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Key Points:
- Diel cycles in beam attenuation are a persistent feature of the NPSG
- The dawn to dusk amplitude in beam attenuation is correlated with ^{14}C-PP
- Daytime particle production and nighttime loss rates are tightly balanced in the NPSG

Supporting Information:
- Supporting Information S1

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Productivity diagnosed from the diel cycle of particulate carbon in the North Pacific Subtropical Gyre

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Abstract The rate of primary production (PP) in the ocean is a critical ecosystem function that contributes to the regulation of air-sea CO_2 exchange. Historically, oceanographers have relied primarily on in vitro measurements of ^{14}C uptake (^{14}C-PP) as a proxy for PP. Yet it can be difficult to reconcile PP rates measured in vitro with in situ rates such as those based on oxygen. Here we present diel cycles of optically derived particulate organic carbon (POC) measured in the North Pacific Subtropical Gyre. We have calculated gross production (^{OPT}GP) from the daytime increase and nighttime decrease of optically derived POC, assuming that the observed change in POC represents the sum of PP and community losses. We have compared these estimates to parallel ^{14}C-PP incubations and considered sources of difference. We find that ^{OPT}GP is strongly related to ^{14}C-PP in this region and that growth and loss rates of POC are tightly coupled.

1. Introduction

Primary production (PP) in the ocean is the first step in energy transfer in all food webs; it is fundamental to the ocean's biological carbon pump and partially serves to regulate air-sea gas exchange of CO_2. The coupling of PP to heterotrophic processes and the effectiveness of remineralization and ballasting throughout the water column [*Wollast*, 1998; *Klaas and Archer*, 2002] ultimately determine the proportion of organic matter available for subsequent export to depth. Yet despite its importance in the Earth's carbon cycle, rates of PP in the ocean are not particularly well constrained. For the last 50 years, the oceanographic community has relied almost exclusively on bottle incubations measuring the rate of ^{14}C-labeled bicarbonate uptake to estimate ocean PP [*Nielsen*, 1952; *Marra*, 2009]. ^{14}C-based PP measurements (^{14}C-PP) have become the PP benchmark and are used not only to define the spatial and temporal variations in ocean PP but also to validate satellite PP algorithms and ocean ecosystem models [*Carr et al.*, 2006; *Friedrichs et al.*, 2009]. Despite the huge impact that the ^{14}C-PP method has had in oceanography, it has known issues concerning the use of clean techniques, incubation durations, consideration of ^{14}C assimilation in the dark, recycling of nonlabeled CO_2, excretion of ^{14}C-labeled dissolved organic carbon (DOC), and other caveats, such that the rate measurement is thought to measure something between net primary productivity (NPP) and gross primary productivity (GPP) [*Peterson*, 1980; *Fitzwater et al.*, 1982; *Karl et al.*, 1998; *Marra*, 2009; *Pei and Laws*, 2013; *Viviani et al.*, 2015]. Additionally, there is a long-standing and difficult to resolve issue of how to reconcile in vitro PP and in situ PP measurements (as discussed in *Marra* [2002] and *Juranek and Quay* [2012]).

In the last decade, alternative methods to measure ocean PP rates in situ have gained traction in the oceanographic community. In particular, measurement of net and gross production based on changes in the ratio of oxygen (O_2) to argon and anomalies of naturally occurring oxygen isotopes introduced by *Luz and Barkan* [2000] has become increasingly widespread. These methods come with their own caveats, most notably due to entrainment/mixing biases or the influence of nonsteady state conditions. Yet in regions where mixing biases are minimal, comparison of in situ oxygen-based productivity metrics to in vitro C-based PP [*Quay et al.*, 2010; *Juranek and Quay*, 2012; *Nicholson et al.*, 2012] consistently found in situ PP estimates to exceed in vitro PP estimates by around 30%, for reasons that are not clear. Another in situ PP method based on measuring diel changes in POC derived from particle beam attenuation was identified over 25 years ago [*Siegel et al.*, 1989] and has recently received renewed interest [e.g., *Claustre et al.*, 2008; *Dall'Olmo et al.*, 2011; *Loisel et al.*, 2011]. The importance of these in situ PP methods cannot be overstated as they provide independent means to estimate the spatial and temporal variations in ocean PP and, importantly, evaluate the traditional in vitro PP methods.

