Further Reading

Broecker WS and Peng, TH (1982) *Tracers in the Sea*. New York: Eldigio Press.

Bullister JL (1989) Chlorofluorocarbons as time-dependent tracers in the ocean. *Oceanography* 2: 12–17.

England MH (1995) Using chlorofluorocarbons to assess ocean climate models. *Geophysical Research Letters* 22: 3051–3054.

England MH and Maier-Reimer E (2001) Using chemical tracers to assess ocean models. *Review of Geophysics* 39: 29–70.

Libers SM (1992) *An Introduction to Marine Biogeochemistry*. New York: John Wiley.

Maier-Reimer E (1993) Design of a 3D biogeochemical tracer model for the ocean. In: Anderson D and Willebrand J (eds) *Modelling Oceanic Climate Interactions*, NATO, ASI Series, Vol. 111, Berlin: Springer-Verlag. 415–464.

Sarmiento JL (1983) A simulation of bomb tritium entry into the Atlantic Ocean. *Journal of Physical Oceanography* 13: 1924–1939.

Toggweiler JR, Dixon K and Bryan K (1989) Simulations of radiocarbon in a coarse-resolution world ocean model. *Journal of Geophysical Research* 94: 8217–8264.

TRACERS OF OCEAN PRODUCTIVITY

W. J. Jenkins, University of Southampton, Southampton, UK

doi:10.1006/rwos.2001.0174

Introduction

Primary production is the process whereby inorganic carbon is fixed in the sunlit (euphotic) zone of the upper ocean, and forms the base of the marine food pyramid. It occurs when marine phytoplankton use sunlight energy and dissolved nutrients to convert inorganic carbon to organic material, thereby releasing oxygen. The total amount of carbon fixed during photosynthesis is called gross production, whereas the amount of carbon fixed in excess of internal metabolic costs is referred to as net production. It is understood that a significant fraction of the carbon fixed in this manner is rapidly recycled by a combination of grazing by zooplankton and *in situ* bacterial oxidation of organic material. New production is that portion of net production that is supported by the introduction of new nutrients into the euphotic zone. Traditionally, this has been regarded as production fueled by nitrate as opposed to more reduced forms of nitrogen, such as ammonia and urea. Some portion of the fixed carbon sinks out of the euphotic zone in particulate form, or is subducted or advected away as dissolved organic material from the surface layers by physical processes. This flux is regarded collectively as export production. The ratio of new (export) to net production, referred to as the f-ratio (e-ratio) can vary between 0 and 1, and is believed to be low in oligotrophic ('blue water'), low productivity regions, and higher in eutrophic, high productivity regions. Finally, net community production is the total productivity in excess of net community metabolic cost. On sufficiently long space- and time-scales, it can be argued that new, net community, and export production should be equivalent in magnitude.

Net production has been measured 'directly' by radiocarbon incubation experiments, whereby water samples are 'spiked' with radiocarbon-labeled bicarbonate, and the net rate of transfer of the radioisotope into organic matter phases determined by comparison of light versus dark incubations. Global maps of net productivity have been constructed on the basis of such measurements, and current estimates indicate a global fixation rate of order 50 GT C a^{-1} (1 GT = 10^{15} g). Rates of export, new, and net community production are more difficult to determine directly, yet are of equal importance as determinants of biogeochemically important fluxes on annual through centennial timescales.

Geochemical tracer techniques have been used to make such estimates, and offer significant advantages in that they are fundamentally nonperturbative, and integrate over relatively large space-scales and long time-scales. Conversely, such determinations must be viewed from the perspective that they are indirect measures of biogeochemical processes, and have characteristic implicit space- and time-scales, as well as boundary conditions, and sometimes ambiguities and model dependence. Further, the specific tracer or physical system used to obtain production estimates determines the type of productivity measured. Thus any treatment of geochemical tracer estimates must include a discussion of these attributes.

