



## Net community production and metabolic balance at the oligotrophic ocean site, station ALOHA

Peter J. le B. Williams<sup>a,\*</sup>, Paul J. Morris<sup>b</sup>, David M. Karl<sup>b</sup>

<sup>a</sup>*Marine Science Laboratories, School of Ocean Sciences, University of Wales, Menai Bridge, Bangor, Gwynedd LL59 5EY, UK*

<sup>b</sup>*School of Ocean and Earth Science and Technology, University of Hawaii, Honolulu, HI, 96822, USA*

Received 18 August 2003; received in revised form 14 June 2004; accepted 14 June 2004

Available online 12 September 2004

### Abstract

To test the hypothesis that in oligotrophic areas of the ocean respiration exceeds production, a 12-month study was undertaken of in vitro-determined net oxygen production and consumption in the top 150 m of the water column at the extreme oligotrophic site, Station ALOHA, in the North Pacific subtropical gyre. Throughout the year the water column was observed to be in metabolic deficit, the calculated cumulative shortfall being  $9 \pm 1.7 \text{ mol O}_2 \text{ m}^{-2} \text{ a}^{-1}$  (approximately  $100 \text{ g C m}^{-2} \text{ a}^{-1}$ ), an amount equivalent to 40% of measured production (annual estimated rates of production and consumption were, respectively, 22 and  $31 \text{ mol O}_2 \text{ m}^{-2} \text{ a}^{-1}$ ).

We consider three possible explanations for the observed deficit:

- (1) the in vitro oxygen rate measurements, in themselves, are fundamentally flawed and should be discounted,
- (2) the observations are correct and the observed deficit is a true account of the balance of oxygen (and organic carbon) at Station ALOHA, or
- (3) the observations are correct as they stand, but need not be interpreted as organic carbon imbalance for that ecosystem.

We find no error unique to the oxygen rate measurements themselves. We find also no evidence that the associated organic carbon deficit can be sustained over the long-term by internal organic reserves or by external subsidy. Accordingly we accept the geochemical findings that calculated in situ oxygen flux requires the euphotic zone of the water column at this site to be slightly (circa  $2 \text{ mol C m}^{-2} \text{ a}^{-1}$ ) autotrophic, in contrast to the simple analysis of our observations which gives a net heterotrophic water column. We discuss a number of processes that may give rise to the observed discrepancy. In part it may derive from the difficulty of reproducing the variations in the light field experienced by an algal cell due to vertical advection. It may also derive from the intermittency of production. This latter effect would manifest itself in the following manner. Because of its universal distribution in the food web, respiration has greater integrating properties than photosynthesis and so will give a more accurate estimate of the long-term mean in studies with coarse sampling frequencies. If the system is undersampled, then short bursts of

\*Corresponding author. Tel.: +44-1248-382-840; fax: +44-1248-716-367.

E-mail address: [pjlw@bangor.ac.uk](mailto:pjlw@bangor.ac.uk) (P.J. le B. Williams).

photosynthesis are prone to be missed from the integration of the production term but will be seen in the consumption term: hence the apparent deficit. The corollary of this line of reasoning is that, in undersampled systems, respiration has the potential to give a more accurate measurement of integrated system production than photosynthesis.

© 2004 Published by Elsevier Ltd.

**Keywords:** N. Pacific Ocean; Station ALOHA; Respiration; Net community production; Oligotrophic ocean; Metabolic balance; Oxygen metabolism

---

## 1. Introduction

The carbon cycle has been a major focus of biological oceanography during the past two decades. There is a growing interest in the export of carbon and the consequential drawdown of atmospheric carbon dioxide. Because the rate of riverine input of organic material ( $34 \text{ T mol C a}^{-1}$ ) exceeds the combined rates of burial in sediments and losses to the atmosphere ( $12.5\text{--}17 \text{ T mol C a}^{-1}$ ) the oceans are net heterotrophic (Smith and Mackenzie, 1987), although as a percentage of overall organic carbon flux the amount is very small (ca. 0.5%) and therefore not well constrained. Furthermore, this implied imbalance is well over an order of magnitude below the capabilities of standard oceanographic field techniques designed to detect these fluxes. With this as a background the conclusion of papers by del Giorgio et al. (1997) and Duarte and Agusti (1998), based on analysis of field observations of production and respiration, that “80% of the ocean’s surface are expected to be heterotrophic...” was surprising. The del Giorgio et al. (1997) paper was criticised by Williams (1998) on the grounds that the data set was small but more particularly that it based its conclusion on an analysis of volumetric rates of oxygen change. It was argued that one needed to resort to depth-integrated rates in order to overcome some of the problems associated with the space and time separation between respiration and production, inherent with discrete incubation measurements. Duarte and Agusti’s (1998) conclusion was that the major sites of net heterotrophy were the oligotrophic regions of the world ocean. This is counter-intuitive because these low nutrient, low biomass ecosystems are a consequence of their physical isolation and leaves them as the least

likely candidates for the external organic subsidy needed to sustain net heterotrophy (Williams and Bowers, 1999). However, a series of subsequent papers (Serret et al., 2001; Robinson et al., 2002) have lent support to the observation of net heterotrophy in low latitude oligotrophic areas. This debate has been reviewed by Cole (1999). With the exception of the early work in the North Pacific subtropical gyre (Williams and Purdie, 1991), made in association with the 1985 PRPOOS (Plankton Rate Processes in Oligotrophic Oceanic Systems) study, all the data published to date for oligotrophic regions have been derived from oceanographic transects and so only provide a snapshot of the balance of community metabolism at a particular site. This leaves open the possibility that the negative balances observed could be supported by a carryover of locally produced organic material from a previous net autotrophic period. Were this to be the case, the time and depth integral of net community production would either be positive or not significantly different from zero. The PRPOOS study, although it was at a fixed station and used very precise methods, did not have the time coverage necessary to resolve this problem, it nonetheless still serves as a valuable set of comparative measurements.

We set out to test the hypothesis of net heterotrophy in oligotrophic systems. Accordingly we undertook a 12-month study of depth dependent rates of respiration, production and net community production at the Hawaii Ocean Time-series (HOT) benchmark site, Station ALOHA. The site was chosen for a number of reasons: there is a well documented history of plankton measurements at this site, spanning some 15 years, the programme was ongoing so that supplementary data would be available and, most

importantly, it is a site of extreme oligotrophy—where chlorophyll concentrations in the upper water column are  $<0.1 \text{ mg m}^{-3}$  and nitrate is  $<10 \text{ nM}$  year round (Karl et al., 2001, 2002). The production versus respiration relationship reported by Duarte and Agusti (1998), predicts a net deficit of  $20\text{--}70 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  ( $7\text{--}26 \text{ mol O}_2 \text{ m}^{-2} \text{ a}^{-1}$ ) at Station ALOHA. Using eight replicates for each determination of oxygen concentration, we calculated that we should be able to achieve a precision of  $0.05 \text{ mmol m}^{-3}$  ( $\text{CV} = 0.02\%$ ) in the measurement of oxygen concentration. Measurements at six depths through the top 150 m of the water column would enable us to achieve a precision of  $7 \text{ mmol O}_2 \text{ m}^{-2} \text{ day}$  in the measurement of depth integrated net community production (NCP), which would be sufficient to test whether or not oligotrophic regions like Station ALOHA conformed with the prediction of Duarte and Agusti (1998) that oligotrophic gyres are in metabolic deficit.

## 2. Methods

### 2.1. Sampling and incubation protocols

Sampling for this investigation took place during 10 HOT cruises between May 2001 and May 2002, on board the R/V *Kaimikai-O-Kanaloa*. The sampling location was Station ALOHA at  $22^\circ 45' \text{N}$  and  $158^\circ 00' \text{W}$  which is an area of the oligotrophic subtropical North Pacific approximately 100 km north of the Hawaiian island of Oahu (Karl and Lukas, 1996).

