Net Community and Gross primary production and carbon export in the transition zone between Peru Current and South Pacific Gyre, as determined with dissolved O$_2$/Ar ratios and oxygen triple isotope composition of O$_2$

Abstract

Marine biological production accounts for half of global primary production and plays an important role in regulating oceanic uptake of atmospheric CO₂. Here we report rates of Net Community and Gross Primary Production (NCP and GPP) in the mixed layer of Eastern Tropical South Pacific (ETSP), relatively understudied region of the Pacific. The region was studied during El Nino (January-February 2010) and during La Nina conditions (March-April 2011). The study area included a transition from the High Nutrient Low Chlorophyll regime at 10S to the oligotrophic conditions on the north-eastern limb of the South Pacific Gyre at 20S, coincident with the transition from the net upwelling to net downwelling advective regimes. NCP rates were derived from continuous underway measurements of O₂/Ar ratios made along 10S and 20S latitudes between 80W and 100W using an Equilibrated Inlet Mass Spectrometer (EIMS) system. GPP rates were estimated from the oxygen triple isotope mass balance within the mixed layer at several hydrographic stations along the cruise tracks. Excluding areas clearly affected by the strong upwelling, the O₂-based NCP rates averaged along 10S were 4.7±1.8 mmol-C m⁻² d⁻¹ and 6.6 ±1.3 in 2010 and 2011 respectively. The NCP along 20S was ~ 3x lower in magnitude, averaging at 1.3 ±0.4 in 2010 and 1.8 ±0.4 mmol-C m⁻² d⁻¹ in 2011. In 2011, we also obtained rates of NCP in the upwelling-influenced eastern region of 10S transect, using upwelling velocities constrained with ⁷Be mass balance in the upper 100 m. Rates of NCP were comparable to the Corg export fluxes determined based on ²³⁴Th-deficit integrated over the upper 200 m of the water column at several hydrographic stations, but approximately an order of magnitude higher than the POC fluxes obtained with floating sediment traps. Along 10S, GPP rates were 113 ± 30 and 198 ± 99 mmol-O₂ m⁻² d⁻¹ in 2010 and 2011 respectively. Along the 20S, the GPP was lower, 75 ±22 and 121 ±39 mmol-O₂ m⁻² d⁻¹ in 2010 and 2011. Significant spatial variability in NCP rates, revealed by the underway O₂/Ar measurements reflects the physics of nutrient supply to the surface along 10S, but may in part result from patchy N₂ fixation along the 20S transect.
I. Introduction

Marine primary production and export of biologically produced carbon ($C_{org}$) are responsible for transformation of CO2 into sedimentary organic matter and accumulation of O2 in the atmosphere on the geologic time scale. On the shorter, decadal to millennial time scales, primary production and $C_{org}$ export play a role in regulating the atmosphere-ocean exchange of CO2. The largest ocean-atmosphere flux of CO2 in the modern ocean is found in the Eastern Equatorial Pacific, where intense upwelling brings nutrient-replete and CO2-supersaturated waters to the surface. A large effort has been dedicated to studies of the primary production within the Equatorial Pacific during several oceanographic campaigns, such as JGOFS Equatorial Pacific study (e.g. Murray et al., 1994, 1995; McCarthy et al., 1997; Bender et al., 1999), as well later studies (Hendricks et al., 2005; Kaiser et al., 2005; Stanley et al., 2010) However, the area immediately to the south from the Equatorial Pacific, referred hereafter as Eastern Tropical South Pacific (ETSP), remains poorly studied.

The ETSP has been proposed to be a region of biological N2 fixation (Deutsch et al., 2007; Westberry and Siegel, 2006; Westberry et al., 2005). The water masses advected offshore from the Peru-Chile denitrification zones are nitrate depleted relative to the average Redfield nutrient stoichiometry (Refs) potentially promoting N2 fixation. Thus, ETSP may be a region of the tight coupling between the sources and sinks in the nitrogen budget (Deutsch et al., 2007) et al., 2007, Knapp et al, in prep).

As part of a multi-disciplinary effort to document and constrain nitrogen fixation in the ETSP, this study assesses rates of both gross and net photosynthesis during two cruises, in January-February 2010 and March-April 2011. We used a dual tracer approach to estimate two components, Net and Gross O2, of the primary production. Rates of Net Oxygen Community Production (NCOP) were determined from the biological O2 supersaturation, measured as dissolved O2/Ar supersaturation (Craig and Hayward, 1987). NCOP was converted to Net Community Production (NCP) with the stoichiometric O2:C ratio of 1.4 assuming that nitrate is the major N source for photosynthesis (Laws, 1991).

Gross Photosynthetic Production (GPP) was derived from the oxygen triple isotope (OIT) mass balance (Luz and Barkan, 2000; Luz and Barkan, 2009). Simultaneous measurements of both production terms were used to derive Net to Gross production ratios (NCP/GPP) which reflect the potential export efficiency of the biological carbon pump (Bender et al., 1999). GPP determinations are compared with: (3) Net Primary Production (NPP) determined with on-deck $^{14}$C incubations, and NPP derived from satellite-based surface Chl concentrations and temperatures using Vertical General Productivity Model algorithm (VGPM, Behrenfeld and Falkowski, 1997).

At steady state, NCP is equivalent to carbon export production plus formation of Dissolved Organic Carbon (DOC) (Bender et al., 1987, Emerson et al., 1995, Emerson et al., 1997). We investigated how the O2-based in situ NCP fluxes are compared to the Particulate Organic Carbon (POC) flux collected during a 1-2 day-long deployments of sediment traps in the upper 100 and 200 m, and POC export derived with measured $^{234}$Th-deficit (Haskell et al., submitted). Finally, we compared the O2-derived productivity with the NPP rates estimated by Vertically Integrated Productivity Model (Behrenfeld and Falkowski, 1997) using satellite (MODIS) remote Chl sensing with
temperature correction.

The methodologies compared in our study examine biological production components on somewhat different timescales. On-deck bottle incubations (24 h) provide a window into daily NPP rates, floating traps represent 1-2 days integrated C$_{org}$ export (Buesseler, 1991; Buesseler and Boyd, 2009)O$_2$/Ar and OTI mass balances integrate the NCP and GPP within 10-20 days (Bender and Grande, 1987; Bender et al., 1987; Emerson et al., 1991; Luz and Barkan, 2009), while 234Th deficit reflects the C$_{org}$ export on the time scale of 20-40 days (Buesseler, 1991; Buesseler et al., 1992). Comparing the multiple methods of determining carbon sequestration rates, we develop a more comprehensive picture of the C cycling pathways in the region, discuss the strengths and the weaknesses of each approach and draw potential links between observed patterns and regional hydrography.

**Hydrography of the study region within Eastern Tropical South Pacific**

The study area (Fig. 1), defined by the tracks of two cruises, in January-February 2010 and March-April 2011) was bounded by 10ºS/20ºS latitude and 80ºW /100ºW longitude. Seven major hydrographic stations were occupied during each cruise, where CTD, [O$_2$] and nutrient profiles were measured; 234Th profiles, on-deck 24-hour incubation for 14C-based primary productivity determination (in 2011 only), and deployment of floating sediment traps were done at selected stations (Fig. 1A). In 2010, five additional stations were sampled for hydrography only and in 2011, five major hydrographic stations were sampled for $^7$Be inventory (Haskell et al., submitted) (Fig. 1A).

The ETSP area bounded by our cruise tracks includes two distinct regimes, the Eastern Boundary Current (Peru Coastal upwelling and Peru Coastal (or Humboldt) Current) and the oligotrophic South Pacific Gyre (SPG). The 10S cruise transect ran 5-6º to the south of the pronounced biogeochemical influence of the Equatorial Upwelling (Hendricks et al., 2005; Kaiser et al., 2005; Kessler, 2006; Wanninkhof et al., 1995), within the southern branch of the westward flowing South Equatorial Current (SEC, Fig. 1B). The 20S transect was within the northern limb of the South Pacific Gyre transitioning into the Humboldt Current eastward of 85ºW (Fig. 1B). A generally offshore surface flow of 5-25 cm/s range has been reported, based on drifter data in the region (Kessler, 2006).

Basin-wide trend driven by the wind trades is deepening westward and southward thermocline (Kessler, 2006, Fiedler and Talley, 2006). The permanent thermocline deepen between 80W and 100W from less than 50m in the east to over 250 m meters in the west, as well as between 10S and 20S (Fig. 3E), reflecting the general transition from the upwelling to downwelling-dominated vertical advection from north-east to south-west (Fiedler and Talley, 2006). The 10S transect was within High Nutrient Low Chlorophyll (HNLC) waters (Pennington et al., 2006, and Fig. 1A, C), as confirmed by the 3-7 μM nitrate concentrations measured in the mixed layer during our cruises (Knapp et al., in prep). The southern transect encountered much more oligotrophic conditions, with nitrate $<0.5μM$ in the mixed layer (Knapp et al, in prep., Claustre et al., 2008a,b; Pennington et al., 2006). A large subsurface Oxygen Deficient Zone extends off the coast of South America, shoaling and intensifying from south-west to north-east (Fig. 1E).