Measuring Oceanic Productivity with Tracers

Just a few approaches will be discussed here. Other techniques have been used with some success, parti-

cularly with relation to particle interceptor traps, but this section will concentrate on basic mass budgeting approaches using water column distributions or seasonal cycling of tracers. There are three basic, yet fundamentally independent approaches that can be used.

1. Aphotic zone oxygen consumption rates that, when vertically integrated, provide a net water column oxygen demand that can then be related stoichiometrically to a carbon export flux.
2. Seasonal timescale euphotic zone mass budgets, particularly of oxygen, carbon, and carbon isotopes, which lead to estimates of net community production.
3. Tracer flux-gauge measurements of physical mechanisms of nutrient supply to the surface ocean, which place lower bounds on rates of new production.

These techniques, summarized in **Figure 1**, yield estimates of subtly different facets of biological production. On annual timescales, however, these different modes of production should be very close to equivalent, and hence the results of these various measurement approaches should be comparable. As shown below, their quantitative agreement coupled with their essential independence lends an inductive support to the validity of their results.

Aphotic Zone Oxygen Consumption Rates

In the surface ocean air–sea gas exchange controls the composition of dissolved gases and phytoplankton release oxygen. Below, in the aphotic (nonsunlit) zone, oxygen is generally undersaturated, because bacterially mediated oxidation of sinking organic material consumes oxygen. Credible estimates of aphotic zone oxygen consumption rates have been made since the 1950s. However, the earliest quantitative linkage to primary production was in 1982. The principle behind it is dating water masses and dividing the age of the water mass into the observed oxygen deficit. Another approach involves correlating water mass age along streamlines with oxygen concentration (older water has less oxygen). This dating can be achieved by a technique such as tritium-^{3}He dating, which uses the ingrowth of the stable, inert noble gas isotope ^{3}He from the decay of the radioactive heavy isotope of hydrogen (tritium), according to:

$$^3\mathrm{H} \xrightarrow{12.45\mathrm{y}} {}^3\mathrm{He}$$

If surface waters are in good gas exchange contact with the atmosphere, then very little ^{3}He will accumulate due to tritium decay. Once isolated from the surface, this ^{3}He can accumulate. From the

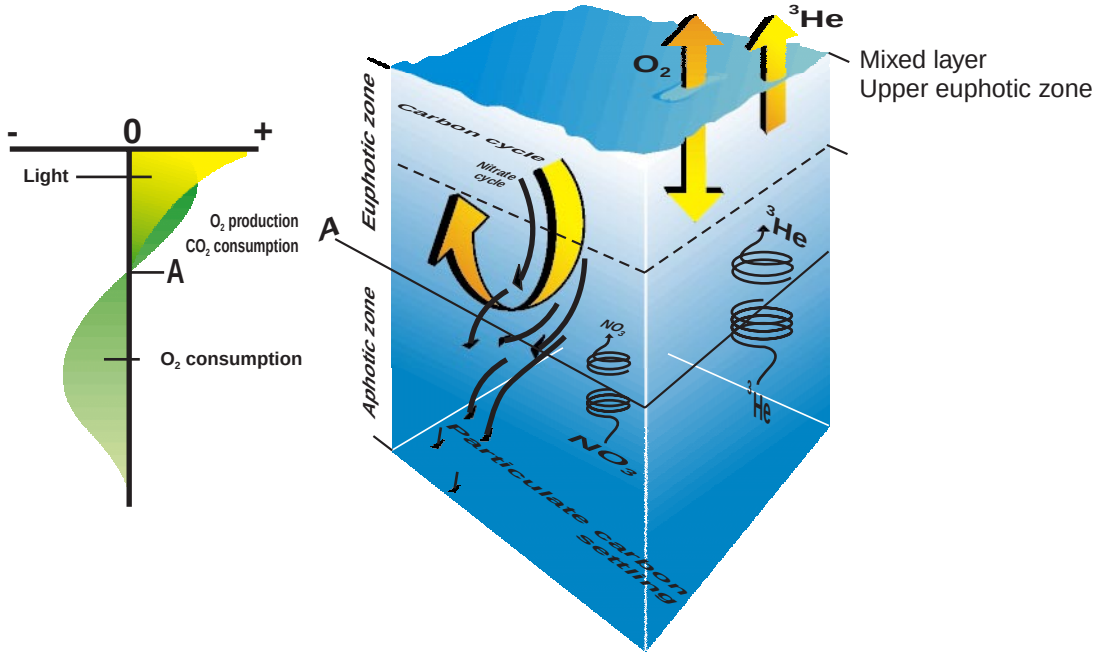

Figure 1 A schematic of the upper ocean, showing material fluxes and various tracer constraints on primary production.

