



Measuring primary production rates in the ocean: Enigmatic results between incubation and non-incubation methods at Station ALOHA

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[1] Primary production (PP) rates were estimated using concurrent ^{14}C and ^{18}O bottle incubations and a non-incubation oxygen isotope ($^{17}\Delta$) based method during monthly cruises to the time series station ALOHA in the subtropical N. Pacific Ocean between March, 2006 and February, 2008. The mean gross oxygen production (GOP) rate in the photic layer (0–200m) at ALOHA was estimated at 103 ± 43 and 78 ± 17 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ from the $^{17}\Delta$ and ^{18}O methods, respectively. In comparison, the mean ^{14}C -PP rate (daytime incubations) in the photic layer was 42 ± 7 $\text{mmol C m}^{-2} \text{ d}^{-1}$ (502 ± 84 $\text{mg C m}^{-2} \text{ d}^{-1}$). Seasonal and depth variability (% change) for GOP rate was 2–3 times that for ^{14}C -PP. The non-incubation $^{17}\Delta$ -GOP rates consistently exceeded the incubation ^{18}O -GOP rates by 25–60%, and possible methodological biases were evaluated. A supersaturation of the dissolved O_2/Ar gas ratio was measured every month yielding a mean annual value of $101.3 \pm 0.1\%$ and indicating a consistent net autotrophic condition in the mixed layer at ALOHA. The mean annual net community production (NCP) rate at ALOHA estimated from dissolved O_2/Ar gas ratio was 14 ± 4 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (120 ± 33 $\text{mg C m}^{-2} \text{ d}^{-1}$ or 3.7 ± 1.0 $\text{mol C m}^{-2} \text{ yr}^{-1}$) for the mixed layer. A NCP/GOP ratio of 0.19 ± 0.08 determined from $^{17}\Delta$ and O_2/Ar measurements indicated that $\sim 20\%$ of gross photosynthetic production was available for export and harvest.

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1. Introduction

[2] Photosynthetic production of organic carbon is the foundation of ocean's food web and biological carbon pump, leading ultimately to fish production, deep sea carbon sequestration and sustained oxygen levels in the atmosphere. Yet accurately measured rates of marine primary production (PP) remain elusive since there is no absolute PP standard against which methodological accuracy can be tested. Historically, the benchmark aquatic PP method has been ^{14}C bottle incubations [Steemann Nielsen, 1952], which have yielded thousands of ocean PP estimates over the last 50 years. Thus our understanding of PP in the ocean is dominated by the ^{14}C incubation method (^{14}C -PP) and yet the method has had acknowledged flaws that persist today [e.g., Peterson, 1980]. The influence of ^{14}C -PP extends to satellite based estimates of PP since most the satellite PP

algorithms rely on ^{14}C -PP measurements to estimate the response of PP to light.

[3] One source of ambiguity of the ^{14}C -PP method is whether this incubation method is a measure of gross primary production (GPP), net primary production (NPP) or some value in between [Marra, 2002, 2009]. In addition to the absence of a reliable physiological model, ^{14}C -PP measurements are influenced to some unknown degree by sampling, manipulation and containment effects that impact all incubation methods. The accuracy of the ^{14}C -PP method is obviously very important because many remineralization-intensive marine ecosystems (e.g., tropical and subtropical habitats) are poised near the balance point between GPP and total community respiration (R). The incubation PP method based on $^{18}\text{O}_2$ production from ^{18}O -labeled H_2O [e.g., Bender et al., 1987] provides a direct estimate of gross oxygen production (GOP). Concurrent ^{18}O - and ^{14}C - incubation PP measurement have been used to improve the interpretation of ^{14}C -PP measurements [e.g., Bender et al., 1999; Laws et al., 2000a; Marra, 2002]. However, the ^{18}O incubation PP method (^{18}O -GOP) is still susceptible to sampling, manipulation and containment effects.

[4] Over the past decade two other PP methods, based on Fast Repetition Rate Fluorometry (FRRF) and the isotopic composition of dissolved oxygen, have begun to yield non-incubation based estimates of gross primary production (GPP)

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rates in the ocean [e.g., *Kolber et al.*, 1998; *Luz and Barkan*, 2000]. These two PP methods have the advantage of avoiding potential methodological flaws inherent to incubation techniques and are capable of yielding GOP estimates over large regions of the ocean via underway sampling. The opportunity to obtain a new look at PP in the ocean using multiple approaches, rather than the reliance on a single method, is bound to provide new insights into PP variability in the ocean and the ecological and biogeochemical implications of this variability.

[5] From the perspective of the ocean's carbon cycle, the most important biological production rate is net community production (NCP), which equals the difference between GPP and R. NCP, at steady state, represents the organic carbon in both dissolved and particulate phase that is available for export or harvest. NCP has been estimated by several methods (e.g., dissolved oxygen and inorganic carbon (DIC) budgets, thorium-234 budgets, sediment traps, bottle O₂ incubations, etc.); however, each approach has substantial uncertainty. Unfortunately, there are only a few sites where multiple NCP methods have been compared (e.g., JGOFS study sites, BATS and ALOHA time series sites). Thus, for most of the ocean NCP is poorly constrained. The lack of accurate NCP estimates may be responsible for reports of net ecosystem heterotrophy in the oligotrophic ocean surface layer based on bottle O₂ incubations [e.g., *Williams et al.*, 2004] that are in contradiction to reports of net ecosystem autotrophy based on mixed layer O₂ budgets at the same location [e.g., *Emerson et al.*, 1997].

[6] We present the results of two years of monthly GOP and NCP rate estimates based on non-incubation methods using the measured isotopic composition of dissolved O₂ and the ratio of dissolved O₂/Ar gases, respectively, and compare these estimates to concurrent ¹⁸O and ¹⁴C incubation based estimates of PP. The study site is the Hawaii Ocean Time series station ALOHA in the subtropical N. Pacific Ocean where PP has been measured by the ¹⁴C incubation method for 20 years and NCP has been estimated previously by several methods. Since the non-incubation oxygen isotope GOP method has been applied at only a few sites to date, the results discussed here provide an excellent opportunity to compare PP rates measured by non-incubation and incubation methods at a well-studied site.

[7] We conclude that the oxygen isotope method yields a mean GOP rate of 103 ± 43 mmol O₂ m⁻² d⁻¹ in the photic layer that was ~25–60% greater than the GOP rate measured using ¹⁸O-bottle incubations and 2–3 times the daytime ¹⁴C-PP rates at ALOHA. We measured a supersaturation in dissolved O₂/Ar gas ratio every month that yielded a mean annual NCP rate of 14 ± 4 mmol O₂ m⁻² d⁻¹ (120 ± 33 mg C m⁻² d⁻¹ or 3.7 ± 1.0 mol C m⁻² yr⁻¹) for the mixed layer that is ~20% of the GOP and ~35% of daytime ¹⁴C-PP. Compared to the historic ¹⁴C-PP data set, the much higher non-incubation based estimates of GPP and NCP at ALOHA may require a re-evaluation of carbon and energy flow in this habitat.

2. Background

2.1. Study Site

[8] The study site is the time series station ALOHA (23°N 158°W) in the subtropical N. Pacific Ocean. Certainly a

major advantage of working at ALOHA is the wealth of historic data available that provides a context for evaluating data collected in any given year. There have been monthly measurements of PP at ALOHA using the ¹⁴C bottle incubations (in situ dawn to dusk incubations) since 1988 for a total of almost 200 individual depth integrated ¹⁴C-PP estimates. The mean daytime ¹⁴C-PP is 514 ± 135 mg C m⁻² d⁻¹ between 1988 and 2008 with a slight seasonality, i.e., in the typical year there is ~16% difference between ¹⁴C-PP measured in winter (Dec–Mar) and summer (Jun–Aug).

[9] Primary production rates at ALOHA have been simulated using a PP model based on measured chlorophyll concentrations, PAR and the empirically derived photosynthesis versus light relationship or quantum yield [*Ondrusek et al.*, 2001]. Although the PP model yielded an annual mean PP rate (460 ± 33 mg C m⁻² d⁻¹) within ~10% of the mean ¹⁴C-PP at ALOHA, it significantly underestimated the variability in PP, which may have been due to a species dependence of maximum quantum yield [*Ondrusek et al.*, 2001]. *Ondrusek et al.* found that satellite based PP at ALOHA underestimated measured ¹⁴C-PP by ~60% and was mainly due to underestimates of chlorophyll and assumed maximum quantum yield.

[10] The importance of stochastic productivity events at ALOHA is somewhat unclear. *Karl et al.* [2003] made the illustrative case that episodes of NCP occurring at rates 3x the mean rate and 10% of the time are sufficient to yield a net annual autotrophic condition despite a background heterotrophic condition. The lesson being that frequent NCP measurements would be required to accurately estimate the mean annual trophic state. *Letelier et al.* [2000] detected an eddy at ALOHA that had 3x background chlorophyll concentrations and a nitracline uplifted by ~100 m, which demonstrated the potential impact of mesoscale features on the ecosystem structure at ALOHA. *Emerson et al.* [2002] used a continuous record of surface dissolved O₂ gas measurements from a moored sensor at ALOHA to demonstrate significant mesoscale variability of O₂ saturation levels and that would, at steady state, correspond to similar variability in NCP. On the other hand, the historic ¹⁴C-PP data from ALOHA do not detect large PP events. Only two out of 172 times between 1988 and 2006 was the measured ¹⁴C-PP greater than twice the long-term mean and never was it $\geq 3x$ the mean. Thus, either PP events are relatively unimportant at ALOHA or the ¹⁴C-PP method doesn't detect them. It is important to point out, however, that episodic events (eddies, storms, fronts, etc.) potentially have a much bigger impact on the rate of NCP than PP. At ALOHA, NCP estimates (~90 mg C m⁻² d⁻¹, see below) represent ~20% of the average ¹⁴C-PP (~500 mg C m⁻² d⁻¹), with most of the PP being supported by recycled nutrients, and thus episodic events that doubled annual NCP would increase ¹⁴C-PP by only ~20%.

