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PART I

In vitro O_2 fluxes compared with ^{14}C production and other rate terms during the JGOFS Equatorial Pacific experiment

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Abstract

We report rates of gross and net O_2 production measured in vitro during JGOFS cruises in the equatorial Pacific in spring and fall, 1992. We scale O_2 productivities to net and gross C production. We then compare the calculated rates with ^{14}C production and with new/export production measured by various techniques. ^{14}C productivities in samples incubated for 24 h are about 45% of gross carbon production rates calculated from gross O_2 production. The difference is compatible with expected rates of the Mehler reaction, photorespiration, excretion, and community mitochondrial respiration. ^{14}C production rates are similar to net carbon production rates in the upper half of the euphotic zone. At lower irradiances, where net C production can be zero or less, ^{14}C productivities lie between net community production and gross primary production. Net carbon production rates in vitro are a factor of $\sim$4–20 times greater than estimates from drifting sediment trap and tracer transport studies. This difference probably reflects anomalous accumulation of POC in bottles because of the exclusion of grazers. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction and background

Rates of gross carbon production and net community production are fundamental properties of oceanic ecosystems. Chlorophyll-normalized gross production itself

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reflects the nutrient sufficiency of the environment and the response of the photosynthetic apparatus to light. The ratio of net/gross production reflects the efficiency of ecosystems in recycling biomass. Net production is linked to new production and the accumulation or export of POC and DOC. Export limits productivity by removing nutrients from surface water. It also enriches the deep ocean with bioactive elements compared to most of the surface ocean.

Important uncertainties attend nearly all experiments to measure rates of net and gross production. Measurements of biological rates in vitro suffer from artifacts associated with enclosing seawater in bottles as well as problems inherent in the individual methods. Enclosure excludes large grazers and may be especially harmful to microzooplankton (Harrison and Harris, 1986). Thus bottle effects can either enhance the growth of certain microzooplankton by excluding their predators, or induce their mortality because of enclosure. Any change in microzooplankton abundance will in turn affect the biomass of the phytoplankton on which they graze. Such changes pose a particularly acute problem with respect to the measurement of net production. This term depends on the difference between rates of photosynthesis and respiration, processes that are not necessarily closely coupled over typical incubation times (up to 24 h). Suppression of respiration by the death of microheterotrophs, together with enhanced phytoplankton production due to the same cause, can lead to high rates of net production in vitro even when the true oceanic value is close to zero. Reduction of microheterotroph mortality might have the same effect, at least for limited periods. Rising chlorophyll concentrations during incubations (Cullen et al., 1992; Martin and Fitzwater, 1988) presumably reflect such processes. The elimination of most turbulence, poor simulation of the light field, and other factors introduce additional errors into metabolic rates measured in vitro.

Some approaches for measuring metabolic rates in vitro have inherent methodological problems that cause them to (generally) underestimate the true rate within the bottle itself, or introduce ambiguity into exactly what is being measured. Remineralization of $PO^{14}C$ will cause ^{14}C productivity to lie between net community and gross primary production (e.g. Eppley, 1980). If $DO^{14}C$ is produced but not measured, ^{14}C productivity can even be less than net community production. $^{15}NO_3^-$ uptake rates are also susceptible to recycling of the label by remineralization and $DO^{15}N$ excretion (Bronk et al., 1994). These problems can be at least partly alleviated by using short incubation times to minimize remineralization and changes in the nature of the enclosed community (McCarthy et al., 1997; Cullen et al., 1992). On the other hand, determining net production becomes increasingly difficult for shorter incubation times, because photosynthesis and respiration are decoupled for time scales shorter than diurnal.

The central equatorial Pacific Ocean is a region of special interest for carbon cycling studies. Divergence here brings cool, nutrient-rich waters to the surface. Chlorophyll is elevated (e.g. Barber et al., 1997; Lindley et al., 1995), although low by comparison with coastal waters of similar nutrient concentration. Along the JGOFS transect, productivity between 2°N–2°S is higher, by about a factor of 3, than in nearly oligotrophic waters at the ends of the transect ($\sim$12°N and 12°S) (Barber et al., 1997).

The U.S. JGOFS Equatorial Pacific study (Murray et al., 1995) included measurements of carbon fluxes by a wide range of methods involving in vitro experiments as well as studies with sediment traps and proxy measures of carbon fluxes (e.g. ^{234}Th). Important goals of EqPac were to determine regional carbon fluxes and investigate the relationships between the various rate processes.

Our experimental contribution to EqPac included measuring net O_2 production, gross O_2 production (Bender et al., 1987), and $PO^{14}C$ production (Barber et al., 1997) in samples incubated for 24 h. We did this work during an 18 day occupation of a station at 0°, 140°W in the (boreal) spring of 1992 (March 23–April 10) and a 19 day occupation in the fall of 1992 (Oct. 2–Oct. 21) at the same location.

We use data on the stoichiometric relationship between O_2 and C_{org} fluxes (Laws, 1991) to scale net and gross O_2 production to carbon fluxes. We compare our measurements of net production with carbon fluxes inferred from ^{15}N uptake studies (McCarthy et al., 1997; Wheeler, unpublished results), particle rain rates measured in drifting sediment traps (Murray et al., 1997), ^{234}Th/C ratios (Buesseler et al., 1995), and water fluxes together with the water column distribution of NO_3^-, DOC and O_2. All data are available on the World Wide Web via the home page of the U. S. Joint Global Ocean Flux Program (http://www.whoi.edu/jgofs.html). We then compare ^{14}C production to net and gross C_{org} production rates inferred from O_2 studies as well as $^{15}NO_3^-$ assimilation rates. Finally we discuss the observed relationships.