measurement of both isotopes in a fluid parcel, a tritium-^{3}He age can be computed according to:

$$\tau = \lambda^{-1}\ln\left(1 + \frac{[^3\mathrm{He}]}{[^3\mathrm{H}]}\right)$$

where λ is the decay probability for tritium, and τ is the tritium-^{3}He age (usually given in years). Under typical Northern Hemispheric conditions with current technology, times ranging from a few months to a few decades can be determined.

Although a conceptually simple approach, under normal circumstances mixing must be accounted for because it can affect the apparent tritium-^{3}He age in a nonlinear fashion. Furthermore, in regions of horizontal oxygen gradients, lateral mixing may significantly affect apparent oxygen consumption rates. For example, following a fluid parcel as it moves down a streamline, mixing of oxygen out of the parcel due to large-scale gradients will masquerade as an augmentation of oxygen consumption rates. These issues can be accounted for by determining the three-dimensional distributions of these properties, and applying the appropriate conservation equations. With additional constraints provided by geostrophic velocity calculations, these effects can be separated and absolute oxygen consumption rates can be computed as a function of depth. **Figure 2** shows profiles of oxygen consumption rates as functions of depth for two locales in the subtropical North Atlantic. Integration of these curves as a function of depth gives net water column oxygen demands of $6.5 \pm 1.0\,\mathrm{mol\,m^{-2}\,a^{-1}}$ for the Sargasso Sea and $4.7 \pm 0.5\,\mathrm{mol\,m^{-2}\,a^{-1}}$ in the eastern subtropical North Atlantic. Using the molar ratio of oxygen consumed to carbon oxidized for organic material (170 : 117), the flux of carbon from the euphotic zone above required to support such an oxygen demand can be calculated for the two regions (4.5 ± 0.7 and $3.2 \pm 0.4\,\mathrm{mol\,C\,m^{-2}\,a^{-1}}$).

The character of these estimates bears some consideration. Firstly, according to the definitions of primary production types described earlier, this represents a determination of export productivity. Secondly, the determinations represent an average over timescales ranging from several years to a decade or more. This is the range of ages of the water masses for which the oxygen utilization rate has been determined. Thirdly, the corresponding space-scales are of order 1000 km, for this is the region over which the age gradients were determined. Fourthly, although the calculation was done assuming that the required carbon flux was particulate material, it cannot distinguish between the destruction of a particulate rain of carbon and the *in situ* degradation of