[11] Rates of NCP at ALOHA have been estimated using several approaches including budgets of O₂, dissolved inorganic carbon (DIC) and ²³⁴Th and sediment traps (Table 1). The NCP estimates range from 30 ± 8 mg C m⁻² d⁻¹ to 135 ± 62 mg C m⁻² d⁻¹ and yield a main rate (excluding sediment traps) of 90 ± 28 mg C m⁻² d⁻¹ (~2.7 ± 0.9 mol C m⁻² yr⁻¹).

Table 1. Estimates of Net Community Production Rate ($\text{mg C m}^{-2} \text{d}^{-1}$) From the Photic Layer at ALOHA

Method	Rate	Time Interval	Reference
Sediment traps	30 ± 8	1989–1997	<i>Karl</i> [1999]
O_2 + Ar budgets	89 ± 56	1992–1995	<i>Emerson et al.</i> [1997]
	46 ± 21	2000–2001	<i>Hamme and Emerson</i> [2006]
DIC + DIC ¹³ budgets	90 ± 45	1994–1999	<i>Quay and Stutsman</i> [2003]
	92 ± 32	1988–2002	<i>Keeling et al.</i> [2004]
²³⁴ Th + OC budgets	88 ± 31	1999–2000	<i>Benitez-Nelson et al.</i> [2001]
Mooring O_2	135 ± 62	2005	<i>Emerson et al.</i> [2008]

2.2. Primary Production Rates

2.2.1. Bottle Incubation Methods

[12] ¹⁴C bottle incubations were performed from dawn to dusk (daytime) in triplicate at six depths (5, 25, 45, 75, 100, and 125m) to estimate daytime PP during each HOT cruise using procedures described by *Karl and Lukas* [1996]. *Marra* [2002] found that the net O_2 production rate measured by bottle incubations during JGOFS was similar to the concurrent daily (24 h incubation) ¹⁴C-PP rate assuming a PQ of 1.4 and, thus, concluded that daily ¹⁴C-PP approximated net autotrophic PP under most conditions. *Letelier et al.* [1996] estimated that 90% of the ¹⁴C-PP between the surface and 200m occurred within the top 100m at ALOHA. Based on a comparison of concurrent daytime and 24 h (daily) ¹⁴C incubation PP measurements at ALOHA, *Karl et al.* [1996] observed that ~15% of the organic matter fixed during the daytime was respired at night as compared to previous estimates of 20–25% observed during JGOFS [*Laws et al.*, 2000a; *Marra and Barber*, 2004]. *Karl et al.* [1998] observed that unmeasured DOC¹⁴ production during the dawn to dusk ¹⁴C incubations at ALOHA could yield a 30–50% underestimate of PP.

[13] Rates of GOP were measured each month in triplicate at five depths (5, 25, 45, 75 and 100m) using bottle incubations (24 h) of ¹⁸O labeled water [*Bender et al.*, 1987]. Specifically, we used acid cleaned quartz bottles and ¹⁸O enriched water that was triple distilled to eliminate nutrient and trace metal contamination following the incubation techniques described by *Juranek and Quay* [2005]. The ¹⁸O method clearly measures GOP and since there is insignificant recycling of the ¹⁸O labeled O_2 produced during the incubation, the measured GOP rate does not depend on incubation duration or diel variations in R [*Bender et al.*, 1999; *Laws et al.*, 2000a]. However, the conversion from GOP to gross carbon production is not straightforward. Recent studies demonstrate an uncoupling of O_2 production from carbon fixation during photosynthesis via, for example, the Mehler reaction, chlororespiration and photorespiration, which can vary depending on light level and nutrient availability [e.g., *Zehr and Kudela*, 2009; *Suggett et al.*, 2009].

[14] Previous comparisons of ¹⁸O-GOP versus daily ¹⁴C-PP indicated that GOP was 2–3 times the ¹⁴C-PP rates ($\text{mol O}_2/\text{mol C}$) based on measurements in the equatorial Pacific and Arabian Sea during JGOFS [*Bender et al.*, 1999; *Laws et al.*, 2000a]. *Marra* [2002] compiled the ¹⁸O-bottle and ¹⁴C-bottle measurements during JGOFS and found an ¹⁸O-GOP/¹⁴C-PP of ~2.7 ($\text{mol O}_2/\text{mol C}$) for daily (24 h)

incubations and ~2.0 for daytime (dawn to dusk) incubations. *Juranek and Quay* [2005] measured a mean ¹⁸O-GOP/¹⁴C-PP (daytime) of 1.7 ± 0.4 during four cruises to station ALOHA in 2002–2003. Recently, however, *Robinson et al.* [2009] reported a significantly higher ¹⁸O-GOP/¹⁴C-PP of 4.5 ± 1.2 based on concurrent 24 h on-deck incubations in waters from the Celtic Sea where the ¹⁴C-PP rate ranged from ~200 to 5000 $\text{mg C m}^{-2} \text{d}^{-1}$.

[15] A difficult question to answer is whether any incubation (or non-incubation) based measurement of PP is accurate. Incubating seawater enclosed in bottles or bags introduces artifacts potentially affecting the measured PP rate (e.g., changes in the quality and quantity of irradiance, the phytoplankton, zooplankton and microbial communities, nutrient supply, turbulence, etc.). There is also the issue of extrapolating incubation-based PP measurements to longer time scales. Daily variations in cloudiness, water clarity, mixed layer depth and spatial patchiness in PP yield uncertainty in spatial or temporal extrapolations of 12- or 24-h incubation-based PP measurements. If infrequent episodes or patches of high PP are superimposed on a background of lower PP conditions, then sporadic bottle measurements of PP will underestimate the true PP. In short, the question of how the PP rate measured by traditional incubation methods compares to the in situ PP rate has remained unanswered because of the lack of an absolute PP standard and alternative non-incubation PP methods.

2.2.2. Oxygen Isotope Method

[16] The rate of aquatic PP has been estimated using the natural isotopic composition of dissolved O_2 [*Luz and Barkan*, 2000]. This method relies on an observed anomalously low ¹⁷O/¹⁶O for O_2 in the atmosphere caused by a mass independent fractionation during reactions between ozone, O_2 , and CO_2 in the stratosphere [*Thiemens et al.*, 1995]. The basis of the oxygen isotope PP method is that air-sea O_2 gas exchange drives the ¹⁷O/¹⁶O and ¹⁸O/¹⁶O of dissolved O_2 in the surface ocean toward that of atmospheric O_2 whereas photosynthesis produces O_2 with a mass dependent (typical) distribution of O isotopes that has a higher ¹⁷O/¹⁶O relative to O_2 in air. As a result, the measurement of the ¹⁷O/¹⁶O and ¹⁸O/¹⁶O of dissolved O_2 in the surface ocean yields a direct estimate of the fractions of O_2 from air and photosynthesis. Therefore, once the rate of air-sea O_2 gas exchange is estimated, one can calculate the rate of GOP from the measured ¹⁷O/¹⁶O and ¹⁸O/¹⁶O of O_2 dissolved in seawater.

[17] Because the ¹⁷O/¹⁶O difference (relative to ¹⁸O/¹⁶O) between O_2 in air and O_2 produced during photosynthesis is small an isotopic notation (¹⁷Δ) expressed in parts per million (per meg), rather than in parts per thousand (per mil) traditionally used in isotopic notation, was adopted [*Luz and Barkan*, 2000; *Angert et al.*, 2003]. The ¹⁷Δ represents the ¹⁷O/¹⁶O anomaly relative to ¹⁸O/¹⁶O and is expressed as:

$${}^{17}\Delta(\text{per meg}) = [\ln(\delta^{17}\text{O}/1000 + 1) - 0.518 \cdot \ln(\delta^{18}\text{O}/1000 + 1)] \cdot 10^6, \quad (1)$$

where $\delta^{18}\text{O}(\text{‰}) = [({}^{18}\text{O}/{}^{16}\text{O})_s / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{std}} - 1] \cdot 1000$, s = sample and std = standard (and similarly for $\delta^{17}\text{O}$). The

expression for $^{17}\Delta$ implies that a process that produces or consumes oxygen with a $^{17}\text{O}/^{16}\text{O}$ to $^{18}\text{O}/^{16}\text{O}$ reaction rate ratio of ~ 0.518 will not change $^{17}\Delta$. This is important since respiration in plankton and bacteria measured in lab experiments yields a mean $^{17}\text{O}/^{16}\text{O}$ to $^{18}\text{O}/^{16}\text{O}$ reaction rate ratio of ~ 0.518 [Luz and Barkan, 2005] and thus has an insignificant effect on the $^{17}\Delta$ of dissolved O_2 .

[18] Luz and Barkan [2000] chose O_2 in air as the standard for $^{17}\Delta$ and thus, by definition, atmospheric O_2 has a $^{17}\Delta = 0$ per meg. The $^{17}\Delta$ of dissolved O_2 in seawater equilibrated with air is 17 ± 4 per meg at $\sim 25^\circ\text{C}$ [Sarma et al., 2006; Luz and Barkan, 2009]. Based on marine plankton culture studies, the O_2 produced during photosynthesis has a $^{17}\Delta_{\text{photo}} = 249 \pm 15$ per meg [Luz and Barkan, 2000]. Thus $^{17}\Delta$ of the dissolved O_2 in the warm surface ocean ranges between extremes of ~ 17 and ~ 249 per meg, depending on the relative rates of air-sea O_2 exchange and gross photosynthesis.