The complete 3-D understanding of a smaller scale regional circulation within the
ETSP is still somewhat limited (Fiedler and Talley, 2006, Kessler, 2006), as only few studies, each focusing on one particular hydrographic regime, addressed dynamic hydrography with the ETSP area (Tsuchiya and Talley, 1998, Toggweiler, 1991, Rowe et al., 1999, O’Connor et al., 2001). Based on these studies, the westward flowing SEC marking the northern ETSP boundary is most likely formed by the confluence of the meridional Humboldt Current veering westward between 10-20S and 80-90W (Fig. 1B) and the coastal waters upwelled along the Peru coast and advected westward.

A third likely source feeding into the South Equatorial Current is the Southern Subsurface Countercurrent (SSSCC, Kessler, 2006), also identified as Tsuchiya Jets flowing eastward across the Pacific basin within 3-10º from the equator and diverging poleward as they move east (Toggweiler, 1991, Tsuchiya and Talley, 1998), though the exact location of the SSSCC outcropping is not well constrained. The map of surface buoyancy (Brunt-Vaisala) frequency constructed based on World Ocean Atlas data (WOA09, Fig. 1D) shows an area of elevated values east of 90ºW between 10-18ºS. We hypothesize that higher buoyancy frequency in this region indicates the locus of the divergence bringing the SSSCC to the surface. One likely driver for the divergence might be Ekman modification of the northward flowing Humboldt/southward flowing Coastal Countercurrent and westward flowing South Equatorial Current, which would be expected based on the regional wind patterns (Kessler, 2006). However, as many regional circulation features remain currently unresolved (Fiddler and Talley, 2006, Kessler, 2006), the connection between SSSCC outcropping and elevated buoyancy field is hypothetical.

II. Methodology

Here we briefly review the terms of biological production used in oceanography. Gross Primary Production (GPP) is a measure of the amount of energy derived from the oxidation of water through the catalytic water-splitting function of photosystem II (Riley, 1940; Platt et al., 1984; Steeman Nielsen, 1963; Odum, 1971; Bender et al., 1987). Net Primary Production (NPP) is the difference between GPP and autotrophic respiration. Net community production (NCP) is defined as the amount of chemical energy produced by primary producers minus that is respired by autotrophs and heterotrophs; thus, it represents the biological organic carbon input to the ocean. The ratio of net to gross primary production (NCP/GPP), to first order, reflects the organic carbon export efficiency out of the ocean surface, provided the formation of Dissolved Organic Carbon (DOC) is negligible (Refs).

2.1 O2/Ar-based Net Community Production

The NOP (Net Oxygen Production, stoichiometrically equivalent to Net Community Production) within a mixed layer can be constrained from the $O_2$ mass balance (Eq. 1) that includes NOP as the difference between Gross Photosynthetic Production (GPP) and respiration (R), (so NOP=GPP-R), atmospheric exchange (driven by the deviation of dissolved $[O_2]$ from equilibrium with atmosphere, and by bubble injection (BI). $J_{tr}$ is a sum of $O_2$ fluxes due to physical transport (both vertical and horizontal) (Bender et al., 1987, Emerson, 1987):

$$NOP = GPP - R - J_{tr}$$
\[ h \frac{\partial O_2}{\partial t} = NOP - \Delta O_2_{\text{BIO}} k_v O_{2\text{eq}} + BI + J_{tr} \]

where \( h \) is a Mixed Layer Depth (MXLD), \( k_v \) is O₂ piston velocity and \( O_{2\text{eq}} \) is an equilibrium [O₂] at \textit{in situ} temperature, salinity and pressure. To factor out the effect of short-term variability in temperature/salinity on O₂ solubility, the term \( \Delta O_2_{\text{BIO}} \) is used instead of total O₂ super-saturation (in percent, %), \( \Delta O_{2\text{bio}} = O_2 / Ar_{\text{supersat}} = \left( O_2 / Ar_{\text{eq}} - 1 \right) \) (Craig and Hayward, 1987, Emerson et al., 1991). The effect of bubble injection (\( BI \)) on dissolved O₂/Ar is small and can be neglected (Reuer et al., 2007, Stanley et al., 2010). \( J_{tr} \) is the transport term used when vertical and/or horizontal advection and/or turbulent mixing measurably affect the O₂/Ar mass balance within a specified biogeochemical domain. Assuming steady state and ignoring the transport term, the NOP flux can be written as:

\[ NOP = GPP - R = O_2 / Ar_{\text{supersat}} \cdot [O_2]_{\text{eq}} \cdot k_v \]

NOP (in mmol-O₂ m⁻² d⁻¹) is equivalent to the Net Community Production through the O₂:C photosynthetic quotient of 1.4 ±0.1 (Laws, 1991), assuming nitrate is the main N source for net (new) phytoplankton growth. Hereafter, we report O₂-based productivity as NCP in carbon units (mmol-C m⁻² d⁻¹).

### 2.1.1 Wind-based and Rn226-based piston velocities

Interpolated and weighted 30-day wind histories (Reuer et al., 2007) from the ASCAT satellite in 0.5° × 0.5° grids around each station, and the parameterization of Nightingale et al (2000), were used to calculate gas-exchange velocities at stations for both 2010 and 2011 cruises. For the underway dataset, piston velocities were obtained using wind speeds centered at whole degrees in 2010 and at even degree longitude in 2011 within 0.5° × 0.5° grid. In 2010, in addition to wind-based estimates, piston velocities were constrained with ²²²Rn mixed layer deficit at several stations (Yeung et al., in review). In the observed range of wind speeds, Yeung et al. reported an agreement within 30%? between ²²²Rn-based piston velocities and Nightingale (2000) parameterization for 0.5° × 0.5° gridded ASCAT winds, the procedure then chosen for obtaining piston velocities in 2011 (when no ²²²Rn measurements were made), as well as underway piston velocities in both years.

### 2.2 Underway and discrete O₂/Ar, and [O₂] measurements

Mixed layer dissolved O₂/Ar ratios were measured as ratios of 32/40 masses continuously through the duration of both cruises with a quadrupole mass spectrometer (Pfeiffer, Prisma Plus 200) equipped with an Equilibrator Inlet (EIMS) following the methodology described in (Cassar et al., 2009). The intake of the science sea water was located 4-5 m below the waterline of R/V Atlantis (in 2010) and 3-4 m below the waterline of R/V Melville (2011). Measurements were taken every 500 ms, and averaged over 2 minutes. The averaging time of the signal of gases supplied by the equilibrator is ~15 minutes. At a ship speed of 5 knots, the EIMS O₂/Ar ratio represents the signal averaged over ~2.5 km. The 32/40 ion current ratio was calibrated every 6-12 hours by admitting for 10 min ambient air into the mass spectrometer through a silica-fused capillary of dimensions identical to the Equilibrator Inlet capillary and interfaced with the inlet through a valve (Valco, HPLC Stream selector valve) (Cassar et al., 2009).
In addition to continuous underway measurements, during the 2011 cruise, O2/Ar ratios were determined on discrete samples collected from Niskin bottles and analyzed with two methods: 1) 4L of sea water was collected into glass bottles and immediately analyzed onboard with the EIMS system, pumping the water through the equilibrator; 2) 0.2-0.4 L samples were collected into glass bottles equipped with Louwers-Hapert (L-H) valves and analyzed within 4 months on Mat253 Isotope Ratio Mass Spectrometers at WHOI or UCLA (see below). The results of the three O2/Ar measurements are compared in Fig. 2, where underway data are averaged over one hour bracketing the time of discrete sample collection. While the underway-EIMS and CTD-EIMS values agreed reasonably well, 4 of 11 O2/Ar supersaturation ratios water samples collected into the L-H-equipped bottles and measured by IRMS were up to 1.5 % higher than the underway 1-hour averaged O2/A signal measured on EIMS at the time IRMS sample was taken. The four “outliers” (Fig. 2) were measured at stations where a large range of underway O2/Ar (up to 3%) was been observed during ~ 30-40 hours the stations were occupied (stations 11 and 9). As discussed below, the rapid change in O2/Ar is likely a result of spatial heterogeneity of this region, and might be responsible for observed discrepancies.

The profiles of dissolved [O2] were obtained at all hydrographic stations with an oxygen SBE sensor mounted on the CTD rosette. As a check on the accuracy of the SBE sensor, Winkler titrations were periodically done on water samples collected at selected intervals with from the rosette bottles. SBE-based [O2] was adjusted with the Winkler-based dataset through the duration of the cruise.