Water samples were collected at midnight using a 24 place-sampling rosette with  $12\text{-dm}^{-3}$  PVC bottles. The bottles were fitted with silicone o-rings and Teflon<sup>®</sup>-coated springs. Separate casts were made for the  $\text{O}_2$ - and  $^{14}\text{C}$ -based rate measurements. With the single exception of HOT 126, three individual bottles were fired at each of six depths: 5, 25, 45, 75, 100 and 150 m, in the case of HOT 126 the deepest sample was at 125 m. Seawater was then transferred into  $25\text{-dm}^{-3}$  carboys with silicone tubing. Prior to use, both the carboys and the tubing were washed with 10% hydrochloric acid and rinsed with distilled deio-

nised water and finally with sample water. For each depth, eight replicates each for a time zero, a light bottle incubation and a dark bottle incubation were subsampled into borosilicate ground glass stoppered bottles with a nominal volume of  $125 \text{ cm}^{-3}$ . The volume of each bottle had previously been calibrated to a mean precision of  $5 \text{ mm}^3$  ( $<0.005\%$ ). All subsampling and initial processing was carried out in low light. Light bottles were attached to polycarbonate racks that were secured within a protective aluminium cubic framework and the dark bottles were housed in light proof boxes and secured to the frame beneath the light bottle incubations. The frames were attached to a free floating array with sample placement at the exact depth of water collection to simulate in situ temperature and light conditions. The array was deployed before sunrise and allowed to drift for approximately 24 h, before it was recovered at first light the following day. Time zero replicates were fixed immediately after the array was deployed and the light and dark incubations were fixed as soon as they were recovered. Samples were fixed for Winkler titration as described by Carritt and Carpenter (1966). Immediately prior to the addition of the fixing reagents, the temperature of every sample was measured to  $0.1^\circ \text{C}$  using a Barnant thermocouple thermometer with a type T small diameter low thermal mass probe for fast response temperature readings. In situ profiles of temperature and salinity were also recorded from the CTD package.

Fixed samples were stored under water to prevent evaporation and resultant gaseous exchange with the atmosphere and were returned to the laboratory for subsequent titration, usually within 7 days.

### 2.2. Dissolved oxygen measurement

Fixed samples were titrated using a computer-controlled Winkler titration with a photometric endpoint detector based on that of Williams and Jenkinson (1982). Using the sample temperature when fixed and in situ temperature and salinity from the CTD records it was possible to correct for thermal expansion of the sampled water and

sample bottles when calculating dissolved oxygen concentration and percentage oxygen saturation.

Over the study the mean standard error and coefficient of variation of the measurements of oxygen concentration of the time zero, light and dark bottles were  $0.035 \text{ mmol O}_2 \text{ m}^{-3}$  (0.016%),  $0.063 \text{ mmol O}_2 \text{ m}^{-3}$  (0.028%) and  $0.047 \text{ mmol O}_2 \text{ m}^{-3}$  (0.021%), respectively, within the target we set ourselves. Each oxygen determination was characteristically derived as a mean of eight replicate bottles, thus permitting a standard error to be calculated. This allowed the changes in concentration due to gross and net  $\text{O}_2$  production and respiration to be measured with a potential precision of 0.078, 0.071 and  $0.059 \text{ mmol O}_2 \text{ m}^{-3}$ . The combined error was calculated as  $\text{SE}_{x-y} = \sqrt{((\text{SE}_x)^2 + (\text{SE}_y)^2)}$ . This rate was corrected for any small departures from a 24 h incubation.

### 2.3. Other measurements

Other relevant biological parameters that were measured routinely as part of the HOT core measurements included chlorophyll *a*,  $^{14}\text{C}$  light bottle productivity rates and mean particle flux measurements obtained from free floating sediment traps (Karl and Lukas, 1996); these and all other HOT program core measurement data, including the oxygen data in this report, are available at: [http://hahana.soest.hawaii.edu/hot/hot\\_jgofs.html](http://hahana.soest.hawaii.edu/hot/hot_jgofs.html).

### 2.4. Terminology

It has been long recognised that the conventional light-dark bottle oxygen technique cannot measure light-associated forms of respiration: Mehler, or ribulose biphosphate carboxylase/oxygenase reactions. As a consequence when net oxidation is corrected for respiratory losses, the part of production that provides the protons and electrons for the above reactions will not be taken into account and so the light-dark bottle approach will not be a true measure of gross production. As the Mehler-peroxidase reaction and to a lesser extent the RUBISCO-oxygenase

reactions are not associated with organic production (see Raven and Beardall, 2004) we shall use the term “production” when referring to that part of gross photosynthesis measured by the oxygen and  $^{14}\text{C}$  techniques and reserve the term “photosynthesis” for true (and in this paper unmeasured) gross photosynthetic production. This usage avoids qualifying the various processes each time we refer to them.

## 3. Results

The full set of the oxygen-determined rates, along with their standard errors, are given in Table 1. Bad weather on the 2nd September 2001 (HOT 130) resulted in the loss of the two upper frames and the associated samples.

The depth distribution of oxygen-determined production rates is shown in Fig. 1a. We found that the summer to autumn profiles (May–October) showed different features from the winter to early spring profiles (November–March). This separation is consistent with the climatology of  $^{14}\text{C}$  production at HOT (Karl et al., 2002). The summer and autumn profiles show a distinct subsurface maximum, characteristically in the 25 m measurement. This may also be seen in the oxygen-derived production rates made in the 1985 PRPOOS study (Fig. 1b). No such intermediate maximum is seen in the HOT 132 and 135–137 profiles (November and March). It is noteworthy that the PRPOOS observations were made in the August/September period. The rates in the upper 50 m in the present study varied from  $0.5$  to  $1.3 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ , again comparable to the PRPOOS observations. Below 50 m they ranged from  $0.5 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  to undetectable ( $<0.08\text{--}0.1 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ).

Respiration rates varied from values in the range of  $0.5\text{--}1.5 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$  in the upper 25 m of the water column to  $0.5 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$  to undetectable ( $<0.06 \text{ mmol O}_2 \text{ m}^{-3} \text{ d}^{-1}$ ) at 150 m. Characteristically, as with production, there is an intermediate maximum between 5 and 45 m (Fig. 2a); the PRPOOS observations (see Fig. 2b) were not extensive enough to reveal any such intermediate depth features. If there is a

Table 1

Measured rates of production, respiration and net community production (volumetric rates as  $\text{mmol O}_2 \text{m}^{-3} \text{d}^{-1}$ , depth-integrated rates as  $\text{mmol O}_2 \text{m}^{-2} \text{d}^{-1}$ )

Code Date	HOT 126 16/05/01	HOT 127 14/06/01	HOT 128 11/07/01	HOT 129 08/08/01	HOT 130 02/10/01	HOT 131 23/10/01	HOT 132 17/11/01	HOT 135 21/02/02	HOT 136 13/03/02	HOT 137 21/05/02
(a) Production <sup>a</sup>										
Depth (m)										
5	0.87±0.07	0.72±0.08	0.74±0.12	0.98±0.08	—	0.73±0.15	1.08±0.09	0.29±0.12	0.60±0.07	0.64±0.07
25	0.90±0.14	1.04±0.11	1.31±0.06	1.12±0.04	—	1.33±0.11	0.87±0.09	0.46±0.14	0.55±0.06	0.84±0.07
45	0.49±0.05	0.67±0.12	1.31±0.32	1.18±0.15	0.70±0.15	1.03±0.05	0.47±0.04	0.31±0.09	0.46±0.04	0.64±0.06
75	0.25±0.02	0.38±0.11	0.51±0.03	0.57±0.11	0.34±0.06	0.20±0.05	0.15±0.06	<b>0.18±0.11</b>	0.12±0.04	0.35±0.04
100	0.13±0.03	0.26±0.07	<b>0.08±0.08</b>	0.13±0.06	<b>0.08±0.06</b>	<b>0.08±0.06</b>	0.16±0.06	0.28±0.13	<b>0.04±0.05</b>	0.13±0.04
150	<b>0.11±0.09<sup>c</sup></b>	<b>-0.02±0.04</b>	<b>0.00±0.04</b>	<b>-0.13±0.11</b>	<b>-0.08±0.05</b>	<b>-0.11±0.06</b>	<b>-0.04±0.11</b>	<b>0.21±0.16</b>	<b>-0.08±0.07</b>	<b>-0.05±0.03</b>
Σ0–Σ150	57+3.9	68+5.7	87+5.5	84+6.0	—	67+4.5	54+4.9	41+8.8	34+3.7	55+3.1
(b) Respiration <sup>a</sup>										
Depth (m)										
5	0.63±0.05	0.67±0.08	0.70±0.05	1.07±0.07	—	0.67±0.06	0.71±0.05	0.76±0.07	1.15±0.15	0.79±0.07
25	0.57±0.14	0.90±0.06	1.36±0.05	1.48±0.11	—	0.85±0.09	0.93±0.05	0.75±0.05	0.80±0.05	0.74±0.03
45	0.31±0.04	1.16±0.10	1.12±0.09	1.22±0.06	0.91±0.04	0.91±0.03	0.67±0.03	0.68±0.07	0.83±0.02	0.51±0.06
75	0.42±0.01	0.52±0.07	0.70±0.04	0.59±0.04	0.52±0.06	0.67±0.03	0.65±0.05	0.73±0.10	0.55±0.05	0.38±0.04
100	0.31±0.03	0.34±0.05	0.29±0.07	0.19±0.04	0.32±0.04	0.42±0.06	0.39±0.05	0.62±0.09	0.50±0.05	0.32±0.02
150	0.29±0.07 <sup>c</sup>	<b>-0.02±0.04</b>	0.09±0.03	<b>-0.03±0.09</b>	<b>0.04±0.05</b>	<b>-0.04±0.04</b>	<b>0.07±0.08</b>	0.49±0.13	0.39±0.03	0.23±0.05
Σ0–Σ150	59+3.1	83+4.1	98+3.7	98+4.3	—	82+3.4	80+3.8	98+6.7	97+3.1	67+2.5
(c) Net community production <sup>b</sup>										
Depth (m)										
5	0.24±0.08	0.04±0.07	0.04±0.12	-0.08±0.06	—	0.06±0.15	0.38±0.10	-0.47±0.12	-0.55±0.17	-0.15±0.09
25	0.33±0.14	0.14±0.10	-0.05±0.04	-0.36±0.12	—	0.48±0.06	-0.06±0.08	-0.29±0.14	-0.25±0.06	0.10±0.07
45	0.18±0.04	-0.49±0.09	0.19±0.31	-0.04±0.14	-0.21±0.15	0.13±0.04	-0.20±0.04	-0.37±0.07	-0.37±0.03	0.13±0.05
75	-0.17±0.02	-0.14±0.10	-0.19±0.05	-0.02±0.11	-0.19±0.06	-0.47±0.05	-0.50±0.04	-0.54±0.08	-0.43±0.06	-0.04±0.04
100	-0.18±0.02	-0.09±0.06	-0.21±0.05	-0.06±0.05	-0.24±0.06	-0.34±0.07	-0.22±0.04	-0.34±0.08	-0.46±0.04	-0.18±0.04
150	-0.18±0.09 <sup>c</sup>	0.00±0.02	-0.09±0.03	-0.11±0.12	-0.13±0.03	-0.12±0.04	-0.11±0.08	-0.28±0.13	-0.47±0.06	-0.28±0.05
Σ0–Σ150	-1.4+3.5	-16+4.4	-11+5.1	-15+6.5	—	-16+3.9	-26+3.8	-57+6.7	-64+3.9	-12+3.4

