myriad refined forms, as plastics, dyes, and chemical feedstocks are so critical to the industrialized world that wars are fought over the ownership of these fossilized hydrocarbons. Since the beginning of civilization, we have used the remains of calcareous nanoplankton, deposited over millions of years in ancient ocean basins, for building materials. Diatomaceous oozes are mined as additives for reflective paints, polishing materials, abrasives, and for insulation. Phytoplankton provided the original source of oxygen for our planet, without which our very existence would not have been possible. The fossil organic carbon, skeletal remains, and oxygen are the cumulative remains of phytoplankton export production that has occurred uninterrupted for over 3 billion years in the upper ocean (Falkowski et al. 1998). In this chapter we examine what we learned during the JGOFS era about how phytoplankton impact contemporary biogeochemical cycles and their role in shaping Earth's geochemical history.

4.1.1 A Brief Introduction to Phytoplankton

Phytoplankton are a taxonomically diverse group of mostly single celled, photosynthetic aquatic organisms that drift with currents. This group of organisms consists of approximately 20 000 species distributed among at least eight taxonomic divisions or phyla (Table 4.1). In contrast, higher plants are comprised of >250 000 species, almost all of which are contained within one class in one division. Thus, unlike terrestrial plants, phytoplankton are species poor but phylogenetically diverse; this deep taxonomic diversity is reflected in ecological function (Falkowski and Raven 1997).

Within this diverse group of organisms, three basic evolutionary lineages are discernable (Delwiche 2000). The first contains all procaryotic oxygenic phytoplankton, all of which belong to one class of bacteria, namely the cyanobacteria. Numerically these organisms dominate the ocean ecosystems. There are approximately 10^{24} cyanobacterial cells in the oceans. To put that in perspective, the number of cyanobacterial cells in the ocean is 2 orders of magnitude more than all the stars in the sky. Cyanobacteria evolved more than 2.8 billion years ago (Summons et al. 1999) and have played fundamental roles in driving much of the ocean carbon, oxygen and nitrogen cycles from that time to present.

All other oxygen producing organisms in the ocean are eucaryotic, that is they contain internal organelles, including a nucleus, one or more chloroplasts, one or more mitochondria, and, most importantly, in many cases they contain a membrane bound storage compartment, or vacuole. Within the eucaryotes we can distinguish two major groups, both of which have descended from a common ancestor thought to be the endosymbiotic appropriation of a cyanobacterium into a heterotrophic host cell. The appropriated cyanobacterium became a chloroplast.

In one group of eucaryotes, chlorophyll *b* was synthesized as a secondary pigment; this group forms the 'green lineage', from which all higher plants have descended. The green lineage played a major role in oceanic food webs and the carbon cycle from ca. 2.2 billion years ago until the end-Permian extinction, approximately 250 million years ago (Lipps 1993). Since that time however, a second group of eucaryotes has risen to ecological prominence; that group is commonly called the 'red lineage' (Fig. 4.1). The red lineage is comprised of several major phytoplankton divisions and classes, of which the diatoms, dinoflagellates, haptophytes (including the coccolithophorids), and the chrysophytes are the most important. All of these groups are comparatively modern organisms; indeed the rise of dinoflagellates and coccolithophorids approximately parallels the rise of dinosaurs, while the rise of diatoms approximates the rise of mammals in the Cenozoic. The burial and subsequent diagenesis of organic carbon, produced primarily by members of the red lineage in shallow seas in the

Table 4.1. The taxonomic classification and species abundances of oxygenic photosynthetic organisms in aquatic and terrestrial ecosystems. Note that terrestrial ecosystems are domianted by relatively few taxa that are species rich, while aquatic ecosystems contain many taxa but are relatively species poor (from Falkowski and Raven (1997))

Taxonomic Group						Known species	Marine	Freshwater
Empire	**Kingdom**	**Subkingdom**	**Division**	**Subdivision**	**Class**			
Bacteria (= Prokaryota)	Eubacteria			Cyanobacteria (sensu strictu) (= Cyanophytes, blue-green algae)		1500	150	1350
				Chloroxybacteria (= Prochlorophyceae)		3	2	1
Eukaryota	Protozoa		Euglenophyta		Euglenophyceae	1050	30	1020
			Dinophyta (Dinoflagellates)		Dinophyceae	2000	1800	200
	Plantae	Biliphyta	Glaucocystophyta		Glaucocystophyceae	13	–	–
			Rhodophyta		Rhodophyceae	6000	5880	120
		Viridiplantae	Chlorophyta		Chlorophyceae	2500	100	2400
					Prasinophyceae	120	100	20
					Ulvophyceae	1100	1000	100
					Charophyceae	12500	100	12400
			Bryophyta (mosses, liverworts)			22000	–	1000
			Lycopsida			1228	–	70
			Filicopsida (ferns)			8400	–	94
			Magnoliophyta (flowering plants)	Monocotyledoneae		52000	55	455
				Dicotyledoneae		188000	–	391
	Chromista	Chlorechnia	Chlorarachniophyta		Chlorarachniophyceae	3 – 4	3 – 4	0
		Euchromista	Crytophyta		Crytophyceae	200	100	100
			Haptophyta		Prymensiophyceae	500	100	400
			Heterokonta		Bacillariophyceae (diatoms)	10000	5000	5000
					Chrysophyceae	1000	800	200
					Eustigmatophyceae	12	6	6
					Fucophyceae (brown algae)	1500	1497	3
					Raphidophyceae	27	10	17
					Synurophyceae	250	–	250
					Tribophyceae (Xanthophyceae)	600	50	500
	Fungi		Ascomycontina (lichens)			13000	15	20

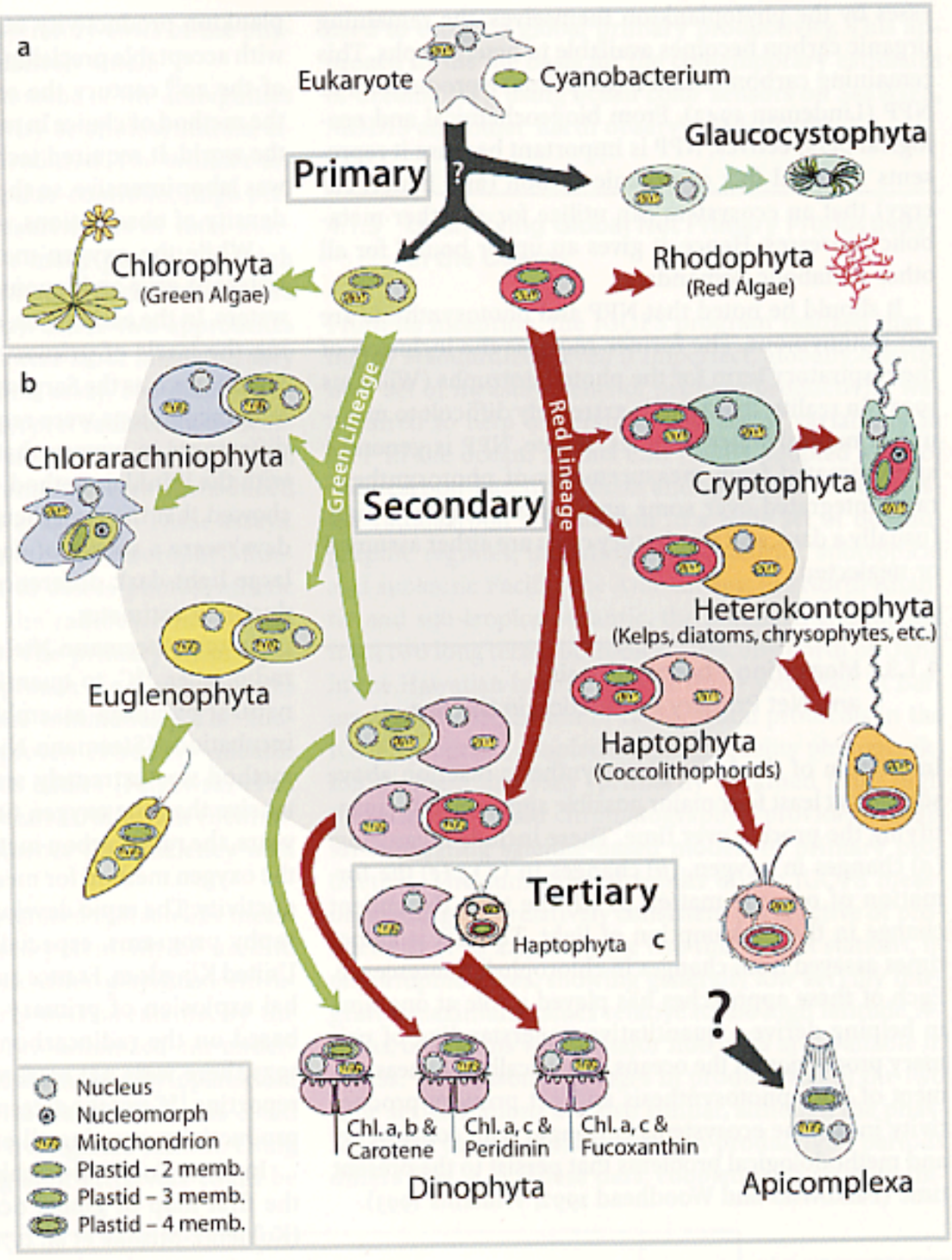

Fig. 4.1.
The basic pathway leading the evolution of eucaryotic algae. The primary symbiosis of a cyanobacterium with a apoplastidic host gave rise to both chlorophyte algae and red algae. The chlorophyte line, through secondary symbioses, gave rise to the 'green' line of algae, one division of which was the predecessor of all higher plants. Secondary symbioses in the red line with various host cells gave rise to all the chromophytes, including diatoms, cryptophytes, and haptophytes (modified from Delwiche CF (1999) Tracing the thread of plastid diversity through the tapestry of life. Am Nat 154:164–177

Jurassic period provide the source rocks for most of the petroleum reservoirs that have been exploited for the past century by humans.

4.1.2 Photosynthesis and Primary Production

The evolution of cyanobacteria was a major turning point in biogeochemistry of Earth. Prior to the appearance of these organisms, all photosynthetic organisms were anaerobic bacteria that used light to couple the reduction of carbon dioxide to the oxidation of low free energy molecules, such as H_2S or preformed organics (Blankenship 1992). Cyanobacteria developed a metabolic system that used the energy of visible light (between 400 and 700 nm) to oxidize water and simultaneously reduce CO_2 to organic carbon. Formally oxygenic photosynthesis can be summarized as:

$$CO_2 + H_2O + \text{light} \xrightarrow{\text{Chl } a} (CH_2O)_n + O_2 \qquad (4.1)$$

In Eq. 4.1, light is specified as a substrate, chlorophyll *a* is a requisite catalytic agent, and $(CH_2O)_n$ represents organic matter reduced to the level of carbohydrate.

Like all organisms, phytoplankton provide biogeochemical as well as ecological 'services'; that is they function to link metabolic sequences and properties to form a continuous, self-perpetuating network of elemental fluxes. The fundamental role of phytoplankton is the solar driven conversion of inorganic materials into organic matter via oxygenic photosynthesis. When we subtract the metabolic costs of all other metabolic proc-

esses by the phytoplankton themselves, the remaining organic carbon becomes available to heterotrophs. This remaining carbon is called net primary production, or NPP (Lindeman 1942). From biogeochemical and ecological perspectives, NPP is important because it represents the total flux of organic carbon (and hence, energy) that an ecosystem can utilize for all other metabolic processes. Hence, it gives an upper bound for all other metabolic demands.

