

## High-resolution estimates of net community production and air-sea CO<sub>2</sub> flux in the northeast Pacific

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[1] Rates of net community production (*NCP*) and air-sea CO<sub>2</sub> flux in the Northeast Pacific subarctic, transition zone and subtropical regions (22°N–50°N, 145°W–152°W) were determined on a cruise in August–September 2008 by continuous measurement of surface values of the ratio of dissolved oxygen to argon (O<sub>2</sub>/Ar) and the partial pressure of CO<sub>2</sub> (*p*CO<sub>2</sub>). These estimates were compared with simultaneous measurements of sea surface temperature (SST), chlorophyll-*a* (*chl-a*), flow cytometry, and discrete surface nutrient concentrations. *NCP* and CO<sub>2</sub> influx were greatest in the subarctic (45°N–50°N, 25.8 ± 4.6 and 4.1 ± 0.9 mmol C m<sup>-2</sup> d<sup>-1</sup>) and northern transition zone (40°N–45°N, 17.1 ± 4.4 and 2.1 ± 0.5 mmol C m<sup>-2</sup> d<sup>-1</sup>), with mean *NCP* ~6–8× greater than mean CO<sub>2</sub> invasion (error estimates reflect 1 σ confidence intervals). Contrastingly, the southern transition zone (32°N–40°N) and subtropics (22°N–32°N) had lower mean *NCP* (5.4 ± 1.8 and 8.1 ± 2.1 mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively) and mean CO<sub>2</sub> efflux (3.0 ± 0.5 and 0.1 ± 0.0 mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively). In the subarctic and transition zone, *NCP* was highly correlated with surface *chl-a* and CO<sub>2</sub> influx, indicating strong coupling between the biological pump and CO<sub>2</sub> uptake. Meridional trends in our *NCP* estimates in the transition zone and subtropics were similar to those for integrated summertime *NCP* along the cruise track determined using an upper ocean climatological carbon budget.

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### 1. Introduction

[2] Surface CO<sub>2</sub> measurements yield a mean global net ocean sink for atmospheric CO<sub>2</sub> of ~2 Pg C yr<sup>-1</sup>, however there is large variation in oceanic CO<sub>2</sub> uptake and release in both space and time [Takahashi *et al.*, 2009] that is controlled by biological drawdown through primary productivity (*PP*) and export to the deep ocean (the biological pump), temperature-driven solubility of CO<sub>2</sub> (the solubility pump) and ocean circulation. The biological pump has been estimated to export organic carbon globally at 8–15 Pg C yr<sup>-1</sup>

[Emerson and Hedges, 2008], but these rates are poorly constrained and vary widely across ocean regions [Boyd and Trull, 2007; Schlitzer, 2000, 2004]. To predict the response of this sink to future changes in Earth's climate, we must understand how the biological and solubility pumps vary spatially, seasonally and interannually, and what factors determine this variability.

[3] A remarkable feature in the surface CO<sub>2</sub> of the North Pacific is the band of strong mean annual air-sea CO<sub>2</sub> uptake (2–9 mol C m<sup>-2</sup> yr<sup>-1</sup>) at ~30°N–45°N, roughly corresponding to the transition zone between the subtropical and subarctic gyres along the path of the Kuroshio current and extension [Takahashi *et al.*, 2009]. Two prominent basin-wide oceanographic features occupy this region: (1) the physically defined North Pacific transition zone (~30°N–45°N), a region of confluence and convergence bounded by temperature and salinity fronts [Rodén, 1991], and (2) the transition zone chlorophyll front (TZCF), a biological hot spot defined by the 0.2 mg m<sup>-3</sup> chlorophyll isopleth that seasonally migrates from 30°N–35°N in winter to 40°N–45°N in summer [Polovina *et al.*, 2001].

[4] Given the biological prominence of the TZCF and the enhanced *PP* found at similar convergent fronts [Longhurst, 2007; Mann and Lazier, 2006], one would expect that *PP* and carbon export contribute substantially to the strong CO<sub>2</sub>

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**Table 1.** Upper Ocean NCP in NE Pacific Subarctic, Subtropics, and Transition Zone<sup>a</sup>

Station	Annual NCP (mol C m <sup>-2</sup> yr <sup>-1</sup> )	Daily NCP (mmol C m <sup>-2</sup> d <sup>-1</sup> )
<i>Subarctic</i>		
OSP Alaska Gyre (~50°N–55°N) Subarctic current (~45°N–50°N)	<b>2.0 ± 0.3</b> 2.1, <sup>b</sup> 1.8, <sup>c</sup> 2.1, <sup>d</sup> 1.6, <sup>e</sup> 2.5 <sup>f</sup> 3.1 <sup>h</sup> 2.6 <sup>h</sup>	<b>14 ± 5</b> 12, <sup>b</sup> 8, <sup>c</sup> 15, <sup>d</sup> 10, <sup>e</sup> 17, <sup>f</sup> 21 <sup>g</sup> 18 <sup>h</sup> 15, <sup>h</sup> 25.8 ± 4.6 <sup>i</sup>
<i>Subtropics</i>		
ALOHA 20°N–25°N 145°W–152°W, 22°N–32°N	<b>2.7 ± 0.9</b> 2.7, <sup>j</sup> 1.7, <sup>k</sup> 4.3, <sup>l</sup> 2.4, <sup>m</sup> 2.7, <sup>n</sup> 2.3 <sup>o</sup> 2.4 <sup>q</sup>	<b>8 ± 4</b> 7, <sup>j</sup> 5, <sup>k</sup> 12, <sup>l</sup> 3, <sup>m</sup> 7, <sup>n</sup> 6, <sup>o</sup> 15 <sup>p</sup> 8.1 ± 2.1 <sup>i</sup>
<i>Transition Zone</i>		
All		<b>9 ± 5</b> (8; 3), <sup>r</sup> (21; 13), <sup>s</sup> 11.8 ± 3.2 <sup>i</sup>
Northern (40°N–45°N)	2.6 <sup>t</sup>	15, <sup>i</sup> 17.1 ± 4.4 <sup>i</sup>
Southern (32°N–40°N)	0.9 <sup>t</sup>	14, <sup>i</sup> 5.4 ± 1.8 <sup>i</sup>

<sup>a</sup>See footnotes for seasonality of daily estimates. Values set in bold type are mean ± s.d. of previous observations cited below.

<sup>b</sup>Wong *et al.* [2002a], NO<sub>3</sub> mixed layer mass balance. Daily average over 6 months.