<sup>a</sup>All data have been tested for significance, those where the measured rate is less than twice that of the standard error are placed in bold.<sup>b</sup>No test can be made for significance on the data, as the value can lie either side of zero.<sup>c</sup>In HOT 126 this sample came from 125 m, in the integration this has been used as a 150 m sample.

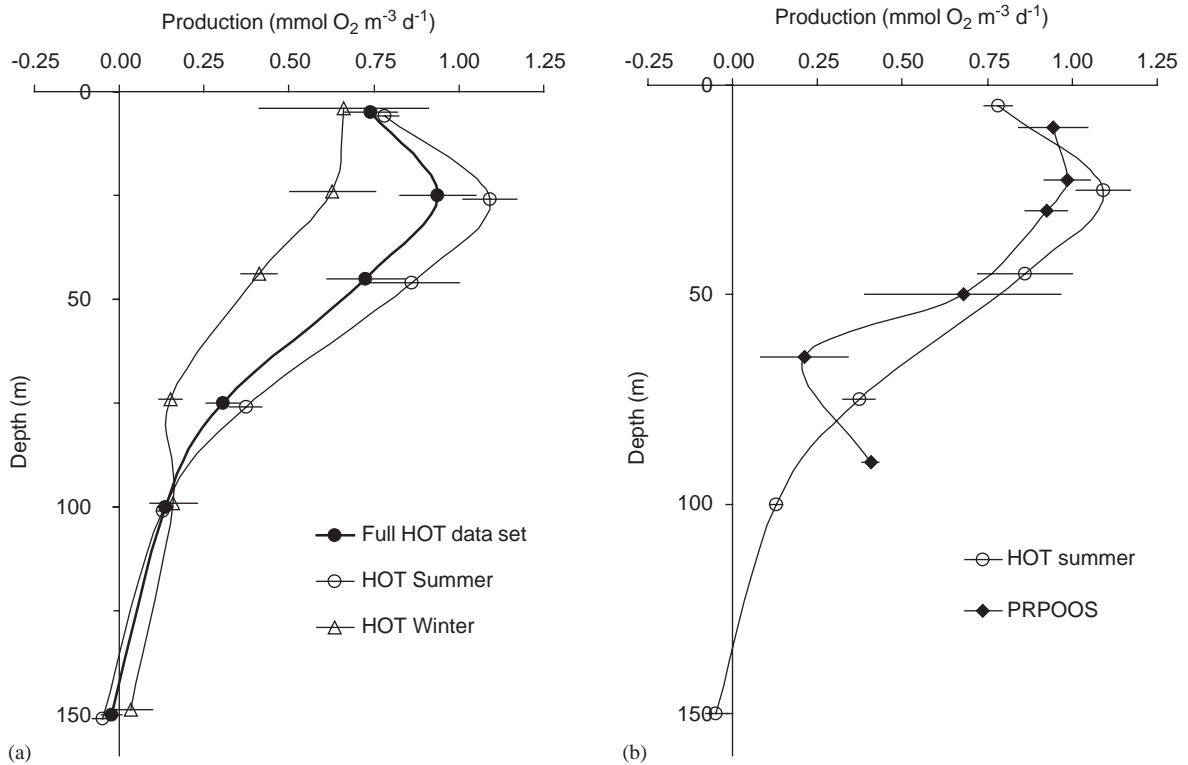


Fig. 1. (a) Depth distribution of the mean of the full data set of O<sub>2</sub>-derived production rates and the means for the “summer/autumn” (May–October) and “winter” (November–March). The error bars are the standard error of the means. The depth for the different profiles have been offset by 1 m to prevent the individual error bars merging. (b) Comparison of production rates obtained during the PRPOOS programme with the “summer/autumn” period of the present study. Details are as in Fig. 1a.

“summer” to “winter” difference associated with the appearance of this maximum, it is not as pronounced as that seen in the production rates. Again, the observed rates of respiration in the present study are similar to those observed in the PRPOOS study.

In principle NCP is the most reliable *in vitro* plankton rate measurement we can make, as there are no complications over isotope cycling or assumptions over processes continuing or not during dark incubations. The observations from the present study, separated into the “winter” and “summer” months are shown in Fig. 3a, a comparison with the PRPOOS data set is given in Fig. 3b. The striking feature is that in the HOT data set the mean NCP rates are negative throughout the water column—particularly so in the winter months.

## 4. Discussion

### 4.1. Production and respiration

As the oxygen-determined rate measurements were embedded in the HOT sampling programme, comparisons are available with <sup>14</sup>C productivity measurements and other core data. A limitation arises from the logistical need to separate the sampling and incubation for the two production rate measurements. The two samplings were 3 h apart. This constrains direct comparison for, whereas the broad shape of depth profile of the two processes should not be affected (in situ incubations were used in both cases), there is some scope for difference in the absolute values arising from heterogeneities in the environment. For example, 3-day variation of  $\pm 20$ –30% of the