It should be noted that NPP and photosynthesis are not synonymous. The former requires the inclusion of the respiratory term for the photoautotrophs (Williams 1993). In reality, that term is extremely difficult to measure in natural water samples. Hence, NPP is generally approximated from measurements of photosynthetic rates integrated over some appropriate length of time (usually a day), and respiratory costs are either assumed or neglected.

4.1.3 Measuring Photosynthesis and Net Primary Production in the Sea

Inspection of the basic photosynthetic reaction above suggests at least four major possible approaches to quantifying the process over time. These include measuring: (*a*) changes in oxygen, (*b*) changes in CO_2, (*c*) the formation of organic matter, or (*d*) the time dependent change in the consumption of light. The last is sometimes assayed from changes in chlorophyll fluorescence. Each of these approaches has played a role at one time in helping derive a quantitative understanding of primary production in the oceans. Historically, the measurement of both photosynthesis and net primary productivity in marine ecosystems is fraught with controversy and methodological problems that persist to the present time (Falkowski and Woodhead 1992; Williams 1993).

4.1.4 A Brief History of the Measurement of Primary Productivity in the Oceans

The first quantitative measurements of phytoplankton productivity were made early in the 20th century by Gran and his colleagues. They realized that oxygen could be used as a proxy for the synthesis of new organic material (Gran 1918). Using a chemical titration method developed by a German chemist, Clement Winkler, Gran measured the difference in oxygen concentrations in clear and opaque glass bottles suspended at various depths in the water column. The net O_2 difference in the water column provided a measure of the net synthesis of new organic matter. The oxygen light-dark method resolved the appropriate timescale (hours), measured the productivity of very small phytoplankton (nanophytoplankton) and was sensitive enough to measure plankton productivity, at least in coastal ocean waters, with acceptable precision and accuracy. For the first half of the 20th century the oxygen light-dark method was the method of choice in marine and fresh waters around the world. It required technically skilled personnel and was labor intensive, so the number of replicates and the density of observations were necessarily limited.

While the oxygen method worked well in coastal waters, it gave ambiguous results in oligotrophic ocean waters. In the early 1950s, disagreements arose concerning the levels of primary productivity in oligotrophic regions such as the Sargasso Sea. In oligotrophic regions, long incubations were required to obtain light vs. dark differences in oxygen that could be resolved manually with the Winkler method. Critics of the oxygen method showed that the long incubations (lasting three or four days) were a source of dark-bottle artifacts that led to large light-dark differences and hence very high productivity estimates.

In 1952, Steemann Nielsen introduced the use of the radiotracer, ^{14}C, to quantify the fixation of carbon by natural plankton assemblages in short-term (hours) incubations (Steemann Nielsen 1952). The radiocarbon method was extremely sensitive and far less labor intensive than the oxygen titration approach. Within five years, the radiocarbon method had completely replaced the oxygen method for measuring oceanic primary productivity. The rapid development of large new oceanography programs, especially in the United States, the United Kingdom, France and the USSR, resulted in a global explosion of primary productivity measurements based on the radiocarbon method. Between 1953 and 1973 there were 221 research papers from 16 countries reporting ^{14}C uptake determinations of oceanic primary productivity covering all of the oceans and major seas.

In 1968, Koblentz-Mishke and co-workers published the first map of global oceanic primary productivity (Koblentz-Mishke et al. 1970). The data, compiled from over 7 000 stations, were used to derive daily surface primary production estimates, from which a global ocean productivity estimate of ca. 24 Pg C yr^{-1} was made. Still widely reproduced in textbooks, the Koblentz-Mishke et al. (1970) map remains one of the most frequently cited articles dealing with global productivity.

By the mid 1970s it was realized that the radiocarbon method also had problems. Depending upon the length of incubation, the assay could be something closer to gross rather than net photosynthesis. Several attempts were made to develop alternative methods for the application of radiocarbon; these led to short-term incubations (<1 h), in which photosynthesis vs. irradiance curves were derived (Platt et al. 1975). The *P* vs. *I* (later to become *P* vs. *E*) curves were then integrated over time, with varying degrees of complexity, to derive an estimate of 'primary productivity'. The degree to which the assays actually measure NPP remains unclear; however,

it is still assumed that the respiratory costs of the phytoplankton themselves are relatively small.

In an effort to help sort out some of the ambiguities of measurements of productivity or photosynthesis, alternative approaches were introduced. The Winkler assay was resurrected with computer-controlled, high precision titration systems. Measurements of total inorganic carbon consumed were made possible by high precision potentiometric titrations with coulombmeters (Williams and Jenkinson 1982). These two approaches still required incubations and were labor intensive; they never replaced the radiocarbon assay, but did help to reveal how difficult it is to interpret radiocarbon measurements as NPP (Grande et al. 1989). In the late 1980s, fluorescence based measurements were introduced (Falkowski et al. 1986; Kolber et al. 1990). These assays, which measure the change in variable chlorophyll fluorescence, were clearly meant to assess photosynthetic activity, and not to replace the radiocarbon method (Kolber and Falkowski 1993). The primary advantages of a variable fluorescence approach are that it requires no incubation and can be done continuously. The fluorescence-based method has proven extremely valuable in mapping processes, such as eddies (Falkowski et al. 1991), fronts, or purposeful ocean fertilization (Behrenfeld et al. 1996), that can influence the efficiency with which light is used in Eq. 4.1.

In the mid-1970s it was recognized that satellite measurements of ocean color could potentially be used to derive global maps of oceanic chlorophyll concentrations (Esaias 1980). The early measurements, by the Coastal Zone Color Scanner, revolutionized our understanding of the global distributions of phytoplankton. The aerial extent and temporal scales of blooms could be seen for the first time in a truly global context. Using productivity models, the pigment retrievals could be used to estimate global primary productivity. This approach forms the basis for the contemporary estimates of oceanic NPP using ocean color sensors on SeaWiFS, MODIS and other Earth observing platforms.

4.1.5 Quantifying Global Net Primary Productivity in the Oceans

From its inception, the JGOFS program realized that a highly standardized, even if imperfect, globally distributed set of measurements of primary productivity was required to help understand sources of variability in NPP in the ocean. To this end JGOFS adopted a set of radiocarbon-based protocols and applied these to measure radiocarbon assimilation in a wide set of oceanographic regimes, including the equatorial, subtropical and subarctic Pacific, the Arabian Sea, the North Atlantic and sub-tropical Atlantic, the Southern Ocean, and from two long term subtropical sites, one north of Oahu in the Hawaiian Islands and the other southeast of Bermuda. Standardization of radiocarbon protocols in the JGOFS program, coupled with high quality phytoplankton pigment analyses (primarily obtained from high performance liquid chromatography), provides a basis for calibrating satellite-based models of primary production. The summarized results of the JGOFS measurements give a relatively consistent perspective of productivity (Fig. 4.2), with the two time series stations, in oligotrophic gyres, showing generally low aerially integrated maximum values relative to the high latitude regions, or regions where major nutrients are available in excess. The seasonal changes in productivity at the two time series stations are also similar, although the phasing of the timing of the maximum productivity periods differs (Fig. 4.3). These data, coupled with satellite im-

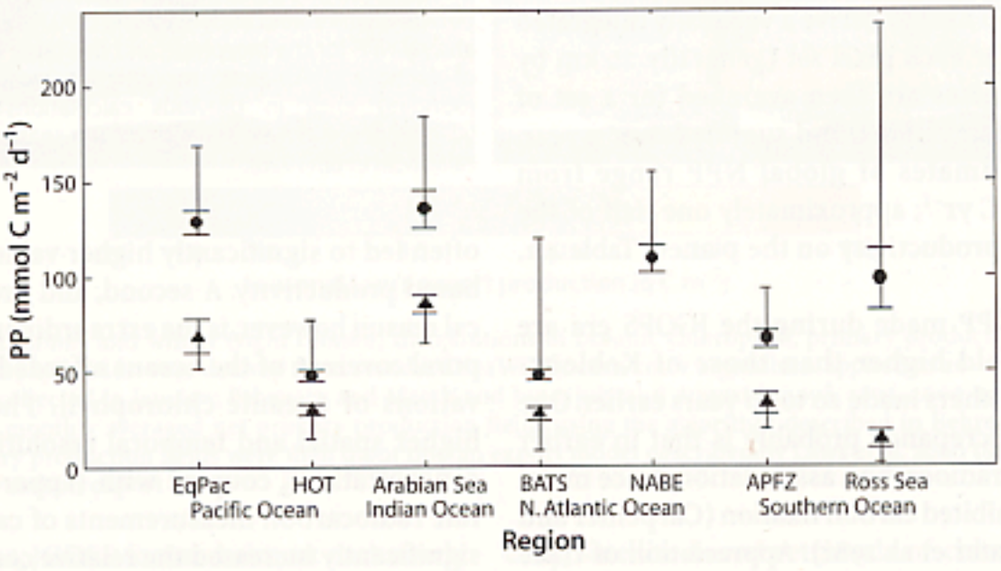

Fig. 4.2. Summary of US JGOFS primary productivity observations from five process studies and two time series studies. The *circles* and their error bars show the mean and standard error of the period of maximum productivity; *triangles* and their error bars show the mean and standard error of the period of minimum productivity. The range of the maximum (minimum) value for both periods is shown by the *thin vertical line*. Data sources are as follows: EqPac (Barber et al. 1996), HOT (Karl et al. 1996), Arabian Sea (Barber et al. 2001), BATS (Steinberg et al. 2000), NABE, APFZ, and Ross Sea (Smith et al. 2000)

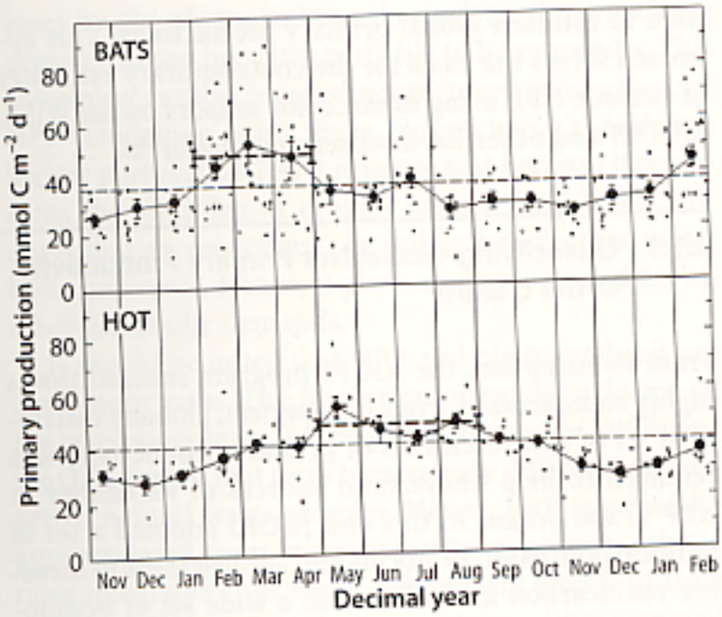

Fig. 4.3. Annual cycle of primary productivity at the two US JGOFS time series studies, the Bermuda Atlantic Time-series Study (BATS) and the Hawaii Ocean Time-series (HOT) from their inception to 2000. *Solid circles* and error bars show the monthly mean and standard error; *small, open circles* represent individual stations; *thin dashed lines* show the annual mean values (BATS = 37 ±1 mmol C m^{-2} d^{-1}; HOT = 40 ±1 mmol C m^{-2} d^{-1}); *thick dashed lines* represent the mean of values during the periods of maximum primary productivity (BATS = 48 ±3 mmol C m^{-2} d^{-1}; HOT = 48 ±2 mmol C m^{-2} d^{-1})