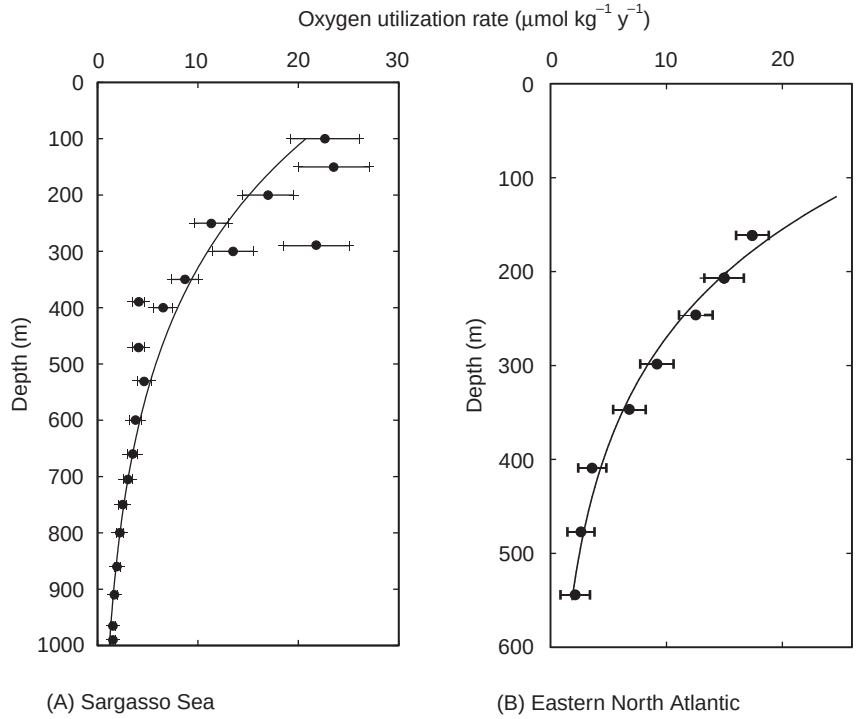

Figure 2 Aphotic zone oxygen consumption rates as a function of depth for two locales in the subtropical North Atlantic. These consumption rates are based on tritium-^{3}He dating and other tracer techniques.

dissolved organic material advected along with the water mass from a different locale. These characteristics must be borne in mind when comparing this with other estimates.

Seasonal Euphotic Zone Mass Budgets

There have been three basically independent approaches to estimating net community production based on observation of the seasonal cycles of oxygen and carbon in the upper ocean. Photosynthesis in the euphotic zone results in the removal of inorganic carbon from the water column, and releases oxygen (**Figure 3**). Recycling of organic material via respiration and oxidation consumes oxygen and produces CO_2 in essentially the same ratios. It is only that carbon fixation that occurs in excess of these processes, i.e., processes that result in an export of organic material from the euphotic zone, or a net biomass increase, that leaves behind an oxygen or total CO_2 (ΣCO_2) signature. Estimates of productivity based on euphotic zone oxygen or carbon budgets are consequently estimates of net community production. Such productivity estimates are

