principle be measured exactly. It is a biological process that cannot proceed unaltered when phytoplankton are removed from their natural surroundings. Artifacts are unavoidable, but many insults to the sampled plankton can be minimized through the exercise of caution and skill. Still, the observed rates will be influenced by the methods chosen for making the measurements. Interpretation is also uncertain: the ^{14}C method is the standard operational technique for measuring marine primary production, yet there are no generally applicable rules for relating ^{14}C measurements to either gross or net primary production.

Fortunately, uncertainties in the measurements and their interpretation, although significant, are not large enough to mask important patterns of primary productivity in nature. Years of data on marine primary production have yielded information that has been centrally important to our understanding of marine ecology and biogeochemical cycling. Clearly, measurements of marine primary production are useful and important for understanding the ocean. It is nonetheless prudent to recognize that the measurements themselves require circumspect interpretation.

See also

Carbon Cycle. Fluorometry for Biological Sensing. Ocean Carbon System, Modelling of. Network Analysis of Food Webs. Ocean Color from Satellites. Primary Production Distribution. Primary Production Processes. Tracers of Ocean Productivity.

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PRIMARY PRODUCTION PROCESSES

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Introduction

This article summarizes the information available on the magnitude of and the spatial and temporal variations in, marine plankton primary productivity. The causes of these variations are discussed in terms of the biological processes involved, the organisms which bring them about, and the relationships to oceanic physics and chemistry. The discussion begins with a definition of primary production.

Primary producers are organisms that rely on external energy sources such as light energy (photolithotrophs) or inorganic chemical reactions (chemolithotrophs). These organisms are further characterized by obtaining their elemental requirements from inorganic sources, e.g. carbon from inorganic carbon such as carbon dioxide and bicarbonate, nitrogen from nitrate and ammonium (and, for some, dinitrogen), and phosphate from inorganic phosphate. These organisms form the basis of food webs, supporting all organisms at higher trophic levels. While chemolithotrophy may well have had a vital role in the origin and early evolution of life, the role of chemolithotrophs in the present ocean is minor in energy and carbon terms (**Table 1**), but is very important in biogeochemical element cycling, for example in the conversion of ammonium to nitrate.

Table 1 Net primary productivity of habitats, and area of the habitats, on a world basis[a]

Habitat	*Total area (m^2)*	*Organisms*	*Global net primary productivity (10^{15} g C $year^{-1}$)*
Marine phytoplankton	370×10^{12}	Cyanobacteria and microalgae	46
Marine planktonic chemolithotrophs converting NH_4^+ to NO_2^- and NO_2^- to NO_3^-	370×10^{12}	Bacteria	≤ 0.19
Marine benthic[b,c]	6.8×10^{12}	Cyanobacteria and microalgae	0.34
		Macroalgae	3.4
Marine benthic[b]	0.35×10^{12}	Angiosperms (salt marshes plus beds of seagrasses)	0.35
Inland waters	2×10^{12}	Phytoplankton (cyanobacteria and microalgae), benthic algae and higher plants	0.58
Terrestrial[d]	150×10^{12}	Mainly higher plants	54

[a]From Raven (1991, 1996) and Falkowski *et al.* (2000). All values are for photolithotrophs unless otherwise indicated.
[b]Area of the habitat the marine benthic cyanobacteria, algae, and marine benthic angiosperm is in series with that of the overlying phytoplankton habitat. The benthic habitat area is included in the habitat area for marine phytoplankton.
[c]The marine benthic cyanobacterial and algal category includes cyanobacteria and algae symbionts with protistans and invertebrates.
[d]As well as higher plants the terrestrial productivity involves cyanobacteria and microalgae, both lichenized and free-living, although there seem to be no estimates of the magnitude of nonhigher plant productivity.

Quantitatively a much more important process in primary productivity on a global scale is photolithotrophy (**Table 1**). Essentially all photolithotrophs which contribute to net inorganic carbon removal from the atmosphere or the surface ocean are O_2-evolvers, using water as electron donor for carbon dioxide reduction, according to eqn [1]:

$$CO_2 + 2H_2^*O + 8\,\text{photons} \rightarrow (CH_2O) + H_2O + {}^*O_2 \quad [1]$$

The contribution of O_2-evolving photolithotrophy from terrestrial environments is greater than that in the oceans, despite the sea occupying more than two-thirds of the surface of the planet (**Table 1**). Sunlight is attenuated by sea water to an extent which limits primary productivity to, at most, the top 300 m of the ocean. Since only a few percent of the ocean floor is within 300 m of the surface, the role of benthic primary producers (i.e. those attached to the ocean floor) is small in terms of the total marine primary production (**Table 1**). Despite the relatively small area of benthic habitat for photolithotrophs in the ocean as a percentage of the total sea area (2%), benthic primary productivity producers account for almost 10% of marine primary productivity (**Table 1**).