2.3 OTI-based estimates of Gross Photosynthetic Production

The GPP can be derived independently from concurrent measurements of δ¹⁷O and δ¹⁸O of the MXL dissolved O2, applying the Oxygen Triple Isotope method (Luz and Barkan, 2000; Luz and Barkan, 2005; Luz and Barkan, 2009). The method takes advantage of the mass independent anomaly in ¹⁷O/¹⁸O ratio in atmospheric O2 relative to ¹⁷O/¹⁸O in photosynthetic (Luz et al., 1999; Thiemens et al., 1995). The mass balance for the three O isotopes can be written as follows (Prokopenko et al., 2011):

\[
\frac{\partial hO_2}{\partial t} = GPP \left[ \frac{r^{17}_p - r^{17}_{eq}}{r^{17}_{eq}} - \frac{r^{18}_p - r^{18}_{eq}}{r^{18}_{eq}} \right] - k \cdot O_{eq} \left[ \frac{r^{17}_{eq} - r^{17}_{dis}}{r^{17}_{dis}} - \frac{r^{18}_{eq} - r^{18}_{dis}}{r^{18}_{dis}} \right] + 17\Delta \rho
\]

where \( r^* = O^{*}/O = (δ^{*}O/1000+1) \cdot r_{std} \), the asterisk referring to either 17 or 18, and \( r_{std} \) is \( O^{*}/O \) in atmospheric O2. In Eq.3, \( \lambda = \frac{1 - \alpha_{17}^{*}}{1 - \alpha_{18}^{*}} \) is the ratio of mass-dependent fractionation factors in respiration, \( \alpha_{17} \) and \( \alpha_{18} \) (Luz and Barkan, 2005). For respective O isotopes, \( r^{*}_{eq} \) is an equilibrium isotopic ratio, \( r^{*}_{p} \) is the *ratio of photosynthetic O2 produced in situ in the mixed layer, and \( r^{*}_{dis} \) are measured ratios of the dissolved O2. The \( 17\Delta \) parameter is defined as shown in Eq. 4. By convention, the units of \( 17\Delta \) are per meg = 0.001‰ (Angert et al., 2003; Kaiser, 2011; Miller, 2002):

\[
\frac{17\Delta}{10^6} = \ln \left( \frac{\delta^{17}O}{1000} + 1 \right) - \lambda \cdot \ln \left( \frac{\delta^{18}O}{1000} + 1 \right).
\]
At steady state, equating the left hand side of the Eq. (3) to zero, the GPP flux can be directly calculated from measured $\delta^{18}O_{\text{dis}}$ and $\delta^{17}O_{\text{dis}}$.

2.4 OTI analysis
Seawater for discrete O$_2$/Ar and $^{17}\Delta$ analysis was drawn into pre-evacuated (< 1 mTorr) and pre-poisoned (100 µL saturated HgCl$_2$ solution) 500-mL Erlenmeyer flasks through the Louwers-Hapert high-vacuum valve on each flask (Emerson et al., 1999; Reuer et al., 2007). O$_2$, N$_2$, and Ar were cryogenically extracted at USC, using gas chromatographic separation of N$_2$ from O$_2$ and Ar at UCLA.

The $\delta^{17}O$ and $\delta^{18}O$ of O$_2$ were analyzed in multi-collection, dual-inlet mode on Thermo-Finnigan MAT 253 isotope ratio mass spectrometers in two laboratories, at UCLA and WHOI (Rachel’s method here?). The UCLA analysis requires manual adjustment of inlet pressure, while the WHOI analyses were done in an automated mode. The isotopic ratios were corrected for mass 40 and 28 isobaric interference (from Ar and residual traces of N$_2$ left after cryogenic purification), imbalance on the bellows and variability of the sample size (Barkan and Luz, 2005, Stanley et al., 2010). Precision on $\delta^{18}O$ and $\delta^{17}O$ measurements was better than 0.02 ‰ and 0.010 ‰ respectively. The O$_2$/Ar ratios on discrete samples were analyzed by peak jumping, and compared to the air-calibrated underway O$_2$/Ar ratios measured on the EIMS through the duration of the cruise (Table 2).

2.5 NPP from space
We obtained 8-day averaged estimates of NPP from the publically available website http://www.science.oregonstate.edu/ocean.productivity/custom.php maintained by the research group of Michael Berehnfeld at Oregon State University. The NPP rates were derived from satellite fluoresce remote sensing using Vertically Generalized Productivity Model algorithm (VGPM, Behrenfeld and Falkowski, 1997a) modified for temperature-dependence, Eplley-VGPM (Eppley, 1972; Berhenfeld and Falkowski, 1997b). The MODIS-NPP rates reported in 8-d intervals were re-averaged to 8-day intervals prior to our sampling instances, representing $\frac{1}{2}$ to $\frac{1}{3}$ oxygen residence time within the mixed layer.

2.6 $^{14}$C incubations, traps and $^{234}$Th deficit
$^{14}$C incubations were performed over 24 hours as described (Doug C. – can you please, add?)

Particulate Organic Carbon (POC) flux was measured with surface-tethered particle interceptor sediment traps (PITs, Knauer et al., 1979), deployed for an average of 40 hours at selected stations at 100m and 200m. Trap material was picked for ‘swimmers’ and combined onto filters for gamma counting and Si analysis at USC, as well as analysis of C, N, and their isotopes at the UC Davis Stable Isotope Facility. For further details, see Haskell et al. 2012, submitted)

POC export was also constrained by integrating the disequilibrium between particle reactive $^{234}$Th (half-life: 24d) and its soluble parent $^{238}$U (half-life: 4.5 byr) (Bhat et al., 1969; Coale and Bruland, 1985; Buesseler, et al., 1992) through the upper 200 m (Haskell, submitted). The deficiency in the surface was calculated with trapezoidal integration of the difference in activities down to the sediment trap depth. In cases of
excess Th, this value was subtracted from the deficiency, under the assumption that this represents remineralization of particles. POC fluxes are calculated using the POC: $^{234}$Th ratio measured in trap samples. A more detailed description of both sediment traps and $^{234}$Th deficit is given by Haskell et al. (2012, submitted).

### III. Results

#### 3.1 Zonal variability in the mixed layer O$_2$/Ar signal

The two longitudinal transects (along 10S and 20S latitudes) of EIMS-measured O$_2$/Ar supersaturation within the mixed layer are shown in Fig. 4 along with the underway temperature (T) and salinity (S) as recorded by shipboard thermosalinographs in both 2010 and 2011.

Along the 10S transect (Fig. 3A), the underway O$_2$/Ar supersaturation within the mixed layer showed a general trend of westward decline, punctuated by regional variability on the scale of 1-2°. In the coastal waters sampled in 2010 between 78°W and 80°W, the O$_2$/Ar trace varied from -5 to +25% supersaturation on a scale of <0.5 degree. The O$_2$/Ar baseline increased from ~0 to ~4% between 78°W and 82°W, accompanied by the increase in the mixed layer T (from 23°C to 25°C) and S (from ~34.5 to 35.3). Further west between 82°-90°W, the O$_2$/Ar trace varied between 0 and a maximum of 6% supersaturation. The sharp peak of 6% in O$_2$/Ar coincided with a local maximum in T (+0.5°C) and minimum in S (-0.5 units). In the most western region of the 10S transect, between 91°W-100°W, the O$_2$/Ar trace varied from ~0 to 1.5% at the scale of approximately 2° (Fig. 3). The zonal segments of higher O$_2$/Ar appeared to coincide with ~0.5°C drop in T and 0.5 increase in S.

In 2011, the O$_2$/Ar supersaturation increased westward between 82°W (the eastern most longitude sampled) and ~ 87° from -1.5% to 3%. Within the 87°W-91°W segment, O$_2$/Ar varied between 0 and 3% supersaturation. The variability in O$_2$/Ar signal was not obviously related to the zonal variability of the underway T and S. Westward of 92°W, the O$_2$/Ar showed a general decline from ~1 to 0%. The general zonal distribution of the O$_2$/Ar within the mixed layer was similar between the two years, but with longitudinal boundaries between different zonal segments appeared to be shifted westward in 2011 relative to 2010.

Along the 20S latitude, the 2010 O$_2$/Ar supersaturations were overall lower than along 10S, varying from -1% to +4%, with maximum values observed as peaks about a degree wide, between 84°W and 94°W (Fig. 3B). The O$_2$/Ar decreased westward to 0 ± 0.5% at St 5 (10S, 100W). In 2010, the general westward increase in both mixed layer T and S was observed along the 20S transect. Note that in 2011, our cruise track cut diagonally from 20S, 90W to 15S, 80W. The diagonal segment of 2011 cruise transect was characterized by the sub-degree scale spatial variability from 0 to 1% of O$_2$/Ar supersaturation. Elevated O$_2$/Ar along 20°S did not appear to correlate, at least qualitatively, with changes in either T or S (Fig. 3B).

