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Particulate organic matter flux and planktonic new production in the deep ocean

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Primary production in the oceans results from alloch-thonous nutrient inputs to the euphotic zone (new production) and from nutrient recycling in the surface waters (regenerated production). Global new production is of the order of 3.4–4.7×10^9 tons of carbon per year and approximates the sinking flux of particulate organic matter to the deep ocean.

THE sinking flux of particulate organic carbon (POC) to the deep sea has been estimated from a geochemical, two-layer box model of the global ocean to be 10% of the surface ocean production[1]. If surface production is in the range 20–45×10^9 tons C yr^{-1} (ref. 2), then the sinking flux would be about 2.0–4.5×10^9 tons C yr^{-1}. We estimate the sinking flux of POC in the deep ocean by assuming that new production, as defined by Dugdale and Goering[3], is quantitatively equivalent to the organic matter that can be exported from the total production in the euphotic zone without the production system running down. Regenerated production constitutes the remaining production and is based on nutrients recycled through the food web of the surface ocean. The principal source of nutrients for new production is the upwelling and diffusion of nutrients from deeper water into the euphotic zone. Secondary sources are terrestrial (rivers, runoff, sewage), atmospheric (nitrate in rain, for example), and nitrogen fixation. Export fates of new production, other than sinking (and with a lower flux rate)[4], include the fish and shellfish catch, deposition of guano on land by marine birds and the like.

Nature of the sinking POC

All the ocean contains sinking particulate matter which is the source of food for the microorganisms and animals of the deep waters and the sea floor. Most of the suspended material in seawater is in very small particles[5,6]. Marine 'snow', consisting of macroscopically visible particles has been seen, however, wherever submersibles have explored. The abundance of deep-sea animals that feed on large food items is much greater than was realised before baited deep-sea cameras[7] were used, suggesting that some of the sinking particles are large.

The herbivorous zooplankton of upwelling areas and of temperate waters are typically calanoid copepods. Copepods and certain other taxonomic groups of herbivorous zooplankton, by producing faecal pellets make a major contribution to the sinking flux of POC. About 20–30% of the organic carbon of the phytoplankton ingested by such creatures is passed in the faeces of the animals and the faeces are encapsulated in durable, fast-sinking packets which can rapidly transport organic carbon to a great depth. This mechanism was first discovered by radio-ecologists studying the vertical flux of radionuclides in the ocean[8]. Typical sinking rates of faecal pellets in laboratory experiments are 50–300 m d^{-1} (ref. 9).

In coastal temperate waters, traps for intercepting particles have caught largely intact phytoplankton during the spring bloom[10] and largely animal faecal material as the zooplankton assemblage developed to graze down the phytoplankton bloom[11,12,15]. Trap catches in the Peru upwelling have been dominated either by intact phytoplankton, by zooplankton faecal pellets and moults, or by the faecal material of the anchoveta, *Engraulis ringens*[13]. Catches with faecal pellets are also reported for oligotrophic, deep ocean situations[5,14,16]. The total flux seems to be approximately proportional to the plankton production in the overlying water. Because of the differential sinking and decomposition rates of large and small particles, the relative importance of faecal pellets as mediators of particulate carbon transport may increase with depth[14].

New production and carbon flux

Primary production in the illuminated surface layer of the ocean—the euphotic zone—can be viewed[3] as depending on two different sources of nitrogenous nutrient supply. One is the supply of ammonia, urea and to a lesser extent amino acids and other dissolved organic nitrogen compounds derived from the excretory activities of animals and the metabolism of hetero-trophic microorganisms. The food or substrate that fuels these activities, including the source of nitrogen, derives from phytoplankton via the food web. The phytoplankton production resulting from this recycled nitrogen is called regenerated production (Fig. 1). In an ideal closed system the cycling of nutrients through an enclosed food web could continue indefinitely with steady-state standing stocks and fluxes. In the real ocean, however, there are losses such as the flux of sinking faecal material and cast off exoskeletons out of the euphotic
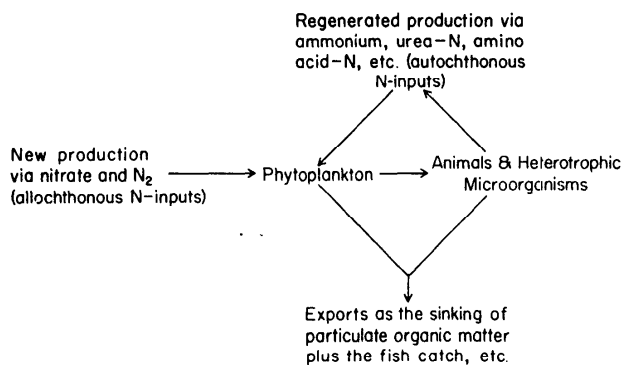
Fig. 1   The production system of the surface ocean, illustrating the concepts of new and regenerated production. Phytoplankton growth is driven by nitrogen inputs of two qualitatively distinct sorts: regenerated and 'new' production. These two pathways leading to phytoplankton production are measured as the phytoplankton assimilation of the various forms of nitrogen using ^{15}N-labelled substrates. This is not possible with other nutrient elements because with carbon or phosphorus, for example, it is not easy to distinguish between autochthonous and allochthonous inputs. To relate new production to export requires that nitrification in the euphotic zone be negligible.