[19] If the mixed layer budget for O_2 and O_2 isotopes approaches steady state (i.e., the time rate of change of O_2 concentration is small compared to the O_2 source and sink rates), then the sources of O_2 resulting from air to sea O_2 gas invasion and GOP equal the O_2 losses resulting from sea to air gas evasion and community respiration (assuming mixing is negligible). Luz and Barkan [2000] showed that the steady state rate of GOP can be expressed in terms of only one field measurement, i.e., the $^{17}\Delta$ of dissolved O_2 ($^{17}\Delta_{\text{diss}}$), and estimates of the O_2 concentration in equilibrium with air ($\text{O}_{2\text{eq}}$) and the air-sea O_2 gas transfer rate (k_{as}).

$$\text{GOP} = k_{\text{as}} \cdot \text{O}_{2\text{eq}} \cdot ({}^{17}\Delta_{\text{diss}} - {}^{17}\Delta_{\text{eq}}) / ({}^{17}\Delta_{\text{photo}} - {}^{17}\Delta_{\text{diss}}) \quad (2)$$

[20] Notably, respiration is not a term in equation (2) because it does not affect $^{17}\Delta$, as discussed above. Here GOP represents the average rate integrated over the depth of the mixed layer. In practice, GOP rates were calculated from $^{17}\Delta$ measurements using the more accurate version of equation (2) from Hendricks et al. [2004], which yielded GOP rates that were $\sim 10\%$ higher than rates calculated from equation (2).

[21] Although GOP estimated from equation (2) ignores the effects of mixing and advection, this assumption is often reasonable because the net advective and diffusive O_2 fluxes are small compared to the gross O_2 flux represented by GOP. However, during periods of mixed layer entrainment (fall and winter), strong upwelling or vertical mixing, GOP can be significantly overestimated by equation (2), as discussed below.

[22] Estimating GOP using the oxygen isotope method (referred to as $^{17}\Delta$ -GOP) has the advantages of eliminating incubation effects and integrating GOP rates over the residence time of O_2 in mixed layer (typically 1–3 weeks) and thus potentially capturing PP events likely missed by 12- or 24-h incubations. Furthermore, since it does not require an incubation, the $^{17}\Delta$ -GOP method can be applied anywhere a surface seawater sample can be collected. The disadvantages of the $^{17}\Delta$ -GOP method are the significant uncertainty in the method ($\sim \pm 40\%$), the extrapolation from mixed layer to total photic layer, possible biases in the GOP estimates due to mixed layer entrainment, upwelling and vertical mixing

and the uncertainty in converting from oxygen production to carbon fixation.

[23] Although the caveats with the $^{17}\Delta$ -GOP method are significant, they are different from the caveats pertaining to ^{14}C -PP incubation method and thus we gain new information about PP in the ocean. However, the lack of an absolute PP standard prevents a determination of accuracy for any PP method. Thus, we must look for consistency (or inconsistency) between PP methods and, in addition, account for the different metrics of PP (e.g., carbon fixation, O_2 production, electron transport, fluorescence, etc.) used by individual PP methods.

[24] The isotopic composition of dissolved O_2 was measured using the analytical procedures described by Juranek and Quay [2005]. Duplicate samples were collected at 9 depths (5, 25, 45, 75, 100, 125, 150, 200, and 300m) on the HOT cruises using the methods described by Emerson et al. [1999]. The typical precision of the repeated $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ measurements averaged 0.05 and 0.01‰ yielding a standard error in the mean (SEM, where $\text{SEM} = \text{SD}/\sqrt{n}$) of ± 5 per meg after 75 individual isotope ratio determinations. The mean standard deviation of $^{17}\Delta$ for paired duplicate samples was ± 8 per meg. In the mixed layer, where typically 4 to 8 samples were collected each month, the average SEM of the mean $^{17}\Delta$ was ± 4 per meg. We estimate the depth of the mixed layer from CTD profiles using a potential density (σ_θ) change of 0.125 kg m^{-3} from the surface as the criterion.

[25] The initial application of the $^{17}\Delta$ -GOP method was at the time series station BATS in the subtropical N. Atlantic in 1998–99 by Luz and Barkan [2000]. They measured a $^{17}\Delta$ range of 30 to 47 per meg (mean = 38 ± 8) during six cruises from which they estimated mean $^{17}\Delta$ -GOP rate of $70 \pm 35 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ that was 3x the long-term average ^{14}C -PP at BATS. (All uncertainties represent ± 1 standard deviation (SD) unless stated otherwise.) A more detailed presentation of these results by Luz and Barkan [2009] indicated that the $^{17}\Delta$ -GOP rates varied from 29 to $107 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in the mixed layer between May and October 2000 and were 3.5–8x the concurrently measured ^{14}C -PP rate. Juranek and Quay [2005] measured a $^{17}\Delta$ range of 31–39 per meg in the mixed layer at ALOHA during four cruises in 2002–2003 that yielded a $^{17}\Delta$ -GOP range of 70–185 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ that was 2–3x daytime ^{14}C -PP rates and $1.8 \pm 0.8\text{x}$ ^{18}O -GOP rates concurrently measured during these cruises. In the eastern equatorial Pacific (95°W – 110°W), Hendricks et al. [2005] measured a $^{17}\Delta$ range of 40 to 100 per meg in surface waters that yielded a mean GOP rate of $102 \pm 65 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ for stations poleward of 2°N and 5°S . In the Southern Ocean (40°S to 70°S), Reuer et al. [2007] measured a $^{17}\Delta$ range of ~ 10 to 50 per meg in surface waters that yielded GOP range of ~ 50 to $500 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (mean = $166 \pm 121 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$). In Sagami Bay on the coast of Japan, Sarma et al. [2005] measured a $^{17}\Delta$ range of ~ 50 to 110 per meg in surface waters that yielded GOP rates of ~ 90 to $350 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$.

2.3. NCP Rates Estimated From O_2/Ar

[26] The net imbalance between GOP and R can be estimated from a mixed layer budget for dissolved oxygen. In

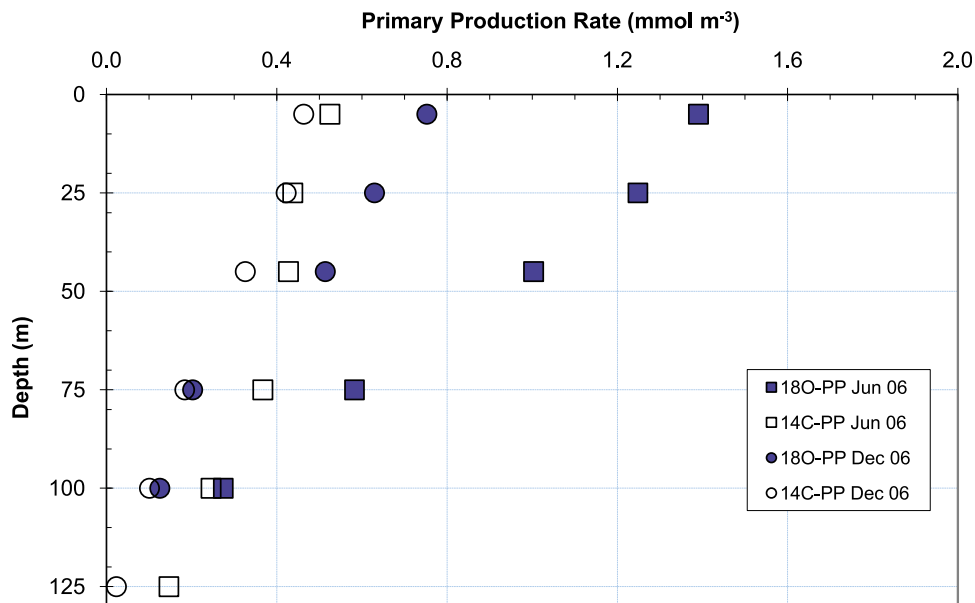


Figure 1. Two representative depth profiles of primary production rates at ALOHA measured by the ^{18}O -GOP ($\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$) and ^{14}C -PP ($\text{mmol C m}^{-2} \text{ d}^{-1}$) incubation methods in June and December 2006.

its simplest form, the budget assumes that the net rate of O_2 gas evasion to the atmosphere is balanced by net biological O_2 production (i.e., $\text{GOP} - \text{R}$). Emerson *et al.* [1997] utilized the similar temperature dependence of gas solubility in seawater for Argon (Ar) and O_2 to determine the biological component of the O_2 saturation. In this way, the O_2/Ar saturation state, i.e., where $(\text{O}_2/\text{Ar})_{\text{sat}}$ equals the O_2/Ar measured divided by the O_2/Ar expected in equilibrium with air, yielded the portion of the net sea to air O_2 flux that was balanced by net biological production of O_2 (or NCP). Thus NCP in the mixed layer is determined from measuring the ratio of dissolved O_2 and Ar gases, calculating $(\text{O}_2/\text{Ar})_{\text{sat}}$ and estimating k_{as} , as follows:

$$\text{NCP} = k_{\text{as}} \cdot \text{O}_{2\text{eq}} \cdot [(\text{O}_2/\text{Ar})_{\text{sat}} - 1] \quad (3)$$

[27] This approach has been applied at ALOHA previously and yielded NCP rates of $10.4 \pm 6.6 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in the 1990s [Emerson *et al.*, 1997], $3\text{--}5 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in 2000–02 [Hamme and Emerson, 2006] and $9\text{--}17 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ during summer 2002–2003 [Juraneck and Quay, 2005]. At BATS, Luz and Barkan [2009] used O_2/Ar measurements to estimate NCP rates of $6\text{--}8 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ for the mixed layer. In the eastern equatorial Pacific, Hendricks *et al.* [2005] used surface O_2/Ar measurements to estimate a mean NCP rate of $10 \pm 9 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. In the Southern Ocean ($45^\circ\text{--}65^\circ\text{S}$), Reuer *et al.* [2007] used surface O_2/Ar measurements to estimate NCP rates of $22\text{--}50 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. Kaiser *et al.* [2005] used continuous underway O_2/Ar measurements during a cruise in the eastern equatorial Pacific to estimate NCP rates of $\sim 0\text{--}18 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. For all the above examples, k_{as} was estimated from observed wind

speeds and an empirical relationship between k_{as} and wind speed [e.g., Wanninkhof, 1992; Nightingale *et al.*, 2000].