<sup>c</sup>Charette *et al.* [1999], <sup>234</sup>Th–<sup>238</sup>U disequilibrium and Th/C ratio, mixed layer. August.

<sup>d</sup>Emerson [1987], O<sub>2</sub> mixed layer mass balance. Summer.

<sup>e</sup>Emerson *et al.* [1991], O<sub>2</sub>, Ar and N<sub>2</sub> mixed layer mass balance. Summer.

<sup>f</sup>Emerson and Stump [2010], in situ O<sub>2</sub> and N<sub>2</sub> mixed layer mass balance. Summer.

<sup>g</sup>Wheeler [1993], 4-month NO<sub>3</sub> drawdown and <sup>15</sup>NO<sub>3</sub> assimilation, mixed layer.

<sup>h</sup>Wong *et al.* [2002b]; NO<sub>3</sub> mixed layer mass balance. Daily average over summer NO<sub>3</sub> drawdown period.

<sup>i</sup>This study.

<sup>j</sup>Emerson *et al.* [1997], O<sub>2</sub> euphotic zone mass balance. Daily average over 12 months.

<sup>k</sup>Hamme and Emerson [2006], O<sub>2</sub> euphotic zone mass balance. Daily average over 12 months.

<sup>l</sup>Emerson *et al.* [2008], O<sub>2</sub> euphotic zone mass balance. Daily average over 12 months.

<sup>m</sup>Benitez-Nelson *et al.* [2001]; <sup>234</sup>Th deficiency over 0–150 m, includes total C output. August steady state POC export rate.

<sup>n</sup>Quay and Stutsman [2003], DIC–δ<sup>13</sup>C mixed layer mass balance. Summer average.

<sup>o</sup>Keeling *et al.* [2004], δ<sup>13</sup>C–DIC mixed layer mass balance. Daily average over 12 months.

<sup>p</sup>Juranek and Quay [2005], in situ mixed layer O<sub>2</sub>/Ar. August.

<sup>q</sup>Quay *et al.* [2009], DIC–δ<sup>13</sup>C mixed layer mass balance.

<sup>r</sup>Howard *et al.* [2010], euphotic zone O<sub>2</sub>/Ar (summer, fall).

<sup>s</sup>Juranek *et al.* [2012], mixed layer O<sub>2</sub>/Ar (spring, summer).

<sup>t</sup>Wong *et al.* [2002b]; NO<sub>3</sub> mixed layer mass balance. Daily average over summer NO<sub>3</sub> drawdown period.

uptake in this region, but the magnitude of this contribution is unclear. Takahashi *et al.* [2002, 2009] attribute the sink to the combined effects of the solubility and biological pumps. In contrast, Ayers and Lozier [2012] recently modeled CO<sub>2</sub> uptake in the transition zone and concluded that although temperature-driven solubility strongly affects seasonal *p*CO<sub>2</sub> trends, it controls only ~17% of the annual sink in this region, with the remainder contributed by biological export and geostrophic divergence of DIC.

[5] In this study, we sought to estimate the contribution of the biological pump to carbon uptake in the North Pacific by making high-resolution estimates of carbon export and uptake. The strength of the biological pump is quantified by estimates of *NCP*, which equals gross *PP* (*GPP*) minus community respiration and is equivalent at steady state to the rate of organic carbon export and transfer up the food chain. In the North Pacific, *NCP* is fairly well constrained at two time series stations, Ocean Station P (OSP) in the subarctic NE Pacific (50°N, 145°W) and Station ALOHA in the subtropical NE Pacific (22°45'N, 158°W) through surface layer budgets of dissolved gases, nutrients, *DIC* and δ<sup>13</sup>C, and through in situ dissolved gas ratios and <sup>234</sup>Th–<sup>238</sup>U disequilibrium (see Table 1). But because there are comparatively fewer estimates in the rest of the basin and only a few snapshot *NCP* estimates for the transition zone [Wong *et al.*, 2002b; Juranek, 2007; Howard *et al.*, 2010; Juranek *et al.*, 2012], it is unclear how representative these sites are of the basin as a whole. On a basin-wide scale, *NCP*

estimated from climatological seasonal *DIC* drawdown [Lee, 2001] is high (2–6 mol C m<sup>-2</sup> yr<sup>-1</sup>) in the transition zone.

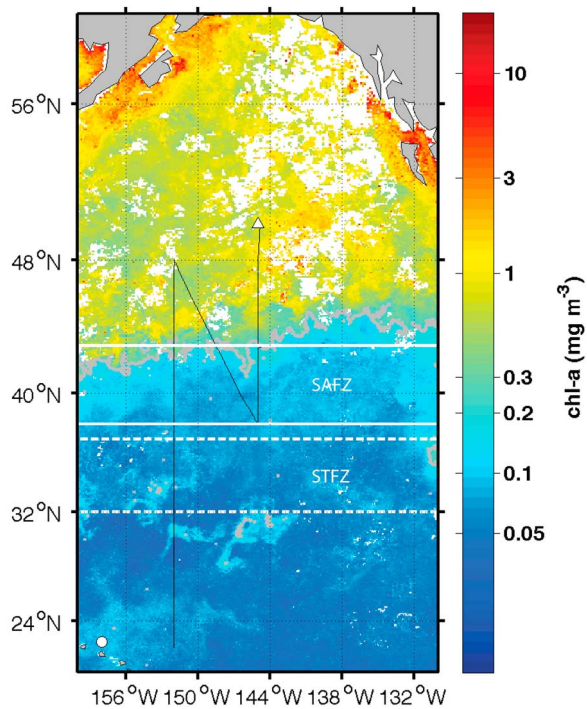
[6] In recent years, fine-scale observations of oceanographic parameters made possible by continuous underway measurements have allowed researchers to better determine rates and controls on ocean biogeochemical processes, including *NCP*. In particular, continuous measurements of the dissolved gases O<sub>2</sub> and Ar using equilibrator inlet mass spectrometry (EIMS) [Tortell, 2005; Kaiser *et al.*, 2005; Cassar *et al.*, 2009], combined with a wind speed parameterization of gas exchange, have led to continuous, kilometer-scale estimates of *NCP* [e.g., Nemcek *et al.* 2008; Guéguen and Tortell, 2008; Stanley *et al.*, 2010; Cassar *et al.*, 2011].