2. Experimental

We measured ^{14}C production by spiking water with $H^{14}CO_3^-$, incubating the samples, and determining the quantity of $PO^{14}C$ collected on a Whatman GF/F glass fiber filter (Barber et al., 1997). ^{14}C samples were incubated in 0.28 l polycarbonate bottles, and net and gross O_2 production experiments were done in $\sim$0.1 l quartz bottles. ^{14}C and oxygen samples were incubated in situ for 24 h beginning at dawn. Samples were incubated at depths corresponding to the following levels of sea-surface irradiance: 100%, 50%, 30%, 14%, 5% and 1%. ^{14}C samples were also incubated at the 7% and 0.1% light levels. ^{15}N assimilation measurements by McCarthy et al. (1997) were done on samples incubated on board ship for 4 h in 2.8 l polycarbonate bottles and filtered onto Whatman GF/F glass fiber filters. Methods for daily irradiance and irradiance-depth profiles are summarized on the JGOFS WWW site.

In those experiments where we measured net production only, we measured this property by determining the $[O_2]$ change from beginning to end of the incubation period. When we measured net production only, we measured initial and final $[O_2]$ by Winkler titration of quadruplicate samples drawn from the same Go-Flo bottle. The reproducibility of initial $[O_2]$ values was about $\pm$ 0.15 μmol/l, with some variability depending on which Go-Flo bottle samples were drawn from. We achieved absolute calibration of our O_2 analyses by comparison with O_2 concentrations measured on samples drawn from the same Go-Flo bottles by the shipboard hydrography group. When we measured gross O_2 production, we measured net production from the

change in the $[O_2]/[Ar]$ ratio before and after the incubation. Duplicate samples were analyzed. Net production was calculated from the formula:

$$\text{Net } O_2\text{production} = [O_2]_i \left(\frac{[O_2]}{[Ar]_f} - \frac{[O_2]}{[Ar]_i} \right) \Big/ \frac{[O_2]}{[Ar]_i}.$$

The subscripts f and i denote final and initial, respectively.

We measured gross O_2 production by spiking seawater with $H_2{}^{18}O$ and determining the transfer rate of the label to O_2 during the incubation (Bender et al., 1987). O_2 collected at the end of the incubation was generally enriched by 10‰ or more with respect to the initial seawater. The corresponding uncertainty in the magnitude of the change in $\delta^{18}O$ of O_2, and hence gross production, is $< 2\%$. A strength of this method comes from the fact that the O_2 concentration of seawater, typically 220 $\mu mol\,l^{-1}$, is much greater than that of biomass ($\sim 5\ \mu mol\,l^{-1}$). If the turnover time of phytoplankton is 1 day, recycling of labeled O_2 will be small (2%) during a 24 h incubation while recycling of labelled $PO^{14}C$ would be very large. A second advantage of the ^{18}O method is that all photosynthetic O_2 goes into a single, well defined pool, the dissolved phase, which we sample quantitatively. ^{14}C-labelled organic matter can be in POC, DOC, or colloidal material, and the $DO^{14}C$ and some colloidal material were not sampled.

We use the procedure of Emerson et al. (1991) to measure the isotopic composition of O_2 and the O_2/Ar ratio. We extract dissolved gases from seawater into pre-evacuated $\sim 0.1\,l^{-1}$ glass flasks sealed with a glass barrel valve and Viton O-ring. In the laboratory, we remove CO_2 and H_2O at liquid N_2 temperatures and quantitatively freeze the remaining gas into a stainless steel tube immersed in liquid He. We allow the gas to warm and mix, then admit the gas into the mass spectrometer and analyze it against an O_2–N_2–Ar mixture with a composition similar to that of gas extracted from saturated seawater (Emerson et al., 1991). We measure $\delta^{18}O$, $\delta^{15}N$, and $\delta O_2/N_2$ (as 32/29) by simultaneous double collection, then measure $\delta(O_2/Ar)$ by peak jumping. Isotope ratios are corrected for the aliasing effects of pressure imbalances between sample and reference gas. The mass spectrometry procedure is described in more detail by Sowers et al. (1989) and Kiddon (1993).

Daily gross O_2 production (GPP) is calculated from the formula:

$$\text{GPP} = \left[\frac{\delta^{18}O(O_2)_{\text{final}} - \delta^{18}O(O_2)_{\text{initial}}}{\delta^{18}O_{\text{water}} - \delta^{18}O(O_2)_{\text{initial}}} \right] \times [O_2]_{\text{initial}}.$$

Based on the stoichiometry of production and respiration given by Laws (1991), we calculate C_{org} production from the formulae:

Net C_{org} production = Net O_2 production/1.4.
Gross C_{org} production = Net C_{org} production + (gross − net O_2 production)/1.1.

These equations invoke the assumption that assimilated N for new production derives from NO_3^- and for regenerated production from NH_4^+.

3. Results and discussion

In Figs. 1 and 2, we plot ^{14}C production, net C production, and gross C production vs. depth for each incubation experiment. All three measures of carbon production decrease with depth in the water column, as expected. In Fig. 3, we plot 24 h production vs. integrated irradiance (calculated at each depth by multiplying daily integrated sea surface irradiance by the fraction of surface irradiance reaching that depth). ^{14}C and gross C production normalized to chlorophyll increase as irradiance rises, with the expected hyperbolic dependence. Given the considerable scatter in the data, the generally hyperbolic shape of the curves of integrated P vs. integrated I does not require that photosynthetic parameters were independent of depth. In fact Cullen et al. (1992) demonstrate that α and P^{B}_{max} are depth dependent on the equator at 150°W, and Lindley et al. (1995) have shown considerable depth dependence in the quantum yield. Cullen et al. (1992) also showed that photosynthetic properties varied with depth as well as with time of day along the Equator at 150°W.