The frequency of O$_2$/Ar supersaturation “peaks” provides insight into their contribution of overall NCOP balance. For instance, 5 peaks per transect, with an average half width of about 0.5 degree and a maximum that is about 5x greater than the baseline supersaturation, they account for about 12% of the transect, and nearly 60% of the background signal (as calculated by multiplying these factors together and dividing by
Thus, failure to capture these spots with discrete stations would under-estimate total production by a factor of about 1.6.

To facilitate broader regional inter-comparison of these heterogeneous datasets, we binned the underway data into longitudinal segments of 1° (corresponding to 109 km and 104 km at 10S and 20S respectively). The average of the binned data for the 10S transect between 80ºW and 100ºW was 0.8±0.4%, in both 2010 and 2011 years. This was 2–4 fold higher than 0.3±0.1% and 0.3±0.05% recorded along the 20S in respective years (±stdm based on n=20 bins). The binned average for the 80W–90W along 20S was 0.5±0.2% in 2010 and 0.16±0.3 (stdm, n=10) for the diagonal transect in 2011.

In addition to spatial variability, at some stations, up to 2.5% temporal variability was observed while on station. For instance, in 2011, at St11 (10ºS, 82ºW) a continuous increase in O2/Ar from -1% to 1.5% was recorded over the 30 hours the station was occupied, accompanied by an increase in surface temperature of ~1ºC (Fig. 4). At the stations occupied over the diurnal cycle, up to 0.5% on O2/Ar supersaturation was observed between day and night time.

### 3.2 Oxygen Triple Isotope composition in the mixed layer and below

At the major hydrographic stations, we measured isotopic composition (δ¹⁸O and δ¹⁷O) of dissolved O₂ at one or two intervals in the mixed layer and just below, typically within the subsurface O₂ maxima (Table 1). Following accepted notation we refer to the OTI composition as ¹⁷Δ defined in Eq. (3). In 2011, similar ¹⁷Δ values of 30-32 per meg were measured within the mixed layer at the most western stations, at both 10S and 20S. The OTI composition remained fairly constant at ~30±4 per meg along the 20S transect, but at 10S, it increased to 50±3 per meg at 90ºW (St 9), and to 70±2 per meg at 82ºW (St11) (±std of replicate measurements). A comparable spatial distribution was observed in 2010, though the ¹⁷Δ were 5 to 20 per meg lower (Table 1). Table 1 also includes the GPP/kvO₂eq term, calculated for the mixed layer from measured δ¹⁸O and δ¹⁷O. Note that GPP/kvO₂eq represents the ratio of GPP flux to the air-sea exchange flux.

Below the mixed layer, ¹⁷Δ was strongly elevated, from 110 per meg at the western stations to 200 per meg in the east. The subsurface ¹⁷Δ maxima is a common phenomenon in the low latitude water column resulting from photosynthesis that occurs at the base of the mixed layer (Juranek and Quay, 2005, 2011; Nicholson et al., 2011).

At St 5 in 2011, we measured a profile of ¹⁷Δ through the 4000 m water column. Samples were analyzed at WHOI and UCLA laboratories (as described in the Methods). At selected intervals, duplicate samples were run at both facilities. For the duplicate measurements, standard deviations are listed in Table 1. The ¹⁷Δ profile is shown in Fig. 5 along with the water masses identified according to Fiedler and Talley (2006) from measured temperatures and salinities. Below the 60 m deep mixed layer (with ¹⁷Δ of 32 per meg), and the thin O₂-maximum zone (with ¹⁷Δ of 110 per meg), the Subtropical Underwater (STUW) is recognized between ~100 and 250 m by salinities of 35.5 ±0.2, with lower ¹⁷Δ of 48 per meg. STUW is a thermostad/halostad separated by a steep pycnocline from the 13ºC Water (13CW, with salinity of 34.5) at 300 m with a higher ¹⁷Δ of 77 per meg. The broad salinity minimum between 350 and 1000 m likely corresponds to the Antarctic Intermediate Water (AAIW) with ¹⁷Δ of 34±1 per meg. Pacific Deep Water (PDW) is marked by T of ~2.5ºC and S of ~34.5 below the depth of ~1500 m. The ¹⁷Δ value of the transition between AAIW and PWD based on the duplicate samples
analyzed at the two laboratories was 51 ±29 per meg. The reason for the poor agreement among the two replicates was not determined, but might be related to the difficulties of analyzing the low O₂/Ar ratio samples and correcting the OTI signal for Ar interference and pressure imbalance between the bellows on a sample and a standard side of the mass spectrometer at the low O₂/Ar ratio of analyzed gas mixtures (Stanley et al., 2010). The lower PDW transitions into the Lower Circumpolar Water (LCW) below 3000 m, with ¹⁷Δ of 29-37 per meg.

IV. DISCUSSION - Primary and export production within ETSP

4.1 Influence of the upwelling on oxygen mass balance within the mixed layer

The 2010/2011 cruise stations along the perimeter of the study region were distributed between hydrographically distinct regimes of the upwelling-dominated Peru-Current system (St 1 and St 11) and the downwelling-dominated South Pacific Gyre (St 5), as well as the transitional zone between the two regimes (Sts 3, 7 and 9) (Fig. 1A). The upwelling of the subsurface waters in the eastern parts of the region stimulating the algal growth by supplying the nutrients to euphotic zone, also directly affects the mixed layer O₂ mass balance by adding O₂-deficient waters from the ODZ extending thousands kilometers west. The influence of the O₂-depleted waters on the mixed layer O₂ intensifies eastward, due to steepening and shallowing of the oxycline from the western to the eastern stations observed in O₂-saturation vertical profiles along both 10S and 20S transects (shown for 2010 in Fig. 6). Along the 10S transect, 50% O₂-undersaturation was measured at ~120 m depth at 100ºW, at ~100 m at 90ºW, and at 55 m at 82ºW, just 20 m below the mixed layer. Much smaller magnitude of O₂ undersaturation, less than -10%, was observed below the mixed layer at stations located along the 20S.

Correcting for upwelling at steady state

At steady state, the mass balance of O₂ within a mixed layer affected by advection of a water mass with differing O₂ saturation is described as shown in eq. (5):

\[ NCP \cdot PQ = NOP = O_2 / Ar_{ss} \cdot [O_2]_{eq} \cdot k_v \cdot w \cdot ([O_2]_d - [O_2]_s) \]

where PQ is the photosynthetic quotient for NCP fueled by nitrate, w is the vertical advection (upwelling velocity), O₂/Ar_{ss} is measured O₂/Ar supersaturation, [O₂]_d is the O₂ concentration upwelled from depth, and [O₂]_s is the mixed layer O₂ concentration.

At steady state, if the NCP is limited by nitrate, and the upwelling brings water containing nitrate and low O₂, the biological O₂ supersaturation depends on the amount of “excess” nitrate remaining after the biological production has compensated for the O₂ undersaturation advected from below. “Excess” nitrate is similar to the pre-formed nitrate (N_{pf}) concept. The difference between the two concepts is that N_{pf} is calculated from Apparent Oxygen Utilization (AOU) within a water mass along the isopycnals to the location of outcropping (N_{pf}=N_m - AOU/10), where N_m is nitrate measured in situ at the depth horizon from which the upwelling occurs. The “excess” nitrate, N_{ex}, is defined as N_{ex}=N_m - (O_{2d}-O_{2eq})/10, where O_{2eq} is the [O₂] in equilibrium with atmosphere at the
Assuming the stoichiometric ratio of photosynthesis supported by nitrate, $O_2:N$, is 10, the Net Oxygen Production can be expressed as:

\[
\text{NOP} = 10w^*(N_{ex} - N_s)
\]

where $w$ = upwelling velocity, $N_s$ = nitrate in the surface water, and $N_{O2}$ is “excess” nitrate. Then, $w$ can be estimate by combining Eqs. (6) and (5).

We applied this approach at St 11, located at 82.3°W on the 10S transect, for both 2010 and 2011 years. A subsurface $O_2$ maximum was observed in the 25-35 m interval in 2010, at ~10% saturation. $N_{ex}$ and $O_{2d}$ were determined by averaging the portion of respective profiles between 25 and 50m. The resulting upwelling velocity, $w$, at St 11 was 0.1 m/d. Using equation (5), the upwelling-corrected NCP (Table 2) was 4.9 mmol-Cm$^{-2}$d$^{-1}$, comparing to originally determined 4.6 mmol-Cm$^{-2}$d$^{-1}$.

In 2011, during the 30 hours of station occupation (3/30/2012 through 3/31/2012), an increase in the underway $O_2$/Ar from -1% to 1.5% was recorded, along with the sea surface water warming by ~1°C (Fig. 4). Moreover, repeated CTD profiling of the water column within 30 hours revealed a rapid change in the upper 100 m of the salinity, temperature and $O_2$ saturation profiles, as well as rapid changes of the mixed layer depth, from 35 to 16 to 20 m (Fig. 7). We interpreted the observed hydrographic changes as a result of horizontal advection, rapidly replacing within the mixed layer and the upper thermocline cooler, $O_2$/Ar undersaturated, and, likely recently upwelled water with warmer and $O_2$/Ar supersaturated water mass, where ongoing photosynthetic production of $O_2$ resulted in the observed $O_2$/Ar supersaturation.