In open ocean regions where highly scattering inorganic material does not appreciably contribute to particle loads, robust relationships have been established between the particulate beam attenuation coefficient (c_p) and the concentration of particulate organic carbon (POC) [e.g., *Gardner et al.*, 2006; *Cetinić et al.*, 2012]. Even before this relationship was well understood and standard protocols were beginning to be put in place for consistent calibration of c_p to POC, it was well known that c_p exhibits a diel cycle in the surface ocean. In a seminal paper, *Siegel et al.* [1989] showed that c_p in the upper 100 m of the oligotrophic North Pacific exhibits a minimum near sunrise which increases toward a maximum near sunset and subsequently declines during the night. Building on this and other earlier work, *Claustre et al.* [2008] describe an approach to quantify net and gross community production based on the diel cycle of POC derived from c_p. The underlying assumption is that the daytime increase in POC can be attributed to photosynthetic production and associated increases in cell size and refractive index that accompany carbon accumulation (not necessarily cell number) [see *Stramski and Reynolds*, 1993]. *Claustre et al.* [2008] propose that the sum of daily carbon increase and carbon loss at night (where losses are assumed to be constant over day/night) can then provide an estimate of gross carbon-based community production (GCP), whereas the difference between daily increases and nighttime losses is a measure of net community production (NCP).

While diel changes in optically derived POC can be used to estimate production, optical approaches also have their limitations: they cannot account for production of DOC, they generally assume a constant carbon-to-c_p conversion factor, and lateral or vertical fluxes of particles over a diel cycle represent fates not "seen" by surface sensors. Perhaps because of these limitations, few comparisons between c_p-based production and more classical productivity measures approaches have been made [*Marra and Ducklow*, 1995; *Walsh et al.*, 1995; *Loisel et al.*, 2011]. Here we evaluate Lagrangian and Eulerian measurements of the diel cycle of beam attenuation and compare the results to traditional ^{14}C-based measurements of primary production collected on a series of cruises in the North Pacific Subtropical Gyre (NPSG).

2. Methods

2.1. Underway Sampling

Underway flow-through particulate attenuation spectra were collected aboard the R/V *Kilo Moana* as a component of a series of Hawaii Ocean Experiment (HOE) cruises that occurred between 5–14 August 2012 (HOE-DYLAN, HD7), 22 August to 11 September 2012 (HOE-DYLAN, HD9), 16–28 September 2013 (HP), 11–25 March 2014 (HOE-BOE, HB), and 24 July to 6 August 2015 (HOE-LEGACY, HL). Notably, HL took a Lagrangian approach and tracked a surface drifter for the entirety of the cruise, whereas the previous cruises were Eulerian and largely centered at Station ALOHA (A Long-Term Oligotrophic Habitat Assessment, at 22.45°N, 158°W, see Figure 1). The uncontaminated seawater line for the ship supplied water from ~7 m below the waterline of the forward hull. This source water was routed through a Vortex debubbler and a valve control device that automatically diverted the inflow to a Pall Supor 0.2 μm membrane filter for the first 10 min of every hour prior to passing through a hyperspectral absorbance and attenuation (ac-spectra, ac-s, Wetlab) meter. For the remaining 50 min of each hour, the valve control device routed water from the debubbler directly to the ac-s.

2.2. Attenuation, Chlorophyll *a*, and Particulate Carbon

Particulate beam attenuation spectra were corrected as per *Slade et al.* [2010]. Briefly, raw data were binned to 1 min intervals, the dissolved absorption and attenuation signal was subtracted from the unfiltered signals to obtain particulate absorption and attenuation spectra (c_p and a_p, respectively), and temperature and salinity corrections were applied. Additional details regarding optically derived carbon and chlorophyll *a* measurements are described in the supporting information [*Bidigare*, 1991; *Bidigare et al.*, 2005].

Duplicate samples (~4 L, $n = 63$) were collected, at dawn and dusk when possible, from the outflow of the ac-s for calibration of c_p (660, m^{-1}) to particulate organic carbon (POC, mg C m^{-3}) as measured by high temperature combustion of particulate matter filtered onto glass fiber filters [*Sharp*, 1974]. Filter blanks were subtracted from all POC samples; these blanks averaged 5 ± 2% of the POC signal (mean ± standard deviation). The coefficient of variation for duplicate POC values ranged from 1 to 13%. For the full data set (n = 30 average POC and c_p values), the slope of a type II regression [*Ricker*, 1973] of POC versus c_p is 519 ± 43 mg C m^{-2} and the intercept is 8.5 ± 2.5 mg C m^{-3} (r^2 = 0.83). This regression is used to