3.1. Comparison of various measured production rates

^{14}C production is plotted vs. gross C production in Fig. 4, and we tabulate values of production integrated to the 1% light level in Table 1. ^{14}C production averages 45% of gross C production for both cruises (Table 1). This number is calculated by dividing average daily depth-integrated values of ^{14}C production by average integrated gross C production. In Fig. 5, we compare ^{14}C and net C production. At low rates of production, ^{14}C production is much greater than net C production. This result is expected, since ^{14}C assimilation must be $\geqslant 0$, whereas net C production will be negative below the compensation depth. At higher rates of production, ^{14}C production is generally comparable to net C production. Gross C production and ^{14}C production were about 50% higher during the fall cruise than during the spring cruise, as discussed by Barber et al. (1977). Net production is only about 11% higher during the fall than during the spring.

In the following sections, we compare three sets of rates: (1) net/new production in the field with net production measured in vitro, (2) ^{14}C production and gross C production measured in vitro, and (3) $^{15}NO_3^-$ uptake and net O_2 production in vitro.

3.2. Comparison of in vitro measurements of net C production with other estimates of net/new C production

There is a wide disparity in rates of net, new, and export production estimated by EqPac investigators using different approaches. We measure net C production to be 79 ± 20 and 90 ± 34 m mol m^{-2} day^{-1} in spring and fall, respectively. Particulate organic carbon export at the equator, measured using ^{234}Th deficiencies and $C/^{234}Th$ ratios in suspended matter, was about 4 m mol m^{-2} day^{-1} at the times of our studies (Buesseler et al., 1995; Bacon et al., 1996). The work of Bacon et al. coincided with ours (same cruise). Rates estimated from POC and ^{234}Th in drifting sediment traps at the

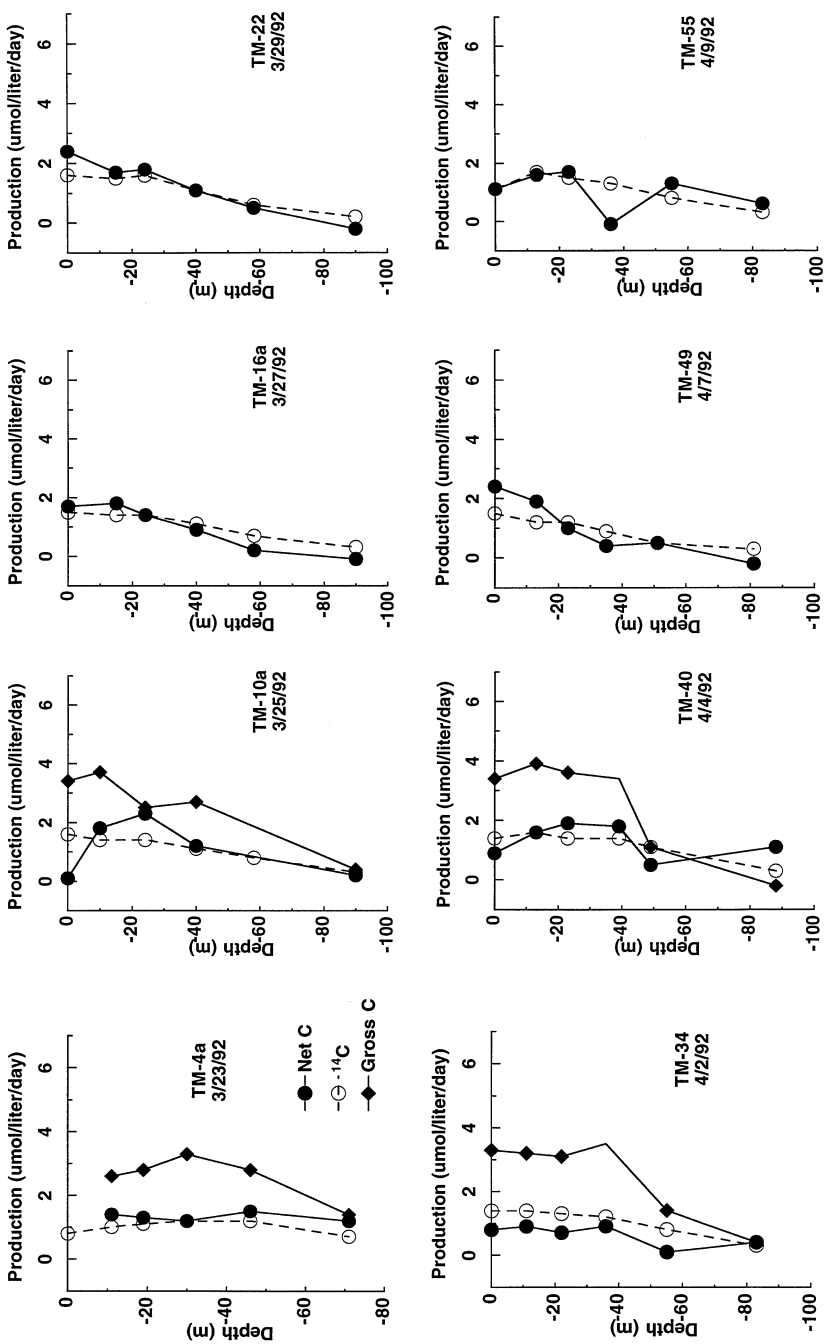

Fig. 1. Net C production, gross C production and ^{14}C production vs. depth during the spring, 1992, EqPac Time Series cruise.