[7] In this study, we continuously measured surface ocean O<sub>2</sub>/Ar, *p*CO<sub>2</sub> and chl-*a* and carried out discrete flow cytometry in the subarctic, transition zone and subtropical Northeast Pacific to determine the heterogeneity in the rates of the biological pump and air-sea CO<sub>2</sub> flux on a cruise (August–September 2008) that crossed the transition zone three times (Figure 1). We compare these results with previous *NCP* estimates at OSP and Station ALOHA and surface CO<sub>2</sub> climatology, and examine the influence of *NCP* on CO<sub>2</sub> uptake in the region.

## 2. Background

### 2.1. Setting

[8] The main circulation features of the Northeast Pacific are the cyclonic subarctic gyre centered in the Gulf of Alaska



**Figure 1.** Cruise track (black) overlain on SeaWiFS 9-km monthly average *chl-a* for September 2008. White triangle, Station P; white circle, Station ALOHA. TZCF is highlighted in gray. Solid white lines bound SAFZ; dashed white lines bound STFZ.

( $\sim 45^{\circ}\text{N}$ – $60^{\circ}\text{N}$ ,  $160^{\circ}\text{W}$ – $135^{\circ}\text{W}$ ), the anticyclonic subtropical gyre ( $\sim 15^{\circ}\text{N}$ – $35^{\circ}\text{N}$ ,  $135^{\circ}\text{E}$ – $135^{\circ}\text{W}$ ), and the transition zone between the two. In the subarctic Alaska gyre, a halocline limits winter mixed layer depths to  $\sim 90$ – $120$  m and strong seasonal variation in temperature and wind speed leads to stratification in summer, with mixed layers shoaling to  $\sim 40$  m [Harrison *et al.*, 2004]. In this high nitrate, low chlorophyll (HNLC) region, iron generally limits the growth of large microphytoplankton like diatoms [Harrison *et al.*, 1999; Boyd *et al.*, 1996], and the phytoplankton community is dominated by small cells  $< 5 \mu\text{m}$ .

[9] The subtropical gyre is a low-nutrient, low-chlorophyll region with lower seasonal variability in temperature, wind speed, productivity and light than in the subarctic gyre; mixed layer depth ranges from 40 m in summer to 100 m in winter [Karl, 1999; Keeling *et al.*, 2004]. *Prochlorococcus* is the dominant photoautotroph, but  $\text{N}_2$  fixation by other cyanobacteria may provide up to half the nitrogen responsible for export [Karl *et al.*, 1997, 2001].

[10] Between these two gyres, the North Pacific transition zone extends across the basin at  $\sim 30^{\circ}\text{N}$ – $45^{\circ}\text{N}$ . Confluence of the Kuroshio and Oyashio currents and Ekman convergence set up two frontal regions with strong meridional gradients in temperature and salinity in winter and salinity in summer, the subarctic frontal zone (SAFZ, defined by 33‰–33.8‰ isohalines,  $\sim 40^{\circ}\text{N}$ – $43^{\circ}\text{N}$ ) and the subtropical frontal zone (STFZ, defined by 34.8‰–35.2‰ isohalines,  $\sim 31^{\circ}\text{N}$ – $34^{\circ}\text{N}$  [Roden, 1991]) (Figure 1). On shorter timescales, these frontal zones are associated with highly temporally and

spatially variable mesoscale perturbations including meandering fronts, jets and eddies [Roden, 1991; Yuan and Talley, 1996].

## 2.2. Previous Estimates of *NCP* in the Northeast Pacific

[11] In the Northeast Pacific, most of our understanding of rates of net community productivity (*NCP*) comes from numerous studies at OSP in the subarctic gyre and Station ALOHA in the subtropical gyre, including mass balances of dissolved gases ( $\text{O}_2$ , Ar and  $\text{N}_2$ ; Emerson, 1987; Emerson *et al.*, 1997, 1991; Hamme and Emerson, 2006; Emerson and Stump, 2010),  $\text{NO}_3$  [Wong *et al.*, 2002a] and  $\text{DIC}$ - $\delta^{13}\text{C}$  [Quay and Stutsman, 2003; Keeling *et al.*, 2004; Quay *et al.*, 2009]; the in situ  $\text{O}_2/\text{Ar}$  method [Juraneck and Quay, 2005; Quay *et al.*, 2010], and the  $^{234}\text{Th}$  method [Charette *et al.*, 1999; Benitez-Nelson *et al.*, 2001].

[12] Notably, despite different limitations to biological productivity at these two sites, annual *NCP* is similar at  $2.0 \pm 0.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$  at OSP and  $2.7 \pm 0.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$  at ALOHA (mean  $\pm$  s.d. of multiple estimates), within the  $\pm 50\%$  uncertainty of the measurements (Table 1) [Emerson *et al.*, 2008]. However, at OSP, *NCP* is primarily confined to spring and summer at high daily rates ( $14 \pm 5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ), whereas at ALOHA, daily rates are lower ( $8 \pm 4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) but *NCP* takes place throughout the year (mean  $\pm$  s.d. of multiple studies, Table 1).

[13] Few studies have examined *NCP* in the transition zone. Wong *et al.* [2002b] estimated *NCP* at  $2.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$  and  $0.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$  based on seasonal  $\text{NO}_3$  drawdown in two regions ( $40^{\circ}\text{N}$ – $45^{\circ}\text{N}$  and  $35^{\circ}\text{N}$ – $40^{\circ}\text{N}$ , respectively). Summertime daily *NCP* for these two provinces was equal at  $14$ – $15 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , but the southern region had a much shorter export season. Juraneck [2007] and Juraneck *et al.* [2012] estimated daily *NCP* in the transition zone mixed layer ( $\sim 32^{\circ}\text{N}$ – $42^{\circ}\text{N}$ ) of 21 and 13  $\text{mmol C m}^{-2} \text{ d}^{-1}$  in spring and summer, respectively, and Howard *et al.* [2010] ( $30^{\circ}\text{N}$ – $45^{\circ}\text{N}$ ) estimated rates of 8  $\text{mmol C m}^{-2} \text{ d}^{-1}$  in summer and 3  $\text{mmol C m}^{-2} \text{ d}^{-1}$  in fall, based on  $\text{O}_2/\text{Ar}$  measurements (Table 1).

## 2.3. $\text{O}_2/\text{Ar}$ Method for Estimating *NCP*

[14] The saturation level of the  $\text{O}_2/\text{Ar}$  gas ratio in the mixed layer coupled with air-sea gas exchange rate yields quantitative estimates of *NCP* that are mostly insensitive to nonbiological gas saturation processes (e.g., warming, bubble injection) because argon is an inert analog of oxygen, as described previously [Craig and Hayward, 1987 and Emerson *et al.*, 1991, 1997].