Table 4.2. Annual and seasonal net primary production (NPP) of the major units of the biosphere (after Field et al. 1998)

	Ocean NPP	Land NPP
Seasonal mean		
April–June	10.9	15.7
July–September	13.0	18.0
October–December	12.3	11.5
January–March	11.3	11.2
Annual mean		
Oligotrophic	11.0	
Mesotrophic	27.4	
Eutrophic	9.1	
Macrophytes	1.0	
Biogeographic regions		
Tropical rainforests		17.8
Broadleaf deciduous forests		1.5
Broadleaf and needleleaf forests		3.1
Needleleaf evergreen forests		3.1
Needleleaf deciduous forest		1.4
Savannas		16.8
Perennial grasslands		2.4
Broadleaf shrubs with bare soil		1.0
Tundra		0.8
Desert		0.5
Cultivation		8.0
Total	48.5	56.4

Source: Field et al. (1998). All values in Gt C. Ocean color data are averages from 1978 to 1983. The land vegetation index is from 1982 to 1990. Ocean NPP estimates are binned into three biogeographic categories on the basis of annual average C_{sat} for each satellite pixel, such that oligotrophic = $C_{sat} < 0.1$ mg m^{-3}, mesotrophic = $0.1 < C_{sat} < 1$ mg m^{-3}, and eutrophic = $C_{sat} > 1$ mg m^{-3} (Antoine et al. 1996). This estimate includes a 1 Gt C contribution from macroalgae (Smith 1981). Differences in ocean NPP estimates between Behrenfeld and Falkowski (1997b) and those in the global annual NPP for the biosphere and this table result from (*i*) addition of Arctic and Antarctic monthly ice masks; (*ii*) correction of a rounding error in previous calculations of pixel area; and (*iii*) changes in the designation of the seasons to correspond with Falkowski et al. (1998).

ages of ocean color, knowledge of sea surface temperature, and the incident solar irradiance, are required for model based estimates of net primary productivity for the world oceans (Antoine et al. 1996; Behrenfeld and Falkowski 1997b; Longhurst et al. 1995).

There are several models for estimating global NPP; these have been classified according to the level of integration/differentiation of specific variables (Behrenfeld and Falkowski 1997a), but fundamentally all the models are conceptually similar. The models basically use satellite-based estimates of phytoplankton chlorophyll biomass and incident solar photosynthetically available radiation (400–700 nm) to derive a vertically integrated estimate of NPP for each pixel set (generally 20 km by 20 km). The estimates are then averaged for a set of monthly global observations, and summed over a year. The resulting estimates of global NPP range from ca. 45 to ca. 57 Pg C yr^{-1}; approximately one half of the total net primary productivity on the planet (Table 4.2, Fig. 4.4).

Estimates of NPP made during the JGOFS era are more than two-fold higher than those of Koblenz-Mishke et al., and others made 20 to 30 years earlier. One reason for this discrepancy probably is that in earlier measurements of radiocarbon assimilation, trace metal contamination inhibited carbon fixation (Carpenter and Lively 1980; Fitzwater et al. 1982). Appreciation of trace metal contamination, especially in oligotrophic open ocean ecosystems, led the JGOFS programs to adopt, insofar as possible, trace metal clean techniques (e.g. Sanderson et al. 1995). When so applied, clean techniques often led to significantly higher values of radiocarbon-based productivity. A second, and probably more critical reason however, is the extraordinary spatial and temporal coverage of the oceans afforded by satellite observations of oceanic chlorophyll. The combination of higher spatial and temporal resolution of chlorophyll concentrations, coupled with (apparently) more accurate radiocarbon measurements of carbon fixation, has significantly increased the relative contribution of large areas of the open ocean to total oceanic NPP.

Somewhat ironically, despite John Ryther's conclusions in 1969 (Ryther 1969) that productivity on continental margins was disproportionate to the aerial ex-

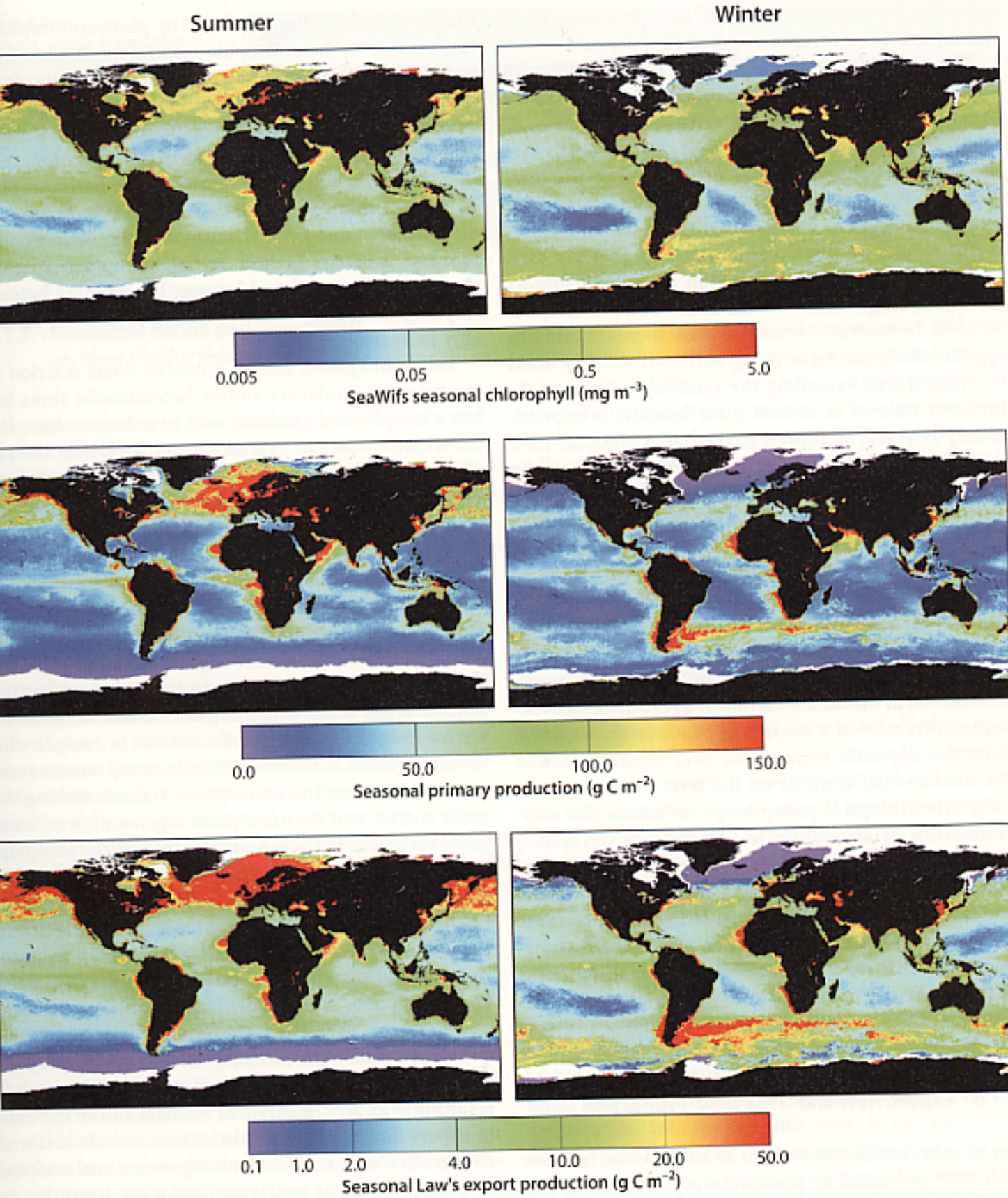

Fig. 4.4. Summer (*left column*) and winter (*right column*) distributions of oceanic chlorophyll, primary production, and export production. Oceanic chlorophyll fields were derived from standard SeaWiFS ocean color algorithms applied to 20 × 20 km pixels for the montly averaged data collected in January, February and March and June, July and August in 1998, 1999, 2000, and 2001. These maps were used to generate monthly averaged net primary production fields using the algorithm described in Behrenfeld and Falkowski (1997a). The net primary production fields were then input into an export model described by Laws et al. 2000 (see Fig. 4.6) to generate global estimates of carbon export

tent of those regions, JGOFS focused almost exclusively on the open ocean (but see the summary of assorted JGOFS studies of continental margin studies by Liu et al. 2000). The resulting extrapolated global NPP emphasizes the open ocean results. Perhaps even more ironically, satellite-based retrievals of chlorophyll on continental margins are often compromised by substances other than phytoplankton that alter the color of the water-leaving radiances. It is entirely conceivable that the estimates of NPP for the ocean provided in Table 4.2

are, in fact, low due to saturation of satellite sensors when chlorophyll concentrations exceed ca. 5 mg m^{-3}.

The results in Table 4.2 compare marine NPP with terrestrial NPP; both are based on satellite compilations of biomass in the respective ecosystems (Field et al. 1998). The striking feature of these calculations is that the contributions of the two ecosystems to the total global NPP are so similar. That is, of the ca. 100 Pg C fixed per annum as NPP on Earth, approximately 45% is due to marine phytoplankton. Given that the total carbon biomass of phytoplankton is <1 Pg, it follows that the average turnover time of the ocean biomass is <1 week. In contrast, terrestrial plant biomass contains approximately 500 Pg of 'living' carbon (including wood in living trees); extending the same logic, the average turnover time of terrestrial plant biomass is approximately 10 years. Moreover, terrestrial ecosystems have much more flexible elemental stoichiometries than marine ecosystems; C/N ratios approach 500 or more. This comparison points out a fundamental difference between the two ecosystems in the context of the global carbon cycle. In terrestrial ecosystems, carbon fixed can be 'stored' in living organic matter (e.g. forests), whereas carbon fixed by marine phytoplankton is rapidly consumed by grazers and transferred from the surface ocean to the ocean interior. In the latter reservoir, the form of 'stored' carbon is overwhelmingly inorganic. Transfer of a fraction of plankton fixed carbon from the euphotic zone to the deep ocean is one of the fundamental controls on the level of atmospheric CO_2. The biological pump helps to reduce the concentration of atmospheric CO_2 by approximately 400 ppm over what it would be if the oceans magically became a sterile reservoir of salty water (see also Watson and Orr, this volume). Thus, elucidating how this transfer occurs, what controls it, how much carbon is transferred via this mechanism, and whether the process is in steady state were primary aims of the JGOFS program.

4.1.6 Export, New and 'True New' Production

Let us now consider some fates of NPP. We can imagine that NPP produced by photoautotrophs in the upper, sunlit regions of the ocean (the euphotic zone) is consumed in the same general region by heterotrophs. In such a case, the basic photosynthetic reaction given above is simply balanced in the reverse direction due to grazing, and no organic matter leaves the ecosystem. This very simple 'balanced state' model, also referred to as the microbial-loop (e.g. Azam 1998), accounts for the fate of most of the organic matter in the oceans (and terrestrial ecosystems as well). In marine ecology, this process is sometimes called 'regenerated production'; that is organic matter produced by photoautotrophs is regenerated by heterotrophic respiration. It should be noted here that with the passage of organic matter from one level of a marine food chain to the next (e.g., from primary producer to heterotrophic consumer), a metabolic 'tax' must be paid in the form of respiration, such that the net metabolic potential of the heterotrophic biomass is always less than that of the primary producers. This does not, a priori, mean that photoautotrophic biomass is always greater, as heterotrophs may grow slowly and accumulate biomass; however, as heterotrophs grow faster, their respiratory rates must invariably increase.