[28] The ratio NCP/GOP in the mixed layer can be estimated by simultaneous $^{17}\Delta$ and O_2/Ar measurements (combining equations (2) and (3)) as follows:

$$\text{NCP/GOP} = [(\text{O}_2/\text{Ar})_{\text{sat}} - 1] \cdot ({}^{17}\Delta_{\text{photo}} - {}^{17}\Delta_{\text{diss}}) / ({}^{17}\Delta_{\text{diss}} - {}^{17}\Delta_{\text{eq}}) \quad (4)$$

Note that NCP/GOP is independent of k_{as} , which means that the calculated NCP/GOP has substantially less uncertainty than either GOP or NCP (except when $(\text{O}_2/\text{Ar})_{\text{sat}}$ approaches 1) and that the numerator and denominator are measured in the same units (O_2 production). Previous NCP/GOP estimates based on $^{17}\Delta$ and O_2/Ar measurements averaged 0.13 ± 0.05 during summer cruises at ALOHA [Juraneck and Quay, 2005], 0.06 ± 0.05 in the eastern equatorial Pacific [Hendricks *et al.*, 2005], 0.13 ± 0.06 for the Southern Ocean [Reuer *et al.*, 2007] and 0.13 ± 0.05 at BATS [Luz and Barkan, 2009].

3. Results

3.1. Incubation-Based Estimates of PP

[29] Depth profiles of ^{14}C -PP and ^{18}O -GOP rates decreased with depth, as expected, through the photic layer (Figure 1). However, ^{18}O -GOP decreased twice as sharply as ^{14}C -PP with depth, i.e., the ^{18}O -GOP at 100m equaled $15 \pm 2\%$ ($\pm\text{SEM}$) of the rate at 5m whereas the ^{14}C -PP at 100m equaled $31 \pm 4\%$ ($\pm\text{SEM}$) of the rate at 5m. The ratio of ^{18}O -GOP to ^{14}C -PP ($\text{mol O}_2/\text{mol C}$) decreased with depth from a mean ($\pm\text{SEM}$) of 2.4 ± 0.3 at 5m, 1.1 ± 0.05 at

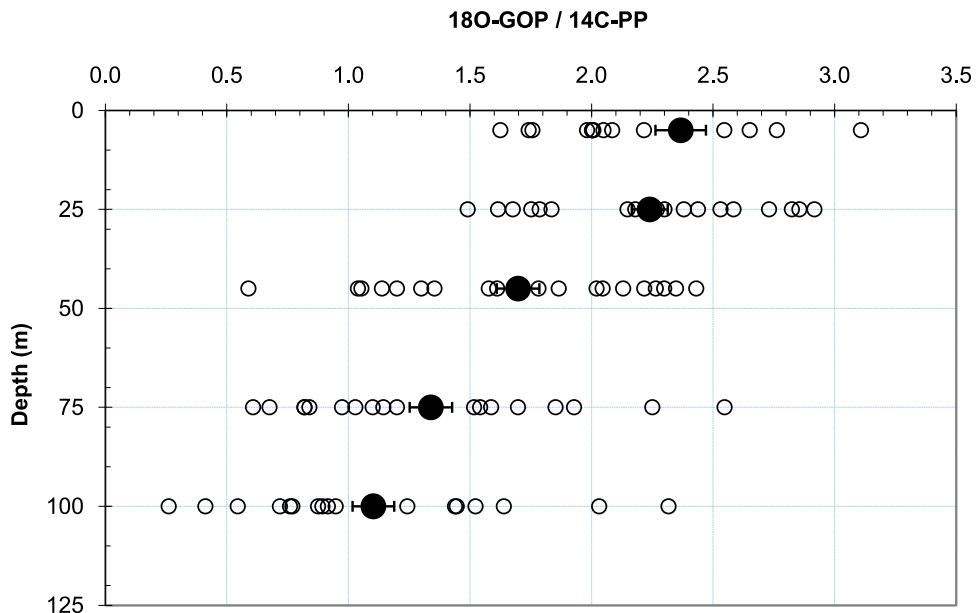


Figure 2. The depth distribution of the $^{18}\text{O-GOP}/^{14}\text{C-PP}$ ratio (mol $\text{O}_2/\text{mol C}$) measured monthly from March 2006 to February 2008 (HOT cruises 179 to 200). The filled circles represent the mean values at each depth and error bars are $\pm\text{SEM}$.

100 m (Figure 2). During the summer (May–Sep), with a mean mixed layer depth (Z_{ml}) of 45m, the depth-integrated mixed layer $^{18}\text{O-GOP}$ was 64% of the $^{18}\text{O-GPP}$ integrated to 100 m, whereas in winter (Nov–Mar) when the mean Z_{ml} was 75 m, the integrated $^{18}\text{O-GPP}$ in the mixed layer was 90% of $^{18}\text{O-GOP}$ to 100m. For $^{14}\text{C-PP}$, similar ratios of 60% and 86% were determined for summer and winter, respectively.

[30] The annual mean $^{18}\text{O-GOP}$ and $^{14}\text{C-PP}$ values were $71 \pm 16 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ and $38 \pm 6 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ($455 \pm 75 \text{ mg C m}^{-2} \text{ d}^{-1}$), respectively, integrated over the top 100m. In comparison, the climatological mean $^{14}\text{C-PP}$ at ALOHA (1988–2008) was $514 \pm 136 \text{ mg C m}^{-2} \text{ d}^{-1}$. Seasonally, $^{18}\text{O-GOP}$ and $^{14}\text{C-PP}$ in summer (May–Sep) exceeded winter (Nov–Mar) rates by 32% and 18%, respectively (Figure 3).

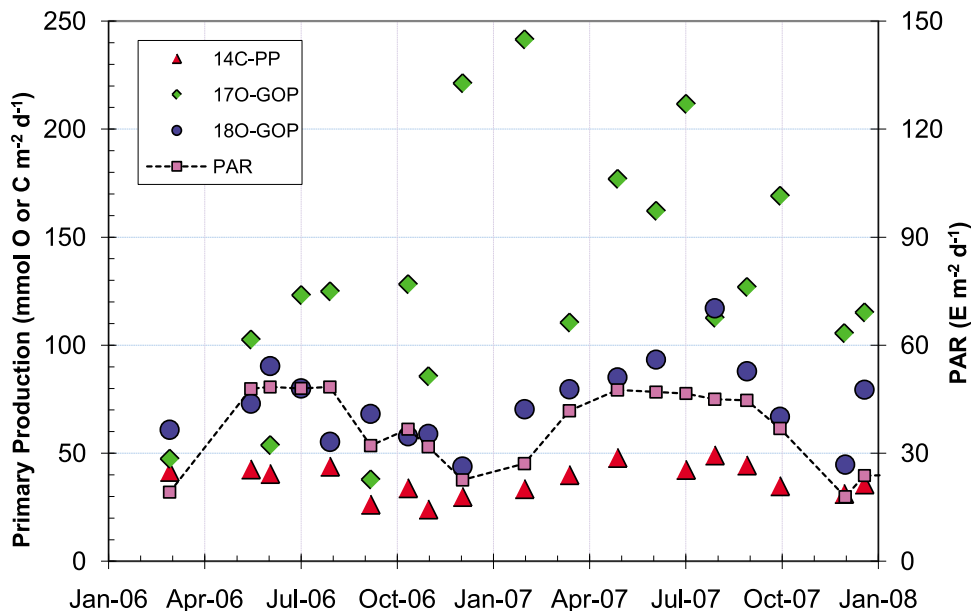


Figure 3. Monthly rates of GOP estimated from the $^{17}\Delta\text{-GOP}$ and $^{18}\text{O-GOP}$ ($\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$) and $^{14}\text{C-PP}$ ($\text{mmol C m}^{-2} \text{ d}^{-1}$) methods depth-integrated to 100 m.

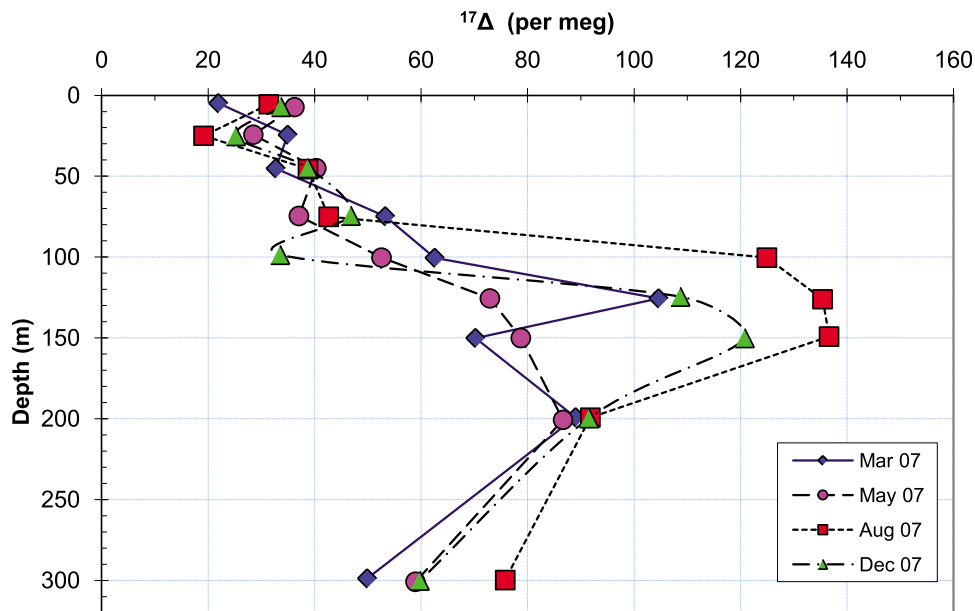


Figure 4. Depth profiles of $^{17}\Delta$ (per meg) measured during four HOT cruises in 2007.