[15] Briefly, the biological  $\text{O}_2$  supersaturation, which quantifies the influence of *NCP* on the  $\text{O}_2$  budget, is defined as:

$$\frac{\Delta \text{O}_2}{\text{Ar}} = \frac{\left[ \frac{\text{O}_2}{\text{Ar}} \right]_{\text{msr}}}{\left[ \frac{\text{O}_2}{\text{Ar}} \right]_{\text{sat}}} - 1 \quad (1)$$

where  $[\text{O}_2/\text{Ar}]_{\text{msr}}$  is the measured dissolved  $\text{O}_2/\text{Ar}$  gas ratio, and  $[\text{O}_2/\text{Ar}]_{\text{sat}}$  is the ratio expected at saturation with air (based on temperature and salinity dependence of  $\text{O}_2$  and Ar solubility [García and Gordon, 1992; Hamme and Emerson,

2004]). The percent biological O<sub>2</sub> supersaturation (%O<sub>2</sub><sub>bio</sub>) equals ( $\Delta O_2/Ar$ )\*100.

[16] *NCP* is calculated using O<sub>2</sub> and Ar mass balances for the mixed layer, typically assuming steady state and negligible physical supply, yielding:

$$NCP = k_{O_2}[O_2]_{\text{sat}} \frac{\Delta O_2}{Ar} \quad (2)$$

where  $k_{O_2}$  is the gas transfer velocity of O<sub>2</sub> (m d<sup>-1</sup>) and  $[O_2]_{\text{sat}}$  is the concentration of O<sub>2</sub> at saturation (mol m<sup>-3</sup>) [García and Gordon, 1992]. We determined  $k_{O_2}$  using winds from QuikScat, the Ho *et al.* [2006] wind speed parameterization using a 60-day time-weighting technique [Reuer *et al.*, 2007], and the temperature- and salinity-dependent Schmidt number [Wanninkhof, 1992]. To convert O<sub>2</sub>-based *NCP* to C-based *NCP*, we used a ratio of 1.4 O<sub>2</sub>:1 C (export or new production) [Laws, 1991]. This estimate of *NCP* integrates over the residence time of O<sub>2</sub> in the mixed layer (i.e., (mixed layer depth)/ $k_{O_2}$ ), which was 8–14 days. The strong vertical stratification and low winds observed during the cruise favored a negligible impact of vertical mixing on the mixed layer O<sub>2</sub> budget.

### 3. Methods

#### 3.1. Underway and Discrete Sampling and Cruise Track

[17] We continuously measured surface O<sub>2</sub>/Ar, *p*CO<sub>2</sub>, temperature, salinity and fluorescence from the underway system of the R/V Thompson (at ~5 m intake) on a cruise between Station P and Honolulu, Hawaii (30 August–15 September 2008; Figure 1). Temperature and salinity were measured using the ship's TSG. Underway chl-*a* was estimated based on continuous fluorometer measurements calibrated with discrete chl-*a* samples measured using standard methods on a shipboard Turner fluorometer [Strickland and Parsons, 1972]. Mixed layer depth was determined using CTD profiles along the ship's cruise track at a resolution of ~1°–2° latitude as a density increase of 0.125 kg m<sup>-3</sup> from the surface value. Concentrations of nitrate, phosphate and silicate were determined on discrete surface samples collected by Niskin using a shipboard autoanalyzer (Technicon AutoAnalyzer II) and standard methods [Intergovernmental Oceanography Commission, 1994].

#### 3.2. Continuous O<sub>2</sub>/Ar Measurements Using EIMS

[18] We continuously measured surface O<sub>2</sub>/Ar using an EIMS system similar to that described in Cassar *et al.* [2009]. Water from the ship's underway line was pumped at ~2 L min<sup>-1</sup> through a coarse filter to screen out particulates into a 1 L graduated cylinder on which the equilibrator cartridge (Membrana MicroModule G569, 0.75" × 1") was mounted. Water from the graduated cylinder was pumped through a 5 μm filter sock sewed inside a 100 μm filter sock (1.5" × 12", McMaster-Carr), and then through the cartridge at ~100 ml min<sup>-1</sup>. To prevent biofouling, the coarse filter was cleaned and the sock filter was replaced daily, and the equilibrator cartridge was replaced weekly. All tubing used was Tygon silver (antimicrobial).

[19] Headspace gas from the equilibrator was delivered through an 0.05 mm fused silica capillary to the quadrupole

mass spectrometer (Pfeiffer Prisma QMS), which was kept at a constant temperature (40° ± 2°C). Individual ion currents (O<sub>2</sub>, Ar) were measured at 1-s intervals, and the ratio of O<sub>2</sub>/Ar currents was averaged to a 10-min timescale. The EIMS system e-folding response time is 7 min [Cassar *et al.*, 2009], yielding a spatial resolution of ~2 km at the average ship speed of 10 knots.

[20] EIMS-based O<sub>2</sub>/Ar measurements were calibrated using the O<sub>2</sub>/Ar of air measured by the EIMS, and O<sub>2</sub>/Ar measured by isotope ratio mass spectrometer (IR-MS) on discrete samples collected from either the underway line or surface (5 m) Niskin bottles approximately every 6–8 h following the collection procedures of Emerson *et al.* [1995] and mass spectrometer procedures of Juranek and Quay [2005] in the University of Washington Stable Isotope Lab. The percent error ([s.d./mean]\*100) in O<sub>2</sub>/Ar of discrete air standards used for IR-MS calibration was 0.2% and that of duplicate samples was 0.1%. The O<sub>2</sub>/Ar of discrete samples measured simultaneously on the ship's underway line and from surface Niskins compared well (0.1% error), showing no evidence of O<sub>2</sub> consumption in the underway line.

[21] We estimated error in *NCP* using a Monte-Carlo approach assigning uncertainty in the following terms:  $k_{O_2} \pm 15\%$  (twice the spread in  $k_{O_2}$  values predicted by three parameterizations recently validated by Ho *et al.* [2011]; Nightingale *et al.* [2000], Ho *et al.* [2006], and Sweeney *et al.* [2007]) and O<sub>2</sub>/Ar ± 0.06 (s.d. of mean in offset between EIMS and discrete samples). Mean *NCP* percentage error ([s.d./mean]\*100) was 18% in the subarctic, 27% in the transition zone and 25% in the subtropics.

