Dissolved O$_2$/Ar and other methods reveal rapid changes in productivity during a Lagrangian experiment in the Southern Ocean

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[1] We use continuous and discrete measurements of the dissolved O$_2$/Ar ratio in the mixed layer to investigate the dynamics of biological productivity during the Southern Ocean Gas Exchange Experiment in March and April 2008. Injections of SF$_6$ defined two water masses (patches) that were followed for up to 2 weeks. In the first patch, dissolved O$_2$/Ar was supersaturated, indicating net biological production of organic carbon. In the second patch, rapidly decreasing O$_2$/Ar could only be reasonably explained if the mixed layer was experiencing a period of net heterotrophy. The observations rule out dominant contributions from vertical mixing, lateral dilution, or respiration in the ship’s underway seawater supply lines. We also compare nine different estimates of net community, new, primary, or gross production made during the experiment. Net community and new production estimates agreed well in the first patch but disagreed in the second patch, both during an initial net heterotrophic period but also during the apparently autotrophic period at the end of the observations. Rapidly changing productivity during the second patch complicated the comparison of methods that integrate over daily and several week timescales. Primary productivity values from on-deck 24 h $^{14}$C incubations and gross carbon production values from photosynthesis-irradiance experiments were nearly identical even during highly dynamic periods of net heterotrophy, while gross oxygen production measurements were 3.5–4.2 times higher but with uncertainties in that ratio near ±2. These comparisons show that the photosynthesis-irradiance experiments based on 1–2 h $^{14}$C incubations underestimated gross carbon production.


1. Introduction

[2] The Southern Ocean Gas Exchange Experiment (SO GasEx) examined air-sea gas exchange in a region with high wind speeds and globally significant CO$_2$ fluxes, with the supplementary goal of understanding processes controlling mixed layer $p$CO$_2$ [Ho et al., 2011a]. Productivity measurements were included in this process study to constrain the carbon mass balance. Our two specific goals for this paper are to elucidate the changing productivity rates during SO GasEx and to compare the many productivity methods used during the experiment.

[3] The SO GasEx site (near 51°S, 38°W), in the southwest Atlantic sector of the Southern Ocean, north of the Polar Front, is a region of net uptake of atmospheric CO$_2$, though $p$CO$_2$ data and inverse models differ as to whether
this region was a natural carbon sink through biological drawdown [Takahashi et al., 2002, 2009; Gruber et al., 2009]. Despite the importance of the Southern Ocean as a CO₂ sink, productivity measurements are relatively sparse in this region and average estimates rely on satellite algorithms [Arrigo et al., 2008]. Spatial surveys have been conducted of net community production from O₂/Ar [e.g., Reuer et al., 2007; Guéguen and Tortell, 2008; Cassar et al., 2011], primary production from ¹³C incubations [e.g., Laubscher et al., 1993; Strutton et al., 2000; Hiscock et al., 2003; Vaillancourt et al., 2003], and export production from sediment traps [Wefer and Fischer, 1991; Trull et al., 2001] and ²³⁴Th measurements [Buesseler et al., 2003].

In contrast to these large surveys, SO GasEx focused on the evolution of biogeochemical properties in two specific water masses that were tracked after injecting ³He/SF₆ into the mixed layer [Ho et al., 2011a]. By following the labeled water masses, or “patches,” in a Lagrangian fashion, observed changes could be attributed to processes within the water mass rather than lateral variability. While other patch experiments in the Southern Ocean have involved iron fertilization [e.g., Boyd et al., 2000; Coale et al., 2004], SO GasEx did not add iron to the tracer patch and so focused on natural processes. Through investigating the variations in productivity rates in this one region and season, we provide insight into the sources of variability within larger spatial surveys and data compilations.

Due to the potential for methodological biases and because the various productivity methods target different timescales and processes, the relationship of productivity measurements to carbon cycle fluxes can be ambiguous. Method intercomparison studies are helping to constrain the relationships between methods and identify accuracy problems [e.g., Robinson et al., 2009; Quay et al., 2010]. However, more comparisons are needed in a wider variety of regions and seasons. We add to this effort to characterize the relationships between productivity measured using different methods by presenting a comparison of nine different productivity methods used during SO GasEx. Our study is noteworthy in that two specific water masses were followed over a relatively long period, allowing us to explore the impact of changing conditions on productivity methods that integrate over different timescales.

2. Methods

Two sequential Lagrangian experiments were conducted during SO GasEx. In each, a patch of ³He/SF₆-enriched water was created by injecting the tracers into the mixed layer in a low pCO₂ (<315 μatm) region. No iron was added to the injected water. These patches were continuously surveyed with surface, underway measurements and sampled by a conductivity-temperature-depth (CTD)/Niskin depth cast approximately twice a day. A drifting buoy with subsurface O₂ and pCO₂ sensors was also deployed in the patches [Moore et al., 2011; Ho et al., 2011a].

2.1. Dissolved Gas Sampling and Analysis

Discrete samples for dissolved O₂/Ar and O₂ isotopes were collected both from Niskin bottles and from the ship’s underway seawater supply following the methods of Emerson et al. [1999] and Reuer et al. [2007]. Briefly, 500 mL glass flasks, with 9 mm Louwers O-ring sealing valves, were poisoned with HgCl₂ and evacuated before the cruise. At sea, seawater was flushed through the flask necks, and then the stopcocks were slightly opened to admit water until the flasks were half full. Sample water was left in the flask necks, which were capped with vinyl.

Back at the lab, following equilibration with the headspace, the water was removed from the flasks. Approximately half the samples were analyzed for O₂/N₂/Ar ratios while the other half were analyzed for O₂/Ar ratios and δ¹⁸O-

2.2. Methods

Continuous O₂/Ar measurements were made on the ship’s underway seawater supply by equilibrator inlet mass spectrometry (EIMS) following Cassar et al. [2009]. Seawater passed over an optode O₂ sensor (Aanderaa Model 4175) and was then pumped through a gas-permeable membrane contactor cartridge. Dissolved gases equilibrated with the gases in the headspace from which a fused silica capillary picked off the headspace gases and transported them to a quadrupole mass spectrometer. Every 2 h, ambient air was introduced to the mass spectrometer through a second capillary in order to calibrate the dissolved O₂/Ar ion current ratio. The continuous O₂/Ar data were further calibrated by comparison to the discrete samples. We measured a positive mean O₂/Ar offset of 0.60 ± 0.09% between the continuous O₂/Ar measurements and discrete samples for the equilibrator cartridge used throughout patch 1, but a small negative offset of −0.08 ± 0.04% for the cartridge used throughout patch 2 (quoted uncertainty is the standard deviation of the mean). These mean offsets were applied as a constant correction to the continuous data. It appears that the membrane of the cartridge used throughout patch 1 was partially clogged (both gas pressure inside the mass spectrometer and measured ΔN₂/Ar ratios were lower than for the two other cartridges used on this cruise). Reduced exchange of gases across the cartridge membrane would tend to increase ΔO₂/Ar, because O₂ is slightly more soluble than Ar, so a smaller fraction of the total dissolved O₂ must cross the membrane to bring the headspace O₂/Ar into
equilibrium with the dissolved phase. We feel that the most accurate way of dealing with potential variability in membrane transmission properties is to calibrate the continuous measurements against the discrete data as we have done.

[10] Additionally, dissolved O2 concentrations were measured at every Niskin depth and with every discrete O2/Ar sampling of the underway system by a variant of the classic Winkler titration with amperometric detection of the endpoint [Culberson and Huang, 1987]. The pooled standard deviation of duplicates for Niskin samples was 0.21 μmol kg⁻¹ (about ±0.07%). No difference was found between O2 measurements from mixed layer Niskin and underway system samples collected at the same time [Juranek et al., 2010], showing that the underway samples were not affected by respiration in the ship’s plumbing during this cruise. Optode O2 concentrations were calibrated against the discrete Winkler samples following Uchida et al. [2008].

2.2. Net Community Production: Discrete and Continuous O2/Ar

[11] Net community production (NCP, the difference between gross production and community respiration) was assessed by O2/Ar mass balance using both discrete and continuous measurements. Because O2 and Ar have very similar physical properties (solubility, temperature dependence, diffusion rates), ΔO2/ΔAr is a measure of the biological O2 supersaturation, with Ar correcting for the impact of physical processes on O2, such as bubble-mediated gas exchange [Craig and Hayward, 1987]. Processes that can cause O2/Ar changes in the mixed layer include air-sea gas exchange, net community production (photosynthesis and respiration), vertical entrainment/mixing, and lateral mixing.

[12] Typically, the contributions of vertical and lateral exchanges are not assessed and ΔO2/ΔAr is assumed to be constant with time in the mixed layer. In this simplest steady state case, net community O2 production is balanced by air-sea exchange of biological O2 and can be estimated by

\[ \text{NCP} = k_w(\Delta O_2/\Delta Ar)[O_2]_{eq}\rho, \]

where \( k_w \) is the weighted gas transfer velocity for O2 (m d⁻¹), \([O_2]_{eq}\) is the equilibrium concentration of O2 in the mixed layer (μmol kg⁻¹), and \( \rho \) is mixed layer density (kg m⁻³) [Reuer et al., 2007]. This calculation of NCP can be applied to any individual ΔO2/ΔAr measurement, but assumes that NCP has been constant over at least the residence time of O2 in the mixed layer, approximately 10 days during this experiment. We refer to this NCP estimate as “prior O2/Ar-NCP” in this paper, since it quantifies NCP over a time period prior to the measurement of mixed layer O2/Ar. We estimate \( k_w \) using QSCAT/NCEP Blended Ocean Winds from Colorado Research Associates (data set number ds4744.4 [Chin et al., 1998]), the wind speed parameterization of Ho et al. [2006], and the gas exchange weighting algorithm of Reuer et al. [2007], which accounts for variable wind speeds up to 60 days prior to the O2/Ar measurement. Gas transfer velocities from \(^3\)He/SF₆ measurements during SO GasEx confirm that Ho et al. [2006] is an appropriate gas exchange parameterization for this experiment [Ho et al., 2011b]. NCP values in O₂ units were converted to C units using a O₂/C ratio of 1.4, appropriate for growth on nitrate [Laws, 1991].