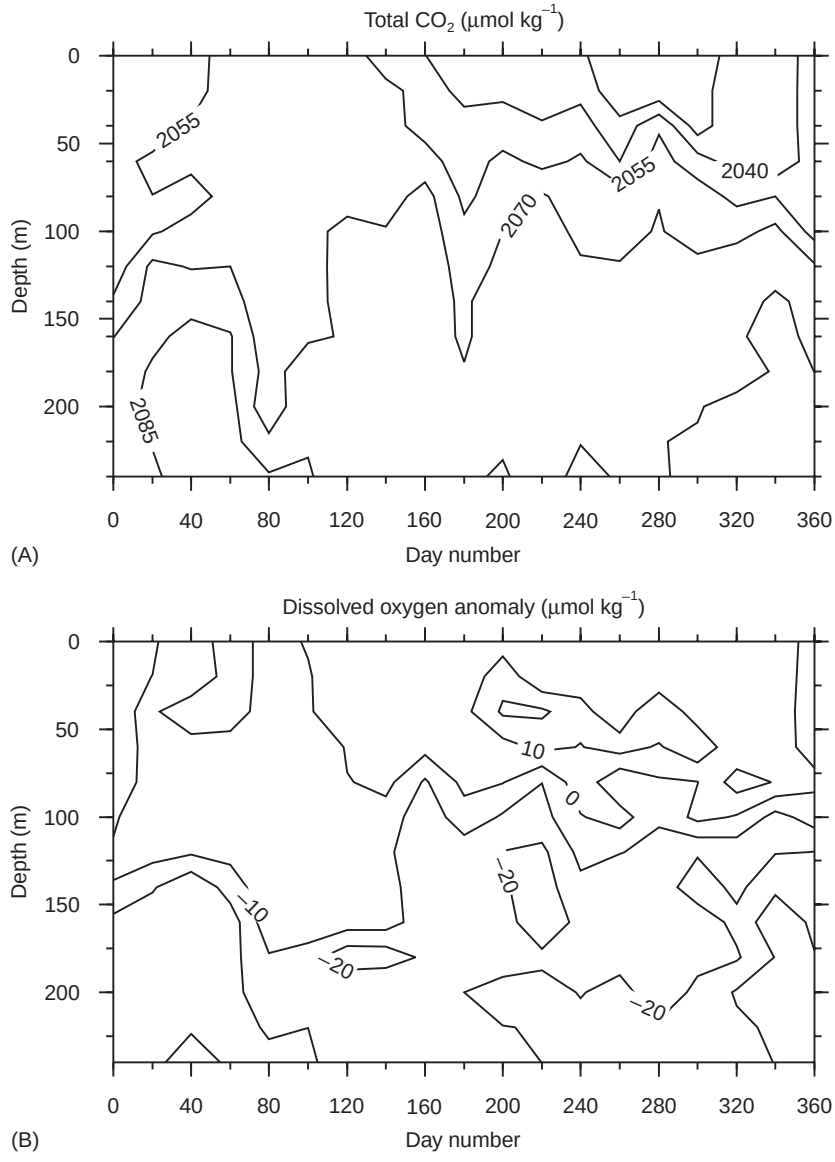

Figure 3 Euphotic zone seasonal cycles of total inorganic carbon (A) and oxygen (B) near Bermuda. Note the build-up of oxygen anomaly and reduction of total CO_2 in the euphotic zone during the summer months due to photosynthetic activity.

characterized by seasonal to annual timescales, and space-scales of order of a few hundred kilometers.

In subtropical waters, excess oxygen appears within the euphotic zone just after the onset of stratification, and continues to build up throughout summer months. Use of the seasonal accumulation of photosynthetic oxygen in the upper ocean to estimate primary production is complicated by the fact that it tends to be lost to the atmosphere by gas exchange at the surface. Furthermore, temperature changes due to seasonal heating and cooling will change the solubility of the gas, further driving fluxes of oxygen across the air–sea interface. In addition, bubble trapping by surface waves can create small supersaturations. While such processes conspire to complicate the resultant picture, it is possible to use observations of noble gases (which do not undergo biological and chemical processing) and upper ocean physical models to interpret the seasonal cycle of oxygen. These calculations have been successfully carried out at a variety of locations, including the subtropical North Atlantic and the North Pacific. In the Sargasso Sea, estimates of oxygen productivity range from 4.3 to $4.7\,\mathrm{mol\,m^{-2}\,a^{-1}}$. Using the molar ratio of oxygen released to carbon fixed in photosynthesis of 1.4 : 1, the carbon fixation rate is estimated to be $3.2 \pm 0.4\,\mathrm{mol\,m^{-2}\,a^{-1}}$.

There is also a net seasonal decrease in ΣCO_2 attributable to photosynthesis at these locations. Such decreases are simpler to use in productivity estimates, principally because air–sea interaction has a much weaker influence on ΣCO_2. On the other hand, precise measurements are required because the photosynthetically driven changes are much smaller compared with the background ΣCO_2 levels. Because of these differences, estimates based on ΣCO_2 seasonal cycles offer an independent measure of euphotic zone mass budgets.

Finally, differences in the carbon isotopic ratio between organic and inorganic carbon, as well as atmospheric CO_2, allow the construction of yet a third mass budget for the euphotic zone. There is a clear carbon isotope signature that can be modeled as a function of primary production, air–sea exchange, and mixing with deeper waters.

Tracer Flux-Gauge Determinations

The third tracer constraint that may be used to determine primary production involves the use of 'tracer flux gauges' to estimate the flux of nutrients to the euphotic zone. This approach relies on the premise that the physical mechanisms that serve to transport nutrients to the euphotic zone from the nutrient-rich waters below also carry other tracers in fixed proportion. If the rate at which these other tracers are transported can be determined, and the nutrient to tracer ratio at the 'source' is known, then the corresponding nutrient flux may be inferred; that is:

$$F_{\mathrm{Nutrient}} = \left[\frac{\mathrm{Nutrient}}{\mathrm{Tracer}}\right]_{\mathrm{Source}} \times F_{\mathrm{Tracer}}$$

Inasmuch as there may be alternate, biologically mediated pathways (such as zooplankton migration), such a calculation would serve as an underestimate to the total nutrient flux.