#### 3.3. Measurements of *p*CO<sub>2</sub> and Estimate of CO<sub>2</sub> Flux

[22] We continuously measured the *p*CO<sub>2</sub> in surface water from the ship's underway line and air from the bow with an automated IR-detection-based underway *p*CO<sub>2</sub> measuring system that has been described in detail elsewhere [Feely *et al.*, 1998; Pierrot *et al.*, 2009]. We calculated the air-sea *p*CO<sub>2</sub> gradient ( $\Delta pCO_2$ ) as  $\Delta pCO_2 = pCO_{2\text{SW}} - pCO_{2\text{atm}}$ , where  $pCO_{2\text{SW}}$  is the calculated *p*CO<sub>2</sub> of the seawater (after correction for water temperature difference between in situ and the *p*CO<sub>2</sub> equilibrator) and  $pCO_{2\text{atm}}$  is the measured atmospheric *p*CO<sub>2</sub>. After correction, the accuracy of the data is within 0.1 μatm for  $pCO_{2\text{atm}}$  and 2 μatm for  $pCO_{2\text{SW}}$  [Pierrot *et al.*, 2009], and the equilibrator integration time is 30–45 s. *p*CO<sub>2</sub> data were averaged to match the 10-min integration time of the EIMS data.

[23] The air-sea flux of CO<sub>2</sub> is calculated based on  $\Delta pCO_2$  and the solubility ( $k_H$ ) [Stumm and Morgan, 1996] and gas transfer velocity of CO<sub>2</sub> ( $k_{CO_2}$ ):

$$CO_2 \text{ flux} = k_{CO_2} k_H \Delta pCO_2 \quad (3)$$

Defined in this way,  $CO_2 \text{ flux}$  from the atmosphere into the ocean (influx) is negative, and efflux is positive.  $k_{CO_2}$  was calculated as described above for  $k_{O_2}$  using the Ho *et al.* [2006] wind speed parameterization with time-weighting [Reuer *et al.*, 2007], and the Schmidt number for CO<sub>2</sub> [Wanninkhof, 1992].

#### 3.4. Flow Cytometry Measurements

[24] Cell counts of phytoplankton groups were collected from the flow-through system of the R/V Thompson at

various intervals along the ship track or from surface (5 m) Niskins. Samples were preserved in liquid nitrogen and processed later in the lab. Cells were enumerated and classified using a FACS-Caliber flow cytometer [Sherr *et al.*, 2005]. Following the protocol of Sherr *et al.* [2005], prokaryotes were stained with SYBR-green; *Prochlorococcus* counts were subtracted from heterotrophic bacteria counts. We binned data into microphytoplankton (10–60  $\mu\text{m}$ ), nanophytoplankton (2–10  $\mu\text{m}$ ) and picophytoplankton (1–2  $\mu\text{m}$ ); the picophytoplankton fraction was dominated by *Synechococcus* north of the TZCF and *Prochlorococcus* south of it.

### 3.5. Climatological $p\text{CO}_2$ , $\text{CO}_2$ Flux, Alkalinity and DIC

[25] We used a recent climatological surface  $p\text{CO}_2$  data set [Takahashi *et al.*, 2009] to compare our  $p\text{CO}_2$  measurements with the seasonal cycle of  $p\text{CO}_2$  and DIC over our cruise track (section 5.3). This data set includes monthly  $p\text{CO}_{2\text{SW}}$ ,  $p\text{CO}_{2\text{atm}}$ , SST, salinity and wind speed data at resolution of  $4^\circ$  latitude  $\times$   $5^\circ$  longitude, with  $p\text{CO}_2$  data normalized to reference year 2000. We calculated climatological monthly  $\text{CO}_2$  flux using the climatological  $p\text{CO}_{2\text{SW}}$ ,  $p\text{CO}_{2\text{atm}}$ , temperature, salinity, wind speed and Ho *et al.* [2006] parameterization of gas transfer velocity and compared it to our continuous  $\text{CO}_2$  flux estimates in September 2008 (normalized to year 2000).

[26] To estimate the seasonal climatological DIC cycle for the region covered on our cruise, we used the climatological temperature and salinity data to calculate monthly alkalinity with the latitude-dependent parameterization of Lee *et al.* [2006], and used these alkalinity values and  $p\text{CO}_2$  to calculate monthly DIC with the program CO2sys [Lewis and Wallace, 1998]. We used monthly climatological mixed layer depth from Monterey and Levitus [1997] at  $1^\circ$  resolution, bin-averaged to the  $4^\circ$  latitude  $\times$   $5^\circ$  longitude boxes of the Takahashi *et al.* [2009] data set.

## 4. Results

### 4.1. Regional Setting

[27] We categorize our results into three regions: the subarctic ( $45^\circ\text{N}$ – $50^\circ\text{N}$ ), transition zone ( $32^\circ\text{N}$ – $45^\circ\text{N}$ ) and subtropics ( $22^\circ\text{N}$ – $32^\circ\text{N}$ ). Sea surface temperature and salinity generally increased and density decreased from the subarctic to the subtropical gyre, with a local density minimum at  $\sim 35^\circ\text{N}$  within the transition zone (Figure 2). The strong gradients in surface salinity (and weaker SST gradients) of the SAFZ and STFZ are apparent (Figure 2) at  $\sim 38^\circ\text{N}$ – $43^\circ\text{N}$ , and  $\sim 32^\circ\text{N}$ – $37^\circ\text{N}$ , respectively, extending slightly farther than their climatological positions ( $40^\circ\text{N}$ – $43^\circ\text{N}$  and  $31^\circ\text{N}$ – $34^\circ\text{N}$ , respectively). The strongest surface density gradients were in the northern transition zone ( $40^\circ\text{N}$ – $45^\circ\text{N}$ ) and subtropics ( $22^\circ\text{N}$ – $24^\circ\text{N}$ ) (Figure 2). The TZCF (location of the  $0.2 \text{ mg m}^{-3}$  chl-*a* isopleth) ranged from  $42^\circ\text{N}$  to  $44^\circ\text{N}$  within the northern transition zone (Figure 3), consistent with its climatological late summer position ( $40^\circ\text{N}$ – $45^\circ\text{N}$ ) [Polovina *et al.*, 2001].

[28] Mixed layer was relatively shallow, reflecting late summer conditions; mean depths decreased from 32 m in the subarctic to a local minimum (26 m) in the transition zone, and then increased to 51 m in the subtropics (Figure 2).  $k_{\text{O}_2}$  was fairly low ( $3$ – $5 \text{ m d}^{-1}$ ), and was highest in the subarctic

and northern transition and lowest in the southern transition zone (Figure 3). Due to variation in mixed layer depth and  $k_{\text{O}_2}$ , the  $\text{O}_2$  residence time in the surface layer increased southward from a mean of 8 days in the subarctic and transition to 14 days in the subtropics.