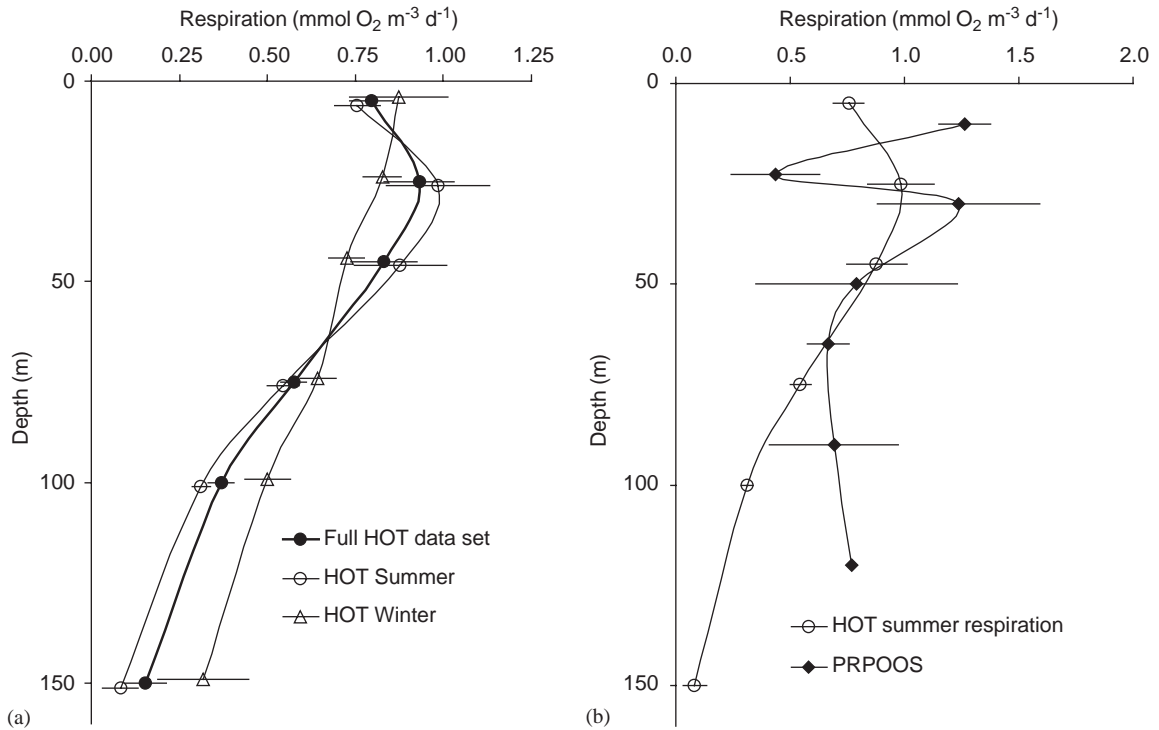


Fig. 2. (a) Depth distribution of the mean of the full data set of respiration and the means for the “summer/autumn” (May–October) and “winter” (November–March). Details are as in Fig. 1a. (b) Comparison of respiration rates obtained during the PRPOOS programme with the “summer/autumn” period of the present study. Details are as in Fig. 1a.

mean was observed on HOT 15 (Karl et al., 1996). Quantitatively, the oxygen-derived rates are of the same order as the <sup>14</sup>C-based rates (Fig. 4). The molar ratios (as  $\Delta\text{O}_2/^{14}\text{C}$ ; i.e. the quotient of the rate of oxygen production and <sup>14</sup>C-based organic carbon production) lay in the range 1.2–1.5 in the upper 50 m in the present study, falling to values less than unity below 50 m. A similar pattern is seen in the PRPOOS observations. The average <sup>14</sup>C-based production profiles show no pronounced intermediate depth maximum. However, if the winter and summer/autumn data in the HOT <sup>14</sup>C data sets are analysed separately then a small intermediate maximum is again seen in the summer/autumn observations. As well as a general downward shift in the  $\Delta\text{O}_2/^{14}\text{C}$  ratio with depth, there appear to be seasonal shifts in the ratio. In the “summer/autumn” period the molar  $\Delta\text{O}_2/^{14}\text{C}$  ratios in the upper part of the water column are in the range 1.2–1.8, in the winter period these ratios

fall to 0.8–1.2. In the deeper part of the water column the relative errors of the two rate measurements become high and so the  $\Delta\text{O}_2/^{14}\text{C}$  ratio is poorly constrained.

We may explain the temporal and spatial shifts in the  $\Delta\text{O}_2/^{14}\text{C}$  ratio in the following manner. The lower boundary of the  $\Delta\text{O}_2/^{14}\text{C}$  ratio is set by the photosynthetic quotient ( $\text{PQ} = \Delta\text{O}_2 / -\Delta\text{CO}_2$ ) when the <sup>14</sup>C technique is measuring gross carbon production. Assuming the population to be assimilating a reduced nitrogen source (e.g. ammonia), the PQ would have a theoretical value of about 1.1 (Laws, 1991; Williams and Robertson, 1991). This order of value is seen in the deeper part of the HOT euphotic zone and in the winter months. Values for the  $\Delta\text{O}_2/^{14}\text{C}$  ratio above the theoretical PQ value would be obtained when the <sup>14</sup>C technique is measuring a net primary production, the ratio would approximate the algal photosynthesis/respiration ( $P/R$ ) ratio and so

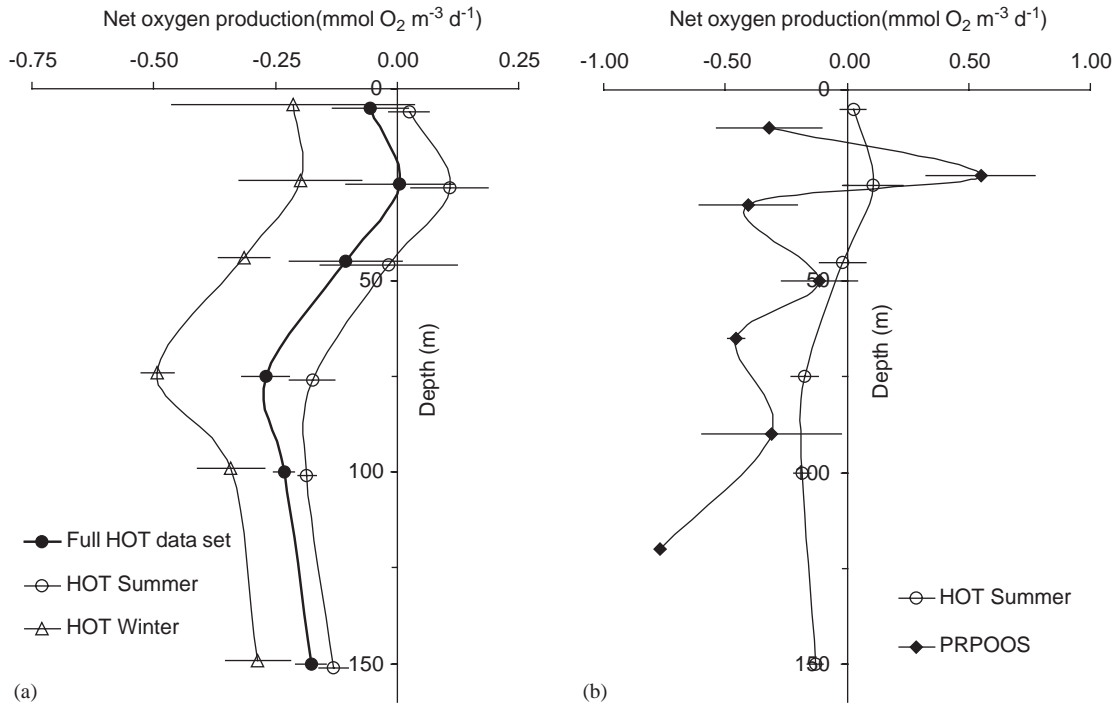


Fig. 3. (a) Depth distribution of the mean of the full data set of net oxygen production and the means for the “summer/autumn” (May–October) and “winter” (November–March). Details are as in Fig. 1a. (b) Comparison of net community production rates obtained during the PRPOOS programme with the “summer/autumn” period of the present study. Details are as in Fig. 1a.

could have values from 3 to 5 (Langdon, 1993). A commonly observed high value for the  $\Delta\text{O}_2/^{14}\text{C}$  quotient is in the region of 2 (Williams et al., 1979; Williams, 1993). These generalisations allow an explanation of the observations at the HOT (and PRPOOS) site. In the upper part of the water column, during the summer months, the <sup>14</sup>C method appears to be measuring a process closer to net than gross primary production, in the winter months and in the deeper part of the water column the rates appear to approach those of gross production. One may surmise that this is associated with changes in in situ irradiance. DiTullio and Laws (1986) showed that algal cultures grown in continuous light appeared to give <sup>14</sup>C rates closer to net production than those grown in a light-dark cycle. It would appear that light limitation tends to drive the <sup>14</sup>C technique from a measurement of net towards to gross photosynthesis. The reason for this may be that, when light is not limiting, CO<sub>2</sub> may become somewhat

more so and the cell may then draw to a greater extent upon internal sources of CO<sub>2</sub> (respiratory CO<sub>2</sub>), which being richer in <sup>12</sup>C than the added external <sup>14</sup>C-enriched CO<sub>2</sub> will result in calculated rates being closer to net than gross primary production.