[13] Our unique observations of the evolution of ΔO2/ΔAr over time in the patches allow us to refine the O2/Ar mass balance to include the rate of change in ΔO2/ΔAr in the mixed layer [Cassar et al., 2011]

\[ \text{NCP} = k_c(\Delta O_2/\Delta Ar)[O_2]_{eq}\rho + h\frac{d(\Delta O_2/\Delta Ar)}{dt}[O_2]_{eq}\rho, \]

where \( k_c \) is the (nonweighted) gas transfer velocity for O2 (m d⁻¹), and \( h \) is the mixed layer depth (m). To estimate the rate of change in ΔO2/ΔAr, we fit a linear regression to 1 h means of the continuous, underway ΔO2/ΔAr data within the tracer patch, as defined by the underway SF₆ measurements. We choose data segments several days long to estimate the rate of change in ΔO2/ΔAr, starting and ending the segment at the same time of day to avoid biasing the slope by diurnal variations in ΔO2/ΔAr (i.e., 72 or 96 h data segments). For the gas exchange term, we integrated gas exchange estimates over the same several day time period using the 1 h means of the continuous, underway ΔO2/ΔAr and 1 h means of \( k_w \), based on wind speeds measured at the ship and the Ho et al. [2006] parameterization. The error in NCP was estimated by propagating uncertainty in the following individual terms: \( k_w \pm 10\% [Ho et al., 2011b], \) mean ΔO2/ΔAr ± 0.09 or 0.04% (the standard deviation of the mean in the EIMS versus discrete sample offset for each patch), \( h \pm 5 \) m [Ho et al., 2011a], and \( d(\Delta O_2/\Delta Ar)/dt \) plus or minus the standard deviation in the slope estimate (typically 0.02–0.04% d⁻¹). Contributions from vertical and lateral exchanges are assessed in section 3. We refer to this method of estimating NCP as “real-time O2/Ar-NCP” in this paper, since it quantifies NCP during the time period of the measurements.

2.3. Gross O2 Production: Triple O2 Isotopes

[14] Gross production of O2 (GOP) in the mixed layer was determined from the \( \delta^{17}\text{O}-\text{O}_2 \) and \( \delta^{18}\text{O}-\text{O}_2 \) isotopic measurements of the discrete dissolved gas samples. We assume that the dominant processes affecting mixed layer oxygen isotopes are air-sea gas exchange, photosynthesis, and respiration. Oxygen in the stratosphere is mass independently fractionated, imparting an anomalously depleted \( \delta^{17}\text{O} \) composition to atmospheric O2. Photosynthesis produces O2 from water [Luz and Barkan, 2011a], with a mass-dependent isotopic distribution. Respiration preferentially consumes the lighter isotopes, but in a normal mass-dependent fractionation that is well constrained [Luz and Barkan, 2005]. For a mixed layer with high productivity but low gas transfer velocities, the \( \delta^{17}\text{O} \) excess of the dissolved O2 will be high, while low productivity and high gas transfer velocities will yield a lower \( \delta^{17}\text{O} \) excess. Mixed layer mass balances for each of the three oxygen isotopes, involving air-sea gas exchange, photosynthesis, and respiration can be combined to yield the ratio of gross O2 production to sea-to-air evasion (GOP/\( k_o[O_2]_{eq} \)) from dissolved oxygen isotopic compositions and isotopic fractionation factors [Kaiser, 2011; Prokopenko et al., 2011]. See Appendix A for complete details of this calculation. Gross O2 production can then be estimated from the weighted gas transfer velocity, calculated as in section 2.2, and the dissolved concentration of O2 at equilibrium [Garcia and Gordon, 1992, 1993].
2.4. Gross O$_2$ Production: Diurnal O$_2$/Ar Changes (Diurnal-O$_2$ GOP)

[15] The continuous, underway $\Delta$O$_2$/Ar measurements in the tracer patches showed consistent diurnal changes, creating the opportunity for a second estimate of gross O$_2$ production. Nighttime changes in $\Delta$O$_2$/Ar are caused by a combination of respiration and air-sea gas exchange, while daytime changes include gross O$_2$ production in addition to these other two processes. We calculated the minimum and maximum $\Delta$O$_2$/Ar each day as the average of the continuous $\Delta$O$_2$/Ar measurements within the patch, as determined by the underway SF$_6$ measurements, in 3 h windows centered on dawn and dusk. Gross O$_2$ production was calculated from the daytime change in $\Delta$O$_2$/Ar minus the average of the nighttime change for the previous and subsequent nights. Essentially, this technique is an in situ light–dark experiment with the added complication that O$_2$ concentration changes reflect air-sea gas exchange as well as photosynthesis and respiration. It assumes that nighttime gas transfer velocities and respiration are characteristic of those during daytime, ignoring possible effects such as enhanced gas exchange due to convection, light enhancement of O$_2$ consumption, and diurnal vertical migration of zooplankton.

[16] Wind speeds, and hence gas transfer velocities, were not characterized by diurnal variations during SO GasEx. Light-enhanced autotrophic respiration has been observed in both pure phytoplankton cultures and natural populations, with ratios of respiration rates in the light to those in the dark ranging from near 1 to over 5 [e.g., Grande et al., 1989; Pringault et al., 2007]. If daytime respiration rates were higher than nighttime rates during SO GasEx, this would bias our Diurnal-O$_2$/Ar GOP estimates too low. We estimate the potential impact of zooplankton migration based on abundance and respiration rates of Antarctic krill. Average summer abundance for krill in the region of our station is $\sim$10 individuals m$^{-2}$, with each individual having a mean dry mass of $\sim$600 mg [Atkinson et al., 2008, 2009]. Conversion to O$_2$ consumption rates using the relationship of Ikeda [1984] and assuming that krill are only present in the mixed layer at night suggests a decrease of 0.02 $\mu$mol O$_2$ kg$^{-1}$ each night due to the presence of migrating zooplankton, which would not have a significant impact on our GOP estimate. We conclude that the most likely source of systematic error in Diurnal-O$_2$ GOP estimates is an underestimate due to light-enhanced respiration.

2.5. New and Primary Production: On-Deck Incubations ($^{15}$N-NewP and $^{14}$C-PP)

[17] Incubation techniques for new and primary production measurements during SO GasEx are fully described by V. P. Lance et al. (Primary productivity, new productivity and carbon export during two Southern Ocean Gas Exchange (SO GasEx) tracer experiments, submitted to Journal of Geophysical Research, 2011). Briefly, water was collected at depths representing six light levels during the night CTD cast. Just prior to dawn, water was spiked with either a Na$_2^{14}$CO$_3$ or K$_2^{15}$NO$_3$ solution. Samples were then placed in an on-deck incubator screened to simulate the six ambient light levels and with temperature maintained by continuously circulating surface seawater. After 24 h, incubations were ended by gentle filtration onto Whatman GF/F filters, followed by $^{14}$C activity measured on board or $^{15}$N isotopic abundance measured later at the Marine Sciences Institute, UC Santa Barbara. Water column production was calculated by trapezoidal integration of discrete values to the 1% light level, which was estimated from in situ PAR (photosynthetically active radiation, 400 to 700 nm) measured during the daytime cast prior to sample collection. New production ($^{15}$N-NewP) was converted from N to C units using the canonical 6.6 Redfield ratio, similar to measured particulate organic carbon (POC):particulate organic nitrogen values of 5.7–6.5 during SO GasEx (Lance et al., submitted manuscript, 2011).

2.6. Gross Primary Production: Photosynthesis-Irradiance Experiments (PE-GPP)

[18] Gross primary production was estimated from photosynthesis versus irradiance experiments conducted on seawater from 8 to 10 depths within the upper 75–100 m. This technique is thought to approximate gross productivity because the incubation times are short (1–2 h) relative to the time that newly fixed carbon becomes available for respiration [Dring and Juxson, 1982]. Briefly, water samples collected at each depth were split into thirteen subsamples that were incubated with NaH$^{14}$CO$_3$ for 1–2 h at mixed layer temperatures within a photosynthetron chamber that provided each subsample with a different light level. At the end of the incubation, water samples were filtered and the $^{14}$C activity of the particulate fraction measured. The carbon uptake versus irradiance data for each depth was then fitted with a nonlinear equation relating irradiance levels to carbon uptake to derive photosynthetic efficiency, $\alpha$ (mmol C (mg Chla)$^{-1}$ h$^{-1}$ ($\mu$mol quanta m$^{-2}$ s$^{-1}$)$^{-1}$), and the maximum photosynthetic rate, $P_{max}$ (mmol C (mg Chla)$^{-1}$ h$^{-1}$). These parameters were then applied to the daily light levels at each depth to produce daily photosynthesis rates at those depths. Depth-integrated productivity was calculated from the surface to the base of the euphotic zone at 50 m using trapezoidal integration of the discrete depth values. See Appendix B for further methodological details and an example carbon uptake versus irradiance curve.