### 4.2. Subarctic

[29] In the subarctic, we observed high biological  $\text{O}_2$  saturation ( $\%O_{2\text{bio}}$ ) and chl-*a* and low  $\Delta p\text{CO}_2$ , with high meridional and zonal variability (Figure 3).  $\%O_{2\text{bio}}$  and chl-*a* were highly correlated.  $p\text{CO}_2$  was highly negatively correlated with  $\%O_{2\text{bio}}$  and chl-*a*, and only weakly correlated with SST (Table 2). At the southern edge of the subarctic along  $145^\circ\text{W}$ , strong peaks in  $\%O_{2\text{bio}}$  and chl-*a* were coupled with troughs in  $\Delta p\text{CO}_2$  (Figure 3). Surface nutrient concentrations at OSP (6  $\mu\text{M}$  nitrate and 4  $\mu\text{M}$  silicate, respectively) were lower than typical late summer concentrations of 9  $\mu\text{M}$  nitrate and 14  $\mu\text{M}$  silicate [Harrison *et al.*, 2004] (Figure 3).

[30] NCP and  $\text{CO}_2$  influx had similar spatial trends to  $\%O_{2\text{bio}}$  and  $\Delta p\text{CO}_2$ , and their mean values were highest in the subarctic among cruise regions ( $25.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$  and  $4.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , respectively; Figure 4). NCP was highly correlated with  $\text{CO}_2$  influx ( $r = 0.89$ ), with a slope of 2.6 (Table 2). Flow cytometry results (Figure 4) show high concentrations of all three phytoplankton classes in the subarctic. NCP was most highly correlated with concentrations of microphytoplankton ( $r = 0.50$ ) in this region.

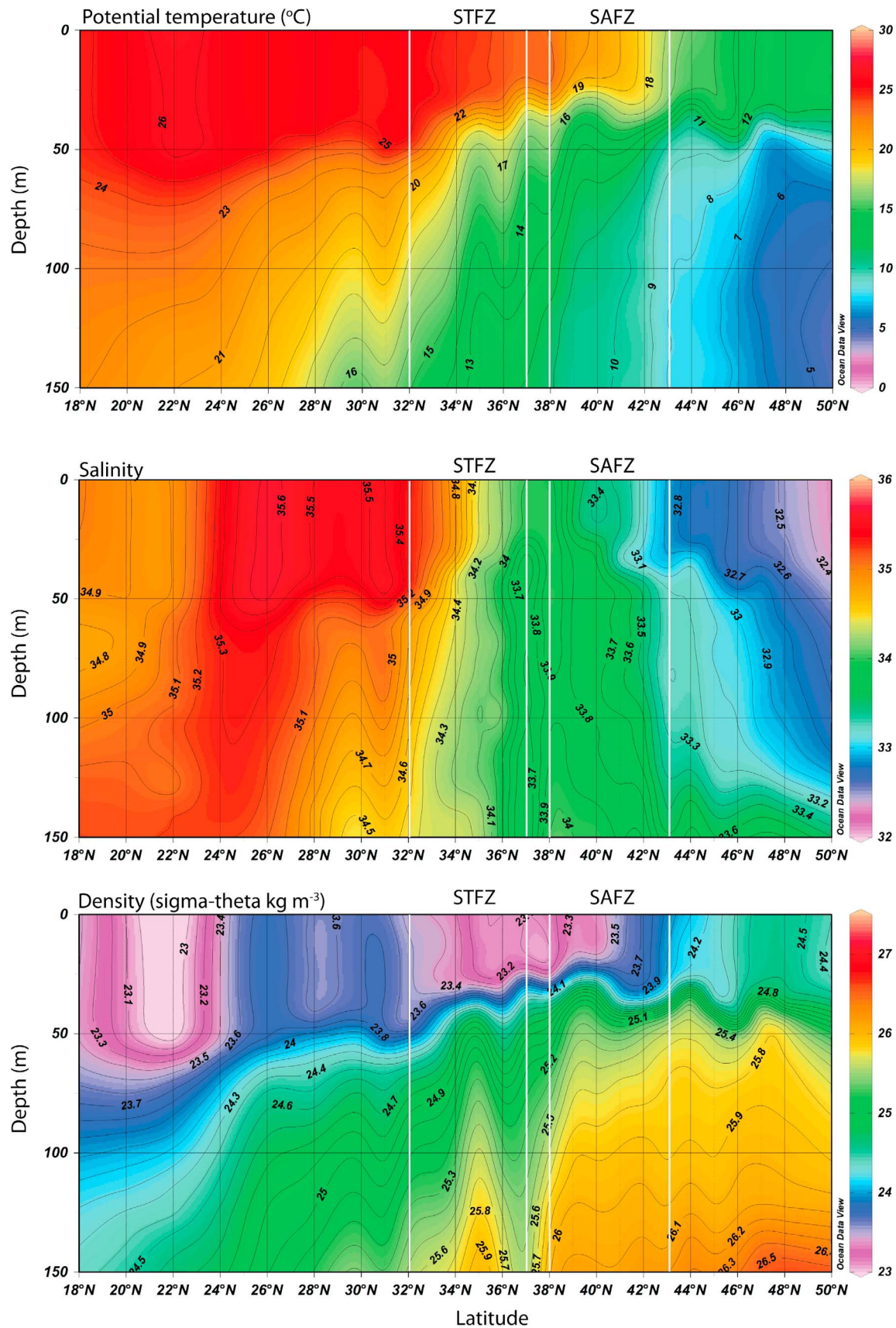
### 4.3. Transition Zone

[31] The transition zone represented a shift from the high-chl-*a*, high- $\%O_{2\text{bio}}$ , low- $p\text{CO}_2$ , high-nutrient conditions of the subarctic to opposite conditions in the subtropics. At the boundary between the northern transition zone and subarctic, in the vicinity of the TZCF, we observed coincident peaks in  $\%O_{2\text{bio}}$  and chl-*a* and troughs in  $\Delta p\text{CO}_2$ , with high zonal variability (Figure 3). In the southern transition zone ( $32^\circ\text{N}$ – $40^\circ\text{N}$ ),  $\%O_{2\text{bio}}$  and chl-*a* decreased. At  $\sim 42^\circ\text{N}$ ,  $p\text{CO}_2$  shifted from undersaturated values to the north to supersaturated values to the south, and remained supersaturated in the southern transition zone.