#### 4.2. Net community production

Assuming there is net downward transport of organic material, either by advection of DOC, gravitational settling of particles or vertical migration of mesozooplankton/fish we would expect positive NCP in the upper part of the water column and negative NCP below. The general pattern is broadly met in the PRPOOS data set, but clearly not in the current study (Fig. 3a and b); although the HOT summer NCP rates do approach this general pattern. A further feature which is common, although not invariable,

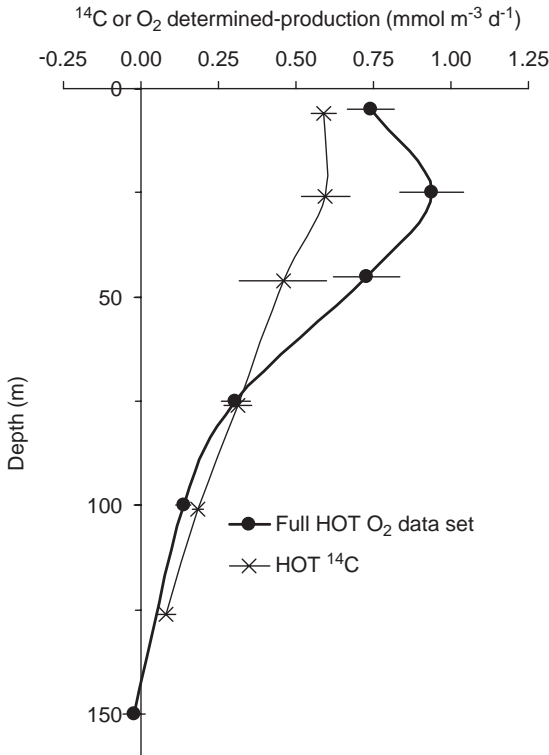


Fig. 4. Comparison of oxygen and <sup>14</sup>C-based production rates. Details as Fig. 1a.

is a maximum in negative NCP at an intermediate depth, in this case 75 m.

4.3. Production/respiration ratios

In Fig. 5, the relationship between photosynthetic and respiration rates has been analysed in the context of the range of P/R ratios obtained at other oceanic areas. The HOT (plus PRPOOS) data set represents the low end-member of the data series. These data are examined as log–log photosynthesis versus respiration plots. Characteristically the slopes are less than unity (a model II major reduced axis fitting procedure is used); the HOT (plus PRPOOS) data set has an essentially identical slope as that of the global data base, although they do not show the high respiration tail at low production rates, seen in other (mainly equatorial and subequatorial Atlantic) data sets. In many respects this correspondence between the

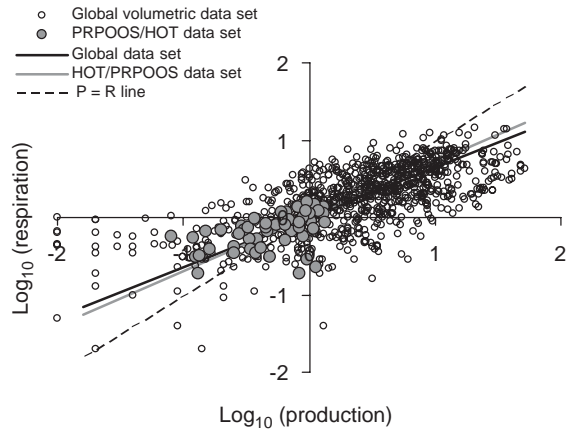


Fig. 5. Comparison of the HOT (+PRPOOS) volumetric rates of production and respiration with a global data set. A double log plot is used to normalise errors—the fitted lines are a Model II regression fit (a major reduced axis). Rates as mmol O<sub>2</sub> m<sup>-3</sup> d<sup>-1</sup>. The slopes of the two lines are: 0.62 (global data set) and 0.56 (HOT/PRPOOS data sets). The global data set comprises 1931 paired observations.

HOT and PRPOOS and the global data sets is remarkable, as relationship on a single curve would place the HOT photosynthesis versus respiration relationship equivalent to the deeper part of the euphotic zone of more productive areas. The reason this is surprising is that in productive areas a photosynthetic rate of, for example, 1 mmol O<sub>2</sub> m<sup>-3</sup> d<sup>-1</sup>, would occur at some intermediate depth and so receive a subsidy from the water column above it thus providing the basis for respiration to exceed production. No such subsidy would be available in an oligotrophic environment, where such rates would occur at the surface. This, in part, was the argument of Williams and Bowers (1999) which, it would appear, is not sustained.

4.4. Depth integrated rates

The in vitro measured rates of oxygen flux allow depth integrated rates to be calculated. These and the associated standard errors are given in Table 1 and shown in Fig. 6. The annual rates, with the associated errors, are summarised in Table 2. The present estimate of gross annual production is 22 mol O<sub>2</sub> m<sup>-2</sup> a<sup>-1</sup> (equivalent to 243 g C m<sup>-2</sup> a<sup>-1</sup>);

a value of  $181 \text{ g C m}^{-2} \text{ a}^{-1}$  was estimated by Karl and Lukas (1996). These observations are markedly at variance with estimates derived from many published models (Behrenfeld et al., 2002), which report values less than  $100 \text{ g C m}^{-2} \text{ a}^{-1}$  (Ondrusek et al., 2001). If we take a figure of  $40\text{--}50 \text{ Pg C a}^{-1}$  (Field et al., 1998; Behrenfeld et al., 2002) for global productivity, we obtain a range of

$117\text{--}147 \text{ g C m}^{-2} \text{ a}^{-1}$  for mean oceanic productivity; these figures put the annual rates at HOT as 23–53% above the oceanic average. Thus, the productivity at HOT, on an annual basis, is comparable to or above the oceanic average, rather than a minimum as the maps depict, alternatively the estimates for global production maybe generally wrong.

In Fig. 7, the areal rates observed in the present study are analysed in conjunction with a global data set. The global data set shows no close correlation between depth-integrated photosynthesis and respiration ( $r^2 = 0.13$ ). Similarly the HOT data set as a whole shows no clear relationship between photosynthesis and respiration, although the two rates appear to correspond to some extent through the summer months.

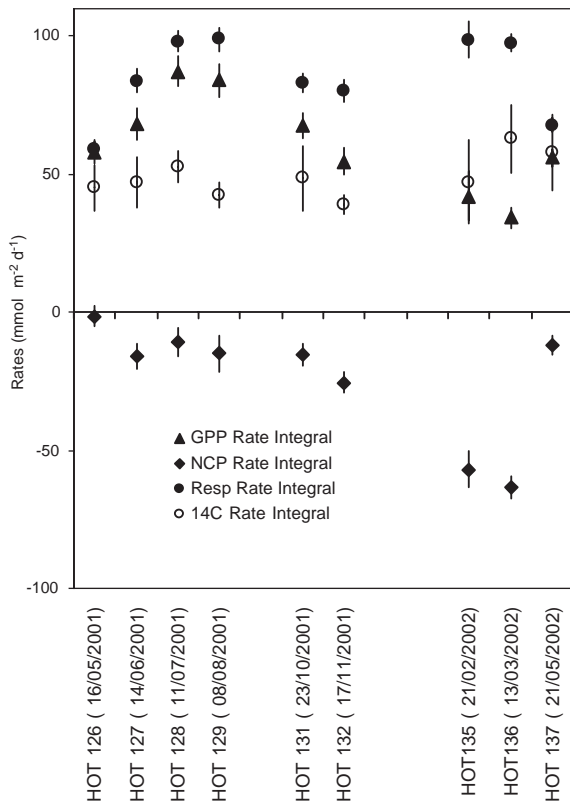


Fig. 6. Seasonal changes in the depth-integrated rates of  $\text{O}_2$ -determined production, respiration, net community production and the associated  $^{14}\text{C}$ -based rates (as  $\text{mmol C m}^{-2} \text{ d}^{-1}$ ). The errors shown are the standard errors of the mean.

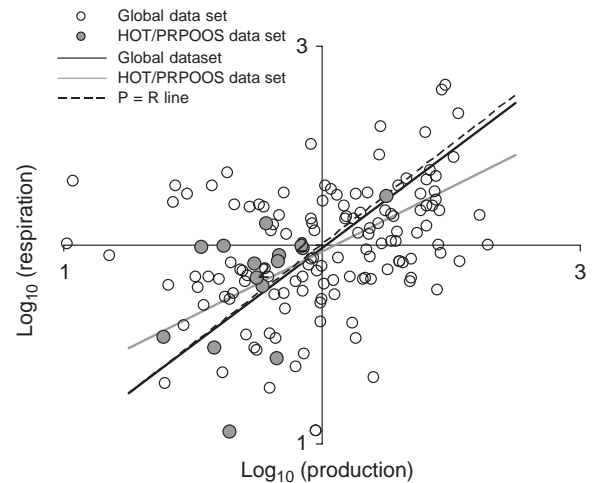


Fig. 7. HOT depth integrated rates, compared with the global data set of integrated production and respiration rate measurements (as  $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ). The global data set comprises 214 observations.