2.7. Net Community Production: Drifter O$_2$ and pCO$_2$ Mass Balance

[19] NCP was also assessed from pCO$_2$ and O$_2$ sensors on the MAP-CO$_2$ drifter, fully described by Moore et al. [2011]. Briefly, the drifter was deployed twice in patch 1 and once in patch 2, with SAMI-CO$_2$ and Aanderaa optode sensors measuring pCO$_2$ and O$_2$ at six depths from 5 to 105 m. Dissolved inorganic carbon (DIC) concentrations were calculated from the in situ pCO$_2$, temperature, and salinity observations, and shipboard alkalinity. NCP estimates from both the C and O$_2$ measurements were derived from mass balances that incorporated air-sea gas exchange based on the wind speed parameterization of Ho et al. [2006], entrainment fluxes when the mixed layer deepened, and bubble-mediated gas exchange for O$_2$. Equilibrium O$_2$ concentrations for gas exchange calculations were corrected for the persistently low atmospheric pressure. We only consider the first and third deployments of the drifter here, because the second deployment occurred mainly when the ship was off-site, so there are few overlapping measurements. During
the third deployment (patch 2), the drifter separated from the main patch sampled by the ship around 26 March 2008.

2.8. Ancillary Measurements

[20] Discrete DIC samples were collected at every Niskin depth into cleaned, precombusted, 300 mL Pyrex bottles and poisoned with 0.2 mL of 50% saturated HgCl2. Samples were analyzed within 12 h using a Single Operator Multi-parameter Metabolic Analyzer (SOMMA)-coulometer system based on the principles outlined by Johnson et al. [1985, 1987]. The precision and accuracy of the SOMMA DIC system is estimated to be about ±1 μmol kg−1 based on the analysis of duplicate samples and certified reference materials (CRMs) prepared by A. Dickson of Scripps Institution of Oceanography (http://andrew.ucsd.edu/co2qc/).

[21] Discrete chlorophyll samples were collected from Niskin casts, gently vacuum filtered onto Whatman GF/F filters, extracted into 100% methanol for 24 h in the dark at −20°C, and read on a Turner 700 fluorometer that had been calibrated with a commercial chlorophyll standard (Lance et al., submitted manuscript, 2011). Underway, surface chlorophyll fluorescence from the ship’s seawater system was measured at a 1–10 s frequency with a Turner Designs Cyclops7 sensor with wiper, attached to a C6 instrument. Incident PAR data (Lance et al., submitted manuscript, 2011) were used to adjust daytime chlorophyll fluorescence, suppressed by nonphotochemical quenching, to match nighttime average values each day, and were further calibrated against the discrete chlorophyll concentrations in units of mg chl-a m−3.

[22] Underway SF6 measurements were made using an automated continuous SF6 analysis system [Ho et al., 2002] and used to identify when underway measurements were within the tracer patches. Briefly, a gas extraction unit continuously stripped SF6 from the ship’s seawater line, which was then analyzed by a gas chromatograph (GC) equipped with an electron capture detector (ECD). The system had a sampling and measurement interval of 1 min and a detection limit of 1 × 10−14 mol L−1.

[23] Wind speeds were measured on the ship by three sonic anemometer packages on the forward mast [Ho et al., 2011a]. Underway temperature was measured with a Sea-Bird SBE 21 at the ship’s intake, and underway salinity with a Sea-Bird SBE 45 as part of another underway system in the main lab. Underway salinity values were calibrated against the CTD/Rosette surface salinities. Mixed layer depths at discrete sampling stations were defined as the shallowest depth in the 1 dbar bin-averaged downcasts with a density at least 0.01 kg m−3 greater than the density at 5 dbar [Ho et al., 2011a]. Euphotic zone depths were defined as the 1% light level based on the diffuse attenuation coefficient of PAR (calculated from the log-transformed linear regression of PAR versus depth for daytime CTD casts).

3. Patch Dynamics

3.1. Patch 1: Net Autotrophic

[24] Tracer patch 1 was injected on 8 March 2008, creating a tagged water mass approximately 50 km2. Surface surveys of the wider region (approximately 2° latitude × 2° longitude) prior to patch injection showed significant physical and biological patchiness with prior O2/Ar-NCP ranging from 5 to over 30 mmol C m−2 d−1 [Ho et al., 2011a]. Underway measurements of the tracer patch began immediately after injection, with CTD/Niskin casts near the patch center starting 10 March. Observations of this patch were halted on 14 March to take shelter from a storm, with the patch remnant resampled once on 18 March. We focus on the 9–14 March time period in the following analysis when the availability of frequent, ship-based observations allows us to make estimates of the potential impact of entrainment and lateral advection on mixed layer budgets. The impact of the storm (14–17 March) is examined qualitatively.

[25] Discrete observations from the CTD/Niskin casts during the initial 4 days of patch 1 demonstrated net autotrophy, photosynthesis exceeding community respiration. Mixed layer temperature increased slightly while salinity was stable (Figure 1). The mean mixed layer depth based on the CTD casts for the first 4 days of patch 1 was 37 m, but varied from 46 m at the start to a brief shoaling to 14 m on 12 March followed by a return to 48 m by 14 March (Figure 1). In this period, the mean O2 transfer velocity was 4.2 m d−1, yielding a mean residence time for O2 of approximately 9 days. Mixed layer depths estimated from temperature sensors at discrete depths on the drifter were 35 m on average during 9–12 March. Mixed layer ΔO2/Ar ratios were supersaturated, indicating recent net biological O2 production, but were slowly decreasing (Figure 1). Oxygen concentrations decreased by ~3 μmol kg−1 over the first 4 days of patch 1, while chlorophyll, DIC (Figure 1), and nutrient (Figure 4 of Lance et al., submitted manuscript, 2011) concentrations showed some variability but no significant trend. Means and standard deviations for mixed layer nutrient concentrations during patch 1 were 16.9 ± 0.4 μmol kg−1 for nitrate, 1.15 ± 0.04 μmol kg−1 for phosphate, and 0.6 ± 0.3 μmol kg−1 for silicic acid (Lance et al., submitted manuscript, 2011).

[26] The underway ΔO2/Ar measurements revealed large diurnal changes as well as a secular decrease of 0.15 ± 0.04% d−1 (Figure 2). Prior O2/Ar-NCP during the first 4 days of patch 1 was 17 ± 5 mmol C m−2 d−1, estimated using a steady state assumption where biological production balances gas exchange. This value characterizes the mixed layer roughly 9 days (the residence time) before samples were collected, approximately 2–11 March. Decreasing ΔO2/Ar over time in the underway measurements shows that the system was not at steady state during the 9–13 March occupation of the patch. The mass balance for this period, invoking the observed ΔO2/Ar decrease, resulted in a ~60% lower real-time O2/Ar-NCP estimate of 7 ± 5 mmol C m−2 d−1.

[27] Given that this relatively modest time-dependent change in ΔO2/Ar had a large effect on the NCP mass balance calculation, we need to evaluate whether the decrease in ΔO2/Ar over 9–13 March may have arisen from physical processes such as vertical or lateral mixing rather than biological productivity and respiration. Profiles of O2 concentration from the CTD sensor showed that there was little vertical gradient in O2 directly below the mixed layer (Figure 3). However, ΔO2/Ar ratios decreased below the mixed layer due to increasing Ar concentrations, here estimated from Ar solubility based on depth profiles of potential temperature and salinity [Hamme and Emerson, 2004]. Mixed layer depths determined from the CTD downcasts in patch 1 were never more than 2 m deeper than the value
from the first cast (Figure 1). However, diagnosing the true extent of mixed layer entrainment from the CTD casts is complicated by an internal wavefield that caused displacements of the base of the mixed layer on timescales of 12 h [Moore et al., 2011]. Mixed layer density decreased during patch 1, arguing against large-scale entrainment, but mixed layer depths derived from the drifter temperature sensors suggested a 4–5 m deepening over the observation period. Taking 5 m as the maximum likely entrainment, we calculated the expected change in mixed layer properties for each CTD profile if the upper water column was mixed to a depth 5 m deeper than the CTD-determined mixed layer depth. This yielded maximum contributions to ΔO2/Ar of −0.1%, to O2 concentrations of −0.15 μmol kg⁻¹, and to DIC concentrations of +1–2 μmol kg⁻¹ over the 3 day observation period, which are of similar magnitude to the O2 and DIC entrainment estimates of Moore et al. [2011]. Including this maximum estimated contribution of entrainment to mixed layer ΔO2/Ar results in an entrainment-corrected real-time O2/Ar-NCP of 9 ± 4 mmol C m⁻² d⁻¹.

To diagnose the potential effect of diapycnal mixing (by which we mean vertical mixing fluxes that do not result in a deeper mixed layer), we implemented a Price-Weller-Pinkel (PWP) model for O2 and Ar during patch 1 [Price et al., 1986; Hamme and Emerson, 2006]. This one-dimensional, mixed layer model was initiated with the first patch 1 CTD profiles of temperature, salinity, and O2, and an Ar profile estimated from temperature, salinity, and measured Ar saturations in the mixed layer. Ship-based meteorological heat fluxes and wind speeds [Ho et al., 2011a] were used to drive the model. Using an upper bound, eddy diffusivity of 1.0 cm² s⁻¹, vertical mixing in the model contributed only a 0.025% d⁻¹ decrease to mixed layer ΔO2/Ar. This potential contribution from diapycnal mixing was within the error of the slope for the observed decrease in ΔO2/Ar (±0.04% d⁻¹).