3.2. Estimates of GOP Based on $^{17}\Delta$

[31] In the mixed layer, where 4–8 individual $^{17}\Delta$ values were measured, the monthly $^{17}\Delta$ ranged from 23 to 45 per meg ($n = 131$) with a typical SEM of ± 4 per meg. The annual mean $^{17}\Delta$ of 33 ± 2 per meg (\pm SEM) implied that 7% of the dissolved O_2 in the mixed layer at ALOHA is from photosynthesis and 93% from air. The $^{17}\Delta$ increased with depth reaching a subsurface maximum at 75–100m that peaked (~ 140 per meg) during the late summer (Figure 4). This sub-surface $^{17}\Delta$ build up was a result of photosynthesis occurring within the photic layer at depths isolated from air-sea O_2 gas exchange. Similar $^{17}\Delta$ depth profiles and mixed layer values have been observed at BATS [Luz and Barkan, 2009].

[32] The monthly GOP rates in the mixed layer calculated from $^{17}\Delta$, using the rigorous version of equation (2), ranged from 40 to 242 $mmol O_2 m^{-2} d^{-1}$, with an annual mean of $100 \pm 51 mmol O_2 m^{-2} d^{-1}$. The two highest mixed layer $^{17}\Delta$ -GOP estimates of 210 and 241 $mmol O_2 m^{-2} d^{-1}$ occurred in December 2006 and February 2007 when the mixed layer was deepest at 90–110m (Figure 3). There is substantially more variability in the monthly $^{17}\Delta$ -GOP estimates compared to ^{18}O -GOP and ^{14}C -PP and no significant annual trend (Figure 3).

[33] The $^{17}\Delta$ -GOP values calculated using equation (2) are overestimated during fall and winter, when subsurface water with elevated $^{17}\Delta$ (Figure 4) is entrained into the mixed layer. To avoid this bias in the $^{17}\Delta$ method, GOP rates were calculated from $^{17}\Delta$ using a time dependent depth-integration of $^{17}\Delta$. This approach calculated the time rate of change of the monthly mean $^{17}\Delta$ integrated to a constant depth, i.e., a depth below the base of the photic layer at which $^{17}\Delta$ varies little during the year (e.g., mean $^{17}\Delta = 85 \pm 3$ (SEM) per meg at 200m) (Figure 4). This

estimate of $^{17}\Delta$ -GOP_{int} (integrated to Z_{int}) is expressed as follows:

$$GOP_{int} = [k_{as} \cdot O_{2eq} \cdot (^{17}\Delta_{diss} - ^{17}\Delta_{sat}) + Z_{int} \cdot d(O_2 \cdot ^{17}\Delta)/dt] / [^{17}\Delta_{photo} - ^{17}\Delta_{diss}] \quad (5)$$

In essence, a time rate of change term is added to the numerator of equation (2). This approach avoids an over-estimation of GOP caused by entrainment and vertical mixing by accounting for the observed depth-integrated $^{17}\Delta$ increase (oxygen concentration weighted) during the summer and decrease during winter (Figure 5).

[34] The average $^{17}\Delta$ -GOP_{int} rate (integrated to 200m) was $123 \pm 44 mmol O_2 m^{-2} d^{-1}$ for summer (May–Sep) and $83 \pm 42 mmol O_2 m^{-2} d^{-1}$ for winter (Nov–Mar) yielding an annual average rate of $103 \pm 43 mmol O_2 m^{-2} d^{-1}$ (Table 2). (The mean annual $^{17}\Delta$ -GOP_{int} rate integrated to 150m was 5% lower). The $^{17}\Delta$ -GOP_{int} rates were higher by $\sim 50\%$ in summer than winter, in marked contrast to the $^{17}\Delta$ -GOP rates calculated using equation (2) which were about equal in winter than summer (Table 2).

3.3. Estimates of NCP Based on O_2/Ar

[35] The measured mixed layer O_2/Ar exceeded that expected at equilibrium with air every month (Figure 6) yielding an annual mean O_2/Ar saturation of $101.3 \pm 0.1\%$ (SEM). In summer, the O_2/Ar saturation at $101.4 \pm 0.1\%$ (SEM) was slightly greater than in winter at $101.0 \pm 0.1\%$ (SEM) and was inversely correlated with mixed layer depth and, in 2007, correlated with ^{18}O -GOP (Figure 6). Vertical mixing had a small effect on O_2/Ar in the mixed layer, i.e., a vertical mixing rate (K_z) of $10^{-4} m^2 s^{-1}$ decreased the annual average mixed layer $(O_2/Ar)_{sat}$ by 0.1%, implying that the measured O_2/Ar is predominantly controlled by air-sea O_2 gas exchange and

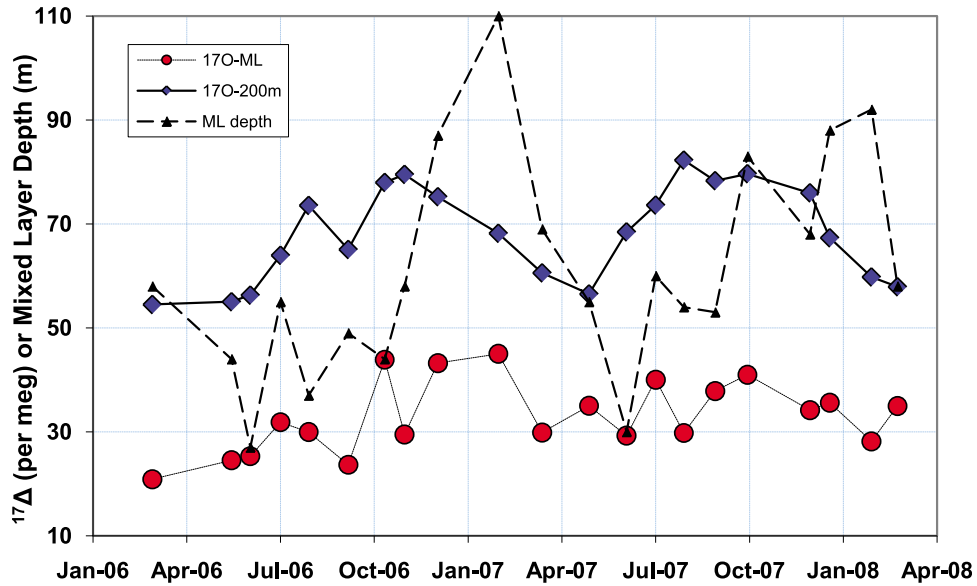


Figure 5. The monthly measurements of the $^{17}\Delta$ (per meg) in the mixed layer and depth-integrated to 200m and depth of mixed layer (m) at ALOHA from Mar 2006 to Feb 2008.

NCP. An annual mean rate of NCP of $14 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ for the mixed layer was calculated using equation (3), monthly measured $(\text{O}_2/\text{Ar})_{\text{sat}}$ and estimated air-sea O_2 gas transfer rates [Nightingale et al., 2000], which converts to $120 \pm 35 \text{ mg C m}^{-2} \text{ d}^{-1}$ ($3.7 \pm 1.0 \text{ mol C m}^{-2} \text{ yr}^{-1}$) assuming a PQ of 1.4.

3.4. Error Analysis

[36] The uncertainty in the GOP, NCP and NCP/GOP estimated from $^{17}\Delta$ and O_2/Ar measurements was determined using a Monte Carlo approach. An error was assigned for

each term in the equations for GOP, NCP and NCP/GOP. A value for each term in these equations was randomly selected assuming a normal distribution based on its mean value and uncertainty ($\pm 1 \text{ SD}$). For example, a value of GOP was calculated for a given set of values for each term in equation (2) and this procedure was repeated 3000 times. The variability ($\pm 1 \text{ SD}$) of the calculated mean GOP was determined from the 3000 individual estimates of GOP.

[37] The following errors in the terms were used: $\pm 25\%$ for k_{as} representing the range between *Liss and Merlivat*

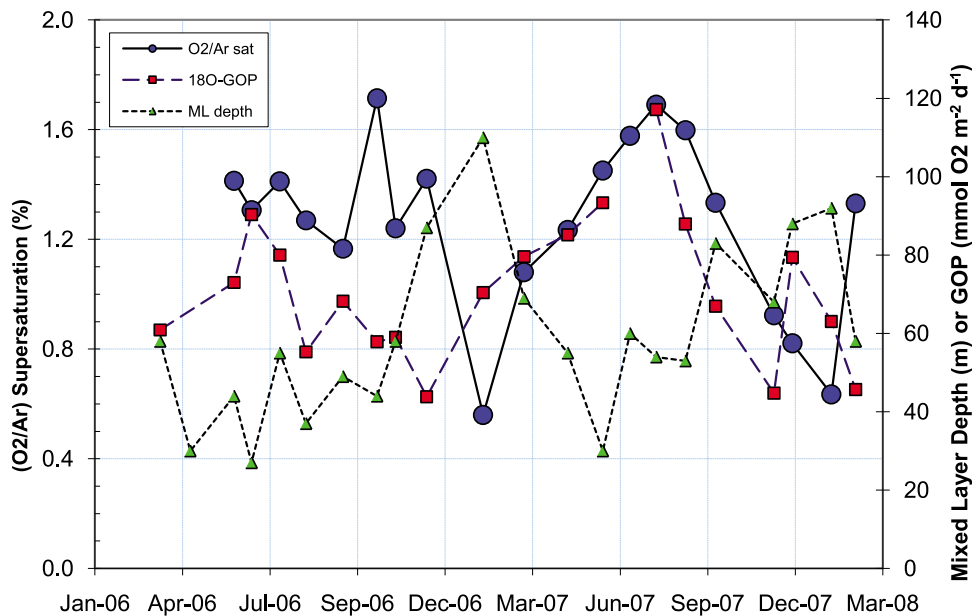


Figure 6. The supersaturation (%) state of the dissolved O_2/Ar gas ratio (i.e., $[(\text{O}_2/\text{Ar})_{\text{meas}} / (\text{O}_2/\text{Ar})_{\text{eq}} - 1] \cdot 100$) in the mixed layer, $^{18}\text{O-GOP}$ ($\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$) and mixed layer depth (m) measured monthly at ALOHA.