zone to deep water. The fish catch is another example of such a loss[4], amounting to $<10^7$ tons per year of organic carbon. Seabirds feeding in the ocean but depositing guano on land is another. There is also a concentration gradient of dissolved organic carbon and nitrogen between the surface and deep ocean, the surface values being higher. Rates of physical mixing[1] and concentrations[17] suggest a downward dissolved organic carbon flux of $0.1-0.3 \times 10^9$ tons C yr^{-1}.

The nutrients lost must be replaced by external inputs to avoid a decline in the productivity of the system. The fossil record shows that production has indeed fallen to low levels in the geological past[18,19]. Renewal takes place naturally by the injection of nutrients from deep water into the euphotic zone. Although the flux of nitrate from deep water is the predominant method of renewal in the ocean there are other sources: the fixation of molecular nitrogen by free-living and symbiotic blue-green algae (Fig. 1); and the nitrogen from terrestrial and atmospheric sources[20]. This so called 'new' production, resulting from the assimilation of nitrogen from these sources, can be exported from the productive system without its reducing and, as such, drives both the fish catch and the downward flux of organic matter to bathypelagic and benthic food webs.

To what extent does the sinking flux of particulate organic carbon constitutes a 'sink' for atmospheric CO_2 from fossil fuel burning? Since dissolved inorganic carbon moves upward along with the vertically transported nitrate, in approximately the Redfield ratio[21] of 106 C atoms : 16 N atoms, only the sinking flux due to new production associated with nitrogen fixation and nutrient inputs from terrestrial and atmospheric sources can be identified as a biologically-mediated transport of atmospheric carbon dioxide to the deep ocean.

Estimation of global new production

The geographical and seasonal data on new production estimates, including measurements of nitrate assimilation and nitrogen fixation, are insufficient to assess global new production directly. Total primary production, however, is quantitatively related to new production (Fig. 2) so that the measurements of total production, based on the photosynthetic assimilation of ^{14}C-labelled CO_2, can be used to provide preliminary estimates of global new production.

In Fig. 2, the ratio of new production to total production was calculated in terms of nitrogen from the rate of nitrate incorporation (new production) and the sum of nitrate plus ammonium plus an estimate of the incorporation of urea and other organic nitrogen used by phytoplankton (total production). McCarthy[22] found urea-N incorporation averaged 28% of the total N incorporation measured as nitrate + ammonium plus urea-N in southern California coastal waters. In the central North Pacific, urea-N incorporation averaged about one-half that of ammonium-N[23]. The line of Fig. 2 was not very sensitive to the estimate of organic-N incorporation. Total N incorporation was similar when calculated either as 1.3 (nitrate plus ammonium incorporation, Fig. 2a) or as (nitrate + 1.5 ammonium incorporation, Fig. 2b). Figure 2b shows values for individual stations in the offshore (depth > 300 m) portion of the Southern California Bight, and provides a measure of the station–station variability; it also reveals some interesting exceptions to the expected values.

Data for shallow (<200 m) inshore waters of the Southern California Bight are not shown in Fig. 2b and they often fall below the line drawn in Fig. 2. This is probably because of the increased supply rate of ammonium from sediments and benthos in the shallow waters. The generality of Fig. 2a is applied here only for deep waters not under the influence of terrestrial runoff or the bottom—for waters where the vertical flux of nitrate is the principal driving force for new production[24-26].