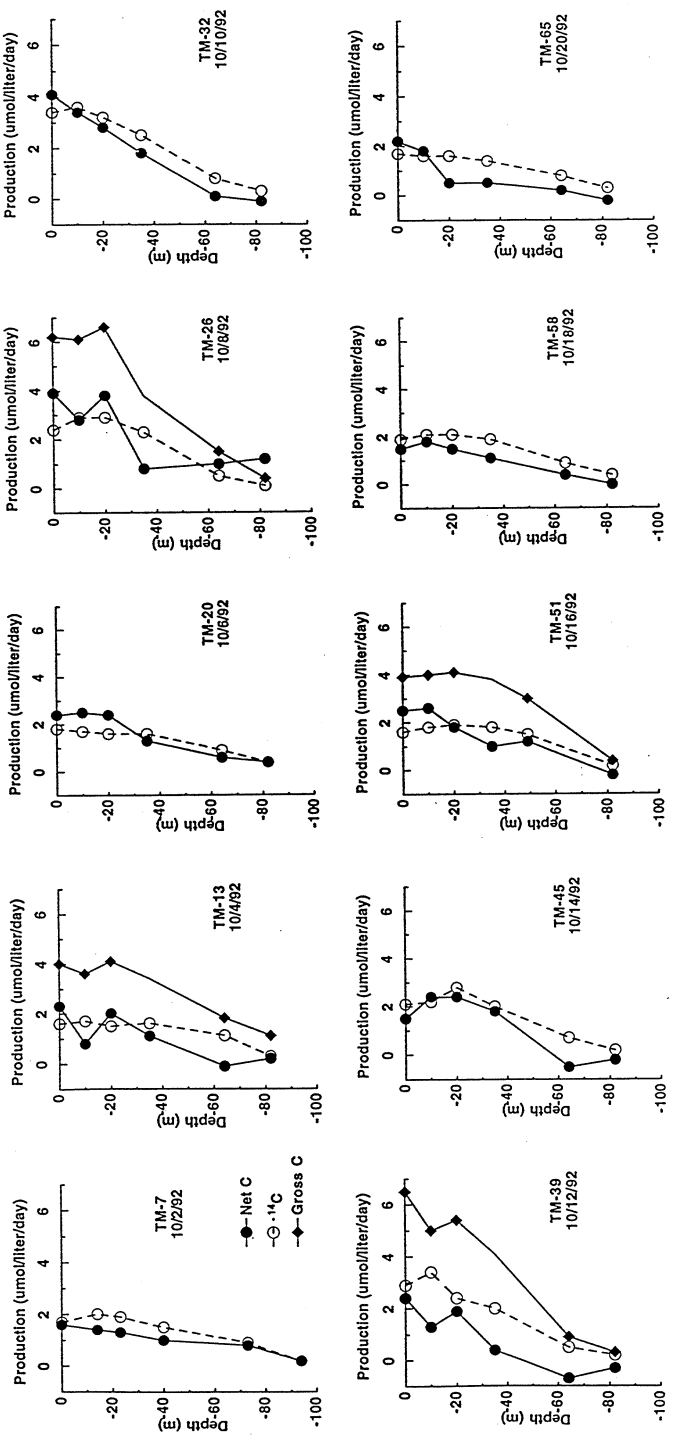

Fig. 2. Net C production, gross C production and ^{14}C production vs. depth during the fall, 1992, EqPac Time Series cruise.

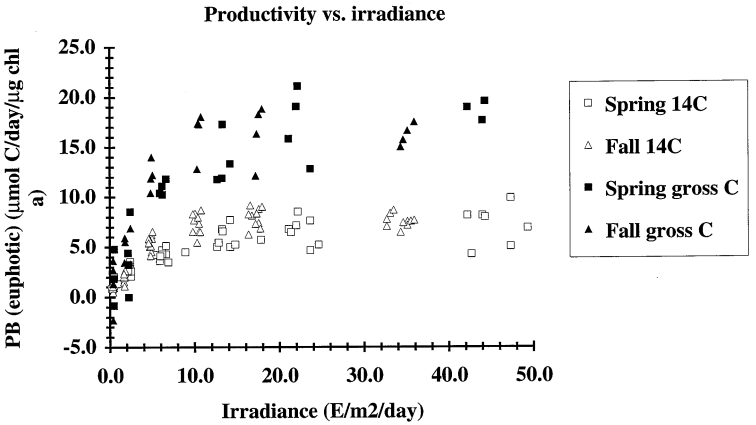

Fig. 3. 24 h ^{14}C and gross C productivity normalized to chl a and plotted vs. irradiance for the spring and fall cruises.

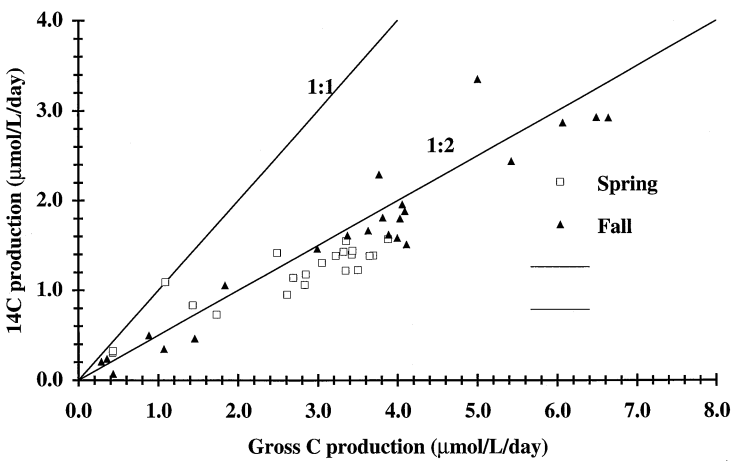

Fig. 4. 24 h ^{14}C production vs. gross production for spring and fall cruises.