Until very recently it has been assumed that the photosynthetic primary producers in the marine phytoplankton are the O_2-evolvers with two photochemical reactions involved in moving each electron from water to carbon dioxide, although molecular genetic data from around 1990 indicated the presence of erythrobacteria in surface ocean waters. Recent work has shown that both rhodopsin-based and bacteriochlorophyll-based phototrophy is widespread in the surface ocean. This phototrophy does not involve O_2 evolution and, while it does not necessarily involve net carbon dioxide fixation, it may impact on surface ocean carbon dioxide dynamics. Thus, growth of prokaryotes using dissolved organic carbon can occur with less carbon dioxide produced per unit dissolved organic carbon incorporated into organic carbon by the use of energy from photons to replace energy that would otherwise be transformed by oxidation of dissolved organic carbon. It is probable that these phototrophs which do not evolve O_2 contribute $< 1\%$ to gross carbon dioxide fixation by the surface ocean.

This article investigates the reasons for this constrained planktonic primary production in the ocean in terms of the marine pelagic habitat and the diversity of the organisms involved in terms of their phylogeny and life-form.

The Habitat

The surface ocean absorbs solar radiation via the properties of sea water, as well as of any dissolved organic material and of particles. A very small fraction ($\leq 1\%$ in most areas) of the 400–700 nm com-

ponent is converted to energy in organic matter in photosynthesis, while the rest is converted to thermal energy. In the absence of wind shear and ocean currents, themselves ultimately caused by solar energy input, the thermal expansion of the surface water would cause permanent stratification, except near the poles in winter.

Such an ocean is approximated by most parts of the tropical ocean, where ocean currents and wind are inadequate to cause breakdown of thermal stratification; the upper mixed layer shows very little seasonal variation. By contrast, at higher latitudes the varying solar energy inputs throughout the year, combined with wind shear and ocean current influences, lead to stratification with a relatively shallow upper mixed layer in the (local) summer and a much deeper one in the (local) winter, usually giving a winter mixing depth so great that net primary production is not possible as a result of the inadequate mean photon flux density (light-energy) incident on the cells.

A very important impact of stratification is the isolation of the upper mixed layer, where inorganic nutrients are taken up by phytoplankton, from the lower, dark, ocean where nutrients are regenerated by heterotrophy. The movement of organic particles from the upper to lower zones is gravitational. While there is significant recycling of inorganic nutrients in the upper mixed layer via primary productivity and activities of other parts of the food web, ultimately there is loss of particles containing nutrient elements across the thermocline. Seasonal variations in mixing depth, and upwellings, are the main processes bringing nutrient solutes back to the euphotic zone.

Global biogeochemical cycling considerations suggest that the nutrient element that limits the extent of global primary production each year is, over long time periods, phosphorus. This element has a shorter residence time than the other nutrients (such as iron) which are supplied solely from terrestrial sources. Nitrogen, by contrast, is present in the atmosphere and dissolved in the ocean as dinitrogen in such large quantities that any limitation of marine phytoplankton primary productivity by the availability of such universally available nitrogen formed as ammonium and nitrate could be offset by diazotrophy, i.e. biologically dinitrogen fixation, which can only be brought about by certain Archea and Bacteria. In the ocean the phytoplanktonic cyanobacteria are the predominant diazotrophs, as the free-living *Trichodesmium* and as symbionts such as *Richia* in such diatoms as *Hemiaulis* and *Rhizosolenia*. Diazotrophy needs energy (ultimately from solar radiation) and trace elements such as iron (always), molybdenum (usually), and vanadium (sometimes). These trace elements all have longer oceanic residence times than phosphorus, and so are less likely to limit primary productivity than is phosphorus over geologically significant time intervals. However, the balance of evidence for the present ocean suggests that nitrogen is a limiting resource for the rate and extent of primary productivity over much of the world ocean, while iron seems to be the limiting nutrient in the 'high nutrient (nitrogen, phosphorus), low chlorophyll' areas of the ocean. Even where nitrogen does appear to be limiting, this could be a result of restricted iron supply which restricts the assimilation of combined nitrogen, and especially of nitrate.