Lateral dilution of the patch by surrounding water masses may explain some of the observed variability, but is unlikely to have caused the observed decrease in ΔO2/Ar. Underway surveys between each CTD cast demonstrated lateral variability in temperature, salinity, and O2, and an Ar profile estimated from temperature, salinity, and measured Ar saturations in the mixed layer. Ship-based meteorological heat fluxes and wind speeds [Ho et al., 2011a] were used to drive the model. Using an upper bound, eddy diffusivity of 1.0 cm² s⁻¹, vertical mixing in the model contributed only a 0.025% d⁻¹ decrease to mixed layer ΔO2/Ar. This potential contribution from diapycnal mixing was within the error of the slope for the observed decrease in ΔO2/Ar (±0.04% d⁻¹).

Figure 1. Patch 1 discrete mixed layer values of (a) potential temperature, (b) salinity, (c) mixed layer and euphotic zone depths from CTD downcasts, (d) ΔO2/Ar, (e) O2 concentration, (f) DIC concentration, and (g) chlorophyll concentration from CTD/Niskin casts. Line in Figure 1e indicates equilibrium O2 concentration (mainly driven by variations in atmospheric pressure).
[30] Given that the maximum likely contribution of vertical processes to mixed layer $\Delta O_2/Ar$ during 9–13 March could account for only a third of the observed decrease over this time and that lateral processes appear to have played a minimal role, we conclude that the observed decrease in $\Delta O_2/Ar$ must have been mainly a result of lower NCP compared to the time period before patch 1 observations began. This fits with the higher prior $O_2/Ar$-NCP estimate, which integrates NCP mostly over the time period before patch 1 observations began, compared with the real-time $O_2/Ar$-NCP estimate, which integrates only over the period of observations during patch 1. Finally, we note that an NCP of 9 mmol C m$^{-2}$ d$^{-1}$ over a 47 m mixed layer translates into an expected mixed layer DIC decrease of less than 1 mmol kg$^{-1}$ over the first 4 days of patch 1, while air-sea gas exchange is expected to have increased DIC by 0.9 mmol C m$^{-2}$ d$^{-1}$ –9 mmol C m$^{-2}$ d$^{-1}$ –9 mmol C m$^{-2}$ d$^{-1}$ over the first 4 days of patch 1, while air-sea gas exchange is expected to have increased DIC by 0.9 mmol C m$^{-2}$ d$^{-1}$ –9 mmol C m$^{-2}$ d$^{-1}$ over the first 4 days of patch 1, while air-sea gas exchange is expected to have increased DIC by 0.9 mmol C m$^{-2}$ d$^{-1}$ –9 mmol C m$^{-2}$ d$^{-1}$ –9 mmol C m$^{-2}$ d$^{-1}$ over the first 4 days of patch 1, while air-sea gas exchange is expected to have increased DIC by 0.9 mmol C m$^{-2}$ d$^{-1}$ over this period. A combined DIC change near zero is well within the variability of the DIC observations (Figure 1).

[31] After the storm, the remnant of patch 1 was sampled on 18 March 2008. Compared to earlier observations of this patch, $\Delta O_2/Ar$ ratios and $O_2$ concentrations were lower, while DIC values were higher (Figure 1). Mixed layer nutrient and POC concentrations were similar to prestorm values (Figures 4 and 9 of Lance et al., submitted manuscript, 2011). These trends suggest that entrainment and high rates of gas exchange, caused by high wind speeds during the storm, brought mixed layer gas concentrations closer to equilibrium values. The mixed layer depth was shallower after the storm, but this could have been caused by a temporary restratification and does not indicate low entrainment during the storm. Significant SF$_6$ tracer concentrations were detected to a depth of 77 m on 18 March [Ho et al., 2011a], but depth levels of the density horizons from this cast indicate considerable depression of the isopycnals throughout the shallow portion of the water column, likely by internal waves. Without observations of the patch during the storm period, the contributions of gas exchange, respiration, and especially entrainment to the $O_2/Ar$ mass balance are not easily constrained, so we do not attempt a calculation of NCP during this latter period of patch 1.

3.2. Patch 2: Net Heterotrophic

[32] Tracer patch 2 was injected on 21 March 2008, approximately 60 km to the south of the patch 1 injection site, creating a smaller tagged water mass of approximately 12.5 km$^2$. Surface surveys of the wider region (approximately 1° latitude × 2° longitude) prior to patch injection generally showed lower prior $O_2/Ar$-NCP than near the patch 1 site, ranging from 0 to 10 mmol C m$^{-2}$ d$^{-1}$ [Ho et al., 2011a]. Given the separate locations of the injection sites and the strong advection of both patches to the southeast, patch 2 cannot be considered a continuation of patch 1 but instead a separate water mass with an unknown prior history. Underway measurements began after the injection, and CTD/Niskin casts commenced 22 March. The productivity dynamics of patch 2 were very different from patch 1, with rapidly changing mixed layer properties over the first 4 days of observations suggesting strong net heterotrophy.

[33] Between 22 and 26 March 2008, mixed layer $\Delta O_2/Ar$ and $O_2$ concentrations decreased rapidly with $\Delta O_2/Ar$ values becoming undersaturated (Figure 5). Mean $O_2$ transfer velocities were 7.1 m d$^{-1}$, yielding an $O_2$ residence time of 8 days. Mixed layer chlorophyll decreased to half its initial concentration (Figure 5), while POC concentrations decreased by one third, and fucoxanthin concentrations (a diagnostic pigment for diatoms) decreased by one half (Figures 8 and 9 of Lance et al., submitted manuscript, 2011). These properties all changed most rapidly in the first 2 days of observations, continuing their decreases at a slower rate over the following 2 days. Mixed layer DIC concentrations increased ~5 mmol kg$^{-1}$ (Figure 5), while nitrate concentrations increased from 14.0 to 14.7 mmol kg$^{-1}$, phosphate increased slightly from 1.00 to 1.08 mmol kg$^{-1}$, and silicic acid increased from 2.1 to 2.6 mmol kg$^{-1}$ (Lance et al., submitted manuscript, 2011). Finally, mixed layer temperature decreased ~0.15°C and salinity increased nearly 0.01 (Figure 5). These changes in DIC, nutrients, temperature, and salinity were most pronounced during days 3 and 4 of the patch 2 observations (24–26 March).

[34] Following a rainstorm on 26 March, fresh water caused the mixed layer to shoal to 12 m, returning to
previously observed depths of $\sim$55 m by 29 March (Figure 5) [Ho et al., 2011a]. Throughout the rest of the patch 2 observations, discrete $\Delta O_2/Ar$ measurements showed continued undersaturation (Figure 5). Oxygen concentrations were near equilibrium through this period, and mixed layer chlorophyll increased slightly. Nutrients and DIC continued to increase slowly (Figure 4 of Lance et al., submitted manuscript, 2011 and Figure 5).

The underway $\Delta O_2/Ar$ observations also showed a rapid decrease over the first 4 days of patch 2, slowing but still decreasing after the rainstorm, and increasing over the last 4 days (Figure 6). During the initial 4 days, changes in $\Delta O_2/Ar$ data observed in the underway data indicate strongly heterotrophic conditions with an apparent real-time $O_2/Ar$-NCP of $-48 \pm 6$ mmol C m$^{-2}$ d$^{-1}$. Heterotrophic conditions persisted after the rainstorm with an estimated real-time $O_2/Ar$-NCP of $-21 \pm 3$ mmol C m$^{-2}$ d$^{-1}$ from 28 March to 1 April, becoming net autotrophic with a real-time $O_2/Ar$-NCP of $13 \pm 4$ mmol C m$^{-2}$ d$^{-1}$ from 1 to 5 April. The contribution to the $\Delta O_2/Ar$ mass balance from the rate of change in mixed layer $\Delta O_2/Ar$ dominated the contribution from air-sea gas exchange during all three of these periods. We refrained from estimating NCP during 26–28 March when the mixed layer depth was changing rapidly.

**Figure 3.** Example profiles of (a) potential temperature, (b) salinity, (c) density ($\sigma_b$), (d) $O_2$ concentration (lines are the CTD-$O_2$ sensor and dots are discrete samples), (e) predicted $\Delta O_2/Ar$, and (f) DIC concentration. Here $\Delta O_2/Ar$ is predicted from the CTD $O_2$ assuming $\Delta Ar$ is constant with depth. Shown are profiles from the beginning of patch 1 (10 March), beginning of patch 2 (22 March), and just before the large rainstorm on 26 March. Example profiles of nitrate and phosphate are presented by Lance et al. (submitted manuscript, 2011).
We can only conclude that high rates of net heterotrophy were indeed observed if contributions from vertical and lateral mixing to the ΔO2/Ar mass balance were small. The trends in mixed layer temperature, salinity, ΔO2/Ar, DIC, nutrients, chlorophyll, and POC were all in the direction expected for vertical entrainment by a deepening mixed layer (Figures 3 and 5 of Lance et al., submitted manuscript, 2011). However, we will show, based on two different calculations as well as on the chlorophyll and POC changes, that entrainment can explain less than half of the observed changes in ΔO2/Ar and that significant changes to the biological community accompanied the physical alterations to the mixed layer during the 22–26 March period.