Most of the recent estimates of the total ocean primary production are between 20 and 45×10^9 tons C yr^{-1}. To estimate global new production we have used two estimates of total production which distinguish between production over deep water where Fig. 2 might be valid and production in shallow waters where it would not. New production was calculated from these, using Fig. 2a to judge what fraction of total production might be new production. The initial slope of the line of Fig. 2a, for total production <200 g C m^{-2} yr^{-1}, is described by

$$\text{New/Total} = 0.0025 \text{ (Total)} \qquad (1)$$

Tables 1 and 2 offer different regional groupings of the production data. New production from the Koblentz-Mishke *et al.* compilation[27] and excluding their "neritic water" category (Table 1) is 18% of total production or 3.4×10^9 tons C yr^{-1}.

Estimates of Table 2 are based on the most recent measurements of total primary production in the oceans[28]. The estimate of total and new production for waters of depth >200 m, is the highest of those considered and suggests new production is nearly 20% of total production or about 4.7×10^9 tons C yr^{-1}.

Table 1   Ocean primary production by water type* and estimates of new production based on Fig. 2

	Area ($\times 10^6$ km^2)	Primary production (g C m^{-2} yr^{-1})	Primary production ($\times 10^9$ tons C yr^{-1})	New production (% total)	New production ($\times 10^9$ tons C yr^{-1})
Oligotrophic waters of the central parts of subtropical halistatic areas	148	25.6	3.79	6	0.24
Transitional waters between subtropical and subpolar zones; extremity of the area of equatorial divergences	83	51	4.22	13	0.54
Waters of equatorial divergence and oceanic regions of subpolar zones	86	73	6.31	18	1.15
Inshore waters	39	124	4.80	30	1.45
Neritic waters	11	365	(3.90)	46	(1.85)
Totals	356		19.1		3.4

* From ref. 27.

Table 2 Ocean primary production in offshore ocean areas* and estimates of new production based on Fig. 2

| Ocean | Offshore area ($\times 10^6$ km^2) | Primary production ($\times 10^9$) | | New production ($\times 10^9$) | |
		(g C m^{-2} yr^{-1})	tons C yr^{-1}	(% total)	tons C yr^{-1}
Indian	71.0	84	5.96	21	1.25
Atlantic	83.9	102	8.56	26	2.18
Pacific	167	55	9.14	14	1.26
Antarctic	11.8–23.8	325	(3.30)	45	(1.49)
Arctic	13.1	1	(0.13)	0	(0)
Totals	347–359		23.7		4.7

Production over continental shelves and in other areas of water depth <200 m, including coastal upwelling areas, is omitted. Values in parentheses were considered under the <200 m category by Platt and Subba Rao and are omitted from the total estimates.
* From ref. 28.

The polar oceans were not included in the calculations as equation (1) may not apply where growing seasons are short while ambient nutrients are high as in the Antarctic.

The large variation between the estimates of both total and new production for the global ocean leads to the conclusion that new production over the deep ocean may be between 3 and 5×10^9 tons C yr^{-1}, excluding the polar oceans. The lower estimate seems more reasonable in view of estimated rates of the decomposition of organic matter and the attendant oxygen consumption and nutrient regeneration rates in the deep water column. For example, if 18% of total production sinks to the deep ocean (Table 1), and 3.0% reaches the sediments[30], then about 15% or about 2.8×10^9 tons C yr^{-1} would be decomposed in the water column. This decomposition would, in a homogeneous ocean, require about 10 μl O$_2$ l^{-1} yr^{-1} on average. Menzel's[30] oxygen consumption rates are 9.2–13.4 at 500 m depth and 2.1 μl O$_2$ l^{-1} yr^{-1} at 4,000 m. The regeneration of

nitrate from organic nitrogen from such a flux would be about 26×10^{-6} mol m^{-3} yr^{-1} based on Redfield's elemental ratios for particulate organic matter[21] and ignoring losses that could result from the formation of N$_2$ and N$_2$O. If the average nitrate concentration of the deep ocean is 30 mmol m^{-3}, its regeneration or formation time would be ~1,200 yr, a value similar to other estimates of the average residence time of the deep water[1]; Table 2 gives 800 yr for this time. If only 1% of the production reached the sediments this time would be decreased to about 1,000 and 720 yr, respectively. Thus the new production estimates of the sinking of particulate organic matter to the deep sea are not inconsistent with other estimates of the rate of decomposition of organic matter. However, this would incorporate[1,29] a fairly wide range of estimates of such rates and for the flux of particulate organic carbon.