Applying the equations (5) and (6) to the initially observed $O_2$/Ar of -1%, results in negative values of $w$ – likely due to violation of the steady state assumption. Applying the same set of equations to the final observed $O_2$/Ar of 1.5% supersaturation yields $w=0.4$ m/d. In these calculations, the $N_{ex}$ and $O_{2d}$ were obtained by averaging the respective profiles between 35 and 50 m. The results were not very sensitive to the choice of depth for $N_{ex}$ and $O_{2d}$. Using $w=0.4$ m/d, the upwelling correct NCP of 19.6 mmol-Cm$^{-2}$d$^{-1}$ was obtained (comparing to NCP = 8.6 mmol-Cm$^{-2}$d$^{-1}$ calculated from $O_2$/Ar supersaturation only).

At St 11, the upwelling rate of 1.9 ± 0.8 m/d was estimated, which was significantly higher than $w$ obtained with a steady state assumption described above. The discrepancy is likely to originate from the non-steady state $O_2$ mass balance within the mixed layer. Applying Eq. (5) NCP for the $O_2$/Ar for -1% to and +1.5% of saturation, the minimum and the maximum values measured while on station. For $O_{2d}$ the average $[O_2]$ between 35 and 50 m was used, so that $(O_{2d} - O_{2s}) = -32 \mu$M. For $^7$Be-derived $w$ of 1.9 ±0.8, and averaging the max and the min of observed $O_2$/Ar, the NCP rate of 41.4 ± 17.7 mmol-Cm$^{-2}$d$^{-1}$. This estimate is 2x higher than the one obtained with the equations (5) and (6) and the steady state assumption (Table 2).
**Mixed layer O$_2$ inventory under steady state and non-steady state conditions**

We investigated the temporal and spatial distribution of the effect of the O$_2$-deficient waters addition on the mixed layer O$_2$ inventory, using a simple box model simulating the biological O$_2$ production within the mixed layer through time (for details of the model Prokopenko et al., in review). The results of several model runs (Fig. 8), were obtained with the initial condition of the O2-deficit of -35 μM (-15% un, based on O$_2$ observed at St 11), resulting from a single instantaneous upwelling event into the mixed layer (MXL) isolated from the water column below otherwise.

The evolution of mixed layer O$_2$-supersaturation was investigated for three different mixed layer depths (20, 30 and 40 m) and two values of wind speeds bracketing the range of wind velocities obtained from ASCAT satellite for the time of both cruises as described in the Method section (5 m/s and 8 m/s, corresponding to the piston velocities of 2 m/d and 4.5 m/d (Nightingale et al., 2000)). T and S were kept constant, to eliminate the effect of the two parameters on the O$_2$ solubility.

First, two steady state scenarios were considered, one without biological O$_2$ production (Fig. 8A) and another one assuming a constant net O$_2$ production of 70 mmol-O$_2$m$^{-2}$d$^{-1}$ corresponding to NCP of 50 mmol-Cm$^{-2}$d$^{-1}$ (Fig. 8B). In both scenarios, for the considered range of physical parameters (MXLD, S, T and k$_v$), the MXL O$_2$ reaches a steady state after 20-60 day. This range is consistent with the time scale, estimated by Hendricks et al. (2005) for the influence of equatorial upwelling on the MXL O$_2$.

Without additional nutrient supply, the biological production within a vertically isolated mixed layer is not in a steady state. Thus, we also simulated biological O$_2$ production which would result from a single injection of a limiting nutrient, linking the specific rate of biological O$_2$ production (growth rate) to the availability of this limiting nutrient (Fig. 8B). Assuming nitrate a limiting nutrient, the model was initiated with [NO$_3$] of 8 μM, measured in 2011 at St 11 at depth of -35μM O$_2$-deficit at 40 m. At an arbitrarily chosen maximum growth rate of 0.5, nitrate was exhausted within ~20 days causing an abrupt drop in modeled NCP ('modeled NCP' Fig. 8C). Fig. 8C also shows the NCP flux ('steady state NCP') that would be obtained with a steady state equation (2) using the modeled biological O$_2$ supersaturation shown in Fig. 8B.

The net westward flow, associated with the South Pacific Equatorial current adects the upwelling O$_2$ signal (both of O$_2$-deficiency and O$_2$ biological production fueled by upwelling) offshore. Calculated time scales of mixed layer ventilation can be used to constrain the spatial extent of the horizontal transport of the upwelling signal of the MXL O$_2$ inventory. Based on in situ observations of float arrays, the westward surface flow in ETSP is 5-20 cm/sec. Averaging these estimates to 12.5 ±8 cm/sec, a O$_2$-saturation signal of a single upwelling event may be advected as far as 600 ± 400 km before MXL is completely ventilated by the air-sea gas exchange (spatial scale is given for comparison in Fig. 8A).

At St 11 in 2011, the minimum observed biological supersaturation at the time of sampling was -1%, and surface [NO$_3$] was 3.5 μM (Knapp et al., in prep). Within the framework of the model, at least 5-10 days must have passed between the introduction of the upwelling signal and our sampling at St 11. Thus, taking into account westward horizontal advection, the upwelling event might have occurred as far as 100 ±50 km further east from the location of St 11 at 82.3ºW, and the ~10% of the O$_2$ signal of this
event would be present in a 20-40 m deep MXLD as far west as ~88-90ºW.

Besides St 11, upwelling velocities of 0.7 ±0.4 m/d, 0.3 ±0.3 and 0.1 ±0.2 m/d were estimated for St7, St 11.1 and St 1 respectively, though the high uncertainty for small values admits a possibility of no vertical advection at St 11.1 and St1 (Haskell et al., in prep). In 2011, the subsurface O2 maxima developed below the mixed layer at St7, St 11.1 and St. 1 (Fig. 9). We reasoned that the subsurface O2 maximum developed just below the mixed layer at the time of observations is likely to eliminate or greatly reduce the transfer of O2-deficient signal into the mixed layer from below. At St 5, Haskell et al. reported the net downwelling of -0.15 ±0.15 m/d (Haskell et al., in prep).

4.2 Mixed layer NCP derived from oxygen mass balance at hydrographic stations compared to POC export

The rates of NCP within the mixed layer at major hydrographic stations (excluding St 11) were computed with Eq. (2) from the O2/Ar supersaturation, obtained as an average between the discrete EIMS- and IRMS-based measurements and the underway EIMS-based O2/Ar recorded during an hour bracketing the discrete sampling (Table 2). Table 2 also includes the NCP rates obtained with Eq. (2) from the continuous underway O2/Ar, binned in one-degree bands centered on the station coordinates. The discrete and binned estimates of NCP agreed with each other within 50% at eight of the thirteen stations. At the remaining five stations, the difference between the discrete and binned NCP rates was significant, up to a factor of 2.5 likely due to spatial heterogeneity on the scale of tens kilometers. At St 11, the 7Be-based upwelling correction was applied to the NCP determined from discrete and binned O2/Ar supersaturation (Table 2).

The NCP rates computed from O2/Ar supersaturation were compared to the POC fluxes estimated from Th234 deficit and by quantifying POC collected during 24 hour floating sediment trap deployments (see Haskell et al., subm) (Table 2 and Fig. 10). The detailed comparison between the traps and 234Th POC fluxes is given in Haskell et al. (submitted). Briefly, the average NCP over the two years exceeded the trap-based POC flux by the factors of 4-5 (see Table 2), the difference similar in magnitude to the difference between the traps and Th234 method. The relatively good agreement between Th234 and the O2/Ar approach suggests that the sediment traps maybe have underestimated the POC export in this region. We attribute this methodology disagreement to: a) declining production prior to cruises and the longer time constant for O2/Ar and 234Th to respond; b) under-trapping of particulates that may be slowly settling.