Let us imagine a second scenario. Some fraction of the primary producers and/or heterotrophs sinks below a key physical gradient, such as a thermocline, and for whatever reason cannot ascend back into the euphotic zone. If the water column is very deep, sinking organic matter will most likely be consumed by heterotrophic microbes in the ocean interior. This sinking flux of organic matter is said to be 'exported' from the surface waters, and the fraction of NPP that meets such a fate is called the export production or EP. Export production is of biogeochemical interest because, in the steady state, the oxidation of organic matter in the ocean interior, rather than in the surface waters, enriches the interior of the ocean with inorganic carbon. Because the waters from the ocean interior are not in contact with the atmosphere, the enrichment effectively removes carbon dioxide from the atmosphere. Indeed, sinking organic matter and its subsequent regeneration to inorganic carbon in the ocean interior effectively 'pump up' the inorganic carbon content in the ocean to values that are significantly higher than predicted from equilibration with the atmosphere. This process, where NPP from the ocean surface sinks and is regenerated in the interior is called the biological pump. The intensity of the biological pump is especially important when the food web has been perturbed. Under such conditions (the 'perturbed state'), the mechanisms controlling production and consumption of organic matter are decoupled, resulting in an accumulation of biomass and an increase in export flux. Types of perturbations include seasonal changes in irradiance, wind mixing events, and seasonal or pulsed inputs of nutrients (including iron) due to changes in nutricline depth, upwelling and atmospheric events.

Criteria, which distinguish balanced and perturbed states, are summarized in Table 4.3.

The argument is that the balanced microbial loop is always present, while during non-steady state conditions the perturbed state with larger plankton is added on. A major challenge in the JGOFS synthesis has been to describe these two states mathematically with simple numerical models.

Table 4.3.
Criteria, which distinguish balanced and perturbed states

Criteria	'Balanced' state	'Perturbed' state
Temporal forcing	Constant	Episodic
Vertical stratification	High	Low
Phytoplankton	Small – nano/pico	Large – diatom/coccolith
Dominant grazers	Microzooplankton/protists	Mesozooplankton
Food web function	Coupled	Uncoupled
Plankton specific rates	Growth = mortality	Growth > mortality then growth < mortality

4.1.7 Elemental Ratios and Constraints on New Production

All organisms consist of six major 'light' elements, and approximately 54 trace elements (Williams 1981). Let us consider, for the moment, only the former; these are H, C, N, O, P, and S. The amount of S required to satisfy the demands of most organisms is relatively small, and we can ignore it in the following discussion. In 1934, Redfield pointed out that the chemistry of four major elements in the ocean, namely C, N, P, and O, was strongly affected by biological processes (Redfield 1934). Absent biological N_2 fixation on land or in the ocean, there would be virtually no fixed nitrogen in the oceans. In the ocean interior, the ratio of fixed inorganic N to PO_4 in the dissolved phase is remarkably close to the ratios of the two elements in living plankton. Hence, it seemed reasonable to assume that the ratio of the two elements in the dissolved phase was the result of the sinking, grazing and or autocatalyzed cell death, and subsequent remineralization of the elements in the plankton. Further, as carbon and nitrogen in the living organisms is largely reduced, while remineralized forms are virtually all oxidized, the remineralization of organic matter was coupled to the depletion of oxygen. The relationship could be expressed stoichiometrically as:

$$[106(CH_2O)16NH_3 1PO_4^{3-}] + 138O_2 \longrightarrow 106CO_2 + 122H_2O + 16NO_3^- + PO_4^{2-} + 16H^+ \quad (4.2)$$

Hidden within this balanced chemical formulation are biochemical oxidation-reduction reactions and hydrolytic processes, some of which are contained within specific functional groups of organisms. In the oxidation of organic matter, there is some ambiguity about the stoichiometry of O_2/P. Assuming that the mean oxidation level of organic carbon is that of carbohydrate (as is the case in Eq. 4.1), then the oxidation of that carbon is equimolar with O. On the other hand, some organic matter may be more or less reduced than carbohydrate, and therefore require more or less O for oxidation. Note also that the oxidation of NH_3 to NO_3^- requires 4 atoms of O, and leads to the formation of 1 H_2O and 1 H^+. Let us examine how these sets of metabolic sequences emerged in the ocean on evolutionary and ecological scales. Effectively, Eq. 4.2 is an expanded version of Eq. 4.1, but written in reverse, to emphasize the remineralization of organic matter. When the reactions primarily occur at depth, Eq. 4.2 is driven to the right, while when the reactions primarily occur in the euphotic zone they are driven to the left. Note that in addition to reducing CO_2 to organic matter, formation of organic matter by photoautotrophs requires reduction of nitrate to ammonia. These two forms of nitrogen are critically important in helping to quantify new and export production. Moreover, JGOFS syntheses studies have shown that the oxidation state of plankton carbon is more reduced than carbohydrate; thus more oxygen is required to combust this organic matter during respiration than predicted by Eq. 4.2 (Li and Peng 2002). Hedges et al. (2002) used NMR analyses to estimate that average plankton composition is best represented as 65% protein, 19% lipid and 16% carbohydrate. Complete oxidation of 106 moles of C in this average organism requires 154 rather than 138 moles of O_2.

4.1.8 New Production, Export Production, and Net Community Production

In our previous thought experiment regarding regenerated production, assimilation and metabolism of NPP by heterotrophs leads primarily to excretion of ammonium and other reduced forms of nitrogen (urea and amino acids) into the euphotic zone. In contrast, when waters from the ocean interior are mixed into the euphotic zone, nitrate is the primary form of nitrogen that becomes available. Realizing that the form of nitrogen could be used to identify its source, Dugdale and Goering (1967) developed the concepts of 'new' and 'regenerated' production. They defined new production to be "all primary production associated with newly available nitrogen, for example NO_3-N and N_2-N". In a confined system such as the mixed layer of the ocean, new production is therefore the portion of primary production supported by exogenous nitrogen inputs (Williams et al. 1989). The exogenous nitrogen could include the sources

explicitly noted by Dugdale and Goering (1967), but could also include atmospheric inputs of nitrate or ammonium, and in coastal and shelf regions might also include riverine inputs.

The fraction of total production accounted for by new production is referred to as the *f*-ratio, which can be calculated either in terms of new and regenerated nitrogen uptake or in terms of carbon uptake. Note that in Eq. 4.3 nitrogen fixation is not specified in the numerator of the new production equation. This omission is related to methodological limitations on deriving N_2 fixation rates robustly. In high latitude or upwelling regions, where the upward NO_3 flux is high, N_2 fixation is negligible, however, in subtropical gyres, the fraction of new production supported by N_2 fixation may be significant – but remains poorly constrained.

$$f = \frac{\text{new production}}{\text{new} + \text{regenerated production}} \equiv \frac{NO_3^- \text{ uptake}}{(NO_3^- + NH_4^+ + NO_2^- + \text{DON})\,\text{uptake}} \equiv \frac{^{15}NO_3^- \text{ uptake}}{^{14}CO_2 \text{ uptake}} \times \left(\frac{C}{N}\right)_{\text{plankton}} \quad (4.3)$$

Related to the concept of new production is the term export production, first coined by Berger et al. (1987). Export production refers to the transfer of biogenic material from one region of the ocean to another. Export production is frequently used to describe transfers from the surface waters to the interior of the ocean by processes such as particle sinking, advection or diffusion of dissolved organic matter (DOM), and vertical migration of zooplankton. However, in zones such as the equatorial upwelling system, a substantial amount of export may occur through lateral advection (Landry et al. 1997). "Export production from the primary system, the photosynthetic zone, or on time scales longer than a year will be equal to new production, although they may, or in most cases will, be separated both in space and time" (Williams et al. 1989). The ratio of export production to primary production is sometimes referred to as the *e*-ratio (Murray et al. 1989)

$$e = \frac{\text{export production}}{\text{primary production}} \quad (4.4)$$

Net community production is the difference between net primary production and heterotrophic respiration. It is an old concept that is operationally defined from net changes in oxygen or biomass concentrations over an appropriate period of time.

In a strictly steady state system, new production, export production, and net community production should be equal. However, the ocean is a dynamic system. On a time frame of days or weeks, biomass in the mixed layer may change dramatically. These changes can occur as a result of imbalances in the rates of biological processes or when physical mechanisms transfer biomass across spatial gradients (McGillicuddy et al. 1995). Because new production, export production, and net community production are measured by fundamentally different methods, there is no reason that these measurements should yield identical results unless the system under study is truly in steady state or unless the measurements are averaged over appropriate scales of time and space. All three approaches were used in JGOFS studies but unfortunately never all at the same time. Given this fact, a measurement that targets new production should not be reported as a measure of export production or net community production, and a measure of net community production should not be reported as a measure of new production or export production.

4.1.9 Measurement of New Production

Throughout the mid 1970s several research groups around the world adopted the measurement of assimilation of $^{15}N\text{-}NO_3$ to estimate new production. This approach, originally introduced by Dugdale and Goering (1967), remains conceptually unchanged. ^{15}N labeled NO_3 that is assimilated and converted to PON by phytoplankton over a known incubation period is filtered and analyzed by mass spectrometry or optical emission spectrometry. Incubation rates are kept short to minimize ^{15}N recycling (e.g., McCarthy et al. 1996). Complementary uptake rates of ammonium and urea are also occasionally measured for regenerated production (e.g., Varela and Harrison 1999; Bury et al. 1995). Failure to correct for release of $DO^{15}N$ from cells during incubations may result in underestimation of new production rates (Bronk et al. 1994). The method is difficult to apply when the ambient concentrations of NO_3 are low, such as in the subtropical gyres, because addition of labeled NO_3 frequently violates the concept of a tracer. Due to analytical limitations, for many years ^{15}N-labeled substrates were never added at concentrations less than 30 nM (Glibert and McCarthy 1984). In recent years analytical improvements have allowed investigators to add spikes as small as 3 nM (McCarthy et al. 1999), but even such small additions may amount to significant perturbations at oligotrophic oceanographic sites. At Station ALOHA, off the north coast of Oahu (22.75° N, 158° W), for example, nitrate concentrations in the upper 50 m of the water column average 2 nM, and 95% of the concentrations are less than 7 nM. Hence despite recent improvements in sensitivity, the ^{15}N technique still does not lend itself to truly oligotrophic conditions. Most applications have been in the vast high-nitrate, low-chlorophyll (HNLC) regions – where incomplete utilization of new nutrients leaves surface CO_2 partial pressures

elevated with respect to the atmosphere (Chavez and Barber 1987; Dugdale et al. 1992; Kurz and Maier-Reimer 1993). The equatorial Pacific upwelling zone has been one of the most well studied HNLC regions on the globe with respect to ^{15}N-new production (Aufdenkampe et al. 2001). In the JGOFS program, ^{15}N based estimates were broadly applied in all field campaigns, with the exception of the North Atlantic Bloom Experiment (NABE) and the subtropical ocean time series.