New: total production and nutrient recycling

Figure 2a implies that the extent of nutrient recycling within the euphotic zone varies regionally with the total production rate. If f is the new: total production ratio, then f is the probability that a nitrogen atom is assimilated by phytoplankton via new production and $(1 - f)$ is the probability of assimilation via regenerated production. The number of times a nutrient element is recycled in the euphotic zone before sinking out in particulate form (r) is given by $(1 - f)/f$. For the central North Pacific (Fig. 2a), $f = 0.05$ and $r = 19$. If $f = 0.5$ (the asymptote of Fig. 2a), $r = 1$. Maximum observed values of f are about 0.8 implying that $r = 0.25$, and only one-quarter of the nutrient is recycled while three-quarters sinks out after being assimilated by phytoplankton. This could occur only if intact phytoplankton accounted for a major fraction of the sinking POC, as observed at the end of a spring bloom[10,11], and transiently in the Peru upwelling[13]. The ratio f thus provides qualitative information on the nature of the sinking POC as well as quantitative information on the extent of nutrient recycling within the euphotic zone.
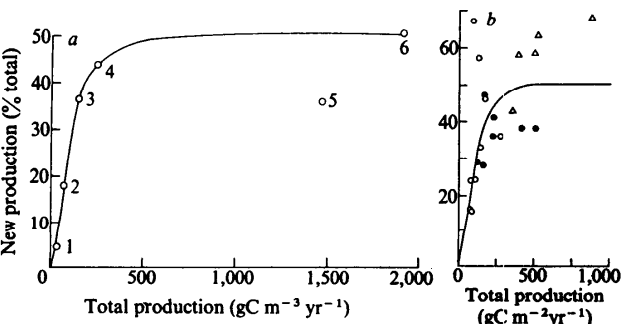
Broecker's geochemical model for the global ocean[1] suggests that an element such as nitrogen is recycled about 10 times in the surface layer before sinking out. Thus $r = 10$, $f \cong 0.1$ and new production is ~10% of the total primary production. Slightly higher values are suggested in Tables 1 and 2 where new production may be about 18 or 20% of total production, respectively.

Checking the validity of the approach

Broecker *et al.*[31] estimated a mean upwelling rate of 27 m yr^{-1} for the equatorial Atlantic between 15° S and 15° N latitude. No measurements of the new: total production ratio have been made there to our knowledge. If the deep-water nitrate concentration is ~15 mmol m^{-3} the nitrate flux to surface waters would be 405 mmol m^{-2} yr^{-1}. From the Redfield ratio, this would support a photosynthetic new production rate of 32.2 g C m^{-2} yr^{-1}; from equation (1) the total primary production would then be $(32/0.0025)^{1/2} = 113$ g C m^{-2} yr^{-1}. Suschenya and Finenko's[32] earlier measurements with the ^{14}C method of primary production in this area gave for the (Northern Hemisphere) fall season an average of 201 g C m^{-2} yr^{-1}. Earlier data for the spring season averaged 88 g C m^{-2}. If annual production were the mean of these values, 145 g C m^{-2} yr^{-1}, this would give fair agreement between the calculated and measured values. Although the result is encouraging, the spatial and temporal variation in the total production measurements suggests that care should be taken in estimating regional averages from a few scattered stations.

Fig. 2 *a*, New production as % of the total primary production versus total production for various ocean areas: (1) Central North pacific, (2) eastern Mediterranean Sea, (3) Southern California Bight, (4) eastern Tropical Pacific, (5) Costa Rica Dome, and (6) Peru upwelling. Total production was measured by the ^{14}C method. New: total production ratio measurements are based on the assimilation of ^{15}N-labelled nitrate and ammonium. Assimilation of urea and other organic-N was assumed to be either 30% of the total N assimilation[22] or one-half of the ammonium assimilation rate[23]. Results were similar with either correction. No correction was applied for new production as molecular nitrogen fixation as this is assumed to be small[33,34]. Values are regional averages from Dugdale[35] (points 2, 4, 5, 6) and from this laboratory[26] (points 1, 3). The total production rates, from ^{14}C measurements of photosynthesis, are not annual averages but are daily rates × 365 for particular sets of measurements. For example, the annual production of the Peru upwelling area is probably less than the 1,900 C m^{-2} yr^{-1} shown here. *b*, New: total production ratio versus total primary production at individual stations in the Southern California Bight. Nearshore stations in water depth <300 m are omitted. New: total production ratio was calculated as nitrate incorporation rate: (nitrate + 1.5 ammonium incorporation rates). For details see ref. 26. Symbols represent different cruises.