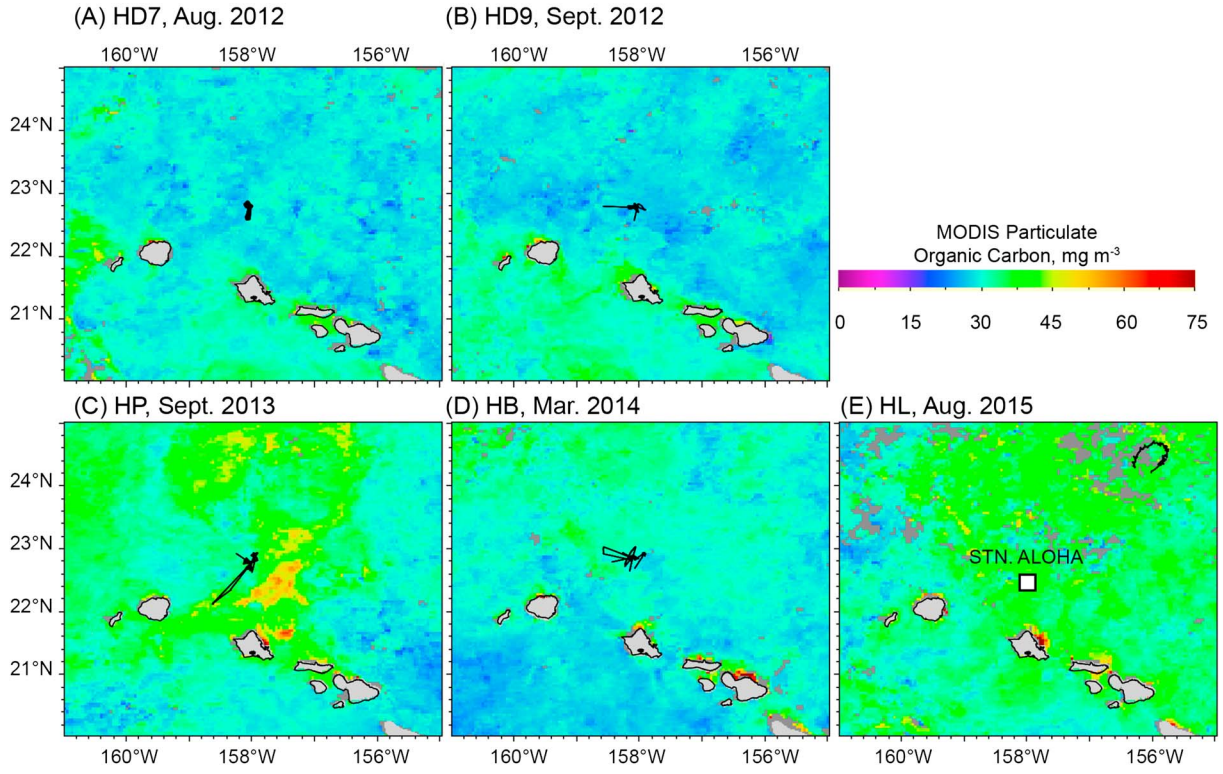


Figure 1. (a–e) Spatial extent of cruise tracks (in black) in the NPSG spanning August 2012–2015. For reference, the location of the Hawaii Ocean Time-series (HOT) Station ALOHA is 22.75°N, 158°W and is shown in Figure 1e. The transit to and from Oahu, Hawaii, is not shown. All tracks overlay the monthly composite MODIS POC fields for the primary month of the each cruise. Note the elevated POC during HP and HL (Figures 1c and 1e).

transform the full corrected c_p (660) data set to POC values. This relationship is consistent with that reported for the Hawaii Ocean Time-series (HOT) by *Fennel and Boss* [2003] and *Gardner et al.* [2006] (POC = $632c_p + 3.8$ and POC = $559c_p + 4.6$, respectively), albeit it is important to note that these earlier ratios were determined by using SeaTech transmissometers with an acceptance angle of 1.03°, whereas the ac-s used in this study has an acceptance angle of 0.93°. *Boss et al.* [2009] have shown that this change in acceptance angle would result in c_p measurements for an ac-s that is 1.2 times higher than those measured by instruments with an acceptance angle of 1.03° due to volume scattering considerations. Using this correction, the POC:c_p slope would be 526 and 466 mg C m^{-2} for the *Fennel and Boss* [2003] and *Gardner et al.* [2006] data sets, respectively. Importantly, the slope we use (equivalent to 1.92 m^2 g C^{-1}) is within the range determined for cultures of *Prochlorococcus* (~1 m^2 g C^{-1}) [*Claustre et al.*, 2002] and *Synechococcus* (~3 m^2 g C^{-1}) [*Stramski et al.*, 1995], which are known to dominate phytoplankton communities in the NPSG [*Campbell et al.*, 1997]. For regional context, MODIS Aqua, level 3, 4 km monthly POC fields were downloaded from the NOAA ERDDAP server (http://coastwatch.pfeg.noaa.gov/erddap/).