Table 2  
Summary of integral rates

	Units	Production	Respiration	Net production
Average daily rate	$(\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1})$	$61 \pm 5$	$86 \pm 4$	$-24 \pm 5$
Annual rate	$(\text{mol O}_2 \text{ m}^{-2} \text{ a}^{-1})$	$22 \pm 1.9$	$31 \pm 1.4$	$-9 \pm 1.6$
Annual rate <sup>a</sup>	$(\text{mol C m}^{-2} \text{ a}^{-1})$	$20 \pm 1.6$	$28 \pm 1.2$	$-8.2 \pm 1.5$

<sup>a</sup>Calculated assuming a PQ = 1.1.

#### 4.5. Balance of metabolism

In the present study, in all instances where full profiles are available, the depth integral (0–150 m) of net community production is negative. The calculated annual deficit is  $9 \pm 1.7 \text{ mol O}_2 \text{ m}^{-2}$  (equivalent to approximately  $100 \text{ g C m}^{-2} \text{ a}^{-1}$ ) at the lower end of that predicted by the approach used by Duarte and Agusti (1998), but none the less statistically significant. The calculated annual deficit over the range of 0–150 m must be a minimal figure, as in addition there will be particulate carbon export into the mesopelagic zone. The mean rate at 150 m as recorded by free floating sediment traps during the period of these  $\text{O}_2$  flux measurements (May 2001–May 2002) is approximately  $1 \text{ mol C m}^{-2} \text{ a}^{-1}$  (Karl et al., 1996). Approximately 90% of the C exported at 150 m is consumed in the mesopelagic zone (150–2000 m; Martin et al., 1987), and will account for much of the additional respiration sink not measured in the present study (del Giorgio and Duarte, 2002).

Thus, the system gives the impression of being net heterotrophic. There are previous observations of negative net areal production in oligotrophic systems (del Giorgio et al., 1997; Duarte and Agusti, 1998; Duarte et al., 2001; Robinson et al., 2002; Serret et al., 2001, 2002). As discussed earlier these were open to criticism in their interpretation as a persistent property of oligotrophic systems as they suffered from two limitations. First, they only could be considered snapshots of the annual cycle and so left open the possibility that the deficit may have been made up at some unstudied period of the year. Second, none of these areas are as physically isolated as the North Pacific subtropical gyre, so the possibility was also open that the observations had been made on water advected in from a (previously) net autotrophic zone (Harrison et al., 2001).

The observed significant and substantial deficit (about 40% of the observed gross  $\text{O}_2$  production in the euphotic zone carbon budget) is counter-intuitive. It has at least three possible explanations:

- (1) the in vitro oxygen rate measurements, in themselves, are fundamentally flawed and should be discounted,
- (2) the observations are correct and the observed deficit is a true account of the balance of oxygen (and organic carbon) at ALOHA, or
- (3) the observations are correct as they stand, but need not be interpreted as organic carbon imbalance for that ecosystem.

We now examine these three possibilities.

*Explanation (1): The in vitro oxygen rate measurements, in themselves, are fundamentally flawed and should be discounted.*

There are generic problems associated with in vitro techniques: sampling, incubation and the projection of their rates to larger time and space scales—these issues are dealt with under explanation (3). Here we limit the discussion to the oxygen rate measurement per se and its interpretation.

Oxygen flux measurements, made chemically, electrochemically and manometrically have been the basis of the classical physiological work on respiration and production of tissues and whole organisms. Their pedigree is thus far more formidable than any other rate measurement used in biological oceanography. Nonetheless we recognise a number of limitations of in vitro measurement of oxygen flux.

At least two forms of algal respiration—the Mehler-peroxidase and the RUBISCO oxygenase/phosphoglycollate reactions—occur only in the light and so are not accounted for in the classical light/dark bottle approach. This will result in an underestimate of community respiration in its entirety and so also an underestimate of true gross photosynthesis. As these light-associated respiration reactions precede the photosynthetic reduction of carbon, failing to take account of them probably does not result in a material underestimate of primary organic carbon production. A form of light-stimulated heterotrophic metabolism has been reported at Station ALOHA (M. Church *pers com.*) which would be overlooked by the dark respiration measurements. As this will be at the cost of organic production it would give rise to an underestimate of primary organic production by the oxygen technique. However, neither of these potential sources of error would bias the measurement of net community production—the subject

of this paper—at least based on present understanding.

The biological oceanographic literature contains concerns over so called “bottle effects” associated with the in vitro rate measurements. For reasons that are far from clear, concern is mainly directed to oxygen rate measurements. Because of the near impossibility of making the appropriate controls when undertaking “bottle effect” studies, the studies fail to meet the basic requirement of a scientific experiment and it is difficult to know how much credence to give the conclusions drawn from such studies. One of the few studies that directly addressed the problem of the validity of in vitro methodology and that did have controls, i.e. associated in situ measurements, was made by Williams and Purdie (1991) during the PRPOOS study and so is very pertinent to the present discussion. They obtained essentially the same photosynthetic index (production rate/chlorophyll concentration) for in vitro as in situ oxygen changes, giving no evidence for substantial “bottle effects”.

Thus, whilst noting the need for caution in their interpretation, we see no grounds to reject the in vitro oxygen rate measurements out of hand.

*Explanation (2): The observations are correct and the observed deficit is a true account of the balance of oxygen (and organic carbon) at ALOHA.*

Two categories of observations have bearing on this issue: first the potential (or lack thereof) for any organic deficit to be made up by an external subsidy and second the findings of in situ observations of long-term net gas flux across the air–sea interface.

The organic reservoir of the upper mixed layer of the ocean is small relative to carbon flux. Dissolved organic carbon (DOC) represents the major organic pool and is approximately  $12 \text{ mol C m}^{-2}$ , i.e. only one and a half times the observed annual deficit. The evidence is that the DOC is rising, not falling, at Station ALOHA (Church et al., 2002). Thus, if there is an imbalance, then organic material must be imported into the area, either from above, below or laterally. The concentrations of DOC decrease with depth at Station ALOHA from  $80\text{--}90 \text{ mmol C m}^{-3}$  in the upper

mixed layer to  $50 \text{ mmol C m}^{-3}$  in the underlying deeper water (Church et al., 2002)—thus mixing processes would give rise to a net downward transport of DOC, i.e. an export rather than import of organic carbon. Likewise, as discussed earlier, the net transfer of POC will be out of the euphotic zone by gravitational settling. The transport of organic material from the atmosphere to the oceans is poorly constrained (Williams, 2000) but it probably amounts to no more than  $8 \text{ T mol Ca}^{-1}$  to the ocean as a whole; thus a maximum figure for Station ALOHA would be in the region of  $0.025 \text{ mol C m}^{-2} \text{ a}^{-1}$ , which would make up very little of the calculated deficit of  $9 \text{ mol C m}^{-2} \text{ a}^{-1}$ . DOC concentrations decrease horizontally from about  $85 \text{ mmol C m}^{-3}$  at the centre of the oligotrophic gyre to  $60 \text{ mmol C m}^{-3}$  or less in the more productive areas to the north and south (Abell et al., 2000). All the above observations require the upper water column to be net autotrophic, rather than net heterotrophic.

Measurement of net gas exchange is also consistent with the euphotic zone at Station ALOHA as a site of net organic carbon production. The surface waters are saturated with respect to oxygen, whereas if they were net heterotrophic and so importing oxygen to meet the deficit implied by our measurements they would need to be 2% or more undersaturated at the surface. Emerson et al. (1993) calculated the net oxygen flux at ALOHA. They found periods of positive and negative oxygen export ranging from about  $-16$  to  $+45 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ , the annual integral being  $1 \text{ mol O}_2 \text{ m}^{-2} \text{ a}^{-1}$ . This figure has been refined and substantiated by subsequent work and a summary (taken from Quay and Stutsman, 2003) is given in Table 3.

We accordingly find it impossible to ignore the overwhelming weight of the geochemical evidence that the area of study is one of net organic carbon production, thus favour the final explanation for our observations.

*Explanation (3): The observations are correct as they stand but need not be interpreted as organic carbon imbalance for this ecosystem.*

First, there is a general problem in in vitro studies, in that the samples are incubated at either

Table 3  
Net annual carbon production calculated from in situ and other observations

Author	Approach	Annual net production Mol Cm <sup>-2</sup> a <sup>-1</sup>
Emerson et al. (1997)	Surface oxygen budget	+2.7±1.7
Benitez-Nelson et al. (2001)	Organic carbon export rates, based on <sup>234</sup> Th budget, DOC gradients and zooplankton migration rates	+2.4±0.9
Sonnerup et al. (1999)	Subsurface O <sub>2</sub> utilisation rates	+2.2±0.5
Quay and Stutsman (2003)	DIC and δ <sup>13</sup> C measurements	+2.7±1.3

Abstracted from Quay and Stutsman (2003).

constant irradiance or constant depth, whereas in nature turbulent processes will result in the populations being subject to changes in depth and varying light fields. In the case of samples from the upper water column, the fixed depth/fixed irradiance incubation procedures are more likely to give rise to suboptimal rather than supraoptimal conditions. As the rates from these depths make a significant contribution to the depth integrals of gross production, and, more importantly in the present work, net production will be underestimated.