Conclusions

New production depends on mixing and vertical advective processes associated with the circulation. Total production also depends on new production and is roughly proportional to it at low to moderate production rates[26]. Thus over geological time climatic changes that reduced vertical mixing and advection must have greatly affected the planktonic production process.

Note that both too little and too much mixing will reduce production, the latter by increasing the critical depth below that which will support net growth of phytoplankton. How increasing levels of atmospheric CO_2 from fossil fuel burning and forest destruction will affect climate-related ocean mixing and hence future plankton production and fisheries harvests is not clear.

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Molecular structure of a left-handed double helical DNA fragment at atomic resolution

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The DNA fragment d(CpGpCpGpCpG) crystallises as a left-handed double helical molecule with Watson–Crick base pairs and an antiparallel organisation of the sugar phosphate chains. The helix has two nucleotides in the asymmetric unit and contains twelve base pairs per turn. It differs significantly from right-handed B-DNA.

MANY biological and chemical phenomena are analysed in the context of the molecular structure of the Watson and Crick[1] double helix of DNA; the B form of DNA is believed to be the predominant form in biological systems. Alternative conformations of the double helix have also been discussed, including modifications of the helical parameters with altered tilting of the bases. Most of our knowledge about the molecular structure of DNA arises from X-ray diffraction studies of DNA fibres[2]. This technique has considerable constraints—the amount of experimental data is small, so the interpretations have to be limited, and atoms are not resolved. To understand the structure of double helical DNA in more detail, it is desirable to crystallise DNA fragments of fixed sequence and solve their three-dimensional structure at atomic resolution. Here we report the crystallisation and structural analysis of a double helical fragment of DNA containing six base pairs with the sequence d(CpGpCpGpCpG). DNA with an alternating dG–dC sequence is of considerable interest as it is known to exist in two distinctly different conformations which are stable in both low or high salt solutions[3]. The crystal structure of this self-complementary hexamer has been solved to atomic resolution at 0.9 Å. The structure is found to be a left-handed double helix with a novel three-dimensional structure which is quite distinct from the familiar right-handed helical B form of DNA.

Crystallisation and structure solution

The ammonium salt of the deoxy hexamer d(CG)₃ was prepared by a slight modification of the recently developed[4,5] phosphotriester approach. The crystals were grown from a solution containing 30 mM sodium cacodylate buffer (pH 7.0), 10 mM spermine tetrachloride, 15 mM $MgCl_2$ and 2 mM d (CG)₃ using the vapour diffusion method as developed for tRNA crystallisation[6]. The precipitating agent was 5% isopropanol. Crystals grew in the form of truncated rectangular plates over a period of 3 weeks and crystals measuring up to $0.7 \times 0.7 \times 0.5$ mm were obtained for X-ray diffraction analysis. Crystals were mounted in a sealed glass capillary together with a droplet of mother liquor. The crystal was orthorhombic with space group P2₁2₁2₁ and cell dimensions $a = 17.88$, $b = 31.55$ and $c = 44.58$ Å. The h01 precession photograph revealed strong reflections in the region 3.4–3.7 Å along the c axis which suggested that the molecules were aligned with their bases perpendicular to the c axis. From the unit cell dimensions, we estimated that there would be one duplex containing 12 nucleotides in the asymmetric unit. The crystals were highly ordered and complete three-dimensional data were collected to a resolution of 0.9 Å using a Picker diffractometer.

The structure was solved by the method of multiple isomorphous replacement using three different heavy atom derivatives, Ba^{2+}, Co^{2+} and Cu^{2+}. Phase determination was carried out using the method of Blow and Crick[7], yielding a mean figure of merit $\bar{m} = 0.76$ to 2 Å resolution and the 'best' Fourier map was calculated[8]. The structure was traced from this electron density map and rough atomic coordinates were measured directly from the map. The structure was refined using the Konnert–Hendrickson refinement procedures[9]. Several cycles of difference Fourier and sum function Fourier ($2F_0 - F_c$) maps were calculated in order to locate all the atoms of the molecule as well as 62 water molecules, 1 hydrated Mg^{2+} ion and 2 spermine molecules. The mass of the asymmetric unit is