[1986] and *Wanninkhof* [1992], ± 4 per meg for the mean monthly $^{17}\Delta_{\text{diss}}$ in the mixed layer representing the typical SEM, ± 15 per meg for $^{17}\Delta_{\text{photo}}$ and ± 3 per meg for $^{17}\Delta_{\text{eq}}$ [*Luz and Barkan*, 2009], $\pm 0.2\%$ for $\text{O}_{2\text{eq}}$, $\pm 0.1\%$ for $(\text{O}_2/\text{Ar})_{\text{sat}}$ representing the observed SEM for mean monthly O_2/Ar in the mixed layer. For the calculation of GOP using equation (5), the error in the time rate of change term ($d^{17}\Delta/dt$) was the error in the slope of $^{17}\Delta$ versus time regression. This analysis yielded errors of $\pm 40\%$ for GOP (equation (2)), $\pm 35\%$ (summer) and $\pm 50\%$ (winter) for GOP_{int} (equation (5)), $\pm 25\%$ for NCP (equation (3)) and ± 0.1 for NCP/GOP (equation (4)).

4. Discussion

4.1. Estimates of PP Based on Incubations

[38] The overall ratio of $^{18}\text{O-GOP}$ to $^{14}\text{C-PP}$ (daytime incubation) at ALOHA is 1.9 ± 0.1 (mol $\text{O}_2/\text{mol C}$) based on a regression of individual bottle measurements made at the same depths on each HOT cruise. This value is slightly higher than the 1.4 ± 0.2 value previously observed during a single day incubation experiment at a nearby PRPOOS study site by *Grande et al.* [1989] but similar to the 2.0 value based on a compilation of JGOFS data [*Marra*, 2002]. Assuming 15% of organic carbon produced during the daytime is respired at night at ALOHA, as estimated by *Karl et al.* [1996], then the ratio of $^{18}\text{O-GOP}$ to daily (24-h) $^{14}\text{C-PP}$ would have been 2.2 ± 0.1 and slightly lower than the 2.7 value observed during JGOFS [*Bender et al.*, 1999; *Marra*, 2002].

[39] In the deeper portion of the photic layer where growth rates are light limited and slower, however, the $^{14}\text{C-PP}$ rate approaches the $^{18}\text{O-GOP}$ rate (Figure 2) as previously observed [*Grande et al.*, 1989; *Bender et al.*, 1999; *Juranek and Quay*, 2005]. There are several possible explanations of these observations. There could have been a decrease with depth in the photic layer of the O_2 production to carbon fixation ratio, the autotrophic respiration to photosynthesis ratio, or the proportions of recycled $^{14}\text{CO}_2$ or unmeasured DOC^{14} production.

[40] There was a stronger seasonality in $^{18}\text{O-GOP}$, with summertime (May–Sep) rates exceeding wintertime (Nov–Mar) rates by 32%, compared to $^{14}\text{C-PP}$ that varied by 18%, between seasons.

4.2. Estimates of GOP Based on $^{17}\Delta$

[41] The ALOHA site is a tough test for the $^{17}\Delta\text{-GOP}$ method because the PP rates are low and have low variability (based on historic $^{14}\text{C-PP}$). The annual mean mixed layer $^{17}\Delta$ of 32 ± 2 (SEM) per meg is close to the atmospheric equilibrium value ($^{17}\Delta_{\text{eq}}$) of 17 ± 3 per meg. Since $^{17}\Delta\text{-GOP}$ is proportional to the difference between the measured $^{17}\Delta$ and $^{17}\Delta_{\text{eq}}$ (see equation (2)), an SEM of ± 4 per meg for each monthly $^{17}\Delta$ measured in the mixed layer typically yields $\sim \pm 25\%$ uncertainty in GOP. Adding the $\pm 25\%$ error in air-sea gas transfer rates increases the overall uncertainty of the monthly GPP estimates to $\sim \pm 40\%$, as discussed above. If the seasonality of GOP at ALOHA was $\sim 30\%$, as indicated by the bottle $^{18}\text{O-GPP}$ measurements, then the uncertainty in an individual $^{17}\Delta\text{-GOP}$

determination precludes detection of monthly variations in GOP. Nonetheless, the $^{17}\Delta\text{-GOP}$ method yields useful estimates of seasonal and annual mean GOP rates, as discussed below.

[42] During the summer, under well-stratified conditions, the mean mixed layer $^{17}\Delta\text{-GOP}$ was 81 ± 39 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. This mixed layer $^{17}\Delta\text{-GOP}$ value was extrapolated to 200 m by assuming that the proportion of $^{17}\Delta\text{-GOP}$ integrated to 100 m that occurred in the mixed layer equaled the measured proportion of $^{18}\text{O-GOP}$ (integrated to 100 m) that occurred in the mixed layer and that 10% of GOP occurred between 100 and 200m as observed for $^{14}\text{C-PP}$ by *Letelier et al.* [1996]. This extrapolated summertime $^{17}\Delta\text{-GOP}$ estimate (0–200m) of 136 ± 51 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ exceeded by only 10% the summertime $^{17}\Delta\text{-GOP}_{\text{int}}$ value of 123 ± 44 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ calculated using the time dependent and depth-integrated (0–200 m) version of the $^{17}\Delta\text{-GOP}$ method (equation (5)); see Table 2. Given the uncertainties in each GOP estimate, this difference is insignificant (although most of the errors in the two estimates are correlated except for the time rate of change term) and suggests that the $^{17}\Delta\text{-GOP}$ method as typically applied to the mixed layer (equation (2)) under well stratified conditions may be only slightly overestimated due to mixing of subsurface waters. Similarly, *Sarma et al.* [2005] estimated that mixing with subsurface waters caused a slight ($< 14\%$) overestimate in mixed layer $^{17}\Delta\text{-GOP}$ rates during summer in Sagami Bay.

[43] The situation during winter at ALOHA is very different when the mean $^{17}\Delta\text{-GOP}$ of 144 ± 66 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (equation (2) and extrapolated to 200 m, as described above) exceeded by $\sim 75\%$ the mean $^{17}\Delta\text{-GOP}_{\text{int}}$ of 83 ± 42 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (0–200 m); see Table 2. Subtropical locations like ALOHA (and BATS) are particularly sensitive to entrainment induced biases in mixed layer $^{17}\Delta\text{-GOP}$ estimates (equation (2)) because GOP rates are low and elevated subsurface $^{17}\Delta$ levels exist during early fall at the onset of the mixed layer deepening (Figure 4). The bias in $^{17}\Delta\text{-GOP}$ caused by entrainment explains why mixed layer $^{17}\Delta\text{-GOP}$ rates (equation (2)) were higher in winter than in summer, opposite to the measured seasonal trends in $^{18}\text{O-GOP}$, $^{14}\text{C-PP}$ and PAR (Figure 3). In contrast, the mean depth-integrated $^{17}\Delta\text{-GOP}_{\text{int}}$ (0–200m) in summer exceeded winter $^{17}\Delta\text{-GOP}_{\text{int}}$ by $\sim 50\%$, which was similar in magnitude to the 40% difference in PAR between summer and winter.

[44] One test of the validity of the $^{17}\Delta\text{-GOP}_{\text{int}}$ approach is whether the depth-integrated $^{17}\Delta$ increase observed during the summer was balanced by the $^{17}\Delta$ decrease observed during the winter so that the depth profile of $^{17}\Delta$ is reset after an annual cycle. This was the situation at ALOHA where the wintertime depth-integrated $^{17}\Delta$ decrease to 200 m was within 2% of the summertime depth-integrated $^{17}\Delta$ increase. This balance is demonstrated by the observation that the annual mean $^{17}\Delta\text{-GOP}_{\text{int}}$ of 103 ± 43 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ integrated over summer and winter equaled the mean annual mixed layer $^{17}\Delta\text{-GOP}$ of 100 ± 51 $\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (equation (2)) and occurs because equation (5) reduces to equation (2) when the time rate of change term approaches zero. One benefit of this observation is that the calculated standard error in the mean (SEM) for the annual mixed layer

Table 2. Rates of Primary Production in the Photic Layer Based on $^{17}\Delta$ -GOP, ^{18}O -GOP ($\text{mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$), and ^{14}C -PP ($\text{mmol C m}^{-2} \text{ d}^{-1}$) for Summer (Jun–Sep), Winter (Dec–Mar), and Annually at ALOHA Between March 2006 and February 2008

$^{17}\Delta$ -GOP ^a	$^{17}\Delta$ -GOP _{int} ^b	^{18}O -GOP ^c	^{14}C -PP ^c	$\frac{^{17}\Delta\text{-GOP}_{\text{int}}}{^{18}\text{O-GOP}}$	$\frac{^{18}\text{O-GOP}}{^{14}\text{C-PP}}$
<i>Summer</i>					
136 ± 51	123 ± 44	89 ± 18	45 ± 8	1.4 ± 0.6	2.0 ± 0.5
<i>Winter</i>					
144 ± 66	83 ± 42	67 ± 13	38 ± 6	1.2 ± 0.7	1.8 ± 0.4
<i>Annual</i>					
140 ± 58	103 ± 43	78 ± 17	42 ± 7	1.3 ± 0.6	1.9 ± 0.5

^aEstimated from rigorous version of equation (2), assuming steady-state mixed layer $^{17}\Delta$ conditions and extrapolated to 200m assuming the relative depth decrease of ^{18}O -GPP rates measured to 100m applied to $^{17}\Delta$ -GPP rates and 10% of PP occurred between 100 and 200m based on comparison of ^{14}C -PP incubations [Letelier *et al.*, 1996].