At approximately half of stations, an agreement within the uncertainty of either of the methods was documented between O2-based NCP and 234Th-POC fluxes (Table 2, Fig. 10). The largest discrepancy was observed at St 11 in 2010 (note that the NCP at St 11 is shown in Figure 10 as an average between the two rates, computed with Eq. 2 and Eq. 5). The horizontal advection and the non-steady state of the mixed layer O2 pool in this area are likely to drive the observed difference between 234Th-POC and O2/Ar-NCP. If the epicenter of the upwelling, as well as substantial fraction of biological production occurs to the east of St11, as shown in Section 4.1, the O2 trace of NCP and the POC export are likely to be decoupled in time and space. Several subsurface 234Th maxima were observed between 50 and 120m at this station in 2011 (Haskell et al, in review), which indicate that vertical 234Th inventory may be affected by a subsurface horizontal
flow (Haskell et al., -Willie, did you say so there?). The surface flow, advecting O$_2$ signal within the mixed layer is likely to differ in velocity from the subsurface flow which may have modified the vertical $^{234}$Th distribution, causing the discrepancy between the carbon flux estimates obtained with the two approaches. The large discrepancy between NCP (-0.9 ±3.4 mmol-C m$^{-2}$ d$^{-1}$) and POC (9.2 ±3.5 mmol-C m$^{-2}$ d$^{-1}$) fluxes was also observed in 2010 at St 5 (Table 2, Fig. 10). At St5, located on the northern limb of the South Pacific Gyre (Fig. 1A-B), the deepest mixed layer and subsurface [O$_2$] max were observed in both 2010 and 2011 (Fig. 6 and 9). Thus, it is possible that a large fraction of net carbon production had occurred in this area below the mixed layer, probably within the subsurface O$_2$ max. If the vertical exchange between the O$_2$ inventories within the mixed layer and the subsurface O$_2$ maximum had not reached a steady state at the time of sampling in 2010, the rates of NCP computed from the mixed layer O$_2$/Ar would be underestimated. On the other hand, it is possible that Th-$^{234}$ flux may also be overestimated through an analytical error. In fact, it is unlikely that POC export at the oligotrophic location of St5 is comparable in magnitude to the export at St11, located in upwelling-fed waters (Table 2). Note that in 2011 the POC and NCP fluxes at St 5 agreed with each other within the analytical uncertainty of the two estimates (Table 2). Compared to the vertical O$_2$ profile in 2010, the 2011 profile showed larger and shallower subsurface O$_2$ max (Fig. 9). It is possible that the 2011 profile represents a later stage of the seasonal subsurface O$_2$ accumulation (Johnson et al., 2009), when vertical O$_2$ profile had already reached the seasonal steady state.

4.3 GPP, NPP and export ratio estimates

At all major stations, rates of GPP (Table 2) were determined applying Eq. (3) at steady state to the $\delta^{18}O$ and $\delta^{17}O$ ratios of dissolved O$_2$ within the mixed layer. Table 2 also includes the 8-day averaged rates of NPP-VGPM (Net Primary Production) obtained as described in Section 2.5 with a VGPM algorithm (Behrenfeld, 1997b) from MODIS remote measurements of Chl and surface temperature for both 2010 and 2011. Table 2 also includes NPP fluxes measured as $^{14}$C uptake rates in ondeck incubations in 2011 only (Table 2). On average, the NPP-$^{14}$C fluxes were ~2x greater than NPP-VGPM values. One exception was St5, where the fluxes values were within 10%. The largest discrepancy between NPP-VGPM and NPP-$^{14}$C was observed on the eastern station, which is consistent with previous reports of underestimation of PP coastal regions by the remote sensing approaches (Pennington et al., 2006).

**GPP/NPP ratios**

Using $^{17}$Δ-based GPP within the mixed layer and $^{14}$C-NPP, we calculated GPP/NPP ratios (Table 2) for 2011, for which $^{14}$C incubations were available. The average GPP/NPP ratio based on data from seven stations was 2.7±0.5 (±stdm), calculated excluding the ratio of <1 at St7 as physiologically impossible. Including the St7 ratio into consideration would the average of GPP/NPP ratios to 2.5±0.5. The GPP/NPP ratio of marine photosynthesis was suggested to have a constant value of 2.7, derived from a compilation of multiple datasets of $^{18}$O-H$_2$O and $^{14}$C incubations run in parallel (Bender et al., 1987; Marra, 2002) and confirmed by culture studies (Halsey et al., 2010). As $^{17}$Δ-GPP is an *in situ* method equivalent to the *in vitro* $^{18}$O-H$_2$O incubation, the ratio obtained from either method should be the same. However, deviations, up to a
factor of 2-3, from the 2.7 value were also reported (Quay 2010, Nicholson, 2012, Luz and Barkan, 2009). The discrepancy may stem from certain artifacts, methodological and hydrographic (such as the entrainment of deep waters with a differing $^{17}\Delta$ signal into the mixed layer (Nicholson et al., 2012; Quay et al., 2010). In our dataset, at station 5, where the GPP/NPP ratio was 4.8 exceeding the “canonical” value by 78%, the periodic entrainment of the subsurface elevated $^{17}\Delta$ (Fig. 6) might have lead to overestimation of $^{17}\Delta$-based GPP (Quay et al., 2010, Nicholson et al., 2012).

Export production and e-ratios

The efficiency of organic carbon export (traditionally referred to as e-ratio, and defined as the ratio of POC export to Net Primary Production, Laws et al., 2000) was estimated from the two independent datasets: the O$_2$/Ar-based NCP and $^{17}\Delta$-based GPP, and from $^{234}$Th deficit combined with NPP obtained with 14C incubations or based on satellite estimates (Table 2).

In the first approach, the NCP/GPP ratios were obtained from simultaneously measured O$_2$/Ar saturation (upwelling-corrected at St 11) and OTI of dissolved O$_2$. The average NCP/GPP for all stations in 2010 was 0.03 ± 0.03, and 0.05 ± 0.03 in 2011. The NCP/GPP ratios were converted to NCP/NPP ratios multiplying the value by the average of the GPP/NPP ratios, 2.7. The resulting NCP/NPP ratios are equivalent to more traditional e-ratios, assuming that only a small fraction of NCP is exported as DOC. The average e-ratios values for 2010 and 2011 cruises were 0.09 ± 0.08 and 0.14±0.07 respectively (Table 2). In both years, the O$_2$-based e-ratios were ~2x higher along the 10S then along 20S transect, were on average higher on at the eastern stations than those obtained for the western stations (Table 2). The lowest NCP/NPP ratios are found at oligotrophic St5 (negative in 2010). The highest NCP/NPP ratios were found at station 9, located at 90°W at the 10S transect.

The O$_2$-derived e-ratios were compared with e-ratios obtained from 234Th-based POC flux and NPP determined with either the VGPM algorithm or 14C incubations (the latter for 2011 only). Excluding the data point at St5, which was, most likely, an outlier (see Table 2), the average POC$_{234\text{Th}}$/NPP$_{\text{VGPM}}$ was 0.17±0.07 in 2010 and 0.11 ± 0.4 in 2011. The POC$_{234\text{Th}}$/NPP$_{\text{VGPM}}$ ratios in 2011 were ~20% lower than POC$_{234\text{Th}}$/NPP$_{\text{14C}}$, which is expected as $^{14}$C-based NPP was on average higher than satellite-based NPP. Overall, the e-ratios estimated with both approaches, in situ O$_2$-based estimates and combination of in situ $^{234}$Th-based with incubations were found in statistically significant agreement (see Table 2).

No previous measurements of NCP/GPP ratios were made in the ETSP region. Geographically the closest, average NCP/NPP of 0.12±0.10 was reported as f-ratio for the Equatorial Pacific between 8S-8N along the 95W (Hendricks et al., 2005) and were in good agreement with our estimates. The averaged ETSP NCP/GPP ratios obtained in this study are, on average, 2x lower than the ratios of Net to Gross Production reported from the Southern Ocean, Equatorial Pacific, North Atlantic (BATS) and North Pacific (REFS, Fig. 10).

Only a handful of previous studies have measured Primary Production in the ESTP region (Pennington et al., 2006). A large-scale survey undertaken by Pennington et al. (2006) demonstrated, as expected, an overall E-W gradient and N-S gradient in the rates of GPP (determined via on-deck incubations), with high values, up to 3500
mgC/m²d in the coastal region, decreasing to 600-1000 mgC/m²d in the equatorial upwelling region, 300-500 mgC/m²d in the Eastern Boundary (Peru-Chile) transition zone, and a somewhat surprisingly high value ~ 400 mgC/m²d in the SPG. In regard to the latter, the authors themselves indicated that these rates seemed too high, and exceed by 100% the rates VGPM satellite-based estimates (Behrenfeld and Falkowski, 1997). Pennington and co-workers also report a large discrepancy between satellite based estimates and on-deck incubations for the coastal regions, with satellite based numbers ~40% lower. Using optical methods, Claustre et al. (2008b) determined very high PP rates in the SP gyre (>800 mgC/m²d GPP), and overall net autotrophic conditions in this region. These results were in contrast with incubation studies conducted by the same workers, which gave the net heterotrophic conditions in the gyre and half the GPP rates.

Need to compare to Hendricks, Stanley, Kaiser.

4.4 Spatial distribution of NCP determined from the underway O₂/Ar supersaturation within the mixed layer

The underway NCP rates were obtained with equation (2) from continuously measured O₂/Ar ratios and piston velocities determined as described in Section 2.3. Figure 10 shows NCP rates zonally binned in one degree bands along the 10S and 20S transects, compared with the NPP rates derived with VGPM described in Section 2.5. The common feature observed along all transects in both years is lack of agreement between NCP and NPP east of 82-85ºW band at all but 20S transect in 2011. The 80-90W segment of this last transect was diagonal to the north (Fig. 1A), thus it reflects the change in both zonal and meridional directions. In the western segments of the transects, the agreement between NCP and NPP improves, and the same 1-3º wide features are recognized in both parameters (Fig. 10).