Equator were higher, about 2–19 m mol m^{-2} d^{-1} between 3°N and 3°S (Murray et al., 1997). Wanninkhof et al. (1995) estimated mixed layer new production at about 11 m mol m^{-2} day^{-1} from the CO_2 balance on the equator. They calculate the upwelling velocity from the rate at which upwelling water is resaturated with O_2, and calculate CO_2 uptake from the upwelling rate and the TCO_2 gradient. Their flux estimate thus reflects conditions at the site and time of our study. Chai et al. (1996) used a 3-D model of equatorial Pacific circulation and climatological $[NO_3^-]$ fields to estimate new production at 0°, 140° W, at 22 m mol m^{-2} day^{-1}. Ku et al. (1995) used ^{228}Ra constraints to estimate 17 m mol m^{-2} day^{-1}. McCarthy et al. (1997) measured rates of

Table 1

Summary of integrated EqPac data from this study. All productivities are in units of m mol m^{-2} day^{-1}. ^{14}C/chl a and Gross C/chl a are in units of m mol mg^{-1} day^{-1}, and surface irradiance is in units of Einsteins m^{-2} day^{-1}

Cast	Date	Chl a	Net O_2	Net C	^{14}C	Gross O_2	Gross C	^{14}C/chl a	Gross G/chl a	C resp.	Surf. Irrad.
TM-4a	3/23/92	20	110	78	74	230	191	3.7	9.6	113	47
TM-10a	3/25/92	22	142	101	90	235	198	4.2	9.1	97	44
TM-16a	3/27/92	20	99	71	87			4.5			47
TM-22	3/29/92	25	124	88	88			3.5			49
TM-34	4/2/92	23	65	46	84	222	189	3.7	8.3	143	42
TM-40	4/492	24	148	106	97	231	181	4.1	7.6	76	44
TM-49	4/7/92	25	87	62	64			2.5			18
TM-55	4/9/92	22	115	82	88			4.0			43
TM-7	10/2/92	28	129	92	123			4.5			35
TM-13	10/4/92	24	95	68	107	303	257	4.4	10.5	189	35
TM-20	10/6/92	22	159	114	104			4.6			36
TM-26	10/6/92	23	205	147	139	358	285	6.2	12.6	139	36
TM-32	10/10/92	36	184	131	170			4.8			33
TM-39	10/12/92	37	54	38	136	353	311	3.7	8.4	272	34
TM-45	10/14/92	27	123	88	131			4.8			34
TM-51	10/16/92	25	141	101	114	301	246	4.5	9.7	145	35
TM-58	10/18/92	27	108	77	122			4.5			33
TM-65	10/20/92	23	67	48	97			4.2			33
Spring	Average	23	111	79	84	230	190	3.8	8.6	107	42
	std. deviation	2	28	20	11	6	7	0.6	0.9	28	10
Fall	Average	27	127	90	124	329	275	4.6	10.3	186	34
	std. deviation	5	48	34	21	31	29	0.6	1.8	62	1

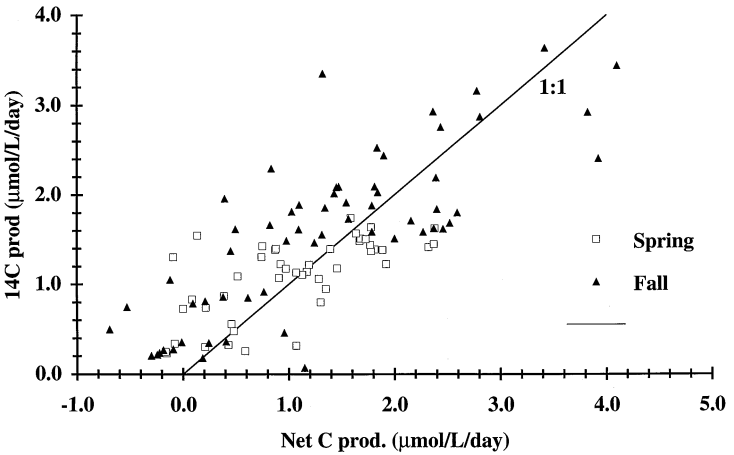

Fig. 5. 24 h ^{14}C production vs. 24 h net C production fo spring and fall cruises.

new production of about 3 and 18 m mol C m^{-2} day^{-1} on the Equator for spring and fall, respectively, from simulated in situ $^{15}NO_3^-$ uptake studies on the JGOFS survey cruises. The survey cruises preceded our cruises by $\sim$35–50 days. New carbon production measured on time series cruises by Wheeler (unpublished results) from $^{15}NO_3^-$ measurements were approximately 15–20 m mol m^{-2} day^{-1}.

One can suggest at least four ways in which the mismatch between net production we measure in vitro and lower values measured by other methods is due to the fact that they represent different rate terms. We discuss each here briefly, and conclude that large discrepancies reflect errors associated with in vitro measurements of net production rather than a real-world mismatch of correctly measured rates. The reasons are as follows. First, net production will be greater than new production if there is net uptake of NH_4^+ from the ecosystem. Such an imbalance may well be present over the course of a day. However, there is never enough NH_4^+ (ambient concentration: about 0.1 μmol l^{-1} above 50 m depth) present in the water to sustain the large imbalance we would require if NH_4^+ supports new carbon production over a period of weeks. Second, carbon may be accumulating in the upper water column as POC. In this case, net production would be much higher than the POC rain. In EqPac, observations show that this process is unlikely to be important. POC concentrations in the upper 30 m are about 7 ± 2 μmol l^{-1} (H. Ducklow, unpublished results). About 30% of this POC derives from pre-existing suspended particles present at the depth of upwelling, roughly 100 m (H. Ducklow, unpublished results). The remainder, about 3–6 μmol l^{-1}, is from recent production. The upwelling rate during the fall is about 1–2 m day^{-1} (Wanninkhof et al., 1995), and we typically measure net production to be 2 m mol m^{-3} day^{-1} throughout the upper 30 m. Given these values, it is clear that POC accumulates at a rate much less than the net C production rate we measured in vitro. Third, the discrepancy might be resolved by invoking DOC accumulation. Here the same objection arises. Semi-labile and refractory DOC, like