^bDepth-integrated to 200m using time dependent method (equation (5)).

^cDepth integrated to 100 m using bottle measurements at five depths and extrapolated to 200 m, as described above.

$^{17}\Delta$ -GOP at $\pm 17 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ is significantly smaller than the error in the $^{17}\Delta$ -GOP_{int} method at $\pm 43 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$, which will help in the comparison between $^{17}\Delta$ -GOP and ^{18}O -GOP estimates discussed below.

4.3. Incubation Versus Non-Incubation Estimates of GOP

[45] The concurrent monthly measurements of $^{17}\Delta$ and ^{18}O -bottle incubations at ALOHA for two years provided an unprecedented opportunity to compare incubation and non-incubation estimates of GOP (Table 2). We find that $^{17}\Delta$ -GOP always exceeds ^{18}O -GOP. During the well-stratified summer season (May–Sep), the mean mixed layer $^{17}\Delta$ -GOP (rigorous version of equation (2)) of $81 \pm 39 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (SEM = 12, based on the eleven individual monthly $^{17}\Delta$ -GOP estimates that comprised the summer mean value) exceeded by $60 \pm 12\%$ (based on SEMs) the mixed layer ^{18}O -GOP of $51 \pm 14 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (SEM = 4). Similarly, but with greater uncertainty, the summertime $^{17}\Delta$ -GOP_{int} (integrated to 200 m) of $123 \pm 44 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ was $38 \pm 57\%$ higher than the average ^{18}O -GOP of $89 \pm 18 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ and the wintertime $^{17}\Delta$ -GOP_{int} of $83 \pm 42 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ was $25 \pm 66\%$ higher than the mean wintertime ^{18}O -GOP of $67 \pm 13 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ (where ^{18}O -GOP was integrated to 100 m and extrapolated to 200 m, as described above). Thus $^{17}\Delta$ -GOP consistently exceeded ^{18}O -GOP at ALOHA, yet there is substantial uncertainty in whether this difference is significant. If the difference (~ 25 – 60%) between $^{17}\Delta$ -GOP and ^{18}O -GOP estimates at ALOHA is accurate, then either the ^{18}O method underestimated GOP, most likely because of bottle incubation effects or missed stochastic PP events, and/or the $^{17}\Delta$ -method overestimated GOP most likely because of an overestimated air-sea O_2 gas exchange rate.

[46] Let's first consider the air-sea O_2 gas transfer rate used in the $^{17}\Delta$ -GOP method. Estimates of k_{as} at ALOHA were derived from wind speeds measured at a nearby National Data Buoy Center buoy site 51001 (23.5°N , 162.2°W)

weighted following Reuer *et al.* [2007] and the empirical relationship between k_{as} and wind speed reported by Nightingale *et al.* [2000]. At ALOHA, k_{as} estimates would have been $\sim 20\%$ higher and lower based on the work of Wanninkhof [1992] and Liss and Merlivat [1986], respectively. The k_{as} values used here are in the middle of the possible range, agree with recently determined k_{as} versus wind speed relationships [Ho *et al.*, 2006; Sweeney *et al.*, 2007] and likely overestimated by no more than 20%. In short, the 25–60% difference between $^{17}\Delta$ -GOP and ^{18}O -GOP is unlikely to be solely a result of overestimated $^{17}\Delta$ -GOP.

[47] Next, let's consider the likely impact of episodic PP events on $^{17}\Delta$ -GOP and ^{18}O -GOP due to the different integration times of the two methods. Infrequent PP events (either spatially or temporally) that contribute to the overall productivity of a region would cause periodic (monthly) single day incubations to underestimate the average PP [Karl *et al.*, 2003]. In contrast, the $^{17}\Delta$ -GOP method integrates GOP over the residence time of O_2 in the mixed layer (typically 1–2 weeks at ALOHA) and thus would more often capture PP events and could yield a mean $^{17}\Delta$ -GOP rate higher than the mean incubation-based ^{18}O -GOP rate. However, there is no evidence from the 20 year record of monthly ^{14}C -PP measurements at ALOHA that pulses of enhanced PP are important. To illustrate this point, let's assume that a 40% higher rate of (non-incubation) $^{17}\Delta$ -GOP compared to (incubation) ^{18}O -GOP was the result of episodic PP events. This difference would result from PP events that were 5x stronger than the background PP rate occurring 10% of the time. In contrast, the historic ^{14}C -PP data at ALOHA indicate that only two out of 172 ^{14}C -PP measurements (1%) exceeded the mean ^{14}C -PP rate by $>2x$ and none of the 172 ^{14}C -PP measurements exceeded the mean by $3x$. Thus there is no evidence from the historic ^{14}C -PP data that PP events occur with sufficient frequency or magnitude to explain the 25–60% difference between non-incubation $^{17}\Delta$ -GOP and incubation-based ^{18}O -GOP. Although storm events or eddies can have a significant impact on annual rates of NCP at ALOHA [e.g., Emerson *et al.*, 2002] such events will have a much smaller impact on rates of PP. At ALOHA, estimates of NCP at $\sim 90 \text{ mg C m}^{-2} \text{ d}^{-1}$ (Table 1) are $\sim 20\%$ of the mean ^{14}C -PP ($\sim 500 \text{ mg C m}^{-2} \text{ d}^{-1}$), thus a hypothetical doubling of the annual mean NCP due to episodic events would only increase PP by $\sim 20\%$.

[48] Finally, let's consider possible biases in incubation-based PP methods. Once seawater is enclosed in bottles and incubated at fixed depths, the characteristics of the environment change (e.g., light, biological community composition, nutrients, excretion products, grazing, turbulence, etc.), which in turn potentially impacts the PP rate. However, neither the magnitude nor even direction of these incubation effects is well known. If the 25–60% difference between $^{17}\Delta$ -GOP and ^{18}O -GOP estimates observed at ALOHA is too large to be explained by uncertainty of the $^{17}\Delta$ -GOP method or differences in integrating episodic PP events, as discussed above, then one should consider whether the difference may be caused by a bias in the incubation method. If so, the environmental changes inherent to isolating seawater in bottles (or bags) could cause biases in all rate

measurement based on incubation methods (e.g., ^{18}O , ^{14}C , and O_2).

4.4. Estimates of NCP and NCP/GOP Based on O_2/Ar and $^{17}\Delta$

[49] A mean NCP rate of $14 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($120 \pm 35 \text{ mg C m}^{-2} \text{ d}^{-1}$ or $3.7 \pm 1.0 \text{ mol C m}^{-2} \text{ yr}^{-1}$, assuming a $\text{PQ} = 1.4$) for the mixed layer at ALOHA for 2006–2008 was estimated from the measured monthly saturation state of the dissolved O_2/Ar gases in the surface layer and estimates of k_{as} (equation (3)). Previously, O_2/Ar measurements at ALOHA yielded NCP estimates for the mixed layer of $10.4 \pm 6.6 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in the 1990s [Emerson *et al.*, 1997], $3\text{--}4.7 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in 2000 [Hamme and Emerson, 2006] and $9\text{--}17 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ in summer 2004 [Juraneck and Quay, 2005]. Emerson *et al.* [2008] used a continuous record of dissolved O_2 in 2005 from a moored O_2 sensor at ALOHA to estimate a NCP rate of $13.1 \pm 7.2 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. The NCP rate below the mixed layer has been estimated at $6.0 \pm 0.8 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ using the annual cycle in dissolved O_2 measured by a profiling float near ALOHA [Riser and Johnson, 2008] and $3.5 \pm 0.4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ using the subsurface O_2 field at ALOHA measured by a SeaGlider survey [Nicholson *et al.*, 2008]. Combining these sub mixed layer NCP estimates with our O_2/Ar derived NCP estimate for the mixed layer yields an NCP of $\sim 19 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ for the photic layer, which corresponds to NCP of $5 \pm 1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (for a $\text{PQ} = 1.4$).

[50] The ratio of net community oxygen production to gross oxygen production (NCP/GOP) in the mixed layer was estimated from measured $^{17}\Delta$ and O_2/Ar using equation (4). During the summer, the mean NCP/GOP was 0.22 ± 0.08 . During winter the mean NCP/GOP was lower at 0.12 ± 0.05 but likely underestimated because entrainment elevated mixed layer $^{17}\Delta$ values significantly, as discussed above. The summertime NCP/GOP estimate is slightly higher than previous range of estimates of NCP/GOP (0.08 ± 0.05 to 0.13 ± 0.05) based on $^{17}\Delta$ and O_2/Ar measurements at ALOHA, BATS, equatorial Pacific and Southern Ocean, as discussed above. An annual mean NCP/GOP of 0.19 ± 0.08 for the photic layer at ALOHA was estimated by dividing the mean NCP of $19 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ for the photic layer, as discussed above, by the mean $^{17}\Delta\text{-GOP}_{\text{int}}$ (0–200m) of $103 \pm 43 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$.