The difference in agreement between NCP and NPP spatial patterns within the eastern and western regions of both transects likely reflects the influence of upwelling on the O₂ mass balance within the mixed layer discussed in section 4.2. Based on the analysis in Section 4.1, we divide 10S and 20S transects into eastern, central and western segments (Table 3). In the eastern segments, the O₂/Ar and corresponding NCP estimates are likely affected by the horizontal advection of the upwelling to the east. The central and western segments lay beyond the significant influence of the horizontal transport of the coastal upwelling signal, thus other processes must affect the O₂/Ar-based NCP in those regions.

Table 3 summarizes the averaged NCP estimates for the whole transects, as well as mean values for each of the transect segments. In both 2010 and 2011, the NCP along the 10S was 2-4x higher than along 20S. In 2011, the total 10S NCP was ~ 20% higher than in 2010, though not statistically significant. The 2010 10S transect showed overall decline in NCP from east to west. In contrast, the 80-97W band in 2011 along 10S had negative NCP likely due to low-O2 upwelling, as shown in Fig. 8. We conclude that in 2011 O2-budget within the mixed layer was affected by the upwelling of low O2 much stronger than in 2010. If eastern segment of 10S is excluded from comparison, the NCP in 2011 was almost 2x higher than in 2010.

The significance of the patches with elevated NCP was considered in the context of a regional nutrient balance:
(7) \( \text{NCP}_{O2} = w \cdot R_s \cdot (\text{LN}_{pf} - \text{LN}_s) \),

where \( w \) is the advection of nutrient, \( R_s \) is a stoichiometric coefficient of photosynthesis and \( \text{LN}_{pf} \) and \( \text{LN}_s \) is a limiting nutrient, pre-formed and in the surface waters respectively. From eq (8), the in NCP should represent isolated areas where either gas exchange is unusually low, upwelling is unusually high, or \( \text{LN}_{pf} \) is unusually high compared to surrounding regions. Gas exchange was relatively similar across most of the region (Yeung et al., in revision). Thus, either higher vertical advection or higher \( \text{LN}_{pf} \) drive the elevated NCP in the patches.

We ran a simple multiple linear regression (MLR) analysis to evaluate the links between estimated NCP and regional hydrography (Temperature, Salinity and Piston Velocity). All data were treated with Z-scoring procedure normalizing the differences among independent variables (predictors), as well as predicted (NCP) variable to the same scale. In Table 3 those segments are highlighted, for which MLR explained at least 60% of the observed variability (based on R value shown in Table 3).

The NCP in the Eastern segments of 10S positively correlated with temperature and salinity in 2011, and negatively in 2010 (though in 2010, less than 50% NCP variability was explained by the three considered predictors). The positive correlation between NCP and temperature and salinity in 2011, once again confirmed stronger influence of the upwelling of O2-deficient waters on the mixed layer O2 inventory in 2011.

In the Western segments of 10S, the NCP correlated positively with salinity in both years. NCP was negatively correlated with temperature in 2010, and positively in 2011, however, the positive coefficients for 2011 was smaller. Thus, it appears that patches of higher NCP within ~91-100ºW zonal band result from the episodic low-level upwelling originating at the depth of salinity maximum and bring a limiting nutrient to the surface. The \(^{7}\text{Be}\)-based upwelling of 0.7 m/d reported by Haskell et al. (in review) for St 7 corroborates this conclusion. The surface waters along 10S transect are likely not N limited, as evident from elevated surface nitrate measured everywhere west of 82ºW. Thus, a different nutrient is likely to be advected to the surface (ANGIE? LET’S TALK) – either silicate or iron. While 10S transects is located within HNLC regime with respect to nitrate, it is not so with respect to Si (Fig. 1C) (Also, Refs). Therefore, Si brought to the surface surface may fuel diatom production (Refs).

A distinct subsurface salinity maximum impinging from west to east from 200 to 100 m and disappearing at ~90-91ºW is present between 12-9ºS (data are from WOA09 climatology, Fig. 12). The formation of this salinity maximum is likely driven by the downwelling of high salinity surface waters in the center of South Pacific Gyre. In the region of the transition to the lower salinities subequatorial waters, a subsurface maximum of buoyancy frequencies is present (Fig. 12). This higher buoyancy zone is likely to vertically amplify the propagation of internal waves of various origins passing in the zonal direction through the Tropical Pacific (REFS).

In the Central segment of 10S transects in both years, the simple MLR analysis failed to find statistically significant predictors for NCP among temperature, salinity and piston velocities. From the numerical simulations (Fig. 8), the horizontal advection of productivity signal from the east does not reach beyond 89-90ºW. Therefore, the substantial NCP fluxes observed within the central segment in both years are supported
by a physical supply of a limiting nutrient through local circulation, not reflect in a
simple statistical analysis of hydrography.

Along the 20S transect, the mixed layer overlies a 100-200 m think
thermostad/halostad layer (Fig. 12?) of lower salinity and temperature than surface
waters. Thus, if the vertical transport of nutrients from below controls the NCP, we
expect to find negative correlation between NCP and temperature/salinity. Neither of the
three segments (Western, Central and Eastern) showed a pattern consistent with this
prediction (Table 3), except for probably the central region, but the MLR explained only
32% of observed variability within this segment.

The lack of hydrographic (temperature/salinity) signal that correspond to the NCP
patches along 20S suggest that upwelling may not be the dominant driver of increased
productivity, unless the upwelled water has a minimal temperature/salinity contrast with
the mixed layer water (which might be the case due to shallower depth gradients of these
properties along 20S than along 10S). Alternatively, as the waters along 20S are devoid
of surface nitrate and thus might be N limited, the patches of higher NCP may represent
areas where the effective pre-formed nitrate is higher than average. The increase in pre-
formed nitrate might be attributable to locations where nitrogen fixation is unusually
high. An alternative might be to attribute the patches to non-steady state behavior, the
presence of a plume that has upwelled episodically, fully converted nitrate to O2, but has
not yet had time for gas exchange to return the mixed layer to the steady state balance.

4.5 Seasonal Variability – TO ADD

5. Summary

From a consideration of Oxygen triple isotope measurements, O2/Ar ratios in the
mixed layer, and other data sets that constrain carbon production and export, we reach the
following conclusions.

1. O2/Ar ratios indicate that either production or upwelling into the mixed layer
is often patchy, with patch sizes that often have half-widths of 150 km and fluxes that are
2-6 times greater than average. In the Eastern half of the transect, patches were
encountered about 10% of the time. Missing these patches with discrete stations could
result in underestimating regional fluxes by about 60%.

2. Patches may be created by localized upwelling of O2-rich water, by localized
upwelling of water that is richer in nitrate than the background water, or by localized
blooms of diazatrophs. Through a comparison of the O2-rich patches with hydrographic
data, it appears that all three of these factors can play a role in the ETSP.

3. Upwelling of low O2 water near the Peruvian coast can be sufficiently rapid
that biological production is insufficient to bring the surface waters to equilibrium with
the atmosphere. Coupling estimates of upwelling rates with budgets for nitrate and O2
allows O2/Ar measurements to be converted to estimates for carbon export, even if
surface waters are undersaturated.

4. Net production based on 234Th and O2/Ar are comparable, and greater than
those for 24 hour floating sediment traps.

5. Estimates of shipboard primary productivity based on 14C incubations and
oxygen triple isotopes are much greater than those estimated from regional satellite
observations, and in reasonable agreement with previous measurements summarized by Pennington et al. (2006).

6. NOP/GOP is about 5%, comparable to, but a bit lower than many other locations. GOP/14C is about $2.7 \pm 0.5$, close to that of 2.7 determined by Marra (2002).

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**Figures and captions**

**Figure 1** Study region with the cruise tracks in 2010 (solid black line) and in 2011 (dashed black line) and stations locations and nitrate (A), temperature (B), silicate (C), Brunt-Vaisala (buoyancy) frequency (D) and O2 saturation (E) maps. Major currents are shown in B. A schematic diagram of net surface circulation is shown in F.

**Figure 2** Comparison between the three estimates of O2/Ar supersaturation

**Figure 3** Continuous measurements of dissolved O2/Ar supersaturation during Jan-Feb 2010 (R/V Atlantis) and March-April 2011 (R/V Melville). A. Transect along 10N. B. Transect along 20S. Sea surface temperature and salinity recorded at the underway sea water intake are also shown. Underway O2/Ar ratios were averaged at 2 minute intervals, and used to calculate 1º-binned O2/Ar ratios also shown.

**Figure 4** Underway record of O2/Ar supersaturation and temperature within the mixed layer during 30 hours of occupying St 11 in 2011.