POC, is in fact accumulating in newly upwelled water at the Equator (Carlson and Ducklow, 1995). However, DOC increases by about the same amount as POC. The accumulation rate is far less than required to account for the difference between net production measured in vitro and the carbon rain measured with field results. (Similarly, POC and DOC accumulation cannot account for the difference between net production estimated by Wanninkhof et al. (1995) and carbon rain estimated by Buesseler et al. (1995).) Fourth, vertical export might be much greater than measured by ^{234}Th/C ratios if vertically migrating zooplankton tranported ^{234}Th-poor organic matter to depth. However, mesozooplankton ingest $< 6\%$ of gross carbon production (Dam et al., 1995), far less than required to resolve the discrepancy.

In fact the covariation of bioactive tracers throughout the equatorial Pacific demonstrates that accumulation of suspended POC and DOC accounts for only about 30% of net production in the region. Sinking of POC, reflected in fluxes inferred from sediment traps and ^{234}Th/C ratios, accounts for the remainder. Jeng et al. (1997) analyzed the changes in DOC (including POC) and DIC in the region. They found that DOC rose about 20% as rapidly as DIC fell. The remaining 80% of net production must have been removed by settling. Hansell et al. (1997) derived a similar estimate. The relative concentration changes in TOC and NO_3^- within the euphotic zone in the region of EqPac studies (Fig. 6) support this conclusion. Between 12°N and 12°S along 140°W, total organic carbon (POC + DOC) is inversely correlated with NO_3^-. Along the flow path of upwelling waters, from $\sim$100 m depth on the equator towards shallower depths and higher latitudes, $[NO_3^-]$ decreases because of biological uptake and POC + DOC rises because of the accumulation of biological material. The slope of covariation, $\Delta[NO_3^-]/\Delta[TOC]$, equals -0.5. If N/C in the accumulating TOC is about 1/7 (e. g. Anderson and Sarmiento, 1994), then about 30% of net carbon production is accumulating in the euphotic zone as DOC + POC and

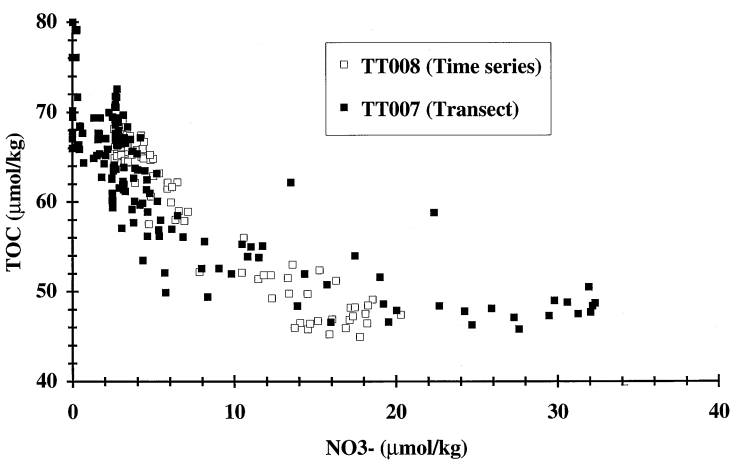

Fig. 6. [Total organic carbon] vs. $[NO_3^-]$ between 12°N and 12°S, along 140°W; depths $\leqslant$ 200 m only. Data are plotted for TT007 (spring transect cruise) and TT 008 (spring time-series cruise).

70% is lost in the particle rain. Again, we cannot invoke accumulation to explain the difference between net production in vitro and the particle rain, and conclude that our in vitro measurements of net production were anomalously high.

As discussed above, net production rates measured in vitro are far higher than rates measured in the field from ^{234}Th/C ratios and other approaches outlined above. Bottle incubations may introduce several artifacts leading to accumulation of organic C in vitro. Phytoplankton incubated in bottles may become better adapted to ambient irradiance than their counterparts in the mixed layer, and photosynthesize more rapidly. The exclusion of large grazers could simply allow the increased accumulation of carbon in microheterotrophs, which flourished during EqPac bottle incubations (Landry et al., 1995). At the same time, ammonium produced as a by-product of microheterotroph grazing would become available to the larger phytoplankton cells, whose large macrozooplankton grazers were excluded from our bottles. Thus conditions in our incubation bottles may have been conducive for enhanced growth of the large phytoplankton cells that consequently resulted in the accumulation of POC. The observation of Cullen et al. (1992) that ^{14}C production is higher in 24 h simulated in situ (shipboard) incubations than values estimated from 1 h photosynthesis-irradiance experiments accords with each of these possibilities.

A simple calculation shows that in vitro effects on photosynthesis and respiration rates would have much larger effects on net production than on gross production or respiration. Consider an oceanic ecosystem in which photosynthesis and respiration are in balance (net production = 0). If bottle artifacts suppress respiration by 20% and enhance photosynthesis by 20%, net production will be measured to be 33% of gross production rather than 0% ((gross production-respiration)/gross production = $(1.2 - 0.8)/1.2 = 33\%$.). Large errors in net production do not imply comparably large errors in gross production or respiration. The artifactually large values of net production we observe are probably due to a combination of enhanced autotrophy and suppressed heterotrophy, as discussed above.