4.1.10 Measurement of Net Community Production

Many estimates of net community production are based on changes in oxygen concentration, either in incubation bottles or in situ. In the latter case, corrections must be made for air/sea gas exchange flux. Empirically, in the euphotic zone, organic matter export production and oxygen export are stoichiometrically related and should be equivalent over an annual cycle. The method of estimating net production from O_2 gas exchange fluxes found wide application before and during JGOFS, especially in the subtropical north Atlantic near Bermuda (Jenkins and Goldman 1985; Spitzer and Jenkins 1989); the subarctic Pacific at Station P (Emerson 1987; Emerson et al. 1991) and the subtropical north Pacific at Station ALOHA (Emerson et al. 1995; Emerson et al. 1997). The method hinges on determining the net biologically produced O_2 in the euphotic zone and calculating its flux across the air-sea interface with gas exchange models. The instantaneous rates will reflect average rates during the prior 2–3 weeks, because the residence time of biologically produced O_2 with respect to gas exchange is about that long. The difficult aspects are separating the biologically produced O_2 from air-injection by bubbles and determining the wind speed dependent gas exchange piston velocity (Liss and Merlivat 1986; Wanninkhof 1992). A high-resolution time series is needed to calculate the time rate of change. Estimates of net production by this approach are significantly higher than those derived from satellite color images (e.g. Laws et al. 2000), possibly because surface water chlorophyll is a poor predictor of integrated productivity in many regions (Letelier et al. 1996).

The accuracy of incubation methods is limited by the requirement to keep incubations short enough to avoid bottle confinement artifacts and by the precision of the oxygen measurements. In recent years considerable improvements have been made in analytical methodology (Williams 1993). The ultimate precision of O_2 methods is probably 0.1–0.2 μmole $O_2\ l^{-1}$ (Laws et al. 2002). For comparative purposes, this is approximately the amount of net community production at Station ALOHA in one day (Laws et al. 2000). Incubations are typically no longer than 24 h. Regardless of the duration of the incubation, estimates of net community production based on bottle incubations may be biased if the biological community in the bottles is somehow not representative of its in situ counterpart. Bender et al. (1999), for example, noted that in vitro estimates of net community production were 4–20 times greater than estimates from drifting sediment trap and tracer transport studies in the Pacific equatorial upwelling system. They postulated that this difference reflected an anomalous accumulation of POC in incubation bottles due to the exclusion of grazers.

A variation on oxygen-based calculations is to use the observed distributions of oxygen in the deep ocean, below the euphotic zone, to calculate export production. Assuming that the distribution is at steady state, the O_2 distribution reflects the balance between in situ consumption of oxygen by respiration and physical transport of O_2 from high latitudes (ventilation) (Riley 1951; Jenkins 1982). The oxygen utilization rate (OUR) is calculated from the decreasing O_2 content (apparent oxygen utilisation or AOU) as a function of age (determined using $^3He/^3H$ and/or chlorofluorocarbon dating; e.g., Doney et al. 1992). This method obviously gives average values over large temporal and spatial scales. By integrating the OUR over a range of density layers below the euphotic zone, areal respiration rates can be calculated. Equating this rate to export production implicitly assumes that the respiration rate below the specified isopycnal surface equals the export of organic matter from the euphotic zone. The respiration rate so calculated is in fact a lower bound on the export flux from the euphotic zone for several reasons. First, there is some accumulation of organic matter in the sediments. Second, no isopycnal surface coincides with the base of the euphotic zone, i.e., there will be some consumption of organic matter below the base of the euphotic zone and the chosen isopycnal surface. Nevertheless, it is reasonable to assume that the consumption of organic matter below an appropriately chosen isopycnal surface is closely correlated with export production from the euphotic zone, and there is evidence that with a suitable time series, decadal scale variability can be detected (Min et al. 2000; Emerson et al. 2002). While this approach was developed prior to JGOFS, the new combined data sets of JGOFS and WOCE have provided excellent opportunities to apply it to different ocean basins (e.g. in the South Atlantic, Warner and Weiss 1992; and North Pacific, Warner et al. 1996).

4.1.11 Measurement of Export Production

Most estimates of export production are in fact estimates of the flux of sinking particulate organic matter. Such calculations need to be augmented to account for other mechanisms of export, including advection of DOM and transport by vertical migrators. Prior to JGOFS free-floating particle interceptor traps (PITS) were the main approach for measuring particle export flux (Martin et al. 1987).

Because of its strong partitioning towards particles, thorium 234 has been widely used as a particle 'scavenging' tracer to determine particle residence times, transformation rates, and sinking rates in the ocean (Santschi et al. 1979; Honeyman and Santschi 1989; Clegg and Whitfield 1990; Dunne et al. 1997). ^{234}Th has a half-life of 24.1 days, which makes it suitable for study of upper ocean processes. The link between ^{234}Th removal from the water and biological processes was demonstrated by Coale and Bruland (1985, 1987) and Bruland and Coale (1986). Based on this evidence, Eppley (1989) suggested that ^{234}Th be used as a tracer for export flux if the particulate Th residence time could be applied to particulate carbon. However, the residence time approach is not used because ^{234}Th and carbon do not always have the same residence times (Murray et al. 1989).

The ^{234}Th method for determining export flux was developed initially by Buesseler et al. (1992) during the JGOFS NABE Study. The basic approach is to use the steady state mass balance for ^{234}Th in the euphotic zone to calculate the export flux of ^{234}Th (P):

$$\partial^{234}\mathrm{Th}/\partial t = (^{238}\mathrm{U} - {}^{234}\mathrm{Th})\lambda^{234}\mathrm{Th} - P + V \qquad (4.5)$$

The method depends on there being a statistically significant deficit of ^{234}Th, a condition that makes application of the method problematic at oligotrophic sites such as BATS (Buesseler et al. 1994) and HOT (Benetiz-Nelson et al. 2001). Various studies have evaluated the importance of the steady state assumption (e.g. Buesseler et al. 1992) and advective and diffusive transport terms (V) in the mass balance (e.g. Buesseler et al. 1995; Bacon et al. 1996; Murray et al. 1996; Dunne and Murray 1999). In general the time rate of change is not significant (e.g. even in the North Atlantic Bloom Experiment; Buesseler et al. 1992), and the transport terms have only been essential in the equatorial and subarctic Pacific and some coastal regions like the Ross Sea (Cochran et al. 2000). The export flux of Th can be converted to carbon (or other elements) knowing the ratio of carbon to ^{234}Th in sinking particles. The relevant equation is:

$$\text{Model POC Flux} = (\text{Model } {}^{234}\text{Th Flux})\,(\mathrm{C}/\mathrm{Th}_{\text{sinking particles}}) \qquad (4.6)$$

One of the stumbling blocks has been the fact that different sampling approaches sometimes lead to different C/Th ratios in sinking particles. In EqPac, for example, the C/Th of trap samples was consistently greater than in situ large volume pump samples. In a study conducted at HOT there was much better agreement (Benetiz-Nelson et al. 2001). The ^{234}Th method has been widely applied in all JGOFS studies.

An alternative to the ^{234}Th method is to quantify the rate of accumulation of organic matter in drifting sediment traps. The most commonly used designs of drifting sediment traps used in JGOFS studies are cylinders (e.g. the cylindrical Particle Interceptor Traps (PITs) of Knauer et al. 1979; Martin et al. 1987) and cones (e.g. Honjo and Doherty 1988; Peterson et al. 1993). The most recent development is a neutrally buoyant trap that should reduce shear at the mouth of the trap and improve trap efficiency due to reduction of hydrodynamic bias (Buesseler et al. 2000).

The question of trap accuracy was addressed by Buesseler (1991) who compared ^{234}Th fluxes measured with traps with ^{234}Th fluxes calculated from a scavenging model. He showed that shallow sediment traps typically display either positive or negative collection biases. Most likely this variability in trap efficiency is due to hydrodynamic effects (e.g. Gust et al. 1992) but vertically migrating organisms may also play a role. One approach for eliminating this bias is to compare the ^{234}Th content in trap samples with the modeled flux from the overlying water column. The relevant equation is:

$$\text{Model POC Flux} = (\text{Trap POC Flux}) \times (\text{model } {}^{234}\text{Th flux}/\text{trap } {}^{234}\text{Th flux}) \qquad (4.7)$$

In this way ^{234}Th can be used as a correction factor for other constituents. However, this approach will only be valid if ^{234}Th and the other components have the same distribution among particles. Note that Eqs. 4.6 and 4.7 are the same when traps are used to collect sinking particles, which means that the model ^{234}Th flux can be viewed alternatively as a tool to correct trap fluxes for hydrodynamic bias or as a primary tool for determining export fluxes if the C/^{234}Th ratio is known from trap samples.

In one study from the equatorial Pacific, Murray et al. (1996) showed a strong correlation between organic carbon and ^{234}Th in PIT type trap samples, supporting the case that ^{234}Th can be used as a tracer for carbon. They then used the comparison of trap and calculated ^{234}Th fluxes as a correction factor for hydrodynamic biases for carbon. Hernes et al. (2001) used the same approach to 'calibrate' traps of a very different design (conical with a large diameter, Peterson et al. 1993), which were deployed at the same times and stations. In the original data the conical POC fluxes were much smaller than the PIT fluxes, in accord with earlier observations reported by Laws et al. (1989). The ^{234}Th correction factors suggest that the conical traps undercollected ^{234}Th while the PIT traps overcollected. When these correction factors are applied to POC, the resulting ^{234}Th corrected POC fluxes are in excellent agreement (Table 4.4). The POC fluxes are about three times larger in the spring (Survey I) than fall (Survey II) and are about 50–70% of the ^{15}N measured new production, which was measured at the same time. The excellent agreement between the ^{234}Th corrected carbon fluxes for these two traps of very different designs verifies the success of this approach.

Table 4.4. Illustration of the ^{234}Th correction approach using conical (105 m) (Hernes et al. 2001) and PIT (100 m) (Murray et al. 1996) data from EqPac, 12° N–12° S at 140° W. Survey I was spring 1992 and Survey II was fall 1992. New production data are from McCarthy et al. (1996). All fluxes given as mmol C m^{-2} d^{-1}

	POC flux		Th correction factor		Th corrected POC flux		New production
	Conical	PIT	Conical	PIT	Conical	PIT	
Survey I	2.2 ±1.5	12.2 ±9.3	1.1 ±0.7	0.3 ±0.2	2.3 ±1.4	2.6 ±0.8	5.7 ±2.2
Survey II	2.4 ±1.3	15.1 ±9.9	4.6 ±1.5	0.6 ±0.2	7.4 ±4.2	8.7 ±5.3	12.4 ±9.2

4.1.12 Summary of Methods

The various methods used to estimate new production, export production, and net community production are clearly not intended to measure the rate of the same process. Although the three rates are equal in a steady state system or when averaged over large enough time and space scales, there is otherwise no a priori reason why the rates should be identical. Comparisons of rates estimated by the various methods should be made with a full awareness of the theoretical differences and practical limitations of the measurements.