Measurements of the rare, inert isotope ^{3}He in the mixed layer of the Sargasso Sea near Bermuda reveal a persistent excess of this isotope over solubility equilibrium with the atmosphere (**Figure 4**). The existence of this excess implies a flux of this isotope to the atmosphere, which can be calculated using the estimated gas exchange rate. Although ^{3}He is produced in the water by the *in situ* decay of tritium, it can be shown that only about 10% of the observed flux can be explained by tritium decay within the euphotic zone. The greater portion of this ^{3}He flux arises from the upward 'exhalation' of old tritium-produced ^{3}He from the waters below. That is, the ^{3}He flux observed leaving the surface ocean is largely the loss of this isotope from the main thermocline.

The ocean–atmosphere flux of ^{3}He shows a pronounced seasonal variation, with the greatest fluxes in the winter months. The winter maximum is due to high rates of gas exchange (more vigorous winter winds lead to higher gas exchange rates) and deeper winter convection. This is the time history of the ^{3}He flux out of the upper ocean. The time history of the ^{3}He flux to the upper ocean may be different. However, the annual mean fluxes must be the same, since the winter mixed layer penetrates below the bottom of the euphotic zone. The annual average ^{3}He flux from the ocean surface near Bermuda is $1.84 \pm 0.25\%\text{-m}\,\mathrm{d^{-1}}$. To estimate the flux of ^{3}He entering the euphotic zone from below, this flux must be corrected for the *in situ* production of ^{3}He by the decay of tritium within the euphotic zone, which produces a ^{3}He flux of $0.20 \pm 0.02\%\text{-m}\,\mathrm{d^{-1}}$. The resultant flux is thus $1.64 \pm 0.25\%\text{-m}\,\mathrm{d^{-1}}$.

Insofar as there is a strong correlation between the concentrations of this isotope and nutrients within the waters below the euphotic zone (older waters are richer in both ^{3}He and nutrients), the ratio of ^{3}He to nutrient can be employed to compute nutrient flux. **Figure 5** is a composite plot of ^{3}He

versus nitrate in the upper 600 m over a 3 year period. The slope of the relationship is $0.87 \pm 0.05\,\mu mol\,kg^{-1}‰^{-1}$.

Applying the flux equation presented above, a nitrate flux of $0.56 \pm 0.16\,mol\,m^{-2}\,a^{-1}$ is computed. Using the average biological C : N ratio of 6.6, this leads to a carbon fixation rate of $3.7 \pm 1.0\,mol\,m^{-2}\,a^{-1}$. The estimate thus obtained is a local, annual-scale measure of new production.

A similar calculation can be made by observing the long-term (decade timescale) trends in thermocline ^{3}He inventories. The long-term evolution of ^{3}He inventory in the thermocline must respond to the opposing processes of production by tritium decay and 'exhalation' upward to the euphotic zone. Knowing the former gives the latter. Using nutrient-^{3}He ratios, a gyre-scale, decadal average estimate of the nutrient flux to the euphotic zone can be