2.3. ^{14}C Primary Productivity

Standard HOT protocols were used on all cruises to measure in vitro dawn to dusk PP via the ^{14}C radiotracer method [*Karl et al.*, 1996]. Water samples were collected from 25 m before dawn and incubated on deck in incubators screened to 55% of surface irradiance and plumbed with flow-through surface seawater for temperature regulation. Given the mean extinction coefficient for photosynthetically available radiation (K_{PAR}) [see *Letelier et al.*, 2004] at Station ALOHA (0.04 m^{-1}), this screening corresponds to light levels at ~15 m, well within the mixed layer which ranged from 36 m to 83 m over the course of this study. Detailed methods and calculation for the ^{14}C PP method are provided in the supporting information (also see *Lee et al.* [2006]).

2.4. Calculating PP and Growth Rates From Diel Beam Attenuation Changes

Measuring the changes in c_p calibrated to POC over a diel cycle yields estimates of in situ productivity and growth rates. Generally following the approach of *Claustre et al.* [2008] we calculate optically derived net

community production ($^{OPT}NCP = \Delta POC_D - \Delta POC_N$) as the balance between the daytime increase in POC from dawn to dusk (ΔPOC_D) due to net production and the decline over the night period (ΔPOC_N) which represent community losses due to respiration, grazing, and sinking. The rate of these losses ($\Delta POC_N\ dt^{-1}$, where dt is the time from dusk to dawn) is assumed to remain constant during the day and night. What *Claustre et al.* [2008] term "gross community productivity" (^{OPT}GCP) is then calculated as the sum of ^{OPT}NCP and $\Delta POC_N\ dt^{-1}$ which should be equivalent to $\Delta POC_D\ dt^{-1}$ in a system where production and loss terms are in close balance. We have chosen to calculate ^{OPT}GCP as $\Delta POC_D\ dt^{-1}$ in order to minimize the impact of advection on particle concentrations. However, given that this approach will underestimate production if there are substantive differences in loss rates between day and night, we argue that this metric must lie closer to GPP than GCP. Accordingly, we denote the derived rate as ^{OPT}GP. A more thorough accounting of this assumption is made in Figure S1 in the supporting information.

Diel POC growth rates, μ_{cp}, are then computed from the c_p value at dawn (c_{p1}) and dusk (c_{p2}) as per *Cullen et al.* [1992] with a modification to correct c_p values for an estimate of the contribution of non-phytoplankton carbon to the c_p signal. We assume this background value (c^*) to be 0.02 m^{-1}, equivalent to 50 ± 12% of mean c_p with a range of 28–70% and consistent with estimates of the contribution of phytoplankton carbon to POC in the open ocean of ~50% [*Graff et al.*, 2015].

$$\mu_{cp} = [1/(t_2 - t_1)]\ \ln\left[(c_{p2} - c^*)/(c_{p1} - c^*)\right] \quad (1)$$

3. Results

3.1. Temporal Variability in Biomass

For the three cruises that remained close to the vicinity of Station ALOHA (Figures 1a, 1b, and 1d), optically derived POC and chlorophyll (chl *a*) were relatively low and stable (average ^{OPT}POC = 27–29 mg C m^{-3} and average chl *a* = 60–92 ng L^{-1}; Figure S2). In September 2013, HP initially began sampling at Station ALOHA and then diverted southward to a region of elevated phytoplankton biomass (on 21–23 September, Figures 1 and 2c). At this site, chl *a* concentrations increased from ~75 ng L^{-1} to 150 ng L^{-1} as we transited into the bloom region (Figure S1) and microscopic enumeration of cells revealed extremely high concentrations of the symbiotic diazotroph *Richelia intracellularis* (1295 ± 64 heterocyst L^{-1}); for reference, non-bloom concentrations of *Richelia intracellularis* are ~10–100 L^{-1} [*Villareal et al.*, 2012].

Field observations in July–August 2015 (HL) followed a Lagrangian drifter initially deployed at 24.5°N, 158°W; phytoplankton standing stocks and productivity were persistently high for the duration of the cruise (^{14}C-PP = 14.7–18.0 mg m^{-3} d^{-1}; ^{OPT}POC = 43 ± 4 mg m^{-3}; chl *a* = 121 ± ng L^{-1}). The magnitude of ^{14}C-PP encountered during HL was ~3× higher than the July–August mean for Station ALOHA (7.5 ± 2.4 mg m^{-3} d^{-1}); albeit, when normalized by chl *a*, rates are 70 ± 8 g C g chl d^{-1} and well within what is typically observed in the upper water column at Station ALOHA in July–August (60–122 g C g chl d^{-1}). Microscopic enumeration of the >10 μm size fraction in the upper 45 m revealed high concentrations of both diatom-diazotroph assemblages (457 ± 150 heterocyst L^{-1}) as well as *Trichodesmium* spp. (859 ± 292 cell L^{-1}) during this cruise, again indicative of "bloom" level abundances of diazotrophs [*Villareal et al.*, 2012].