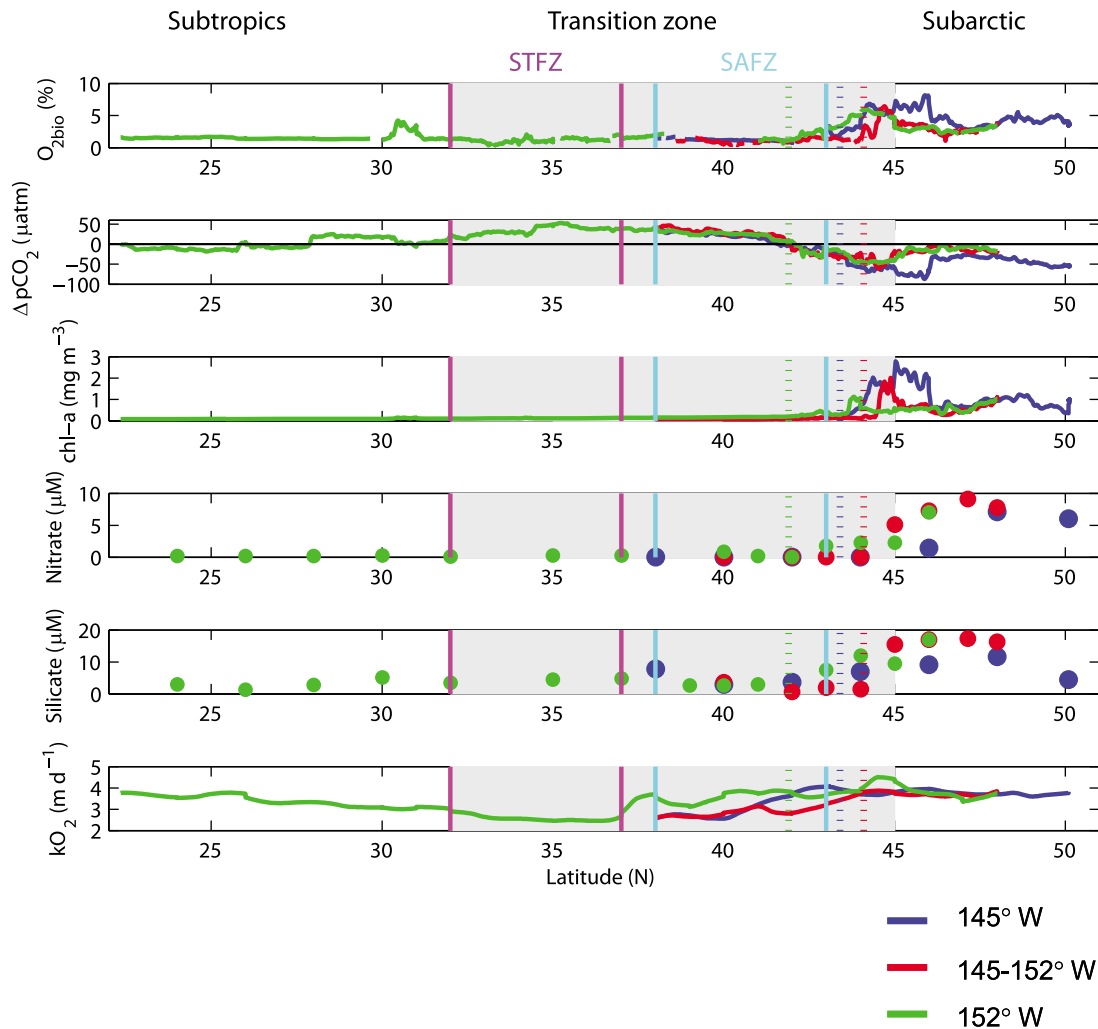
[32] Throughout the transition zone, chl-*a* and  $\%O_{2\text{bio}}$  were positively correlated ( $r = 0.85$ ), and  $p\text{CO}_2$  and  $\%O_{2\text{bio}}$  were negatively correlated ( $r = -0.75$ ), similarly to the subarctic. But in contrast with the subarctic,  $p\text{CO}_2$  was positively correlated with SST ( $r = 0.87$ ; Table 2). Surface nitrate and silicate declined from the subarctic to northern transition zone; nitrate approached the detection limit at the TZCF and remained  $< 1 \mu\text{M}$  in the southern transition zone.

[33] From the northern to the southern transition zone, NCP declined (mean 17.1 and 5.4  $\text{mmol C m}^{-2} \text{ d}^{-1}$ , respectively), and  $\text{CO}_2$  flux varied from an influx to an efflux (Figure 4 and Table 2). Meridional and zonal ( $145^\circ\text{W}$ – $152^\circ\text{W}$ ) variability in fluxes were high in the northern transition zone. Throughout the transition zone, NCP and  $\text{CO}_2$  influx were correlated with a similar  $r$  (0.85) and slope (2.4) to that in the subarctic (Table 2).

[34] Throughout the transition zone, NCP was highly correlated with microphytoplankton and nanoplankton ( $r = 0.89$  and 0.83, respectively), and less strongly correlated with picophytoplankton ( $r = 0.58$ ). NCP was also highly correlated with the fraction of total cell count made up by



**Figure 2.** Depth sections of potential temperature, salinity and potential density ( $\sigma_\theta$ ) measured on cruise along 152°W. The SAFZ and STFZ are bounded with white lines.



**Figure 3.** Continuous underway measurements of surface  $\%O_{2bio}$ ,  $\Delta pCO_2$ ,  $chl-a$ , nitrate, silicate and  $k_{O_2}$  along three legs of cruise track. Blue and magenta lines bound SAFZ and STFZ, respectively. Dotted vertical lines, position of TZCF (colors refer to cruise legs; see key). Transition zone is highlighted in gray.

microphytoplankton ( $r = 0.72$ ). In the northern transition zone, high abundance of micro- and nanophytoplankton coincided with high  $NCP$  and  $CO_2$  uptake (Figure 4).

#### 4.4. Subtropics

[35] In the subtropics,  $\%O_{2bio}$ ,  $chl-a$ , and nutrients were low, similar to conditions in the southern transition zone, with the exception of a small peak in  $\%O_{2bio}$  at  $30.5^\circ N$ .  $\Delta pCO_2$  generally decreased southward from a maximum in the southern transition zone. Throughout the subtropics,  $chl-a$  was highly correlated with  $\%O_{2bio}$  ( $r = 0.86$ ).  $pCO_2$  was weakly negatively correlated with both  $\%O_{2bio}$  and SST (Table 2). Surface nitrate was below detection limit throughout most of the subtropics, and surface silicate averaged  $3 \mu M$ .