Second, the classical in vitro approach to establishing annual rates makes the tacit assumption that the measured rates are representative of the period between the instances of rate determinations and between depths. It has been long recognised that this is not the case, even in areas such as the North Pacific subtropical gyre that were once thought to be stable, climax habitats. The two issues are the scale of this problem and in what manner it would bias the observations. It may be seen from the plots of the volumetric data (Fig. 5) that the variance of production rates at Station ALOHA is greater than that of respiration (the ratio of the two standard deviations is about 1.5). The basis of this is almost certainly the difference between the distribution of photosynthesis and respiration within the planktonic food web. The primary metabolic event is the photosynthetic fixation of organic material, some of this production will be rapidly respired by the primary producers, but the flow of organic material to the heterotrophic component of the plankton will give rise to delays of varying time periods as organic

production flows and cycles through the food web. If the rate of primary production is steady then the autotrophic and heterotrophic systems will be in a state of equilibrium. If, on the other hand autotrophic production is wholly or partially intermittent, then, rather in the manner of a large capacitor, the flow of these pulsed events through the heterotrophic part of the food web will dampen out the variability in production and will give a more constant signal. If the system is under sampled, such that the relatively short-lived autotrophic pulses are prone to be missed, the tendency will be for the damped part of the system (the heterotrophic component) to give a higher signal and, it is important to note, a more accurate integral. In part, this argument was made by Aristegui and Harrison (2002) and has been extended by Karl et al. (2003).

Evidence for intermittency in production at Station ALOHA comes from a gas partial pressure sensor deployed at the HALE ALOHA mooring (Emerson et al., 2002). The sensor was deployed for a 9-month period in 1997 and 8 months in 1998 at 50 m. It logged the changes in oxygen and nitrogen partial pressures at 15 min intervals. There were low frequency changes (weeks–months) in the oxygen signal, presumably due to the slow changes in the balance of metabolism, but in addition to this there were many higher frequency changes of the order of a day or two. They give rise to aperiodic pulses in the oxygen partial pressure equivalent to the order of 1–3% saturation (Karl et al., 2003). This would amount to oxygen increases of about 2.5–7.5 mmol O<sub>2</sub> m<sup>-3</sup> and with infrequent in vitro measurements

a potentially missed and unmeasured rate. To take the analysis further we need to know the distribution of these pulsed events through the mixed layer, however this information currently does not exist. If we assume that these pulses occur through a 50 m mixed layer then the areal rates would be 125–375 mmol O<sub>2</sub>m<sup>-2</sup> produced per event. In order to make up the 9 mol O<sub>2</sub>m<sup>-2</sup> annual deficit these pulses would need to occur at a frequency of once every 10–20 days. Thus even if the system were in metabolic balance, on any single occasion we only have a 5–10% chance of encountering a net autotrophic period and a 90–95% chance of coming to the (false) conclusion that the ecosystem we are studying was heterotrophic. Given that we have sampled on 9 occasions we have a (0.9)<sup>9</sup>–(0.95)<sup>9</sup>, i.e. a 40–60% chance of arriving at the wrong answer. We can invert the calculation to estimate the scale of sampling that would be required to have a statistical certainty (e.g. 95% probability) of coming to the correct answer. We would have needed to have sampled on 30–60 occasions through the seasons before we could expect to reach that level of certainty. At the sampling frequency of the HOT programme to date that would entail a 3–5 year study—a major undertaking.

We have no exact understanding of the circumstances that are the basis of these pulses in oxygen production. González et al. (2001) noted the effect of mesoscale eddies on balance of photosynthesis and respiration, but these were sustained effects. More relevant are Sakamoto et al.'s (in press) observations of nutrient injections into the euphotic zone associated with Rossby waves. However, they estimate the associated increase in phytoplankton production to be less than 5–10% on average, so this phenomenon alone could not account for the observed oxygen pulsed or the presently observed deficit.

A combination of these two broad categories of errors would be our preferred explanation, as it enables us to reconcile the in vitro observations, which we know to be statistically reliable and precise, with the geochemical in situ observations which have a greater accuracy, coming from their better space and particularly time averaging.

If our arguments are correct and we are missing perhaps some 40% of production due to intermittent events, then the very interesting corollary is that respiration, because of its integrating nature, will give a better estimate of production than a direct measurement of productivity itself. It is of course a simpler measurement, as it requires no simulation of the light environment. Contrary to common contention (e.g. Sakshaug et al., 1997) that only the <sup>14</sup>C technique has the requisite sensitivity to measure productivity in extreme oligotrophic waters, the present work (see Fig. 6) makes it clear that this is not the case and that, given care, the performance of the oxygen technique can be comparable to the <sup>14</sup>C technique.

In summary, we have been able to make in vitro measurements of net (and gross) oxygen flux of a quality that has allowed us to produce a budget for depth integrated photosynthesis and respiration at a site of extreme oligotrophy with a precision in the order of 10% or better and observe a deficit in oxygen (and thus organic carbon) production equivalent to about 9 mol Cm<sup>-2</sup>a<sup>-1</sup>, i.e. about 40% of measured production. We are inclined to the view that this deficit in part results from a limitation of the in vitro approach in that it fails to take adequate account of the intermittent nature of primary production. Of the two processes of production and respiration the latter measurement has the potential to give a better time average of upper water column productivity than the former. We conclude this would imply that 28 mol Cm<sup>-2</sup>a<sup>-1</sup> (330 g Cm<sup>-2</sup>a<sup>-1</sup>) is probably a good estimate of water column productivity of the subtropical oligotrophic gyre, far away from rate of 50–100 g Cm<sup>-2</sup>a<sup>-1</sup> frequently cited and adopted for modelling purposes (Behrenfeld et al., 2002).

## Acknowledgements

The authors thank the HOT program staff for their assistance in sample collection and for the ancillary core data sets, and the captain and crew of the R/V *Kaimikai-O-Kanaloa* for their invaluable field assistance. The two British authors (P.J.le B.W. and P.J.M.) wish to express their

sincere thanks for the help and hospitality of their US colleagues during the course of this study. Jon Cole and two other anonymous referees provided invaluable comment on the manuscript. We thank Vivian Ellis for careful calibration of the oxygen glassware and Ray Wilton for updating the titration system. The PRPOOS data were collected in 1985 during a comprehensive investigation of the marine plankton led by Richard Eppley. The present research was supported by grants from the US National Science Foundation (OCE96-17409 to D.M.K and OCE98-11921 to Roger Lukas) and the National Environment Research Council of the UK. This is SOEST contribution 6469 and US-JGOFS contribution 1051.