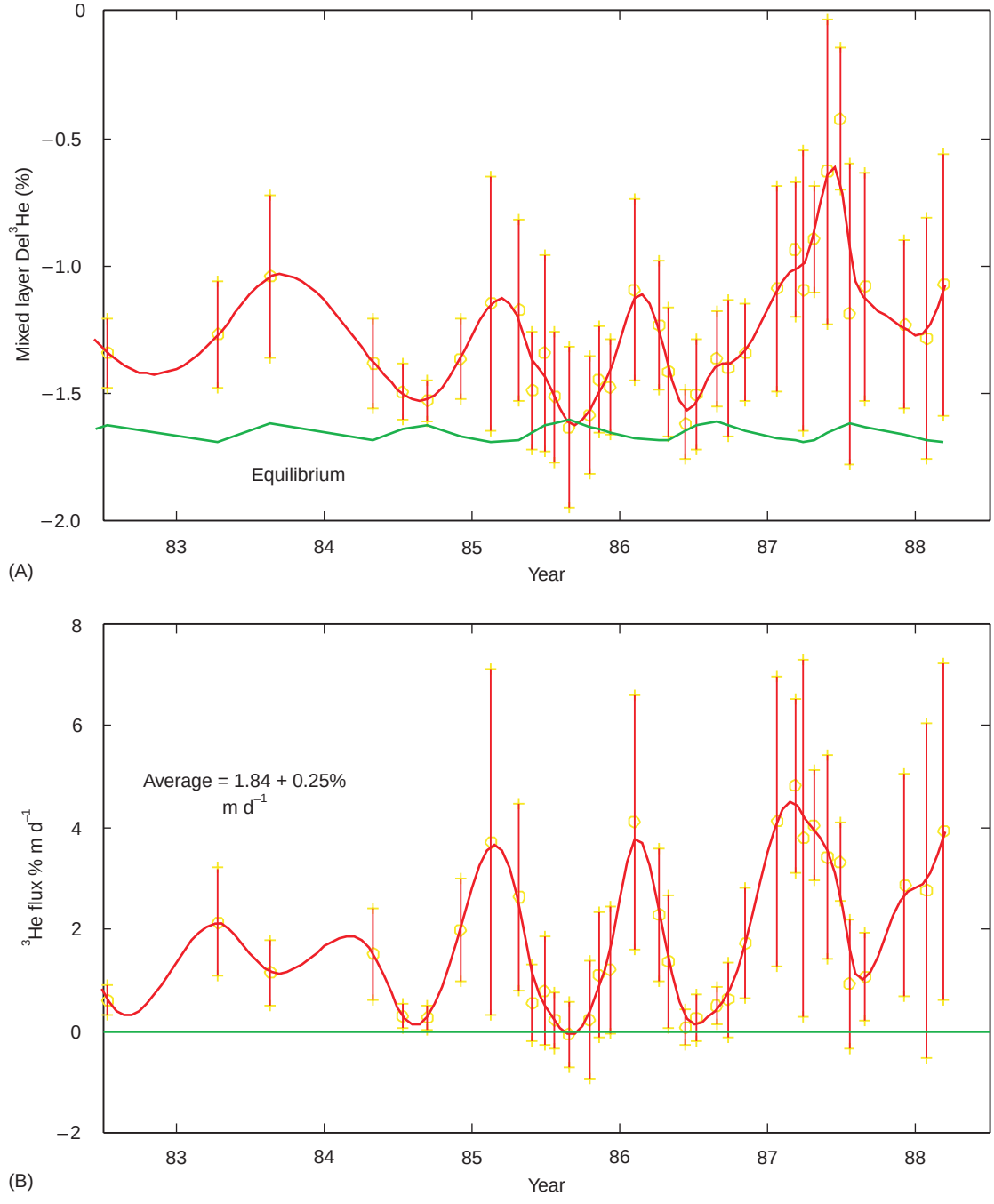

Figure 4 An approximately 6 year history of surface water ^{3}He isotope ratio anomalies (A) and computed flux to the atmosphere near Bermuda (B).