[51] Prior to $^{17}\Delta$ and O_2/Ar measurements, the ratio of new or export production to primary productivity was typically estimated from bottle incubation based measurements of new production (e.g., $^{15}\text{NO}_3$ and/or $^{15}\text{NH}_4$ uptake) or estimates of organic carbon export (e.g., $^{15}\text{NO}_3$ uptake, sediment traps, ^{234}Th budgets, O_2 budgets, etc.) compared to measured ^{14}C -PP. Thus, most previous estimates e- and f-ratios potentially suffer from incubation artifacts. In contrast, the NCP/GOP estimated from $^{17}\Delta$ and O_2/Ar measurements is independent of incubations, has oxygen production as a common currency and is independent of the air-sea gas exchange rate estimate with its substantial uncertainty. Thus NCP/GOP estimates based on $^{17}\Delta$ and O_2/Ar are likely to be more accurate than previous estimates of e- and f-ratios when measured O_2/Ar is significantly greater than 100% saturation. Converting the $^{17}\Delta$ and O_2/Ar based NCP/GOP to an e-ratio

of $\text{NCP}/^{14}\text{C}\text{-PP}$ (mol C/mol C), assuming a PQ of 1.4 and the observed $^{17}\Delta\text{-GOP}/^{14}\text{C}\text{-PP}$ of ~ 2.5 , yields a $\text{NCP}/^{14}\text{C}\text{-PP}$ of 0.34 ± 0.14 for the mixed layer that is about double a previous e-ratio estimate of ~ 0.15 at ALOHA derived from an O_2 budget-based estimate of NCP and measured ^{14}C -PP [Laws *et al.*, 2000b].

5. Oceanic PP: Where Do We Stand?

[52] The oceanographic community has relied overwhelmingly on an incubation-based methodology to obtain PP rates. The recent introduction of non-incubation based $^{17}\Delta$ and FRRF PP methods provide independent means to evaluate incubation-based PP methods. However, since an absolute standard for PP does not exist the accuracy of any method cannot be verified. An additional complication is that the methods measure different metrics of PP (e.g., C fixation, O_2 production, fluorescence, etc.). The best we can do at this time is to compare multiple incubation and non-incubation (including satellite) based PP methods systematically and determine whether consistent relationships exist between methods.

[53] At ALOHA, we found that the non-incubation $^{17}\Delta$ method yielded gross oxygen production (GOP) rates that were consistently $\sim 25\text{--}60\%$ higher than GOP rates measured by ^{18}O incubation method. Yet, the uncertainties in the individual GOP estimates is comparable to the difference between the estimates. Is the non-incubation or incubation GOP method more accurate? Each method has potential biases. High $^{17}\Delta\text{-GOP}$ rates could be a result of an over-estimated air-sea gas transfer rate or a result of mixed layer entrainment of subsurface water. Low $^{18}\text{O}\text{-GOP}$ rates could reflect missed PP events or incubation artifacts. However, the chosen gas transfer rate parameterization was in the middle of the possible range with uncertainties that could explain only up to 20% of the difference between the methods. The depth-integrated $^{17}\Delta\text{-GOP}_{\text{int}}$ method eliminated the entrainment bias. Incubation methods could underestimate mean PP because of missed PP events, however, two decades of ^{14}C -PP measurements at ALOHA indicate that PP events occur too infrequently to be an important factor. Thus the consistent difference between $^{17}\Delta\text{-GOP}$ and $^{18}\text{O}\text{-GOP}$ estimates at ALOHA, despite substantial uncertainty, raises the question whether incubation methods underestimate PP rates in the ocean.

[54] Utilizing multiple methods to estimate PP potentially yields new insights into the ecosystem function as illustrated by the difference in seasonal and depth variability of $^{17}\Delta\text{-GOP}$, $^{18}\text{O}\text{-GOP}$ and $^{14}\text{C}\text{-PP}$ at ALOHA. During summer the mean $^{17}\Delta\text{-GOP}_{\text{int}}$ and $^{18}\text{O}\text{-GOP}$ were 48% and 32% higher, respectively, than winter rates, whereas for $^{14}\text{C}\text{-PP}$ the difference was only 18%. Similarly, $^{18}\text{O}\text{-GOP}$ decreased on average by sixfold between the surface and 100m, whereas $^{14}\text{C}\text{-PP}$ decreased by only threefold. Possible explanations of these observations could involve variations in autotrophic respiration to photosynthesis ratio or the O_2 production to carbon fixation ratio. If true, we need to better understand the physiological reasons for these variations. If on the other hand, the explanation is a result of methodology (e.g., incubation/bottle effects, variations in CO_2 recycling

or DOC excretion, etc.), this needs to be determined experimentally.

[55] There are only a few comparisons of concurrent incubation (^{18}O , ^{14}C and O_2) and non-incubation (FRRF and $^{17}\Delta$ methods) based estimates of PP with which to compare our observations. At ALOHA, *Corno et al.* [2005] found that yearlong FRRF-based estimates of GOP were 1.9 ± 0.2 to 2.9 ± 0.2 times concurrently measured daytime ^{14}C -PP (where the range depended on specific volume, light or chlorophyll normalizations), which was similar to the $^{17}\Delta$ -GOP_{int}/ ^{14}C -PP of 2.7 (summer) and 2.2 (winter) reported here. At BATS, *Luz and Barkan* [2009] determined mixed layer $^{17}\Delta$ -GOP rates during four monthly cruises between May and October 2000 that were much higher (4–8x) than concurrent ^{14}C -PP rate estimates. In Sagami Bay, off the coast of Japan, *Sarma et al.* [2005] found that $^{17}\Delta$ -GOP rates were, on average, $1.8 \pm 0.5\text{x}$ GOP rates estimated from bottle O_2 incubations and $1.6 \pm 0.3\text{x}$ FRRF-GOP rates, where GOP ranged from ~ 100 – $350 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. In the Celtic Sea, *Robinson et al.* [2009] measured mean ^{18}O -GOP rates that were $4.5 \pm 1.2\text{x}$ concurrent ^{14}C -PP rates based on on-deck incubations and measured FRRF-GOP rates that were on average only 14% and 40% of GOP rates estimated by ^{18}O and O_2 bottle incubation methods, respectively.

[56] A potential methodological bias inherent to incubation-based NCP methods would affect our assessment of the metabolic balance of the ocean. At ALOHA, the consistently supersaturated O_2/Ar levels measured every month for two years indicated an autotrophic condition with an annual net O_2 production rate of $14 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$. A similar consistent monthly O_2/Ar supersaturation condition was measured at ALOHA for a one year interval by *Hamme and Emerson* [2006]. Yet, incubation-based net O_2 production rates measured monthly at ALOHA over an annual cycle indicated an overall heterotrophic condition with an annual net O_2 consumption of $25 \pm 4 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ [*Williams et al.*, 2004]. Although *Williams et al.* acknowledge that a net heterotrophic condition at ALOHA is unlikely, they attributed the underestimation of O_2 production by the bottle incubation method to missed productivity events. However, the consistently supersaturated O_2/Ar levels measured at ALOHA (24 consecutive times over two years) and the magnitude of the difference between the incubation and O_2/Ar based NCP estimates make it unlikely that episodic NCP events could explain the difference. Thus, one needs to consider an alternate explanation that O_2 incubation methods underestimate photosynthetic O_2 production and/or overestimate respiratory O_2 consumption rates compared to in situ conditions. Such a bias in the O_2 incubation method would explain the contradiction between the net heterotrophic conditions ($\sim 15 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$) measured by *Williams et al.* every month for one year by the O_2 incubations in the lower half of the photic layer at ALOHA (75–150 m) and net autotrophic conditions ($\sim 1.5 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$) for this same depth interval determined by *Riser and Johnson* [2008] based on the annual cycle in O_2 measured by an ARGO float near station ALOHA. Until possible incubation biases are resolved, conclusions of net

heterotrophic conditions in the photic layer of the oligotrophic ocean based on the O_2 incubation method [e.g., *del Giorgio and Duarte*, 2002; *Robinson et al.*, 2002; *Williams et al.*, 2004; *Gist et al.*, 2009] need to be viewed cautiously.

[57] The non-incubation based estimate of an e-ratio using coupled $^{17}\Delta$ and O_2/Ar measurements provides a much needed alternative to traditional incubation based estimates. Since the e-ratio is a measure of the ocean's biological pump efficiency, it is an important index of ecosystem function and biogeochemical cycling. The $^{17}\Delta$ and O_2/Ar based NCP/GOP estimate of 0.19 ± 0.08 at ALOHA indicates that $\sim 20\%$ of the gross photosynthetic production escapes respiration in the mixed layer (and photic layer) and is available for export or harvest.

[58] Clearly, more systematic comparisons of incubation and non-incubation PP methods are needed over a range of productivity regimes in the ocean. The few available comparisons of simultaneous non-incubation ($^{17}\Delta$, FRRF) and incubation (^{18}O , ^{14}C and O_2) based PP methods yield variable results [e.g., *Sarma et al.*, 2005; *Corno et al.*, 2005; *Luz and Barkan*, 2009; *Robinson et al.*, 2009]. A better understanding about the relationship between photosynthetic O_2 production and carbon fixation under varying light intensities, nutrient supply and photosynthesis rates is needed to accurately convert FRRF and $^{17}\Delta$ based GOP rates to carbon fixation rates. More accurate air-sea gas exchange rates are needed to improve the accuracy of the $^{17}\Delta$ -GOP method. The careful elimination of biases in the $^{17}\Delta$ -GOP method resulting from entrainment and mixing is needed. Despite the uncertainties in the non-incubation PP and NCP methods, however, the $^{17}\Delta$ -GOP and O_2/Ar -NCP results at ALOHA raise a cautionary flag about incubation-based PP and NCP estimates (i.e., including ^{14}C , ^{18}O and O_2 methods) in the open ocean.

[59] Primary production is a fundamental process at the foundation of the ocean's biological pump. Yet, the results of newer non-incubation PP techniques can yield very different estimates of PP rates from traditional incubation methods upon which the oceanographic community has relied heavily. Experiments need to be designed to evaluate multiple PP methods while simultaneously examining the ecosystem composition and plankton physiology in a well constrained physical environment that would be analogous, for example, to the many *GasEx* experiments designed to better constrain air-sea gas exchange rates. If such PP experiments demonstrate that non-incubation methods yield more accurate PP rates than incubation methods, then our current view of the magnitude and variability of biological productivity (including satellite-based estimates) and the efficiency of organic carbon export in the ocean may need significant reassessment.

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