3.3. Comparison of metabolic rates measured in vitro

Our results give insight into the ways in which metabolic processes affect interrelationships between phytoplankton and community rate terms measured in vitro: ^{14}C production, net and gross O_2 production, and net and gross C production. We begin our discussion of this topic by examining the formal relationships. Gross O_2 production, as determined by the $H_2{}^{18}O$ labelling method, measures total O_2 production regardless of the fate of the O_2 produced. The link between gross O_2 production and gross carbon production depends on this fate. One mode of O_2 consumption requires light and is associated with either the Mehler reaction or photorespiration. Chlororespiration fits in this group also but appears to be a minor pathway (Geider, 1992). The other mode of O_2 consumption is mitochondrial respiration, which is carried out by autotrophs as well as heterotrophs.

In the Mehler reaction, O_2 produced by photosystem II is reduced in photosystem I and is therefore not directly linked to carboxylation. Photosynthesis followed by O_2 consumption by the Mehler reaction registers as gross O_2 production because

a molecule of labelled O_2 is produced while a molecule of ambient unlabelled O_2 is consumed. Thus, to the extent that the Mehler reaction is occurring in our incubation experiments, our calculations overestimate the true rate of gross carbon production. Photorespiration involves the oxidation rather than carboxylation of ribulose 1,5-bis-phosphate to phosphoglycolate and 3-phosphoglycerate. If glycolate, the dephosphorylation product of 3-phosphoglycerate, is excreted, then photorespiration is linked to $DO^{14}C$ production. If glycolate is transformed and oxidized by the photorespiration cycle, then photorespiration, like the Mehler reaction, effectively leads to gross production of O_2 without the concomitant accumulation of organic carbon.

In common usage, gross autotrophic production is generally considered to be carbon assimilation after losses due to photorespiration are taken into account (Geider, 1992). We call this term "modified gross carbon production". The values of gross carbon production we calculate from $H_2{}^{18}O$ labelling experiments exceed modified gross carbon production by the extent of O_2 consumption due to the Mehler reaction and decarboxylation due to photorespiration. Gross carbon production values we calculate from ^{18}O exceed net phytoplankton production by the extent of the Mehler reaction, photorespiration, and autotrophic mitochondrial respiration.

Net C_{org} production computed from net O_2 production simply reflects the excess of assimilatory gains over respiratory losses by the community during incubation. Our measurement unambiguously defines net community O_2 production. Uncertainties enter the calculation of net carbon production, because nitrification as well as respiration consume O_2, and more generally because the $\Delta[O_2]/\Delta[CO_2]$ values associated with photosynthesis and respiration are imperfectly known.

Eppley (1980), Peterson (1980) and others have discussed the relationship between ^{14}C production and other metabolic rate processes. We can write the following equations to illustrate the relevant relationships:

> ^{14}C production = net ^{14}C accumulation by phytoplankton, zooplankton and bacteria = modified gross carbon production–assimilation of unlabeled CO_2 injected into the intracellular pool by respiration–phytoplankton respiration of labelled photosynthate–heterotrophic respiration of labelled photosynthate–$DO^{14}C$ excretion + bacterial $DO^{14}C$ accumulation.

^{14}C production rates have been used as indices of three terms of metabolic interest, but are imperfect indices in each case. The first term is gross primary production. This use is implicit in comparisons of ^{14}C productivity with production rates calculated from bio-optical data expressing the activity of photosystem II. ^{14}C production underestimates gross production because of photorespiration, respiratory losses, and $DO^{14}C$ excretion. In addition, it is less than the value of gross C production we calculate from ^{18}O because of the Mehler reaction, photorespiration, and assimilation of unlabelled respiratory CO_2 in the intracellular pool (e.g. Williams and Lefevre, 1996). The second usage of ^{14}C production rates is as net phytoplankton production. ^{14}C production differs from net phytoplankton production because of excretion, because of heterotrophic respiration, and because autotrophs would have continued to remineralize $PO^{14}C$ after the end of the incubation. The third is as net particulate

community production available for transfer up the food web. ^{14}C differs from particulate carbon transferred to higher trophic levels because some labelled particulate carbon present at the end of an incubation would have been respired by autotrophs and microheterotrophs after the incubation rather than progressing up the food chain.

The preceding discussions show that neither ^{18}O nor ^{14}C production corresponds directly to any of the rate terms of interest in studies of ecodynamics and carbon cycling. Net O_2 production and net C production correspond closely to rate terms of great interest in carbon cycling studies, but our measurements of these rates during EqPac are seriously biased by bottle effects.

^{14}C production is generally considered to be intermediate between gross C production and net community production. ^{14}C production will exceed net particulate community C production by the amount of old, unlabelled C_{org} lost to respiration during an incubation. It will be diminished relative to net C production by the amount of $^{14}C_{org}$ which has been excreted during the incubation and remains unassimilated by bacteria.

Five factors will cause ^{14}C production to be less than gross C production calculated from ^{18}O: the Mehler reaction and photorespiration, mitochondrial respiration by phytoplankton, $DO^{14}C$ excretion, assimilation of unlabelled CO_2 during photosynthesis, and heterotrophic respiration of $DO^{14}C$ and $PO^{14}C$. Here we make rough estimates of the first 3 terms and show that they are probably sufficient to account for the difference between gross C production and ^{14}C production we observe.

Measurements of photoenhancement of O_2 consumption provide a way for us to estimate the magnitude of the Mehler reaction and photorespiration. In some phytoplankton culture experiments, O_2 consumption rates are similar in the light and in the dark (e.g. Peltier and Thibault, 1985; Kana, 1992), while in seawater samples and other phytoplankton cultures they may be higher in the light by 10–60% (Kana, 1992; Grande et al., 1991; Bender et al., 1987; Kana, 1990). In an extreme case, Radmer and Kok (1976) found that, for a short period of time after the start of irradiation, the Mehler reaction consumed O_2 at its production rate as *Scenedesmus* produced ATP to be used for carbon assimilation. Some photoenhancement of O_2 consumption is due to photoenhancement of mitochondrial respiration, because phytoplankton are more metabolically active (Elrifi and Turpin, 1985) and because the growth of phytoplankton biomass leads to increased respiration. For the sake of discussion, we assume that the Mehler reaction and photorespiration consume O_2 at 15% of gross O_2 production, and we use this value in the discussion that follows.