In practice by far the most commonly used direct measure of new production is the uptake of nitrate. Traditionally this rate has been estimated using ^{15}N tracer techniques, but with the development of chemiluminescent methods for nitrate analysis (Garside 1985), nitrate uptake can be estimated at low substrate concentrations from the rate of change of nitrate concentration (Allen et al. 1996). Recent studies have suggested that nitrogen fixation may contribute substantially to new production in some parts of the ocean (Karl et al. 1997; Zehr et al. 2001), and nitrification between the 1% and 0.1% light level may confound the interpretation of nitrate as 'newly available nitrogen' (Dore and Karl 1996). Direct estimates of export production are virtually all based on measurements of the downward flux of sinking particles. Very few studies have attempted to directly document the contribution of other mechanisms such as vertical migration (Longhurst et al. 1990; Steinberg et al. 2000) and diapycnal mixing of DOM. The former flux has been estimated to be as much as 20–30% of the sinking POC flux at some locations (Steinberg et al. 2000). These considerations suggest that nitrate uptake and the downward flux of particles are lower bounds on new production and export production if the system in question is defined to be the water column above the 1% light level, i.e., the traditional definition of the euphotic zone. The extent of the bias has often been inferred from estimates of net community production, but comparisons require conversion from an oxygen to a nitrogen or carbon-based budget and implicitly assume that new production, export production, and net community production are equal. Conversions between oxygen, carbon, and nitrogen are usually made assuming Redfield stoichiometry, but this may be a poor assumption in some cases (Sambrotto et al. 1993; Daly et al. 1999). And there is certainly no reason to believe that new production, export production, and net community production are equal when measurements are averaged over different time scales or over equal but short time intervals.

One of the more troubling aspects of all these calculations is the definition of the dimensions of the system being studied. New production and export production are frequently estimated with respect to the euphotic zone, which is conventionally defined to be the water column above the 1% light level. However, this definition is arbitrary. Some photosynthesis certainly occurs between the 1% and 0.1% light level (Hayward and Venrick 1982). During EqPac about 10% of primary production and 20% of new production occurred between the 1% and 0.1% light levels (Murray et al. 1996). Dore and Karl (1996) have reported evidence of nitrification in the same region of the water column. The distinction between new and regenerated production becomes even more confused if one takes physical processes into account. When the mixed layer extends below the depth of the euphotic zone, nutrients regenerated below the depth of the euphotic zone can easily be recycled back into the euphotic zone. This is an important consideration in temperate and high latitudes, where the mixed layer in the winter may be hundreds of meters deep. On an annual basis, recycling of nutrients certainly occurs well below the depth of the euphotic zone in many parts of the ocean. Estimates of net community production based on in situ changes in oxygen concentrations focus on the mixed layer, not the euphotic zone. Comparisons of new production, export production, and net community production will be compromised until a consensus is reached on the vertical dimensions of the system with respect to which these rates are to be calculated.

Subject to these caveats, Table 4.5 summarizes estimates of new production, export production, and net community production based on studies covering a wide range of oceanographic conditions. Much of the work was carried out during the JGOFS program, but results from studies in the Peru upwelling system, at Station P in the subarctic Pacific, and in a Greenland polynya are also included. In most cases the values are estimates of

Table 4.5. Field data and methods of analysis

Area	Z_m	Temperature (°C)	Export or new production (mg N m^{-2} d^{-1})	Method of calculation	Total production (mg N m^{-2} d^{-1})	Method of calculation
BATS	140	21	7.8	Carbon balance assuming Redfield C:N (Michaels et al. 1994)	82	^{14}C production from Michaels et al. (1994) divided by Redfield C:N
HOT	150	25	12.2	Average of O_2 and C mass balances, assuming Redfield ratios (Emerson et al. 1997)	83	^{14}C production from Karl et al. (1996) divided by Redfield C:N
NABE	35	12.5	98	Total production times mean *f* ratio of Bender et al. (1992) and McGillicuddy et al. (1995)	194	^{14}C production from Buesseler et al. (1992) divided by Redfield C:N
EqPac-normal	120	24	32.1	Total production times *f* ratio from McCarthy et al. (1996) based on ^{15}N uptake ratios	260	^{14}C production from Barber et al. (1996) divided by Redfield C:N
EqPac-El Niño	120	27	12.3	Total production times *f* ratio of McCarty et al. (1996) based on ^{15}N uptake ratios	169	^{14}C production from Barber et al. (1996) divided by Redfield C:N
Arabian Sea	65	25	29.2	Total production times *f* ratio of McCarthy et al. (1999) based on ^{15}N uptake ratios	195	^{14}C production from Barber et al. (2001) divided by Redfield C:N
Ross Sea	40	0	165	Total production times *f* ratio of Asper and Smith (1999) from ^{15}N uptake ratios	243	^{14}C production from Asper and Smith (1999) divided by Redfield C:N
Subarctic Pacific-Station P	120	6	40.3	Mean nitrate uptake/utilization from Sambrotto and Lorenzen (1987), Emerson et al. (1993), and Wong et al. (1998)	95	Mean ^{14}C production from Welschmeyer et al. (1991) and Wong et al. (1995) divided by Redfield C:N
Peru-normal	25.5	16.8	339	Nitrate uptake using ^{15}N tracer (Wilkerson et al. 1987)	806	^{14}C production from Wilkerson et al. (1987) divided by Redfield C:N
Peru-El Niño	17.8	17.4	256	Nitrate uptake using ^{15}N tracer (Wilkerson et al. 1987)	867	^{14}C production from Wilkerson et al. (1987) divided by Redfield C:N
Greenland polynya	50	0	35.6	Nitrate uptake using ^{15}N tracer (Smith 1995; Smith et al. 1997)	63.2	^{15}N uptake from Smith (1995) and Smith et al. (1997)

new production based on ^{15}N techniques, but in the absence of ^{15}N results estimates are based on one or a combination of other methods. In all cases the results are based on multiple measurements, and at the time series stations (HOT and BATS) some of the numbers are averages of monthly observations made over a period of several years.

4.2 Synthesis

Following the seminal paper by Eppley and Peterson (1979), it has generally been assumed that a more-or-less hyperbolic relationship existed between primary production and the *f*-ratio, which Eppley and Peterson (1979) defined to be the ratio of new production to primary production. Eppley et al. (1983) suggested that new production and particle sinking are coupled over long time scales and that the residence time of POC in the euphotic zone ranges from 3 to >100 days from shelf to gyre regions. This basic notion was further supported by data from Harrison et al. (1987) that suggested that the *f*-ratio increased hyperbolically with nitrate (i.e., 'new' nitrogen).

The relationship between the ratio of new or export production to primary production, based on the data in Table 4.5, is shown in Fig. 4.5b. The latter ratio is designated the *ef* ratio to indicate that the numerators are in some cases based on estimates of new production and in other cases on export production. There is no significant correlation between primary production and the *ef* ratio in this data set. Similar results have been reported in experimental results summarized by other investigators (e.g., Sarmiento and Armstrong 1997). However, there is excellent agreement (Fig. 4.5a) between the observed *ef* ratios and the *ef* ratios predicted by a model reported by Laws et al. (2000). The model accounts for 97% of the variance in the observed data. The model assumes that primary production is partitioned through both large and small phytoplankton and that the food web adjusts to changes in the rate of exogenous nutrient inputs in a way that maximizes stability,

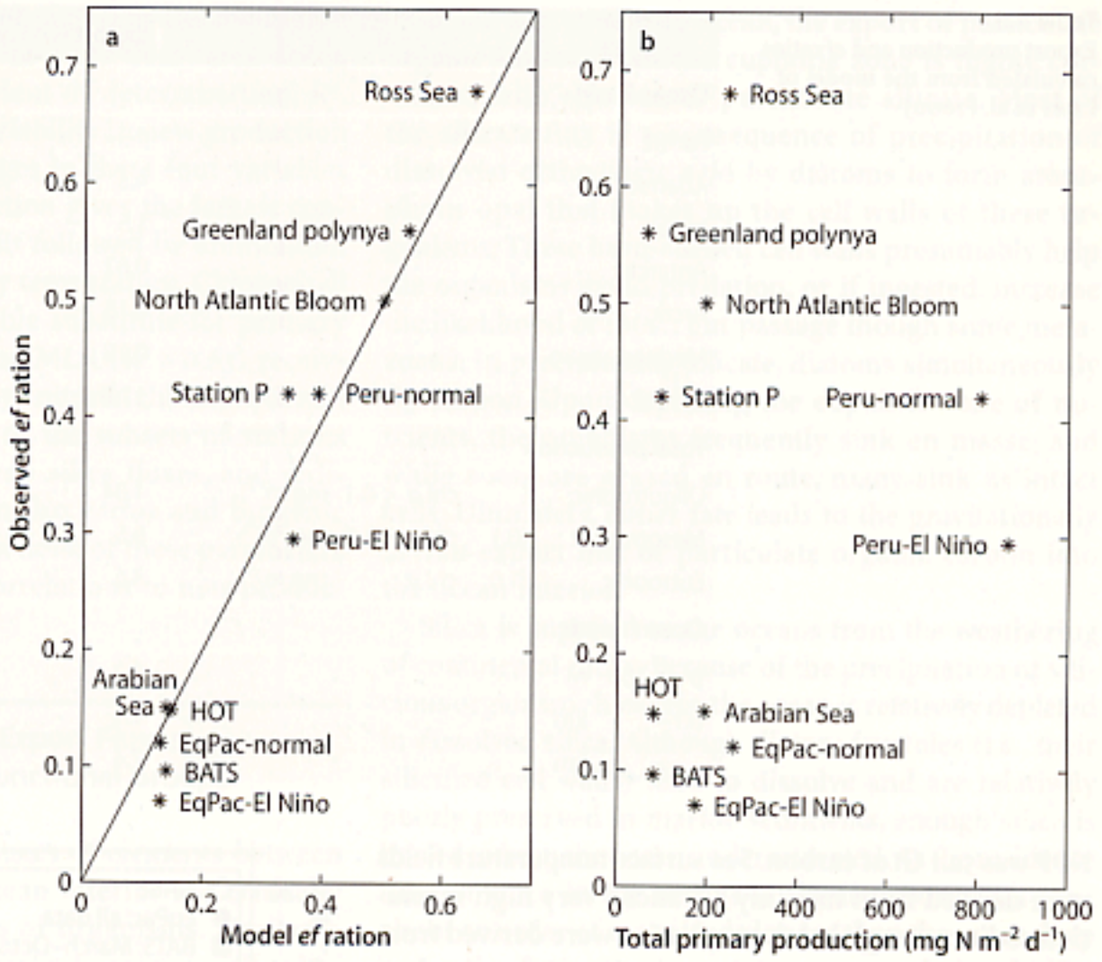

Fig. 4.5.
a Model export ratios vs. observed export ratios at sites summarized by Laws et al. (2000). The *straight line* is the 1:1 line. **b** Total primary production vs. observed export ratios at the same locations (reproduced with permission from Laws et al. (2000) Global Biogeochem Cy 14(4):1231–1246, © 2000 by the American Geophysical Union)