3.2. Variability in Optically Derived Productivity and Relationships to ^{14}C-NPP

As has been documented in many other regions [e.g., *Siegel et al.*, 1989; *Walsh et al.*, 1995; *Claustre et al.*, 2008; *Loisel et al.*, 2011], c_p measurements displayed a minimum at dawn and a maximum at dusk (Figure 2) with the amplitude of the nightly decline (% Δ = 25 ± 10%) approximately equivalent to the amplitude of daily production (% Δ = 22 ± 8%). These values are indistinguishable from the c_p amplitude of 25% measured at Station ALOHA by *Bishop and Wood* [2008]. The remaining 75 ± 10% of the c_p signal, presumably composed of nonliving detrital carbon and the living component of plankton with no diel periodicity, does not oscillate. This fraction can be considered an upper limit to the detrital contribution to total POC and is consistent with the findings of *Chung et al.* [1996] in the equatorial Pacific where detritus accounted for up to 60% of their c_p signal and with adenosine triphosphate-based estimates for Station ALOHA that suggests nonliving POC comprises 75% of the total POC in the upper 50 m of the water column [*Jones et al.*, 1996; *Karl and Dobbs*, 1998].

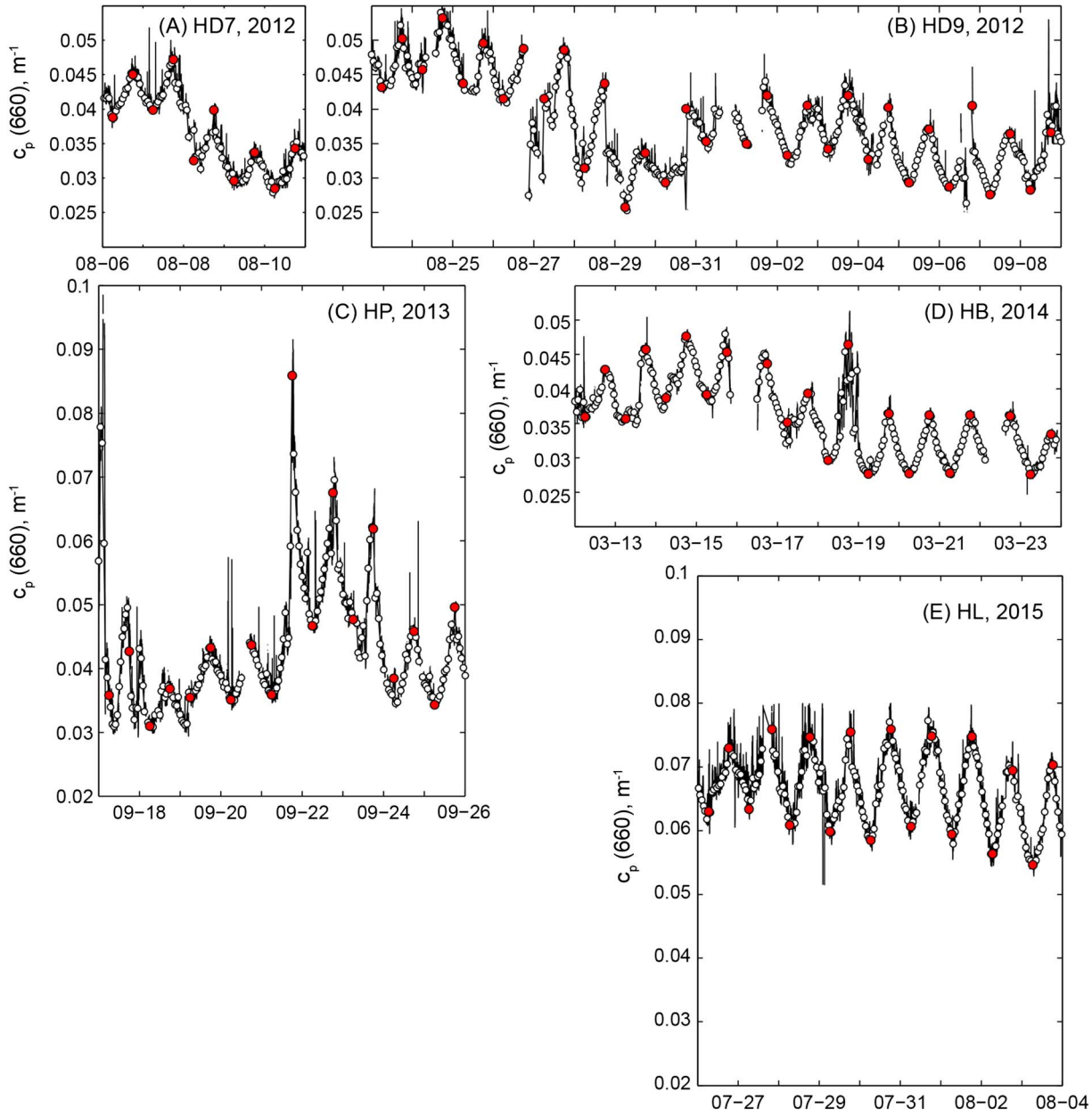


Figure 2. Time series of particulate beam attenuation (c_p) at 660 nm over five cruises in the NPSG spanning August 2012–August 2015. The black lines correspond to 1 min average c_p, whereas the white circles are hourly means and the red circles are the hourly means encompassing dawn and dusk, e.g., ~6 A.M. and ~6 P.M. for this latitude. (a–d) Cruises largely centered at Station ALOHA; however, the 2013 cruise (Figure 2c) diverted SW to a bloom feature on 21–22 September. The (e) 2015 cruise followed a Lagrangian surface drifter in an anticyclonic eddy NE of Station ALOHA where remote sensing suggested elevated biomass.