## References

- Abell, J., Emerson, S., Renaud, P., 2000. Distributions of TOP, TON and TOC in the North Pacific subtropical gyre: implications for nutrient supply in the surface ocean and remineralization in the upper thermocline. *Journal of Marine Research* 58, 203–222.
- Aristegui, J., Harrison, W.G., 2002. Decoupling of primary production and community respiration in the ocean: implications for regional carbon studies. *Aquatic Microbial Ecology* 29, 199–209.
- Behrenfeld, M.J., Esaias, W.E., Turpie, K.R., 2002. In: Williams, P.J.le B., Thomas, D.N., Reynolds, C.S. (Eds.), *Phytoplankton Productivity: Carbon Assimilation in Marine and Freshwater Ecosystems*. Blackwell Publishers, London, pp. 156–186.
- Benitez-Nelson, C.R., Buesseler, K.O., Rutgers van der Loef, M., Andrews, J.E., Ball, L., Crossin, G., Charette, M.A., 2001. Testing a new small volume technique for determining <sup>234</sup>Th in seawater. *Journal of Radioanalytical and Nuclear Chemistry* 248, 795–797.
- Carritt, D.E., Carpenter, J.H., 1966. Comparison and evaluation of currently employed modifications of the Winkler method for determining dissolved oxygen in seawater; A NASCO Report. *Journal of Marine Research* 24, 287–318.
- Church, M.J., Ducklow, H.W., Karl, D.M., 2002. Multiyear increases in dissolved organic matter inventories at Station ALOHA in the North Pacific Subtropical Gyre. *Limnology and Oceanography* 47, 1–10.
- Cole, J.J., 1999. Aquatic microbiology for ecosystem scientists: new and recycled paradigms in ecological microbiology. *Ecosystems* 2, 215–225.
- del Giorgio, P.A., Cole, J.J., Cimleris, A., 1997. Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. *Nature* 385, 148–151.
- del Giorgio, P.A., Duarte, C.M., 2002. Respiration in the open ocean. *Nature* 420, 379–384.
- DiTullio, G., Laws, E.A., 1986. Diel periodicity of nitrogen and carbon assimilation in five species of marine phytoplankton: accuracy of methodology for predicting N-assimilation rates and N/C composition ratios. *Marine Ecology Progress Series* 32, 123–132.
- Duarte, C.M., Agusti, S., 1998. The CO<sub>2</sub> balance of unproductive aquatic ecosystems. *Science* 281, 234–236.
- Duarte, C.M., Agusti, S., Aristegui, J., Gonzalez, N., Anadon, R., 2001. Evidence for a heterotrophic subtropical northeast Atlantic. *Limnology and Oceanography* 46, 425–428.
- Emerson, S., Quay, P., Karl, D.M., Winn, C., Tupas, L., Landry, M., 1997. Experimental determination of the organic carbon flux from open-ocean surface waters. *Nature*, 951–954.
- Emerson, S., Quay, P., Stump, C., Wilbur, D., Schudlich, R., 1993. Determining primary production from the mesoscale oxygen field. *ICES Marine Science Symposium* 197, 196–206.
- Emerson, S., Stump, C., Johnson, B., Karl, D.M., 2002. In situ determination of oxygen and nitrogen dynamics in the upper ocean. *Deep-Sea Research I* 49, 941–952.
- Field, C.B., Behrenfeld, M.J., Randerson, J.T., Falkowski, P., 1998. Primary production in the biosphere: integrating terrestrial and oceanic components. *Science* 281, 237–240.
- González, N., Anadón, R., Mourriño, Fernández, E., Sinha, B., Escáncz, E., de Armas, D., 2001. The metabolic balance of the planktonic community in the North Atlantic subtropical gyre: the role of mesoscale instabilities. *Limnology and Oceanography* 46, 946–952.
- Harrison, W.G., Aristegui, J., Head, E.J.H., Li, W.K.W., Longhurst, A.R., Sameoto, D.D., 2001. Basin-scale variability in plankton biomass and community metabolism in the sub-tropical North Atlantic Ocean. *Deep-Sea Research II* 48, 2241–2269.
- Karl, D.M., Bidigare, R.R., Letelier, R.M., 2002. Sustained and aperiodic variability in organic matter production and phototrophic microbial community structure in the North Pacific Subtropical Gyre. In: Williams, P.J.le B., Thomas, D.R., Reynolds, C.S. (Eds.), *Phytoplankton Productivity and Carbon Assimilation in Marine and Freshwater Ecosystems*. Blackwell Publishers, London, pp. 222–264.
- Karl, D.M., Bjorkman, K.M., Dore, J.E., Fujieki, L., Hebel, D.V., Houlihan, T., Letelier, R.M., Tupas, L.M., 2001. Ecological nitrogen-to-phosphorus stoichiometry at Station ALOHA. *Deep-Sea Research II* 48, 1529–1566.
- Karl, D.M., Christian, J.R., Dore, J.E., Hebel, D.V., Letelier, R.M., Tupas, L.M., Winn, C.D., 1996. Seasonal and interannual variability in primary production and particle flux at Station ALOHA. *Deep-Sea Research II* 43, 539–568.
- Karl, D.M., Laws, E.A., Morris, P., Williams, P.J.le B., Emerson, S., 2003. Metabolic balance in the open sea. *Nature* 426, 32.
- Karl, D.M., Lukas, R., 1996. The Hawaii Ocean Time-series (HOT) Program: background, rationale and field implementation. *Deep-Sea Research II* 43, 129–156.

- Langdon, C., 1993. The significance of respiration in production measurements based on oxygen. ICES Marine Science Symposium 197, 67–78.
- Laws, E.A., 1991. Photosynthetic quotients, new production, net community production in the open ocean. *Deep-Sea Research* 38, 143–167.
- Martin, J.H., Knauer, G.A., Karl, D.M., Broenkow, W.W., 1987. VERTEX: carbon cycling in the northeastern Pacific. *Deep-Sea Res.* I 34, 267–285.
- Ondrusek, M.E., Bidigare, R.R., Waters, K., Karl, D.M., 2001. A predictive model for estimating rates of primary production in the subtropical North Pacific Ocean. *Deep-Sea Research II* 48, 1837–1863.
- Quay, P., Stutsman, J., 2003. Surface layer carbon budget for the subtropical N. Pacific:  $d^{13}C$  constraints at Station ALOHA. *Deep-Sea Research I* 50, 1045–1062.
- Raven, J. A., Beardall, J., 2004. Respiration in aquatic photolithotrophs. In: del Giorgio, P., Williams, P. (Eds.), *Respiration in Aquatic Ecosystems*. Oxford University Press, Oxford.
- Robinson, C., Serret, P., Tilstone, G., Teira, E., Zubkov, M.V., Rees, A.P., Woodward, M.S., 2002. Plankton respiration in the eastern Atlantic Ocean. *Deep-Sea Research I* 49, 787–813.
- Sakamoto, C.M., Karl, D.M., Jannasch, H.W., Bidigare, R.R., Letelier, R.M., Wallz, P.M., Ryan, J.P., Polito, P.S., Johnson, K.S., 2004. Influence of Rossby waves on nutrient dynamics and the plankton community structure in the North Pacific subtropical gyre. *Journal of Geophysical Research* 109, C05032, doi:10.1029/2003JC001976.
- Sakshaug, E., Bricaud, A., Dandonneau, Y., Falkowski, P.G., Kiefer, D.A., Legendre, L., Morel, A., Parslow, J., Takahashi, M., 1997. Parameters of photosynthesis: definitions, theory and interpretation of results. *Journal of Plankton Research* 19, 1637–1760.
- Serret, P., Robinson, C., Fernandez, E., Teira, E., Tilstone, G., 2001. Latitudinal variation of the balance between plankton photosynthesis and respiration in the eastern Atlantic Ocean. *Limnology and Oceanography* 46, 1642–1652.
- Serret, P., Fernandez, E., Robinson, C., 2002. Biogeographic differences in the net ecosystem metabolism of the open ocean. *Ecology* 83, 3225–3234.
- Smith, S.V., Mackenzie, F.T.C., 1987. The oceans as a net heterotrophic system: implications from the carbon biogeochemical cycle. *Global Biogeochemical Cycles* 1, 187–198.
- Sonnerup, R.E., Quay, P.D., Bullister, J.L., 1999. Thermocline ventilation and oxygen utilization rates in the subtropical North Pacific based on CFC distributions during WOCE. *Deep-Sea Research I* 46, 777–805.
- Williams, P.J.le B., 1993. Chemical and Tracer Methods of Measuring Plankton Production: what do they in fact measure? The  $^{14}C$  technique considered. ICES Marine Science Symposium 197, 20–36.
- Williams, P.J.le B., 1998. The balance of plankton respiration and photosynthesis in the open oceans. *Nature* 394, 55–57.
- Williams, P.J.le B., 2000. Micro-heterotrophs and the dynamics of dissolved organic material. In: Kirchman, D.J. (Ed.), *Microbial Ecology of the Oceans*. Wiley-Liss, New York, p. 542.
- Williams, P.J.le B., Bowers, D.G., 1999. Regional carbon imbalances in the oceans. *Science* 284, 173–174.
- Williams, P.J.le B., Jenkinson, N.W., 1982. A transportable microprocessor-controlled precise Winkler titration suitable for field station and shipboard use. *Limnology and Oceanography* 27, 576–584.
- Williams, P.J.le B., Purdie, D.A., 1991. In vitro and in situ derived rates of gross production, net community production and respiration of oxygen in the oligotrophic subtropical gyre of the North Pacific Ocean. *Deep-Sea Research* 38, 891–910.
- Williams, P.J.le B., Raine, R.C.T., Bryan, J.R., 1979. Agreement between the  $^{14}C$  and the oxygen methods of measuring phytoplankton production: a reassessment of photosynthetic quotient. *Oceanologica Acta* 2, 411–416.
- Williams, P.J.le B., Robertson, J.E., 1991. Overall plankton oxygen and carbon dioxide metabolism: the problem of reconciling observations and calculations of photosynthetic quotients. *Journal of Plankton Research* 13, 153–169.