Mitochondrial respiration rates depend on a variety of taxonomic and environmental properties (Geider, 1992; Langdon, 1993). We simply adopt Langdon's (1993) estimate that about 35% of modified gross primary production is recycled by phytoplankton mitochondrial respiration over 24 hours. Again, this estimate is highly uncertain.

Eppley (1980) and Sakshaug (1993) recently estimated that $DO^{14}C$ excretion rates (measured, for example, by Choi, 1972; Nalewajko et al., 1976; Sharp, 1975) total about 10% of $PO^{14}C$ production. We adopt the more recent average of Baines and Pace (1991), 13%. In EqPac, $PO^{14}C$ production is about 45% of gross C

production calculated from 18O. Excretion would account for about 6% of gross carbon production.

To this point, we account for 35% of gross carbon production as phytoplankton mitochondrial respiration (some of which is unlabelled with respect to ^{14}C), 15% as photorespiration and the Mehler reaction, and 6% as excretion. According to our EqPac data, approximately 45% remains as ^{14}C-labelled POC after 24 h. These numbers sum to 101% of gross production. Heterotrophic respiration must also account for a significant fraction of production, given the fact that microheterotrophs graze autotrophs rapidly and turn over about once per day (Landry et al., 1995). As well, some carbon assimilated during our incubations may be unlabelled. We can accomodate some unlabelled CO_2 uptake and significant ^{14}C losses due to heterotrophy by assuming that some CO_2 respired mitochondrially by phytoplankton would be unlabelled, and by recognizing that O_2 consumption by the Mehler reaction and photorespiration may be $<15\%$ of gross production. There are of course uncertainties associated with each of the terms. But the point is that the relationship we observe in EqPac between ^{14}C production and gross C production can be explained with independent evidence of metabolic rates.

According to this balance, net C production would be equal to net $PO^{14}C$ production + net $DO^{14}C$ production–remineralization of unlabelled POC and DOC present at the start of the incubation. At moderate and high irradiances, observed values of ^{14}C and net C production are similar, demonstrating that consumption of old, unlabelled, organic carbon is comparable to $DO^{14}C$ excretion. At low irradiances, ^{14}C production (which can, of course, only be positive) is greater than net production, as expected.

3.4. *Relative rates of net C production and $^{15}NO_3^-$ assimilation in vitro*

As noted above, McCarthy et al. (1997) used $^{15}NO_3^-$ uptake rates to estimate rates of new C production on the equator during EqPac. Their rates were 5–20% of net C production rates reported here. While their measurements and ours were carried out on different cruises, unpublished results of P. Wheeler show that the discrepancy continued during cruises on which we made our measurements (see the U.S. JGOFS data archive). A number of processes may have contributed to the discrepancy between net O_2 production rates and (much lower) $^{15}NO_3^-$ uptake rates scaled to C assuming $C/N = 6.6$. The first is that true $^{15}NO_3^-$ uptake rates are greater than the reported values. This would be the case if most $^{15}NO_3^-$ that is assimilated is excreted by ammonification or as $DO^{15}N$. In fact this process is probably occurring to some extent. Much of the label taken up in $^{15}NO_3^-$ experiments may be transferred to some component other than the PON (Laws, 1984). Bronk et al. (1994) measured $^{15}NO_3^-$ incorporation into DON in various environments. They measured rates of this process to be 30–50% of the total assimilation rate of labelled NO_3^-. Eppley and Renger (1992) measured NO_3^- uptake in equatorial Pacific waters by simply measuring the decrease of $[NO_3^-]$ with time in incubated seawater samples during the WECOMA 8803 cruise. The rates they measured were far higher than rates of $^{15}NO_3^-$ uptake measured in the same seawater sampled by Dugdale et al. (1992); this

difference remains unexplained. On the other hand, McCarthy et al. (1997) argued that their measurements of $^{15}NO_3^-$ uptake were likely to be close to gross uptake, because of short incubation times and other factors.

In our 24 h incubations, uptake of NH_4^+ (ambient concentration $\sim$0.1 μmol l^{-1}) could account for a substantial fraction of the net production we observe. (After 1 day, available NH_4^+ would be used up and could not sustain high net production for the longer periods reflected in the water column carbon balance at the equator.) Rapid degradation of labelled organic N, perhaps by ectoenzymes (Smith et al., 1992), could also stimulate net C production in the absence of NO_3^- uptake. Finally, much of the difference between measured net O_2 production and that estimated from $^{15}NO_3^-$ uptake may well be due to the mismatch in incubation periods (24 h for net O_2 production, 4–6 h for $^{15}NO_3^-$ uptake). In this scenario NO_3^- uptake would eventually rise because of rapid phytoplankton growth linked to the death and exclusion of grazers, as well as the exhaustion of NH_4^+.

4. Conclusions

We have reported rates of net, gross and ^{14}C production in samples from the equatorial Pacific time series study. Net production in vitro is far higher than rates inferred from other data sets, probably because bottle effects reduce heterotrophy and stimulate photosynthesis. In samples incubated for 24 h, ^{14}C production is about 45% of gross C production calculated from $H_2{}^{18}O$ labelling experiments. Estimated rates of the Mehler reaction, photorespiration, phytoplankton mitochondrial respiration, heterotrophic respiration and $DO^{14}C$ excretion can explain the difference between gross C and ^{14}C production.

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