Once c_p is calibrated to POC, we follow the general approach of *Claustre et al.* [2008] to estimate production. Given that $\Delta POC_D\ dt^{-1}$ (10.6 ± 4.5 mg C m^{-3} d^{-1}, n = 45) was statistically equivalent to the sum of ^{OPT}NCP and $\Delta POC_N\ dt^{-1}$ (10.0 ± 4.9 mg C m^{-3} d^{-1}, n = 41), with a two-tailed t test P value of 0.48, we have focused on the former term to minimize the impact of advection. We attribute $\Delta POC_D\ dt^{-1}$ to gross production (^{OPT}GP), e.g., the sum of gross primary production less net transport of particles in or out of the mixed layer and any differences in day/night loss terms (see Figure S1). We have excluded estimates of ^{OPT}GP from 21 September on HP as we were transiting to a large bloom; otherwise, we present the full data set in Table S1 in the supporting information and show the relationship between ^{OPT}GP and ^{14}C-PP in Figure 3. We find a strong agreement between ^{OPT}GP and ^{14}C-PP with r^2 = 0.78 for a geometric mean type II linear regression, a slope of 1.10 ± 0.10, and an intercept not significantly different than zero

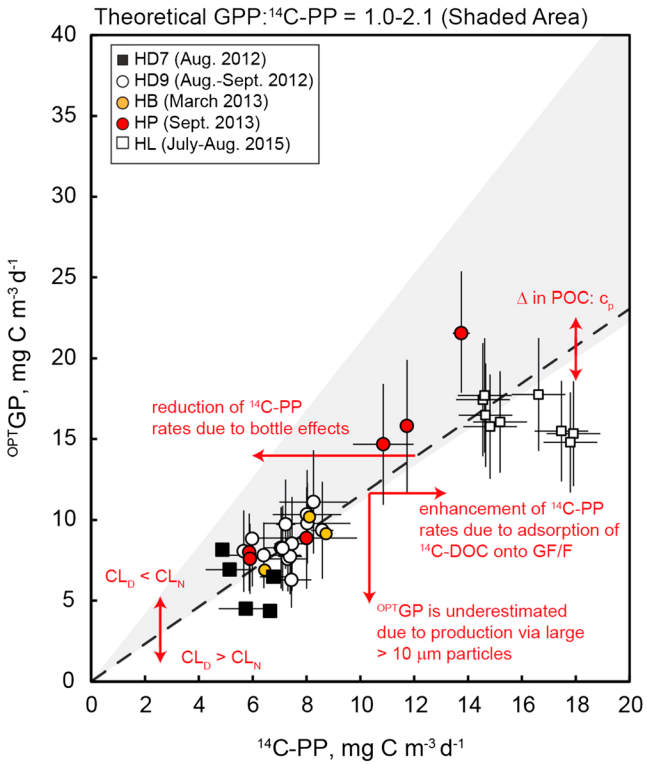


Figure 3. Relationship between PP measured in dark-corrected dawn to dusk ^{14}C incubations (^{14}C-PP) and optically derived gross production (^{OPT}GP). The symbols correspond to concurrent rates measured in a series of cruises spanning 2012–2015. The error bars for ^{14}C-PP are the standard deviation of duplicate incubations, whereas the standard deviation for ^{OPT}GP is calculated by propagating the uncertainty in c_p-derived POC within 30 min of dawn and dusk for the ^{OPT}GP calculation. The black dashed line represents the slope of the composite data set (1.1). For reference, the theoretical range of GPP:^{14}C-PP derived from O_2-based comparisons to ^{14}C-PP is shown as the shaded region (1.0–2.1); see section 4.1. The directions of deviation for known biases from the mean of this relationship are noted with red arrows and text where CL_D and CL_N are community losses including any net transport during the day and night phases, respectively.