Processes at the Cell Level

The photosynthetic primary producers in the marine plankton show great variability in taxonomy, and in size and shape. The taxonomic differences reflect phylogenetic differences, including the prokaryotic bacteria (cyanobacteria, embracing the chlorophyll b-containing chloroxybacteria) and a variety of phyla (divisions) of Eukaryotes. The Eukaryotes include members of the Chlorophyta (green algae), Cryptophyta (cryptophytes), Dinophyta (dinoflagellates), Haptophyta (*Phaeocystis* and coccolithophorids), and Heterokontophyta (of which the diatoms or Bacillariophyceae are the most common marine representatives).

The phylogenetic differences determine pigmentation, with the ubiquitous chlorophyll a accompanied by phycobilins in cyanobacteria *sensu stricto*, chlorophyll b in Chloroxybacteria and green algae, chlorophyll(s) c together with significant quantities of light-harvesting carotenoids in dinoflagellates, haptophytes, and diatoms, and chlorophyll c with phycobilins in cryptophytes. These differences in pigmentation alter the capacity for a given total quantity of pigment per unit volume of cells for photon absorption in a given light field, noting that the deeper a cell lives in open-ocean water, the less longer wavelength (red-orange-yellow) light is available relative to blue-green light. This effect of different light-harvesting pigments on light absorption capacity is greatest in very small cells as a result of the package effect.

Another phylogenetic difference among phytoplankton organisms is a dependence on Si (in diatoms) and on large quantities of Ca (in coccolithophorids) in those algae which have mineralized skeletons. Furthermore, some vegetative cells move relative to their immediate aqueous environment using flagella (almost all planktonic dino-

flagellates, some green algae). Movement relative to the surrounding water occurs in any organism which is denser than the surrounding water sinking (e.g. by many mineralized cells) or less dense than the surrounding water (buoyancy engendered by cyanobacterial gas vacuoles or the ionic content of vacuoles in large vacuolate cells). The variation in cell size among marine phytoplankton organisms is also partly related to taxonomy. The smallest marine phytoplankton cells are prokaryotic, with cells of *Prochlorococcus* (cyanobacteria *sensu lato*) as small as 0.5 μm diameter, while cells of the largest diatoms (*Ethmosdiscus* spp.) and the green *Halosphaera* are at least 1 mm in diameter, i.e. a range of volume from $6.25 \times 10^{-20}\,m^3$ to more than $4.19 \times 10^{-9}\,m^3$. This means a volume of the largest cells which is almost 10^{11} that of the smallest; allowing for the vacuolation of the large cells gives a ratio of almost 10^{10} for cytoplasmic volume. The size range for phytoplankton organisms is expanded by considering colonial organisms (e.g. the cyanobacterium *Trichodesmium*, and the haptophyte *Phaeocystis*) to a range of cytoplasmic volumes up to almost 10^{12}. At the level of the cell size cyanobacteria have a limited volume range, while in organisms size the range is at least 10^{12}; for haptophytes it is at least 10^{11}. Cell (or organism) size is, on physicochemical principles, very important for the effectiveness of light absorption per unit pigment, nutrient uptake as a result of surface area per unit volume, and of diffusion boundary layer thickness, and rate of vertical movement relative to the surrounding water for a given difference in density between the organisms and their environment. These physicochemical predictions are, to some extent, modified by the organisms by, for example, changed pigment per unit volume and light scattering, and modulation of density.

Determinants of Primary Productivity

Despite these variations in phylogenetic origin and in the size of the organisms, that can be related to seasonal and spatial variations over the world ocean, it is not easy to find consistent spatial and temporal variations in the 'major element' ratios (C : N : P, 106 : 16 : 1 by atoms) or Redfield ratio in space or time. This means that we should not look to differences in the phylogeny or size of phytoplankton organisms to account for differences in the requirement for major nutrients (C, N, P) in supporting primary productivity. What is less clear is the possible variations in trace element (Fe, Mn, Zn, Mo, Cu, etc.) requirements in relation to the properties of different bodies of water in the world ocean. The trace metals are essential catalysts of primary productivity through their roles in photosynthesis, respiration, nitrogen assimilation, and protection against damaging active oxygen species. Geochemical evidence for limitation by some factor other than nitrogen and phosphorus is indicated for 'high nutrient' (i.e. available nitrogen and phosphorus) 'low chlorophyll' (i.e. photosynthetic biomass and hence productivity), or HNLC, regions of the ocean (north-eastern subAntarctic Pacific; eastern tropical Pacific; Southern Ocean).