Mixed layer depths from the CTD downcasts suggest that the mixed layer deepened from 44 m to as much as 64 m between 22 and 25 March (Figure 5). However, as with patch 1, the internal wavefield complicates estimation of true mixed layer entrainment from the CTD casts alone. For example, the σθ 26.8 isopycnal on the two casts with the deepest mixed layers during this time was 7 m deeper than the average on the other six casts, so the mixed layer depth was likely temporarily depressed by a similar amount. Instead, we use two alternate methods to estimate the impact of entrainment on mixed layer budgets. Both methods conservatively assume that changes in mixed layer density and temperature during this period can be fully ascribed to entrainment of water from beneath. This is almost certainly an overestimate. A one-dimensional model (GOTM) implemented for the patches shows that local surface forcing is unable to explain the cooling temperatures and increasing densities during the first few days of patch 2 and that colder/saltier water was likely mixed into the patch from the south [Ho et al., 2011a].

First, we turn to density differences to diagnose entrainment of water into the mixed layer. Density in the mixed layer increased from σθ 26.68 to σθ 26.71 over the first 4 days of patch 2 observations. To estimate the maximum possible effect that vertical entrainment might have had on the gas budget for the period 22–26 March, we calculated the expected change in mixed layer properties for each CTD profile if the upper water column was mixed down to the σθ 26.90 isopycnal, which would yield a mixed layer density of 26.71. The maximum effect of vertical entrainment on ΔO2/Ar would have been a decrease of 0.7%, less than half of the 1.7% decrease observed in ΔO2/Ar over these 4 days. Including this maximum estimated contribution of entrainment to mixed layer ΔO2/Ar results in a corrected real-time O2/Ar-NCP of −29 ± 4 mmol C m⁻² d⁻¹. The estimated effect of vertical entrainment on O2 concentrations was a decrease of 0.7 μmol kg⁻¹ compared to an observed decrease of 3.3 μmol kg⁻¹. The possible effect of entrainment on DIC concentration is more difficult to estimate because the gradient beneath the mixed layer was not fully resolved by discrete depth sampling. However, if we interpolate between the discrete samples, we estimate that entrainment contributed up to 5 μmol kg⁻¹ to the DIC increase. These estimated entrainment-induced O2 and DIC changes for 22–26 March are about 50% higher than estimates from the drifter data over the same period [Moore et al., 2011, Figure 7].
Second, we make use of the strong relationships between potential temperature and \( \Delta O_2 \) or DIC beneath the mixed layer to estimate the impact of entrainment. Potential temperature decreased 0.22°C in the mixed layer over the first 4 days of patch 2. We fit linear trends between potential temperature and \( \Delta O_2 \) and between potential temperature and DIC for discrete data collected directly under the mixed layer during patch 2. Combining our estimates of \( \frac{d\Delta O_2}{dT} \) and \( \frac{dDIC}{dT} \) with the observed change in temperature results in an estimated decrease of 0.5% in \( \Delta O_2 \), which should approximate the decrease for \( \Delta O_2/Ar \) and an estimated increase of 4 \( \mu \text{mol kg}^{-1} \) in DIC. These values are similar to but a bit smaller than our density based calculation above.

Finally, this initial period of patch 2 saw significant alterations to the biological community that vertical entrainment cannot explain. Mixed layer chlorophyll and fucoxanthin concentrations decreased by half and POC concentrations by one third over these 4 days (Lance et al., submitted manuscript, 2011). Even if chlorophyll and POC concentrations were zero beneath the mixed layer, vertical entrainment could at most have produced 20% decreases in these quantities, significantly less than observed. Export of particulate matter from the mixed layer, due to bloom senescence or other causes, could explain the decreases in chlorophyll, POC, and fucoxanthin. However, export would not have affected the dissolved constituents, such as \( \Delta O_2/Ar \), and so cannot explain the observed changes in the gas budget.

Following the rainstorm, mixed layer density was reduced by a fresh layer at the surface and increased to only \( \sigma_0 \) 26.72 by the end of patch 2 observations. Also, a one-dimensional mixed layer model (GOTM) implemented for SO GasEx showed that the mixed layer did not reach deeper depths after the rainstorm than it had before [Ho et al., 2011a], suggesting that vertical entrainment was limited during this period. Potential mixed layer \( \Delta O_2/Ar \) changes due to diapycnal mixing (as opposed to actual mixed layer deepening) were at most \(-0.02\% \text{ d}^{-1}\), assessed using the PWP model described in section 3.1 with an eddy diffusion coefficient of 1.0 cm² s⁻¹.

We use the underway surveys to assess the potential for lateral mixing to affect the \( \Delta O_2/Ar \) mass balance during the first 4 days of patch 2. The large-scale spatial survey performed immediately before the tracer injection revealed wide-ranging water properties in the region of the patch 2 injection site including areas of negative \( \Delta O_2/Ar \) [Ho et al., 2011a, Figure 4]. However, in the immediate vicinity of the patch, we observed no areas with significantly lower \( \Delta O_2/Ar \) than the values within the patch. A region with high \( O_2 \) concentration, high \( \Delta O_2/Ar \), high chlorophyll, lower temperature, and higher salinity was present just to the south of the tracer patch (Figure 7), causing occasional high \( \Delta O_2/Ar \) observations in the underway time series as the ship happened to move through this region (Figure 6). Although SF₆

Figure 5. Patch 2 discrete mixed layer values of (a) potential temperature, (b) salinity, (c) mixed layer and euphotic zone depths from CTD downcasts, (d) \( \Delta O_2/Ar \), (e) \( O_2 \) concentration, (f) DIC concentration, and (g) chlorophyll concentration. Line in Figure 5e indicates equilibrium \( O_2 \) concentration.
concentrations were always below detection in this anomalous water mass, the GOTM model results mentioned earlier suggest that this water mass may have influenced patch 2 properties [Ho et al., 2011a]. Therefore, it appears possible that lateral mixing may have acted to increase $\Delta O_2/Ar$, $O_2$, and chlorophyll, but could not have been responsible for the dramatic decreases observed in these properties.

[43] Given the potentially significant but not dominant contribution of vertical entrainment and the apparently small contributions of lateral processes to the $\Delta O_2/Ar$ mass balance in patch 2, we conclude that much of the rapid decrease observed in $\Delta O_2/Ar$ must have been due to a period of net heterotrophy from 22 to 26 March, and likely continuing to 1 April. Unlike conditions observed for patch 1, the mixed layer depth was approximately 10 m deeper than the euphotic zone depth during the first 4 days of patch 2. We do not know how long this condition existed prior to the beginning of sampling. However, if recent, the reduction in light levels over the mixed layer could have been a factor in the observed decreases in primary productivity rates and transition from net autotrophy to net heterotrophy. Effects of irradiance on productivity will be examined in a future paper. Lack of data prevents an assessment of the role of zooplankton population dynamics or iron levels, which may also have been important factors. Lance et al. (submitted manuscript, 2011) infer increased grazing activity during this period based on high ammonia concentrations and rapidly falling fucoxanthin concentrations.

[44] Based on the real-time $O_2/Ar$-NCP estimates, we would expect an increase in mixed layer DIC of 4 $\mu$mol kg$^{-1}$ from 22 March to 1 April, while the observed change was 9 $\mu$mol kg$^{-1}$ (Figure 5). The balance of the DIC increase may be accounted for by air-sea gas exchange (p$CO_2$ was undersaturated) and mixed layer entrainment. Moore et al. [2011] estimate that gas exchange contributed a 3.1 $\mu$mol kg$^{-1}$ increase in DIC during this period of the patch 2 experiment. A similar calculation using the surface discrete sample values gave a comparable DIC increase of 2.5 $\mu$mol kg$^{-1}$ due to gas exchange.

4. Productivity Method Comparisons

4.1. Net and New Production

[45] We turn now to comparing our $O_2/Ar$-derived net community production (NCP) estimates to new production (nitrate uptake) measured by on-deck $^{15}NO_3$ incubations.

Figure 6. Time series of surface, underway $\Delta O_2/Ar$ measurements during patch 2 from 22 March to 6 April 2008. Gray bars indicate local night. Red line segments indicate measurements inside the patch when underwater SF$_6$ concentrations were greater than 75 fmol L$^{-1}$ during 22–27 March, greater than 25 fmol L$^{-1}$ during 27 March to 1 April, or greater than 10 fmol L$^{-1}$ during 1–6 April. Black points show discrete, mixed layer $\Delta O_2/Ar$ measurements. Straight lines show linear regressions of 1 h binned averages of in-patch data with slopes and errors indicated.
(\textsuperscript{15}N-NewP (Lance et al., submitted manuscript, 2011)) and to NCP from a mass balance based on O\textsubscript{2} and pCO\textsubscript{2} sensor data from the MAP-CO\textsubscript{2} drifter [Moore et al., 2011]. To the extent that light inhibits the conversion of respiratory NH\textsubscript{4}+ to NO\textsubscript{3}/CO\textsubscript{2} in the euphotic zone [Müller-Neuglück and Engel, 1961], the uptake of \textsuperscript{15}NO\textsubscript{3} should represent new rather than recycled production, potentially available for export. Barring methodological bias, NCP and \textsuperscript{15}N-NewP could be expected to be equivalent on some timescales; however, rapidly changing conditions, such as patch 2 exhibited, could create differences between the two measures.