(0.77 ± 1.0 mg C m^{-3} d^{-1}). This slope (1.1) is shown in Figure 3. Considering ^{OPT}NCP as ($\Delta POC_D - \Delta POC_N$), the NCP distribution (n = 38) is lognormal and negatively skewed with a mean ± standard deviation of −1.07 ± 2.07 mg C m^{-3} d^{-1} and a median of −0.37 mg C m^{-3} d^{-1} (see Table S1). ^{OPT}NCP estimates are likely to be biased low as NCP is generally strictly defined as the difference between GCP and respiration and optically determined losses also include removal of particles due to sinking [*Claustre et al.*, 2008; *Loisel et al.*, 2011]. Nonetheless, these findings suggest that POC production and losses are tightly coupled in the NPSG, with high frequency oscillations (daily) between net particle production and net particle loss (also evident in oxygen measurements of *Ferrón et al.* [2015]). Work in other regions [*Marra and Ducklow*, 1995; *Walsh et al.*, 1995; *Loisel et al.*, 2011] indicate that this may be a general phenomenon observable if not obscured by spatial heterogeneity of biomass and assuming that the upper water column is stable to mixing.

We have also estimated growth rates for all cruises (Table S1). The magnitude of these rates (0.89 ± 0.41 d^{-1}) compares well to previous rate measurements for the region. Specifically, *Liu et al.* [1997] report *Prochlorococcus* growth rates between 0.53 and 0.57 d^{-1} and bulk phytoplankton growth rates for Station ALOHA range from ~0.5 to 2.0 d^{-1} [*Jones et al.*, 1996; *Laws*, 2013].

4. Discussion

Via repeat sampling in the NPSG, we were able to capture a threefold variation in ^{14}C-PP and ^{OPT}GP and derive a relationship between these in vitro and in situ C-based measurements. Notably, as a result of the low variability in PP rates sampled at the time scale of days-weeks (Table S1), a strong linear relationship is not apparent within cruises, with the exception of HP where strong spatial gradients in PP were observed. While the composite relationship we find is significant, there are several sources of error inherent to both ^{14}C-PP and ^{OPT}GP determinations. Figure 3 represents how specific aspects of ocean metabolism would impact the relationship between ^{14}C-PP and ^{OPT}GP. Here we first consider whether the relationship between ^{OPT}GP and ^{14}C-PP that we have observed is reasonable and then address additional sources of potential disagreement.

4.1. Comparison of ^{14}C-PP to ^{OPT}GP

While neither optical nor ^{14}C radiotracer approaches measure the "true" GPP or NPP, respectively, we can evaluate whether the relationship between ^{OPT}GP and ^{14}C-PP measured here is reasonable via comparison

to the gross O_2 production (GOP):^{14}C-PP ratios reported by *Juranek and Quay* [2012] for a global data set and by *Quay et al.* [2010] for summer months at Station ALOHA; these ratios are 2.7 and 1.3–2.4, respectively. In order to convert GOP to units of C, isotopic GOP measurements first need to be corrected for light-dependent O_2 cycling not associated with C fixation (15% of GOP as per *Bender et al.* [1999]) and we need an estimate of the photosynthetic quotient (PQ, 1.1 assuming growth on NH_4^+ [*Laws*, 1991]) such that

$$\mathrm{GPP} = (0.85 \times \mathrm{GOP}) \times \mathrm{PQ}^{-1} \tag{2}$$

Substituting (1.3–2.7 × ^{14}C-PP) for GOP in equation (2), GPP:^{14}C-PP then becomes

$$\mathrm{GPP}{:}^{14}\mathrm{C\text{-}PP} = \left[\left(0.85 \times 1.3 - 2.7 \times {}^{14}\mathrm{C\text{-}PP} \times \mathrm{PQ}^{-1}\right)\right] \times {}^{14}\mathrm{C\text{-}PP}^{-1} = 1.0 - 2.1 \tag{3}$$

This range (shown on Figure 3) is consistent with the ratio of ^{OPT}GP:^{14}C-PP presented in this study (1.1), suggesting that while ^{OPT}GP is an approximate measure of GPP, it is likely an underestimate of the true rate and may be closer to the rate approximated by ^{14}C-PP (~NPP, see Figure S1). Clearly, no method is perfect, and neither ^{OPT}GP nor ^{14}C-PP corresponds directly to the respective rate terms of interest for quantifying ecosystem metabolism (e.g., GPP and NPP). Nonetheless, given that ^{OPT}GP closely tracks ^{14}C-PP, at a ratio close to what is expected due to metabolic considerations, we conclude that under steady state conditions, optically derived measures of production can provide a valuable in situ measurement for detection of relative change in PP.