Before seeking other geochemical limitations on primary production to explain why these apparently available sources of nitrogen and phosphorus have not been used in primary productivity, we need to consider geophysical or 'bottom up' (mixing depth, surface photon flux density) and ecological or 'top down' factors (involvement of grazers or pathogens). While these nongeochemical 'bottom up' (control of production of biomass) and 'top down' (removal of the product of primary production) constraints on the use of nitrate and phosphate are, in principle, causes of this HNLC phenomenon, *in situ* Fe enrichments show that addition of this trace element causes drawdown of nitrate and phosphate, increases in chlorophyll and primary productivity, and increased abundance, and contribution to primary productivity of large diatoms.

These IRONEX and SOIREE experiments strongly support the notion that iron limits primary productivity in HNLC regions, as well as suggesting that Fe enrichment can impact differentially on primary producers as a function of their taxonomy and cell size. The increased importance of large diatoms as a result of Fe enrichment can be a result of the diffusion boundary layer thicknesses and surface area per unit volume, rather than of the biochemical demand for Fe to catalyze a given rate of metabolism per unit cell volume. While data are not abundant, theoretical considerations suggest that cyanobacteria should, other things being equal, have higher requirements for Fe for growth than do diatoms, haptophytes, or green algae. This prediction contrasts with observations (and production) for major nutrients such as organic C, N, and P, where cell quotas are much less variable phylogenetically than are those for micronutrients. There is, of course, much less elasticity possible for the C content of cells than for other, less abundant, nutrient elements, with the same applying to a lesser extent to N and P. It is clear that the cost of N, P, or Fe in fixing carbon dioxide is higher for growth at low (limiting) as opposed to high (saturating) photon flux densities.

To broaden the issues of limitations on primary productivity, the ultimate limitation on primary productivity in the ocean is presumably the 'geochemical' limiting element P, i.e. the nutrient element with the shortest residence time in the ocean. It has been plausibly argued that, in the short term, nitrogen has become a limiting nutrient indirectly by the short-term (geologically speaking) Fe limitation. Thus, 'new' production, depending on nitrate upwelled or eddy-diffused from the deep ocean, has a greater Fe requirement than the NH_4^+ (or organic N) assimilation in 'recycled' production in which primary production is chemically fuelled by N, P, and Fe generated by zooplankton, and more importantly, by Fe limitation (at least in the geological short-term) is seen as restricting diazotrophy. In the context of the balance of diazotrophy plus atmospheric and riverine inputs of combined N, and denitrification and sedimentation loss of combined N, Fe limitation can reduce the combined N availability relative to that of P to below the 16:1 atomic ration of the Redfield ratio. This, then, restricts the N:P ration in upwelled sea water. Even more immediate Fe limitation is seen in the HNLC ocean, as discussed above.

Conclusions

Marine primary production accounts for almost half of the global primary production, and is carried out by a much greater phylogenetic range of organisms than is the case for terrestrial primary production. As on land, almost all marine primary production involves O_2-evolving photolithotrophs. Marine phytoplankton has a volume of cells of 6.10^{-20}–$4.10^{-9}\,m^3$. While the primary production in the oceans is, on geological grounds, ultimately limited by P, proximal (shorter-term) limitation involves N or Fe.

Glossary

HNLC high nutrient, low chlorophyll. Areas of the ocean in which combined nitrogen and phosphate are present at concentrations which might be expected to give higher rates of primary production and levels of biomass, than are observed unless some 'top down' or 'bottom up' limitation is involved.

IRONEX iron enrichment experiment. Two releases of $FeSO_4$, with SF_6 as a tracer, south of the Galapagos in the Eastern Equatorial Pacific HNLC area.

Photon flux density. Units are mol photon $m^{-2}\,s^{-1}$. Means of expressing incident irradiance in terms of photons, i.e. the aspect of the particle/wave duality of electromagnetic radiation which is appropriate for consideration of photochemical reactions such as photosyntheses. For O_2-evolving photosynthetic organisms the appropriate wavelength range is 400–700 nm.

SOIREE southern ocean iron release experiment. A Southern Ocean analogue of IRONEX, performed between Australasia and Antarctica.

See also

Anthropogenic Trace Elements in the Ocean. Carbon Cycle. Carbon Dioxide (CO_2) Cycle. Nitrogen Cycle. Primary Production Distribution. Primary Production Methods.

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