\[ \text{Prior O}_2/\text{Ar-NCP for patch 1 was about double } \textsuperscript{15}N-\text{NewP estimates (Figure 8 and Table 1); however, this NCP estimate mainly represents conditions prior to the start of patch 1 observations. When we included the observed rate of change in } \Delta \text{O}_2/\text{Ar over time and the potential impact of entrainment, we found that the ratio of real-time } \text{O}_2/\text{Ar-NCP to } \textsuperscript{15}N-\text{NewP was } 1.0 \pm 0.5 \text{ (both in C units). We are aware of only one other study that compared these two methods on the same cruises/stations. Giesbrecht [2010] found that prior } \text{O}_2/\text{Ar-NCP was nearly double } \textsuperscript{15}N-\text{NewP (both in C units)} \text{ under iron-limited conditions in the subarctic NE Pacific, but that prior } \text{O}_2/\text{Ar-NCP was similar to or less than } \textsuperscript{15}N-\text{NewP in coastal upwelling conditions and during an iron-stimulated bloom.} \]

\[ \text{At the beginning of patch 2, mixed layer } \Delta \text{O}_2/\text{Ar was supersaturated, yielding positive prior } \text{O}_2/\text{Ar-NCP estimates, but again these values represent conditions before the start of patch 2. Real-time } \text{O}_2/\text{Ar-NCP for the first 4 days of patch 2 show that this period was actually net heterotrophic, i.e., community respiration exceeded gross photosynthesis, with a real-time } \text{O}_2/\text{Ar-NCP corrected for the potential impact of entrainment of } -29 \pm 4 \text{ mmol C m}^{-2} \text{ d}^{-1}. \text{ High ammonium concentrations of } 2-3 \text{ \textmu M during patch 2 (Lance et al., submitted manuscript, 2011) also support net heterotrophy. Estimates of } \textsuperscript{15}N-\text{NewP were low and decreasing during this early part of patch 2. Because } \textsuperscript{15}NO_3 \text{ incubations measure NO}_3 \text{ uptake rates, they cannot yield negative values, so we expect } \textsuperscript{15}N-\text{NewP to exceed } \text{O}_2/\text{Ar-NCP in net heterotrophic conditions, as observed.} \]

\[ \text{Throughout the rest of patch 2, } \Delta \text{O}_2/\text{Ar remained undersaturated. The real-time } \text{O}_2/\text{Ar-NCP estimate yields net} \]
heterotrophic conditions during the middle period of patch 2 and net autotrophic conditions, with NCP exceeding $^{15}$N-NewP, in the last few days (Figure 8 and Table 1). Throughout this latter period, $^{15}$N-NewP remained low and fairly stable. It is interesting that the real-time O$_2$/Ar-NCP eventually recovers to values significantly higher than $^{15}$N-NewP at the end of patch 2. Together with the high ammonium concentrations observed, these results suggest that net growth on ammonia may have enhanced O$_2$/Ar-NCP relative to $^{15}$N-NewP. Dedicated $^{15}$NH$_4$ incubations in tandem with the $^{15}$NO$_3$ incubations would have confirmed this. If ammonia did fuel much of the NCP in this period, a O$_2$ to C (PQ) ratio closer to 1.1 rather than 1.4 would be more appropriate to convert O$_2$-based production to C units [Laws, 1991], which would create an even larger discrepancy between NCP and $^{15}$N-NewP. Increases in $\Delta$O$_2$/Ar from lateral mixing with the high $\Delta$O$_2$/Ar water mass to the south could also have elevated the real-time O$_2$/Ar-NCP estimates for this time period. Finally, methodological differences may have contributed to the observed discrepancy, including excretion of $^{15}$N as dissolved organic nitrogen [Bronk and Ward, 2000], alteration of productivity rates by confinement in bottles [Quay et al., 2010], and uncertainty in gas exchange parameterizations for the O$_2$/Ar calculations.

50 During patch 1, NCP estimated from O$_2$ sensors on the drifter $(3 \pm 10 \text{ mmol C m}^{-2} \text{ d}^{-1})$ and from pCO$_2$ sensors on the drifter $(7 \pm 9 \text{ mmol C m}^{-2} \text{ d}^{-1})$ agreed within uncertainties with real-time O$_2$/Ar-NCP $(9 \pm 4 \text{ mmol C m}^{-2} \text{ d}^{-1})$, Table 1). During 22-31 March, Moore et al. [2011] also estimate negative NCP (net heterotrophy) from the drifter O$_2$ mass balance $(–5 \pm 7 \text{ mmol C m}^{-2} \text{ d}^{-1})$ and from the DIC mass balance $(–7 \pm 8 \text{ mmol C m}^{-2} \text{ d}^{-1})$ but with much lower rates than the strong net heterotrophy demonstrated by real-time O$_2$/Ar-NCP at this time. During 22–26 March, the ship measurements were in close proximity to the drifter. However, on 26 March the tracer patch split, with the ship continuing to monitor one portion of the patch, while the drifter advected to the southeast in a different portion. Higher O$_2$ concentrations observed by the drifter O$_2$ sensors compared to the ship-based measurements after 26 March suggest that the portion of the tracer patch monitored by the drifter experienced a different evolution in productivity rates, and that drifter NCP averaged over this full time period is not directly comparable to the ship-based estimates. Moreover, the drifter estimates integrate over the time period when the mixed layer rapidly shoaled and deepened after the rainstorm (26–28 March), for which we did not estimate real-time O$_2$/Ar-NCP. The difference between drifter and ship-based estimates emphasizes the spatial heterogeneity of the region around patch 2.

4.2. Primary and Gross Production

50 Primary production was determined by 24 h on-deck $^{14}$C incubations ($^{14}$C-PP) and gross primary production was estimated from photosynthesis-irradiance experiments (PE-GPP). Gross O$_2$ production was estimated from the triple isotopes of dissolved O$_2$ ($^{15}$O$_2$/O$_2$ GOP) and from diurnal changes in $\Delta$O$_2$/Ar (Diurnal-O$_2$ GOP). While we do not expect equivalence among all of these methods, previous studies have seen consistent ratios among some of them [e.g., Quay et al., 2010].

51 Primary productivity values showed rapid changes during patch 2, falling to half their initial values in concert with falling chlorophyll concentrations over the first few days and then slowly recovering to higher values near the end of observations (Figure 9). Estimates of primary production including...

Figure 8. Comparison of NCP estimates with new production ($^{15}$N-NewP) from $^{15}$NO$_3$ incubations. Where replicates exist, only the means are shown. Grey patches for real-time O$_2$/Ar-NCP indicate the uncertainty. Drifter pCO$_2$ and O$_2$ indicate the time-averaged NCP from the pCO$_2$ and O$_2$ measurements on the MAP-CO$_2$ drifter deployments.

Table 1. Summary of Productivity Method Comparisons During SO GasEx

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>Prior O$_2$/Ar-NCP</td>
<td>16.8 ± 5.4</td>
<td>0.9 ± 5.0</td>
<td>−5.8 ± 5.1</td>
<td>−5.1 ± 2.4</td>
</tr>
<tr>
<td>Real-time O$_2$/Ar-NCP</td>
<td>9.4 ± 4.4 (7.4 ± 4.5)</td>
<td>−28.8 ± 4.3 (−48.3 ± 5.8)</td>
<td>−21.1 ± 2.9</td>
<td>12.6 ± 4.0</td>
</tr>
<tr>
<td>$^{15}$N-NewP</td>
<td>9.6 ± 2.8</td>
<td>4.0 ± 2.2</td>
<td>3.3 ± 0.5</td>
<td>3.1 ± 0.6</td>
</tr>
<tr>
<td>Drifter pCO$_2$ NCP</td>
<td>6.7 ± 9.2</td>
<td>−7.3 ± 8.4$^{b}$</td>
<td>not measured</td>
<td>not measured</td>
</tr>
<tr>
<td>Drifter O$_2$ NCP</td>
<td>3.2 ± 9.9</td>
<td>−5.2 ± 6.7$^{b}$</td>
<td>−5.2 ± 6.7$^{b}$</td>
<td>not measured</td>
</tr>
<tr>
<td>24 h $^{14}$C-PP</td>
<td>39.1 ± 8.5</td>
<td>27.1 ± 11</td>
<td>18.4 ± 1.4</td>
<td>25.3 ± 4.9</td>
</tr>
<tr>
<td>PE-GPP</td>
<td>not measured</td>
<td>23.1 ± 4.8</td>
<td>21.3 ± 3.3</td>
<td>28.2 ± 2.6</td>
</tr>
<tr>
<td>$^{15}$O$_2$/O$_2$ GOP</td>
<td>144 ± 29</td>
<td>159 ± 36</td>
<td>21 ± 46</td>
<td>97 ± 47</td>
</tr>
<tr>
<td>Diurnal-O$_2$ GOP</td>
<td>84 ± 11</td>
<td>111 ± 41</td>
<td>45 ± 14</td>
<td>104 ± 27</td>
</tr>
</tbody>
</table>

$^{a}$Units for NCP, NewP, PP, and GPP are mmol C m$^{-2}$ d$^{-1}$. Units for GOP are mmol O$_2$ m$^{-2}$ d$^{-1}$. Real-time O$_2$/Ar-NCP values in parentheses indicate values that do not include potential contributions by entrainment. Errors for real-time O$_2$/Ar-NCP are described in section 2.2 and for drifter NCP estimates by Moore et al. [2011]. Errors given all other estimates are standard deviations of multiple observations in those periods and likely represent some real temporal variability.