**Figure 5** Profiles of $^{17}\Delta$, O2/Ar and O2 saturation, temperature and salinity at St 5.

**Figure 6** Profiles of O2 saturation and salinity at all hydrographic stations in 2010.

**Figure 7** – [O2] profiles at St 11 in 2011

**Figure 8** – Modeled biological O2 supersaturation ($\Delta O_{2\text{bio}}$) within the mixed layer (MXL) and NCP fluxes:

(A) Modeled $\Delta O_{2\text{bio}}$ under an assumption of a steady state NCP rates for three MLX depth (20, 30 and 40 m), and two piston velocities ($k_v = 2$ m/d and 4.5 m/d).

(B) Modeled $\Delta O_{2\text{bio}}$ for a case of a single upwelling event introducing into MXL O2-depleted signal and a limiting nutrient for $k_v = 3$ m/d.
(C) Modeled NCP driving $\Delta O_{2bio}$ shown in (B) and NCP calculated from predicted $\Delta O_{2bio}$, with a steady state assumption (Eq. 2 in the text)

**Figure 9** – Profiles of O2 for 2011 (Still to make)

**Figure 10** – $^{234}$Th-deficit based POC vs. NCP fluxes

**Figure 11** – Binned NCP compared to MODIS-based NPP, and underway temperature and salinity

**Figure 12** - Net vs. Gross Production from studies with O2/Ar and D17O. The ETSP is from this study, other data from: Data from Quay et al. (2010) GBC 24; Bender et al. (1992) DSR 39; Bender et al. (1999); DSR 46; Hendricks et al. (2005) JGR 110; Hendricks et al. (2004) DSR 51; Reurer et al. (2007) DSR 54; Luz and Barkan (1999) Aq.Micro.Ecol 56. Results indicate a slightly lower efficiency for ETSP.

**Figure 13** – to make

**TABLES**

**Table 1** Measured Oxygen Triple Isotope (OTI) composition and GPP/k, O2

**Table 2** Summary of fluxes determined in 2010 and 2011 at major hydrographic stations for NCP based on O2/Ar budget, POC based on $^{234}$Th-deficit and sediment traps, NPP based on MODIS-Chl and $^{14}$C-incubation and GPP derived from oxygen triple isotope mass balance.

**Table 3** NCP fluxes for three segments of 10S and 20S transects: Western (WE), Central (CE) and Eastern (EA) and results of the multiple linear regression (MLR) analysis

**References:**


<table>
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<th>Station</th>
<th>Depth (m)</th>
<th>δ¹⁷O (%)</th>
<th>δ¹⁸O (%)</th>
<th>¹⁷Δ (per meg)</th>
<th>GPP/kO₂ (ratio of fluxes)</th>
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Table 2 Summary of NCP, POC, NPP, GPP fluxes and export ratios

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<th>O$_2$/Ar-based NCP</th>
<th>POC flux</th>
<th>NPP</th>
<th>GPP</th>
<th>GPP/(^{14}$$\text{C}$-NPP ratio</th>
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<td>Ave</td>
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<td>37 ± 6</td>
<td>78 ± 39</td>
<td>162 ± 32</td>
<td>2.7 ± 0.5</td>
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</table>

**1** indicates a second visit to St 1, approximately once month apart from the first visit
* Unreasonably high POC-\(^{234}\text{Th}$/NPP ratio
**GPP/NPP < 1 is not possible, and excluded from calculation of the average
***e-ratio > 1 is not possible, and excluded from calculation of the average

Explanation of table headings and abbreviations

NCP = Net Community Production
POC flux = Particulate Organic Carbon fluxes based on:
- 234Th deficit (POC-\(^{234}\text{Th}$)
- floating traps (POC-Traps) (Haskell et al., sub)
NPP = Net Primary Production based on:
- Satellite data and VGPM algorithm (NPP-\(\text{VGPM}$)
- \(^{14}$$\text{C}$-incubation (NPP-\(^{14}$$\text{C}$)
GPP = Gross Photosynthetic Production

Calculated ratios

- GPP/NPP-\(^{14}$$\text{C}$ = ratio of \(^{17}$$\text{O}$-based GPP to \(^{14}$$\text{C}$-incubation based NPP
- NCP/GPP = ratio of O$_2$/Ar-based NCP binned at 1º longitude to \(^{17}$$\text{O}$-GPP
- e-ratios (carbon export to Net Primary Production ratios)
- NCP/NPP = converted from NCP/GPP ratio using the average observed GPP/NPP-\(^{14}$$\text{C}$ ratio
- POC-\(^{234}\text{Th}$/NPP-\(\text{VGPM}$ = ratio of 234Th-based POC flux to NPP derived from satellite data and VGPM algorithm
- POC-\(^{234}\text{Th}$/NPP-\(^{14}$$\text{C}$ = ratio of 234Th-based POC flux to NPP obtained from \(^{14}$$\text{C}$ ondeck incubations
Table 3 NCP fluxes for three segments of 10S and 20S transects: Western (WE), Central (CE) and Eastern (EA) and results of multiple linear regression analysis
NCP is given in mmol-C/m²d

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Total R of the MLR 0.84 0.09 0.48 0.61 0.32 0.60 0.85 0.37 0.58 0.54 0.62 0.06

* indicates the MLR results are not significant based on calculated confidence intervals (not shown).
The MLR results with R>60% are highlighted in bold.

| Piston Velocity | -0.41 | -0.08 | 1.75 | 0.08 | -0.03* | 0.07 | 0.55 | 0.00 | 1.01 | -0.80 | 1.05 | 0.12 |
| Temperature    | -0.33 | 0.36  | -1.86| 0.17 | -0.03* | 0.75 | -0.88 | -0.39 | 0.37 | 1.08  | -0.01*| 0.11 |
| Salinity       | 0.35  | 0.13  | -0.31| 0.79 | -0.62  | 0.86 | 1.03 | -0.50 | -0.75| -1.20 | -0.42 | 0.04*|

MLR coefficients for

The MLR results with R>60% are highlighted in bold.
Major stations including discrete oxygen samples in both years, 234Th fluxes and sediment traps deployment in 2010 and 14C incubations in 2011

- Major stations including the measurements listed above, and 7Be mass balance and 234Th fluxes in 2011
- Minor hydrographic stations in 2010 only

Legend:

- Geostrophic Currents: SEC = South Equatorial Current
- HC = Humboldt Current
- Subsurface Currents: EUC = Equatorial Undercurrent
- SSSCC (TJs) = Southern Subsurface Countercurrents (Tsuchiya Jets)
- PUC = Peru-Chile Undercurrent
- Near surface (wind-driven) currents

Figure 1

A. Surface NO3- (µM)
B. Surface T (°C)
C. Surface SiO4 (µM)
D. Surface Brunt-Vaisala frequency (cycle/hour)
E. Oxygen saturation (%) at 40 m
F. Depth section showing current flow

- Figure 1A: Surface NO3- (µM)
- Figure 1B: Surface T (°C)
- Figure 1C: Surface SiO4 (µM)
- Figure 1D: Surface Brunt-Vaisala frequency (cycle/hour)
- Figure 1E: Oxygen saturation (%) at 40 m
- Figure 1F: Depth section showing current flow
Comparison of Shipboard Continuous Pump with Niskin sample draw on board and lab analysis

Figure 2
Figure 3

(A) 10S-2010

- Salinity
- Temperature (Temp)
- O$_2$/Ar$_u$ underway
- O$_2$/Ar$_u$ 1°-binned

(B) 20S-2010

- Salinity
- Temperature (Temp)
- O$_2$/Ar$_u$ underway
- O$_2$/Ar$_u$ 1°-binned

10S-2011

- Salinity
- Temperature (Temp)
- O$_2$/Ar$_u$ underway
- O$_2$/Ar$_u$ 1°-binned

20S-2011

- Salinity
- Temperature (Temp)
- O$_2$/Ar$_u$ underway
- O$_2$/Ar$_u$ 1°-binned

Longitude (W) along 10S/20S
Figure 4
**Figure 5**

- **O₂/Ar and O₂ saturation, %**
  - Depth, m: 0, 500, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500
  - O₂/Ar saturation
  - O₂ saturation

- **Temperature, °C**
  - Depth, m: 0, 5, 10, 15, 20, 25
  - Temperature

- **Salinity**
  - Depth, m: 34, 34.5, 35, 35.5, 36
  - Salinity

- **STUW = Subtropical Underwater**
- **13CW = 13C Water**
- **AAIW = Antarctic Bottom Water**
- **LCW = Lower Circumpolar Water**

Legend:
- O₂/Ar saturation
- O₂ saturation
- Δ
- 17Δ
Figure 8

A

NCP=50, k=2
NCP=50, k=4.5
NCP=0, k=2 and 4.5

B

variable NCP
modelled NCP
steady state NCP

C

Distance, km

850 680 510 340 170 0

Degrees longitude (W)

88 86 84 82 80
Figure 10

![Graph showing NCP-O2/Ar vs POC flux - Th234 for All data, 2011, All data, 2010, Series3, and Series1.](image)