4.2. Potential Sources of Error

While the ratio of ^{OPT}GP:^{14}C-PP observed in this study is reasonable given our current understanding of ecosystem processes, there are other sources of error that need be considered. These include advective or vertical fluxes that would bias the diel amplitude of POC, any day-night differences in loss or production terms other than GPP, changes in the c_p:POC ratio, bottle effects, and production by size classes not detectable by transmissometry. Of these terms, entrainment of different water masses that increase or decrease ^{OPT}GP over a day or night period is likely the simplest to address, as step functions or rapid shifts in the rate of particle growth or loss can be used as a proxy to exclude a sample from consideration. In fact, this is what we have done for several samples where we transited into a region of elevated chl *a* (e.g., 22 September, see Figure 2,); the daily amplitude of ^{OPT}POC at this station could not be compared to ^{14}C incubations collected in waters with lower initial biomass. Additionally, for HL where large diazotrophs (>10 μm) were found to be abundant, direct contributions of these particles to PP would be missed by transmissometry, thus leading to underestimates of GPP. In fact, several samples from HL do fall off the curve in a direction consistent with missed contributions from large particles (Figure 3). The role of cell size in the diel cycle of attenuation is discussed thoroughly in *Boss et al.* [2009] and underscores why this approach is best applied to oligotrophic regimes where large phytoplankton are relatively rare.

Arguably, the major caveat inherent to ascribing diel change in POC to GPP is the assumption that no process other than GPP has diel periodicity such that community losses are constant over a diel cycle (see Figure S1). For example, if particle export, grazing losses, or exudation of DOC were higher in the day than the night, then ^{OPT}GP underestimates GPP. Conversely, if the opposite is true, then ^{OPT}GP overestimates GPP. In Figure 3 we outline the impact of how an imbalance of terms other than GPP would impact ^{OPT}GP. Given that the slope of the ^{OPT}GP versus ^{14}C-PP relationship (1.1) falls on the lower range indicated by in situ O_2 based GPP:^{14}C-PP relationships, this would suggest that some portion of community losses or net particle transport are greater during the day than the night.

In this study we assume a static c_p:POC relationship. While we acknowledge that optical properties of cells do vary [*Stramski and Reynolds*, 1993; *Claustre et al.*, 2002], we believe that this is a reasonable assumption for the following reasons: (1) we did not find any clear and systematic variation between c_p and POC relationships between cruises (the coefficient of variation of POC:c_p for n = 30 samples was 19%), (2) the NPSG system is dominated by small cells (*Prochlorococcus*, *Synechococcus*, and picoeukaryotes) and grazers (flagellates) that are within the size range (0.5–10 μm) detectable by commercial transmissometers such as the ac-s [*Stramski and Kiefer*, 1991], and (3) considerations of the impact of changes in cell size and refractive index on the diurnal amplitude of c_p in oligotrophic settings are small (~6% change in c_p) [see *Claustre et al.*, 2008], relative to the amplitude of change we observe (~25%). Accordingly, and in agreement with

Stramski and Reynolds [1993], we consider use of a constant c_p to POC coefficient an acceptable approximation for estimation of carbon production and loss. Other potential sources of error in ^{OPT}GP and ^{14}C-PP are shown in Figure 3.

5. Conclusions

A critical evaluation of PP methods will have significant long-term benefits to our understanding of processes controlling ocean PP and how future climate change will impact the ocean's food web and biological carbon pump. Determining the accuracy of a PP method is, however, not easy as there is no true PP reference standard. Thus, we must rely on the consensus of multiple PP methods to evaluate the accuracy of any individual PP method. Here we have shown that in situ optically derived estimates of PP closely track in vitro ^{14}C-PP in the NPSG. Moreover, this ratio is within the theoretical range of GPP:^{14}C-PP predicted from in situ oxygen-based approaches (1.0–2.1). We have evaluated the major sources of error and outlined the assumptions inherent to calculations of ^{OPT}GP. Given these considerations, we argue that, under steady state conditions, in relatively stable oligotrophic regimes such as the NPSG where particle size is small, optical approaches can provide high-resolution carbon-based measurements of ocean productivity with potential error of the same magnitude as bottle-based incubations. This work can be extended to autonomous sampling platforms such as bio-optical drifters, profiling floats, and instrumented moorings, thus representing a powerful potential to broaden the number and spatiotemporal resolution of productivity measurements in the vast and ecologically important regions of the open ocean. Finally, this work can be coupled to high-resolution and parallel measurements of NCP and GPP via in situ oxygen-based measurements [*Alkire et al.*, 2012; *Nicholson et al.*, 2015].

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