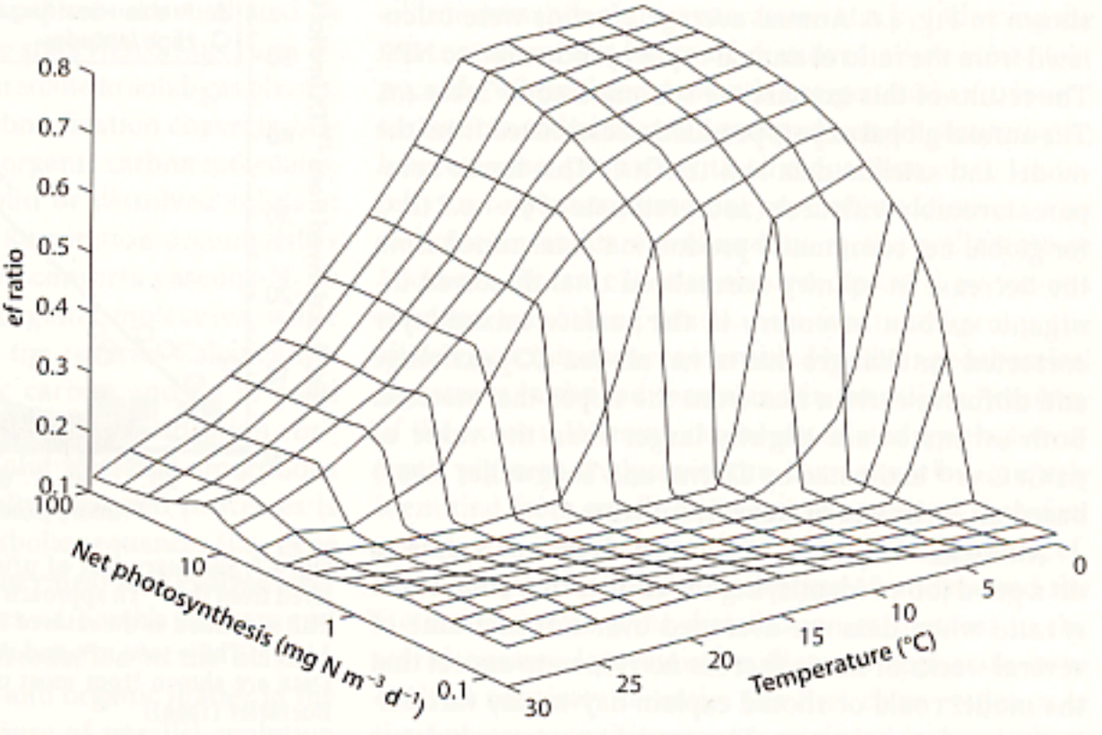

Fig. 4.6.
Calculated export ratios as a function of temperature and net photosynthetic rate (reproduced with permission from Laws et al. (2000) Global Biogeochem Cy 14(4):1231–1246 © 2000 by the American Geophysical Union)

i.e., how rapidly the system returns to steady state following a perturbation. The model predicts that the *ef* ratio will be a function of two variables, primary production per unit volume and temperature. The response curve is shown in Fig. 4.6. At a fixed temperature, the behavior of the response curve is similar to that postulated by Eppley and Peterson (1979). The *ef* ratio is low at low rates of primary production, rises steeply at intermediate rates of primary production, and plateaus at high rates of primary production. The height of the plateau is greatest at low temperatures, and the region of rapid rise shifts to progressively higher rates of primary production as temperature rises.

In order to examine the implications of their model with respect to global export production, Laws et al. (2000) calculated net primary production with the vertically generalized production model of Behrenfeld and Falkowski (1997a,b) using SeaWiFS ocean color data for the 12-month period beginning October 1997 and NASA's derived global chlorophyll fields. The calculated global

Table 4.6.
Export production and *ef* ratios calculated from the model of Laws et al. (2000)

	Export (Gt C yr^{-1})	*ef*
Ocean basin		
Pacific	4.3	0.19
Atlantic	4.3	0.25
Indian	1.5	0.15
Antarctic	0.62	0.28
Arctic	0.15	0.56
Mediterranean	0.19	0.24
Global	11.1	0.21
Total production		
Oligotrophic (chl *a* < 0.1 mg m^{-3})	1.04	0.15
Mesotrophic (0.1 chl *a* < 1.0 mg m^{-3})	6.5	0.18
Eutrophic (1.0 chl *a* mg m^{-3})	3.6	0.36
Ocean depth		
0 – 100 m	2.2	0.31
0.1 – 1 km	1.4	0.33
> 1 km	7.4	0.18

NPP was 52.1 Gt of carbon. Sea surface temperature fields were derived from monthly advanced very high resolution radiometer global data. *ef* ratios were derived from a look-up table generated from the interpolated values shown in Fig. 4.6. Annual average *ef* ratios were calculated from the ratio of annual export production to NPP. The results of this exercise are summarized in Table 4.6. The annual global export production estimated from the model and satellite data was 11.1 Gt C. This figure compares favorably with Lee's (2001) estimate of 9.1–10.8 Gt C for global net community production determined from the decrease in salinity-normalized total dissolved inorganic carbon inventory in the surface mixed layer corrected for changes due to net air-sea CO_2 exchange and diffusive carbon flux from the upper thermocline. Both estimates are slightly larger than the value of 7.2 Gt C yr^{-1} estimated by Chavez and Toggweiler (1995) based on estimates of upwelled nitrate.

Although the model of Laws et al. (2000) seems to do a good job of identifying the factors that control the *ef* ratio when data are averaged over a time frame of several weeks or more, there is no reason to expect that the model could or should explain day-to-day variability in *f*-ratios or *e* ratios. The model assumes a balance between new production and export production, and this assumption may certainly be violated on a short time frame. An alternative approach is needed to describe variability in new or export production on such time scales. Indeed, export production based on ^{234}Th measurements and primary production clearly illustrate the difficulty of extrapolating export from net primary production measurements in highly energetic ecosystems (Fig. 4.7).

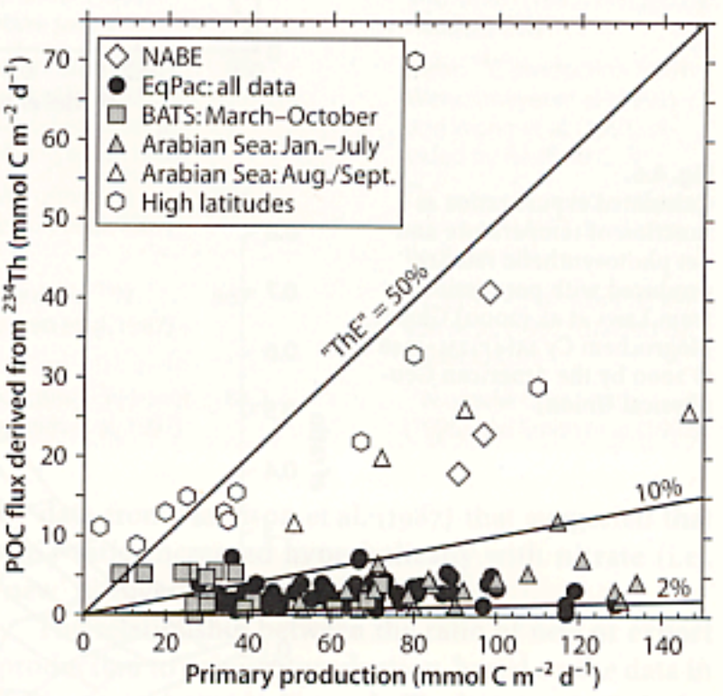

Fig. 4.7. Summary plot of primary production vs. POC flux derived from the ^{234}Th approach (both in terms of mmol C m^{-2} d^{-1}). ThE is defined as the ratio of POC export to primary production. *Lines* of ThE = 50%, 10% and 2% are drawn for comparison to data. Data are shown from most of the JGOFS study regions (after Buesseler (1998))

Aufdenkampe et al. (2001) developed a multiple linear regression (MLR) expression to calculate new production in the tropical Pacific. The model can explain nearly 80% of the variability in new production using four independent variables – rates of primary production (or chlorophyll inventories), inventories of ammonium and nitrate, and temperature. Depth integrated primary production, euphotic zone inventories of ammonium and nitrate, and depth averaged euphotic zone

temperature formed the most significant combination of independent variables from more than three dozen tested. The multiple coefficient of determination, R^2, indicated that 79% of the variability in new production could be explained by changes in these four variables alone. Total primary production gives the largest contribution to the regression fit followed by ammonium inventory, nitrate, and finally temperature. Chlorophyll inventory offered a reasonable substitute for primary production with the resulting MLR ($R^2 = 0.63$) receiving similar contributions from nitrate, chlorophyll, and ammonium. MLR analyses of the subsets of stations having data for sediment-trap silica fluxes, and sediment-trap silica-to-nitrogen flux ratios and biogenic silica inventories showed that none of these parameters exhibited stronger partial correlations to new production than did nitrate.

4.2.1 Physical Controls of Export Fluxes: the Importance of Functional Groups

The biologically mediated fluxes of elements between the upper ocean and the ocean interior are critically dependent upon key groups of organisms. Similarly, fluxes between the atmosphere and ocean as well as between the ocean and the lithosphere are mediated by organisms that catalyze phase state transitions from either gas to solute/solid or from solute to solid/gas phases. For example, autotrophic carbon fixation converts gaseous CO_2 to a wide variety of organic carbon molecules, virtually all of which are solid or dissolved solids at physiological temperatures. Respiration accomplishes the reverse. Nitrogen fixation converts gaseous N_2 to ammonium and thence to organic molecules, while denitrification accomplishes the reverse. Calcification converts dissolved inorganic carbon and Ca to solid phase calcite and aragonite whereas silicification converts soluble silicic acid to solid hydrated amorphous opal. Each of these biologically catalyzed processes is dependent upon specific metabolic sequences (i.e., gene families encoding a suite of enzymes) that evolved over hundreds of millions of years of Earth's history, and have, over corresponding periods, led to the massive accumulation of calcite, opal, and organic matter in the lithosphere. Presumably because of parallel evolution as well as lateral gene transfer, these metabolic sequences have frequently co-evolved in several groups of organisms that, more often than not, are not closely related from a phylogenetic standpoint (Falkowski and Raven 1997). Based on their biogeochemical metabolism, these homologously similar sets of organisms can be clustered into 'functional groups' or 'biogeochemical guilds'; i.e., organisms that are related through common biogeochemical processes rather than phylogenetic affiliation.

In the contemporary ocean, the export of particulate organic carbon from the euphotic zone is highly correlated with the flux of particulate silicate. Most of the silicate flux is a consequence of precipitation of dissolved orthosilicic acid by diatoms to form amorphous opal that makes up the cell walls of these organisms. These hard-shelled cell walls presumably help the organisms avoid predation, or if ingested, increase the likelihood of intact gut passage though some metazoans. In precipitating silicate, diatoms simultaneously fix carbon. Upon depleting the euphotic zone of nutrients, the organisms frequently sink en masse, and while some are grazed en route, many sink as intact cells. Ultimately, either fate leads to the gravitationally driven export flux of particulate organic carbon into the ocean interior.

Silica is supplied to the oceans from the weathering of continental rocks. Because of the precipitation of silicious organisms however, the ocean is relatively depleted in dissolved silica. Although diatom frustules (i.e., their silicified cell walls) tend to dissolve and are relatively poorly preserved in marine sediments, enough silica is buried to keep the ocean undersaturated. As the residence time of silica in the oceans is about 10 000 years (i.e., about an order of magnitude longer than the mean deep water circulation), one can get an appreciation for the silicate demands and regeneration rates by following the concentration gradients of dissolved silica along isopycnals. While these demands are generally attributed to diatoms, radiolarians (a group of non-photosynthetic, heterotrophic protists with silicious tests, that are totally unrelated to diatoms) are not uncommon, and radiolarian shells are abundant in the sediments of Southern Ocean. Silica is also precipitated by various sponges, and other protists. As a functional group, the silicate precipitators are identified by their geochemical signatures in the sediments and in the silica chemistry of the oceans. Diatoms can be elucidated by photosynthetic pigment analyses in situ, but cannot be uniquely identified from satellite imagery. Because of their importance in mediating carbon export, a significant effort was spent in JGOFS attempting to understand the factors controlling the distribution of diatoms in the world oceans. Interestingly, diatoms appear to have evolved relatively recently; the first clear evidence of their presence in the oceans is recorded in fossils from cherts dating to 120 Mybp (i.e. in the early Cretaceous). Thus, although export carbon fluxes are associated with this group of organisms in the contemporary ocean, they usurped that role from an unknown group(s) of phytoplankton that dominated earlier in the Mesozoic. What organisms mediated export of carbon in the Proterozoic (prior to the emergence of eucaryotes) and Paleozoic (prior to the dominance of the chromophyte algae) remains totally unknown.