$^{b}$Value is a mean over 22–31 March.
from 24 h on-deck 14C incubations agreed very well with estimates of gross primary production from the photosynthesis-irradiance experiments (Figure 9 and Table 1). Samples for 14C-PP were collected from nighttime casts, while PE-GPP samples came from daytime casts, but the underway SFO measurements used to choose CTD stations should have ensured that the same water mass was sampled for both. During much of patch 2, the mixed layer depth was deeper than the euphotic zone depth (Figure 5), suggesting that cells were being actively mixed within the light gradient while other environmental conditions (nutrients, etc.) were constant. Also, the observed photosynthetic efficiency (αmax) varied by no more than a factor of two (maximum/minimum) throughout the euphotic layer, and maximum photosynthetic rate (Pmax) varied on average 37%. These changes, likely owing to short-term photoadaptive responses, are small relative to stably stratified marine environments such as the oligotrophic ocean where Babin et al. [1996] found αmax varied by 10 times and Pmax by 4 times in the euphotic zone. The relatively small range in photosynthetic parameters during the two estimates of GOP is complicated by the different timescales of the measurements. The 17O2 GOP estimate assumes a steady state between O2 production in the mixed layer and O2 evasion to the atmosphere. This method integrates over the residence time of O2 in the mixed layer, 8–11 days for a 50 m mixed layer at these wind speeds, so most of our measurements at least partially represent conditions prior to the creation of the patches. In contrast, the Diurnal-O2 GOP method integrates over a single day. However, the 17O2 GOP measurements at the end of patch 2 should represent average conditions over the entire observation period of patch 2, and we do see similar values within errors between 17–24h GOP in the final days of patch 2 (97 ± 47 mmol O2 m−2 d−1 for 1–5 April) and Diurnal-O2 GOP averaged over all of patch 2 (86 ± 40 mmol O2 m−2 d−1 for 23 March to 5 April). We also note that the 17O2 GOP values around 30 March to 1 April were unusually low compared to earlier values (Figures 9 and A1). The residence time of 17O2 with respect to gas exchange is similar to that of dissolved oxygen, about 8 days at the start of patch 2. Even in the complete absence of gross production during the latter half of March, gas exchange should not have been fast enough to draw down mixed layer 17O2 values from the values observed at the start of patch 2 to near equilibrium. Likely, these low values represent either analytical noise, despite the high accuracy of 17O2 analyses, or analytical noise, despite the high accuracy of 17O2 analyses, or uncertainty in a small value is about ±50 mmol m−2 d−1, or lateral variability in 17O2 that we could not evaluate from the limited discrete samples.

Typically, GOP results have been compared to 14C-PP using a ratio of 2.7 based on comparison of GOP from incubations with H218O to 24 h 14C incubations during JGOFS expeditions in the North Atlantic, Arabian Sea, and equatorial Pacific oceans [Bender et al., 1999; Laws et al., 2000; Marra, 2002]. We scaled the axes in Figure 9 such that the PE-GPP results did not yield higher rates than the 24 h 14C-PP estimates could suggest that recycling of the 14C tracer was consistent over time and that autotrophic respiration was very low in the incubations. Low rates of phytoplankton respiration for these experiments are supported by parallel 12 h and 24 h 14C incubations during SO GasEx that yielded similar results [Marra and Barber, 2004; Lance et al., submitted manuscript, 2011]. Another possibility is that the light spectrum within the photosynthetron used in the PE-GPP experiments did not adequately match the spectra of the 24-h 14C-PP incubations, nor did either match the true spectra of the submarine light field. In the incubations themselves, it is also possible that there was more recycling of the 14C tracer or exudation of labeled DO14C at short timescales than expected, or that there was a delay in the uptake of the 14C tracer, for example by reassimilation of recently respired unlabeled CO2. Robinson et al. [2009] also found no significant difference in productivity measurements derived from 24 h, on-deck, 14C incubations and 2 h photosynthesis-irradiance experiments at stations in the North Atlantic during spring.

[53] Diurnal-O2 GOP also demonstrated rapid changes during patch 2, with estimated values dropping to 20% of the initial value over the first week and then returning to higher values by the end of observations (Figure 9). Comparison of the two estimates of GOP is complicated by the different timescales of the measurements. The 17O2 GOP estimate assumes a steady state between O2 production in the mixed layer and O2 evasion to the atmosphere. This method integrates over the residence time of O2 in the mixed layer, 8–11 days for a 50 m mixed layer at these wind speeds, so most of our measurements at least partially represent conditions prior to the creation of the patches. In contrast, the Diurnal-O2 GOP method integrates over a single day. However, the 17O2 -O2 GOP measurements at the end of patch 2 should represent average conditions over the entire observation period of patch 2, and we do see similar values within errors between 17–24h GOP in the final days of patch 2 (97 ± 47 mmol O2 m−2 d−1 for 1–5 April) and Diurnal-O2 GOP averaged over all of patch 2 (86 ± 40 mmol O2 m−2 d−1 for 23 March to 5 April). We also note that the 17O2 GOP values around 30 March to 1 April were unusually low compared to earlier values (Figures 9 and A1). The residence time of 17O2 with respect to gas exchange is similar to that of dissolved oxygen, about 8 days at the start of patch 2. Even in the complete absence of gross production during the latter half of March, gas exchange should not have been fast enough to draw down mixed layer 17O2 values from the values observed at the start of patch 2 to near equilibrium. Likely, these low values represent either analytical noise, despite the high accuracy of 17O2 analyses, or uncertainty in a small value is about ±50 mmol m−2 d−1, or lateral variability in 17O2 that we could not evaluate from the limited discrete samples.

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that the GOP axis on the left-hand side is 2.7 times the PP axis on the right-hand side. During SO GasEx, the ratio of Diurnal-O₂ GOP to $^{14}$C-PP, which have similar measurement timescales, was 3.5 ± 1.7 (GOP in O₂ units and PP in C units). The ratio of the mean $^{18}$O-GOP during the last 4 days of patch 2 to the mean $^{14}$C-PP over all of patch 2 was 4.2 ± 2.5. Neither of these GOP,$^{14}$C-PP ratios is significantly different from the 2.7 ratio typically seen in $^{18}$O-GOP versus 24 h $^{14}$C-PP comparisons [e.g., Quay et al., 2010; Marra, 2002]. The rapidly changing conditions in patch 2, mismatch in timescales, and overall low productivity rates impart high uncertainties to these comparisons.

5. Conclusions and Implications

[57] In recent studies, $\Delta^{18}$O/Ar measurements have been used to assess the trophic status of surface waters. For example, at station ALOHA near Hawaii, year-round $\Delta^{18}$O/Ar supersaturation demonstrates net autotrophy [Emerson et al., 1997], in conflict with in vitro changes in O₂ during light/dark bottle incubations that have suggested net heterotrophy [Williams et al., 2004]. Where $\Delta^{18}$O/Ar undersaturation has been observed previously, it was explained by local upwelling of low O₂ waters [Kaiser et al., 2005; Stanley et al., 2010] or respiration effects in the ship’s underway sampling lines [Juranek et al., 2010]. By monitoring a water mass defined by SF₆ over a period of weeks, we were able to rule out a dominant influence from physical processes on $\Delta^{18}$O/Ar and show that biology was largely responsible for the rapid changes observed. Frequent comparisons of O₂ concentration between Niskin and underway samples also demonstrated that the ship’s underway water supply was free of respiration induced bias [Juranek et al., 2010]. We believe this experiment is the first instance of net heterotrophy identified by $\Delta^{18}$O/Ar measurements, albeit over a short time period.

[58] Continuous measurements of $\Delta^{18}$O/Ar in the tracer patches also allowed us to constrain the rate of change in mixed layer $\Delta^{18}$O/Ar. This term can only be measured in patch experiments, and has not previously been determined [e.g., Reuer et al., 2007; Quay et al., 2010]. The rate of change term was at least as large as the gas exchange term in our NCP mass balance. It dominated the mass balance during patch 2 (−28.3 versus −0.5 mmol C m⁻² d⁻¹) in the first 4 days when $\Delta^{18}$O/Ar was falling rapidly but its average value was near or above saturation and $^{15}$N-NewP was being actively assimilated. In addition, we observed diurnal changes in $\Delta^{18}$O/Ar with a range as large as 0.6%, significant compared with mean supersaturations of −1 to 3%. These
Table A1. Constant Choices for Determining Gross Productivity From Triple Oxygen Isotope Composition (Equation (A1))