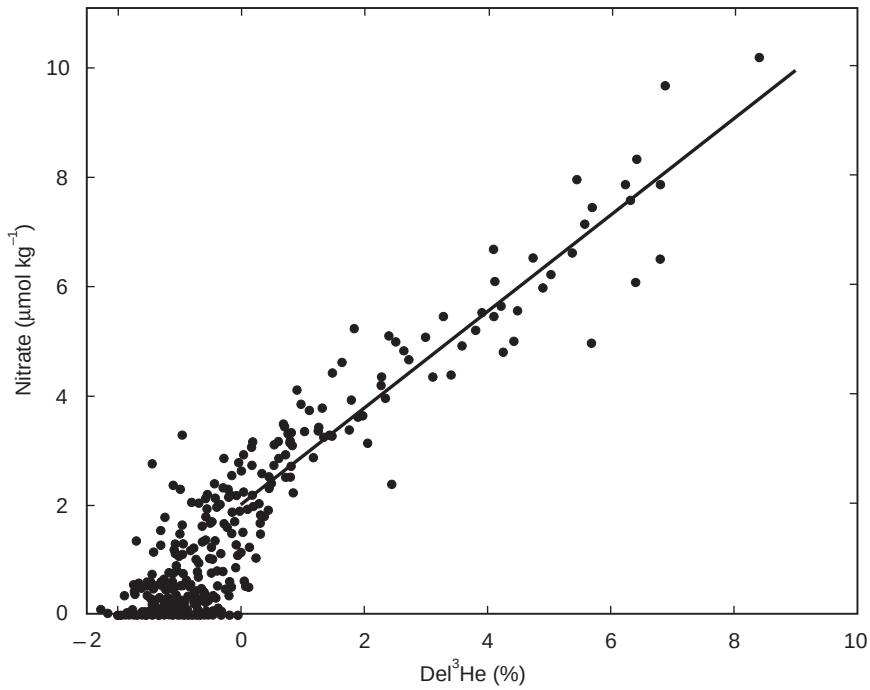

Figure 5 The correlation of ^{3}He isotope ratio anomaly (in %) and nitrate (in μmol kg^{-1}) in the upper ocean near Bermuda for the period 1985–88.

obtained. A detailed analysis of the long-term trends of tritium and ^{3}He in the upper 1000 m of the Sargasso Sea, coupled with the observed nitrate : ^{3}He ratios, yields an estimate of 0.70 ± 0.20 mol m^{-2} a^{-1}. This leads to a somewhat higher carbon fixation rate of 4.6 ± 1.3 mol m^{-2} a^{-1}. This estimate differs from the surface layer flux calculation in that it is a much longer-term average, since it depends on the very long-term evolution of isotopes in the thermocline. Moreover, it represents a very large-scale gyre-scale determination, rather than a local measure: horizons within the thermocline probably connect to regions of higher productivity further north.

Table 1 Comparison of tracer-derived estimates near Bermuda in the Sargasso Sea

Type of determination	*Type of production*	*Technique used*	*Carbon flux (mol m^{-2} a^{-1})*
Aphotic zone oxygen consumption rates	Export production	Tritium-^{3}He dating	4.5 ± 0.7
Euphotic zone cycling	Net community	Oxygen cycling	3.2 ± 0.4
		Carbon isotopes	3.8 ± 1.3
Tracer flux-gauge	New production	Mixed layer ^{3}He	3.7 ± 1.0
		Thermocline budgets	4.6 ± 1.3

Comparing Tracer-Derived Estimates

Although the various techniques described here are based on differing assumptions, and measure different types of production, they should be mutually consistent on annual or greater timescales. **Table 1** is a comparison between the various estimates near Bermuda in the Sargasso Sea. A weighted average of these determinations gives a productivity of 3.6 ± 0.5 mol (C) m^{-2} a^{-1} for the Sargasso Sea near Bermuda. The determinations are within uncertainties of each other, although they utilize different tracer systems, are reliant on different assumptions, and are virtually independent of each other. This agreement provides some confidence as to their accuracy.

See also

Air–Sea Transfer: N_2O, NO, CH_4, CO. Carbon Cycle. Primary Production Distribution. Primary Production Processes. Tritium–Helium Dating.

Further Reading

Falkowski PG, Woodhead AD (1992) *Primary Productivity and Biogeochemical Cycles in the Sea*. New York: Plenum Press.

Jenkins WJ (1995) Tracer based inferences of new and export primary productivity in the oceans. *IUGG, Quadrennial Report* 1263–1269.

Williams PJ leB (1993) On the definition of plankton production terms. *ICES Marine Science Symposium* 197: 9–19.