A major strategy of diatoms is to acquire nutrients rapidly under highly physically dynamic conditions, and to store the nutrients in vacuoles for later cell growth. This strategy simultaneously deprives competing groups of phytoplankton of essential nutrients while allowing diatoms to grow rapidly, forming blooms. In this strategy nitrate, but not ammonium can be stored. Nevertheless, Aufdenkampe et al. (2001) showed that silicate itself does not appear to exert a strong direct control on new production during typical conditions. Diatom-associated chlorophyll did indeed seem to be important in the equatorial Pacific, but only a few stations during uncommonly high new production (NP) dictated much of the NP-Chl_{dia} relationship. These findings are consistent with the conclusion of Dunne et al. (1999) that diatoms regulate new production fluxes only during highly dynamic, non-steady state conditions such as the passage of tropical instability waves (referred to earlier as the 'perturbed' state), but that diatoms do not dominate new production during more common and less dynamic conditions.

4.2.2 Calcium Carbonate Precipitation

Like silica precipitation, calcium carbonate is not confined to a specific phylogenetically distinct group of organisms, but evolved (apparently independently) several times in marine organisms. Carbonate sediments blanket much of the Atlantic Basin, and are formed from the shells of both coccolithophorids and foraminifera. (In the Pacific, the carbon compensation depth is generally higher than the bottom, and hence, in that basin carbonates tend to dissolve rather than become buried.) As the crystal structures of the carbonates in both groups is calcite (as opposed to the more diagenically susceptible aragonite), the preservation of these minerals and their co-precipitating trace elements, provides an invaluable record of ocean history. Although on geological time scales, huge amounts of carbon are stored in the lithosphere as carbonates, on ecological time scales, carbonate formation depletes the ocean of Ca^{2+}, and in so doing, potentiates the efflux of CO_2 from the oceans to the atmosphere. This sequence can be summarized by the following:

$$2HCO_3^- + Ca^{2+} \longrightarrow CaCO_3 + CO_2 + H_2O \qquad (4.8)$$

Unlike silicate precipitation, calcium carbonate precipitation leads to strong optical signatures that can be detected both in situ and remotely. The basic principles of detection are the large, broad band (i.e., 'white') scattering cross sections. The high scattering cross sections are detected by satellites observing the upper ocean as relatively highly reflective properties (i.e., a 'bright' ocean). Using this detection scheme, one can reconstruct global maps of planktonic calcium carbonate precipitating organisms in the upper ocean. In situ analysis can be accompanied by optical rotation properties (polarization) to discriminate calcite from other scattering particles. In situ profiles of calcite can be used to construct the vertical distribution of calcium-carbonate-precipitating planktonic organisms that would otherwise not be detected by satellite remote sensing because they are too deep in the water column.

Unlike diatoms, coccolithophores do not store nutrients very efficiently, but can bloom when nutrients are supplied at slow rates. Hence, coccolithophorids are primarily found at low abundance in tropical and subtropical seas, and at higher concentrations at high latitudes in midsummer, following diatom blooms. Hence, export of inorganic carbon by diatoms in spring at high latitudes can be offset by an efflux of carbon to the atmosphere with the formation of coccolithophore blooms later in the year.

4.2.3 Primary, New and Export Production and the Global Carbon Cycle on Longer Time Scales

Now we come to a feature at the intersection of oceanic biology and geochemistry that sometimes causes some confusion, namely, do changes in export production or the biological pump affect the atmospheric concentration of CO_2? The answer is, "Not necessarily, but they can; it depends how the changes come about."

Let us imagine that we could stir the oceans with a large spoon or egg beater, such that we mixed the ocean interior up and it was exposed to the atmosphere. Initially CO_2 would evade from the oceans to the atmosphere, but the stirring process would also bring up essential nutrients that help stimulate NPP. The two major nutrients are fixed inorganic N (primarily in the form of nitrate) and P (primarily in the form of phosphate). As these nutrients are consumed to make new cells in the upper ocean, inorganic carbon would also be fixed back to organic matter, and hence returned to the oceanic reservoir. Unlike any other ecosystem that we know of, the elemental stoichiometry specified in Eq. 4.2 between C, N, P, and O appears to be relatively constrained in the oceans.

On geological time scales, there is one final fate for NPP we should consider, namely burial in the sediments. By far, the largest reservoir of organic matter on Earth is locked up in rocks (Table 4.7). Virtually all of this organic carbon was the result of the burial of the export production in the oceans over literally billions of years of Earth's history. Indeed, without burial, there would be no net evolution of oxygen in Earth's atmosphere, as the production of oxygen would have been

Table 4.7. Carbon pools in the major reservoirs on Earth (from Falkowski and Raven 1997)

Pools	Quantity ($\times 10^{15}$ g)
Atmosphere	720
Oceans	38400
Total inorganic	37400
Surface layer	670
Deep layer	36730
Dissolved inorganic	600
Total organic	1000
Lithosphere	
Sedimentary carbonates	>60000000
Kerogens	15000000
Terrestrial biosphere (total)	2000
Living biomass	600–1000
Dead biomass	1200
Aquatic biosphere	1–2
Fossil fuels	4130
Coal	3510
Oil	230
Gas	140
Other (peat)	250

balanced by its consumption (e.g. Walker 1974). On geological time scales, the burial of marine NPP effectively removes carbon from biological cycles, and places that carbon into another, much slower, carbon cycle. The latter is driven by tectonics and weathering (discussed by Watson and Orr, this volume), in which the organic (and inorganic; i.e., carbonate) sedimentary rocks are subducted into the upper mantle along tectonic boundaries, and heated in the Earth's interior. The resulting carbon-containing products of this heating process (primarily CO_2 and CH_4) enter the atmosphere through volcanic outgassing. The CH_4 is rapidly oxidized to CO_2 in the upper atmosphere. CO_2 reacts with Ca and Mg silicates to form carbonates through the weathering reactions. On time scales of millions of years, this cycle determines the concentration of O_2 and CO_2 in the atmosphere and oceans.

A very small fraction of the carbon buried in sediments undergoes transformation to become polymers of petroleum (Table 4.7) or exploitable methane. These organic carbon pools are part of the 'slow' carbon cycle; they are effectively removed from the atmosphere for hundreds of millions of years unless they are extracted from the lithosphere and burned. The burial of organic carbon in the modern oceans is primarily confined to a few regions where the supply of sediments from terrestrial sources is extremely high. Such regions include the Amazon outfall and Indonesian mud belts. In contrast, the oxidation of organic matter in the interior of the contemporary ocean is extremely efficient; virtually no carbon is buried in the deep sea. Similarly, on most continental margins, organic carbon that reaches the sediments is consumed by microbes within the sediments, such that very little is actually buried.

As discussed earlier, in the contemporary ocean export of organic carbon to the interior is often associated with diatom blooms. This group has only risen to prominence over the past 40 million years.

Over geological time, the distributions of key functional groups change. For example, relative coccolithophorid abundance generally increases through the Mesozoic, and undergoes a culling at the K/T boundary, followed by numerous alterations in the Cenozoic. The changes in the coccolithophorid abundances appear to trace eustatic sea level variations, suggesting that transgressions lead to higher calcium carbonate fluxes. In contrast, diatom sedimentation increases with regressions and since the K/T impact, diatoms have generally replaced coccolithophorids as ecologically important eucaryotic phytoplankton. On much finer time scales, during the Pleistocene, it would appear that interglacial periods favor coccolithorphorid abundance, while glacial periods favor diatoms. The factors that lead to glacial-interglacial variations between these two functional groups are relevant to elucidating their distributions in the contemporary ecological setting of the ocean.

We shall assert, based on first principles, that the distribution of all planktonic organisms in the oceans obeys a rule of *universal distribution and local selection*. This rule states that in any given body of water, there is a finite probability of finding any organism at any time, but that the local environment will be more conducive to the growth of some organisms than others. This rule implies that, within reason, the rules of 'selection' can be largely elucidated for major functional groups. If, for example, the water column is cold and nutrient rich we may assume that nitrogen fixers will be present but not highly selected while diatoms are more likely to be abundant. Conversely, in warm, stratified, oligotrophic seas, it is unlikely that diatoms will emerge as dominant organisms, while nitrogen fixers are more likely to be abundant.

Over the past ca. 150 years, human energy-related activities have led to a large and rapid injection of CO_2 into Earth's atmosphere, largely through the combustion of fossil fuels. In this process, organic carbon has been extracted from the slow carbon cycle of the lithosphere and placed into the rapid carbon cycle that includes the atmosphere/ocean abiotic exchange, and biologically mediated exchanges that include carbon fixation, respiration, and calcification. To influence the anthropogenic CO_2 emissions, the latter processes must not only

deviate from the steady state, but must become imbalanced over time scales of decades. The JGOFS program forced a discussion of whether or if primary production plays or will play a significant role in sequestering the anthropogenic carbon dioxide.

Inspection of Eq. 4.2 suggests that, like Eq. 4.1, the production of organic matter at the surface and its remineralization at depth is normally in a steady state. Thus, moving nitrate and phosphate (at a fixed ratio of 16:1 by moles) from the right hand side to the left would result in a predictable formation of organic matter. To first order however, there are four mechanisms by which the biological pump can deviate from the steady state and impact the net exchange of CO_2 between the atmosphere and ocean. Given that at the present time there is very little burial of organic matter in ocean sediments, we shall ignore burial. The remaining four options operate on time scales of decades to centuries. First, if a limiting nutrient(s) is added to the ocean from an external source, the utilization of that nutrient by primary producers would increase the net formation of organic matter. Some of that organic material would be exported to the ocean interior and remineralized. Alternatively, there are some regions in the ocean where nitrate and phosphate were brought from depth to the surface but not consumed before these nutrients returned to depth. If the efficiency of nutrient utilization were to be somehow enhanced, in principle more carbon would be stored in the ocean interior. Third, if the elemental ratio of the organic matter were to deviate from that given in Eq. 4.2, then in principle the net new flux of carbon to depth would also be altered. Finally, if the ratio of the fluxes of particulate organic/particulate inorganic carbon were to change, the net flux of carbon could change. These scenarios are not mutually exclusive, but require external perturbation. One perturbation will be climate change forced by the combustion of fossil fuels. While it is presently not possible to determine quantitatively whether this perturbation will have any significant effect on the net rate of uptake of anthropogenic carbon by the ocean, or whether any of the four aforementioned processes that are critical to the biological pump will be altered, it is clear that ocean circulation and stratification almost certainly will change.

Synthesis and modeling of the extraordinary data set was the culmination of the formal JGOFS program. These efforts have led to a greater appreciation for the interactions between physical and biological processes in determining which specific functional group dominates, and how that outcome affects the fluxes of organic and inorganic carbon. While still in its infancy, the modeling efforts have further revealed that changes in ocean circulation and stratification can lead to significant changes in export production. In an increasingly stratified ocean of the future, one might predict that diatom blooms occur less frequently or with lower amplitude, and that coccolothophores might become relatively more abundant. Indeed, a major challenge for the next few decades will be to identify the major rules by which key functional groups are distributed in the ocean, both past and present, and to develop predictive models of their distributions in this first century of the third millennium of the common era. Our work is just beginning and the JGOFS data sets will continue to provide a framework in to explore these issues for years to come.

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