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
<th>Citation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta^17$O_{dis}$</td>
<td>isotopic composition of dissolved $^17$O</td>
<td>measured</td>
<td></td>
</tr>
<tr>
<td>$\delta^18$O_{air}$</td>
<td>isotopic composition of $^18$O in air</td>
<td>0‰</td>
<td></td>
</tr>
<tr>
<td>$\delta^17$O_{water}$</td>
<td>fraction of $^17$O in water (VSMOW)</td>
<td>$-23.324$‰</td>
<td>Barkan and Luz [2011]</td>
</tr>
<tr>
<td>$\delta^18$O_{water}$</td>
<td>fraction of $^18$O in water (VSMOW)</td>
<td>$-11.883$‰</td>
<td>Barkan and Luz [2011]</td>
</tr>
<tr>
<td>$\alpha^{17}_{g}$</td>
<td>fractionation of $^17$O during photosynthesis</td>
<td>$1.0052$</td>
<td></td>
</tr>
<tr>
<td>$\alpha^{18}_{g}$</td>
<td>fractionation of $^18$O during photosynthesis</td>
<td>$1.0052$</td>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
<td>ratio of respiration fractionation factors for $^17$O and $^18$O</td>
<td>$0.5179$</td>
<td></td>
</tr>
<tr>
<td>$\alpha^{17}_{eq}$</td>
<td>equilibrium fractionation factor for $^17$O during air-sea gas exchange</td>
<td>$(-0.730 + \frac{\Delta T}{1000})1000 + 1$ with potential temperature in kelvin</td>
<td>Benson and Krause [1984]</td>
</tr>
<tr>
<td>$\alpha^{18}_{eq}$</td>
<td>equilibrium fractionation factor for $^18$O during air-sea gas exchange</td>
<td>$exp(8<em>10^{-6} + 0.5179</em>ln(\epsilon_{eq}))$</td>
<td>Stanley et al. [2010]</td>
</tr>
<tr>
<td>$\alpha^k_{eq}$</td>
<td>kinetic fractionation factor for air-sea gas exchange</td>
<td>$0.9972$</td>
<td>Knox et al. [1992]</td>
</tr>
<tr>
<td>$\alpha^k_{air}$</td>
<td>kinetic fractionation factor for air-sea gas exchange</td>
<td>$0.998554$</td>
<td>Kaiser [2011]</td>
</tr>
</tbody>
</table>

findings indicate that Prior $^17$O/Ar-NCP derived from single measurements of mixed layer $\Delta^17$O/Ar can differ significantly from NCP at the time of sampling. Some of this bias could be reduced by averaging many measurements over large spatial and temporal scales and by eliminating data collected at the extremes of the diurnal cycle (dusk and dawn). In any case, the trophic status of upper ocean ecosystems may be much more variable than previously implied by $^17$O/Ar and other productivity measurements.

During SO GasEx, estimates of net community, new, primary, or gross production were made using 9 different methods. Export of carbon from the surface layer is one of the most important carbon cycle fluxes that biogeochemists would like to constrain, because it relates to the sequestration of $^12$CO$_2$ in the deeper ocean. Both NCP and NewP methods are used to estimate export. In patch 1, we found good agreement among these methods, suggesting that either of them might provide a fair estimate of export at this time. However, in the more dynamic patch 2, these methods disagreed not only during the net heterotrophic period, but also during the autotrophic period at the end of the patch observations, suggesting that methodological bias of some sort would affect export estimates by at least one of these methods. Incubations using $^{15}$N-labeled ammonium and urea might have allowed us to distinguish whether the higher NCP at the end of patch 2 resulted from net growth on recycled nutrients.

Appendix A: Triple Oxygen Isotope Calculations

We use the calculation method of Kaiser [2011], which is similar to Prokopenko et al. [2011], to calculate the ratio of gross O$_2$ production to sea-to-air evasion (GOP/k$_{wO2}$) from oxygen isotopic compositions and fractionation factors.

\[
\text{GOP} = \frac{\left( X_{\text{dis}}^{17} - X_{\text{air}}^{17} \alpha_{eq}^{17} \alpha_{k}^{17} \right)}{X_{\text{dis}}^{17}} - \gamma \left( X_{\text{dis}}^{18} - X_{\text{air}}^{18} \alpha_{eq}^{18} \alpha_{k}^{18} \right) + \left( \frac{\Delta^17}{\Delta^18} \text{Ar} + 1 \right) \left( \alpha^{17}_{k} - 1 \right) - \gamma \left( \alpha^{18}_{k} - 1 \right). \tag{A1}
\]

where $X^*$ is the ratio of $^{17}$O/$^{16}$O or $^{18}$O/$^{16}$O such that $\delta^*O = \left( \frac{X^*}{X_{\text{air}}^*} - 1 \right)1000$, and $\alpha$ is the fractionation factor for various processes where $\epsilon = (\alpha - 1)1000$. This equation is identical to equation (49) of Kaiser [2011] with different notation, and, if the kinetic fractionation during gas exchange is ignored ($\alpha_k = 1$), it is also identical to equation (7) of.
calculation methods or constants, we present the original measurements to be recalculated pending future revisions in been revised several times. With a view to allowing our has been calculated from triple oxygen isotopic measure-

Figure B1. Diamonds indicate C production at different light levels within the photosynthetron for subsamples collected at 35 m on 4 April 2008. The line is a nonlinear regres-

Appendix B: PE-GPP Methodology

[64] At each depth, 50 mL samples were dispensed from the Niskin through an acid-cleaned silicone tube into 13 new, sterile polystyrene tissue culture flasks (Corning 25 cm²), capped and kept in dark, insulated containers for 5–20 min. Under subdued red light, 10 µCi of NaH¹⁴CO₃ (MP Biomedicals catalog 17441H25) was added to each flask. Twelve flasks were stacked face to face within a photo-
synthetron chamber. The thirteenth flask was kept at 4°C in darkness as a control. An aliquot (100–150 µL) was removed from two random flasks for a total count sample and pipetted into a 20 mL scintillation vial containing either mono-
ethylamine or sodium hydroxide as a CO₂ capturing agent.

[65] The radial photosynthetron, designed after Babin et al. [1994], consisted of ten black Plexiglas, watertight incubator chambers, with a clear window at one end, arranged radially around a Hg halogen lamp (250 Watt, Phillips) wrapped in a sheet of blue optical filter (Lee Filters 354). Attenuation of light through the row of twelve flasks formed a light gradient. Neutral density filters were placed between some adjacent flasks to further reduce the irradiance when necessary. A circulating chiller maintained flask temperature at 5 ± 2°C, the in situ temperature in the upper 100 m during the cruise. Irradiances of 4–570 µmol quanta m⁻² s⁻¹ were achieved across all photosynthetron chambers, and measured at each flask position using a newly calibrated biospherical QSL 2100 scalar irradiance probe with a 2 cm diameter Teflon diffuser head. The light attenuation curves were character-
ized within each incubation box using sample flasks filled with water to simulate a sample series, and were highly reproducible throughout the day.

[66] After an incubation of 1–2 h, each flask was filtered onto 25 mm GF/F filters (nominal pore size 0.7 µm) using low vacuum pressure (≤5 mm Hg). Filters were placed in scintillation vials and acidified with 6N HCl for 12 h, neutral-
ized with 6N NaOH, and then filled with 15 mL of Ecolume scintillation cocktail. Radioactivity was counted with a Perkin Elmer Tri-Carb 2200CA liquid scintillation analyzer. The photosynthetic efficiency, α(¹⁸O = (mmol C (mg Chla)⁻¹ h⁻¹) (µmol quanta m⁻² s⁻¹)⁻¹), and maximum photosynthetic rate, P_max (mmol C (mg Chla)⁻¹ h⁻¹), were determined using a least squares nonlinear fit to the irrita-
dance versus photosynthesis data using the model of Platt et al. [1982] when photoinhibition was present or Webb et al. [1974] when it was not. An example of photosynthe-
sis-irradiance data and the curve fit from samples collected at 35 m during the noon cast on 4 April 2008 is given in Figure B1.

[67] Daily primary production at each sample depth, P(z), was calculated using the depth-resolved PE parameters and

respiration fractionation factors for ¹⁷O and ¹⁸O (γ = 0.5179 in Table A1) or may represent a value appropriate for steady state where photosynthesis is balanced by respiration (θ = 0.5154) [Luz and Barkan, 2005]. Given a NCP/GOP ratio near 0.1 in our data, we might argue that the steady state reference slope is most appropriate. However, the choice of λ in the ¹Δ definition does not affect our GOP estimate, and we simply report both versions of ¹Δ for ease of comparison to other work.
15 min averages of PAR irradiance at each depth, \( E(z,t) \), calculated from

\[
E(z,t) = E(0,t) e^{-k_z}
\]

where \( E(0,t) \) is the PAR irradiance at the surface measured continuously using a LI-COR cosine light sensor mounted near the rear of the ship and averaged in 15 min intervals (Lance et al., submitted manuscript, 2011), and \( k_z \) is the diffuse attenuation coefficient averaged over the upper 50 m of the water column from daily casts with a biospherical 4 m PAR sensor. Irradiances at each depth were then applied to the PE parameters at those depths and integrated over the day to calculate daily production [Webb et al., 1974; Platt et al., 1982]. PE parameters were assumed to be constant throughout each day. Depth-integrated productivity was then calculated using trapezoidal integration from the surface to 50 m depth.

[68] Acknowledgments. We thank Matt Reid and Paul Schneider for making the underway SF, measurements, Greg Johnson for processing the CTD data, and Burke Hales for providing his underway salinity data. Bruce Barnett, Robert Mika, and Cory Beatty are thanked for their help with cruise logistics and sample analysis. We appreciate the comments of Paul Quay and an anonymous reviewer that helped us to improve the manuscript. Funding for this work was provided by NSERC Discovery grant 328290-2006 to R.C.H.; NASA cooperative agreements NNX08AF12G to M.L.B., and NNX07AF12G to M.D.D., NA07OAR4310122 to M.D.D., GC07-129 and GC07-109 NNX07AV23G to B.R.H.; NOAA grants NA07OAR4310088 to P.G.S. and B.Hales, NA07OAR4310122 to M.D.D., GC07-129 and GC07-109 to C.L.S., and NA07OAR4310113 and NA08OAR4310890 to D.T.H.; and NSF grants ANT-0636744 to M.L.B. and OCE-0726784 to M.D.D. This is production and export in the Southern Ocean along 170°W, Deep Sea Res., Part II, 50, 579–603, doi:10.1016/S0967-0645(02)00554-4.