[36] Mean  $NCP$  in the subtropics ( $8.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ; Figure 4) was slightly higher than that in the southern transition zone. Mean  $CO_2$  flux was close to zero, and  $CO_2$  influx was weakly correlated with  $NCP$  (Figure 4 and Table 2).  $NCP$  was weakly correlated with picophytoplankton (*Prochlorococcus*) throughout the subtropics (Table 2). A peak in  $NCP$  at  $\sim 30.5^\circ N$  of  $22 \text{ mmol C m}^{-2} \text{ d}^{-1}$

corresponded to a small  $CO_2$  influx. In the region of this peak ( $30^\circ N$ – $31.2^\circ N$ ),  $NCP$  was highly correlated with  $chl-a$  ( $r = 0.97$ ) and  $CO_2$  influx ( $r = 0.69$ ), and the  $NCP:CO_2$  influx slope (3.3) was similar to that observed in the subarctic and northern transition zone (Table 2).

## 5. Discussion

### 5.1. Rates of $NCP$ and $CO_2$ Uptake

[37] In the subarctic,  $NCP$  ( $25.8 \pm 4.6 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) and  $CO_2$  influx ( $4.1 \pm 0.9 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) reached their highest mean values along the cruise track. These values were  $\sim 2\times$  higher than the mean of previous estimates of  $NCP$  and climatological  $CO_2$  influx for this region (Table 1 and Takahashi et al. [2009, Table 2]). Mean  $chl-a$  ( $0.8 \text{ mg m}^{-3}$ ) was almost twice as high as usual for September based on the SeaWiFS 9-km  $chl-a$  time series for 1997–2010 (Figure 5), reflecting a phytoplankton bloom in this region. This bloom was most likely stimulated by iron deposited with volcanic ash in the early August 2008 eruption of the Aleutian island volcano Kasatochi [Hamme et al., 2010; Langmann et al., 2010].

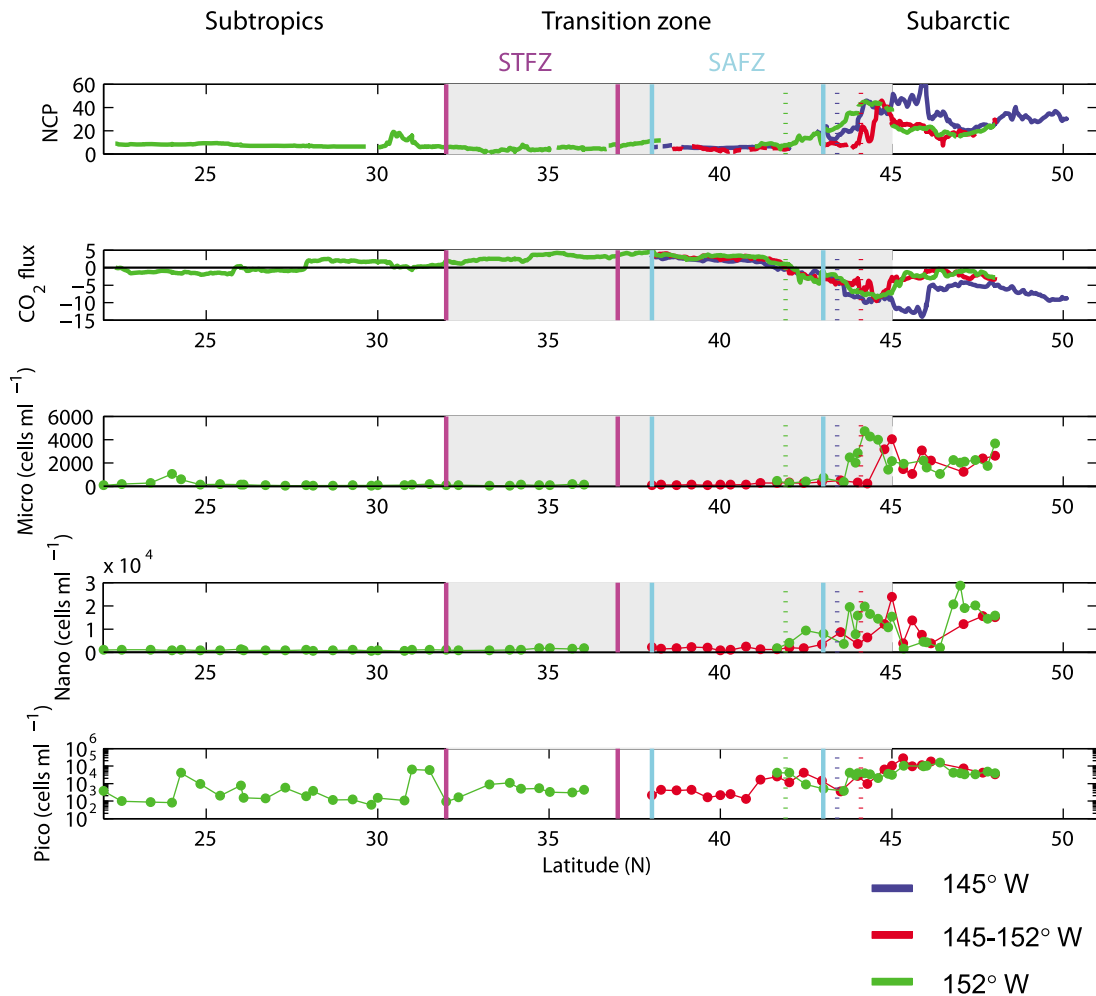
**Table 2.** Mean Values and Correlation Statistics for Underway Measurements

Region	$NCP^a$ (mmol C m <sup>-2</sup> d <sup>-1</sup> )	$CO_2 flux^a$ (mmol C m <sup>-2</sup> d <sup>-1</sup> )	Climatol. $CO_2 flux^b$ (mmol C m <sup>-2</sup> d <sup>-1</sup> )	$chl-a$ ( $\mu g m^{-3}$ )	$\%O_{2bio}^-$ $chl-a$	$\%O_{2bio}^-$ $pCO_2$	Correlation Coefficient ( $r$ )						Slope $NCP-CO_2$ Influx
							$SST-pCO_2$	$SST-CO_2$ Influx	$SST-CO_2$ $flux$	$NCP-micro$ $NCP-f_{micro}$	$NCP-nano$ $NCP-f_{nano}$	$NCP-pico$ $NCP-f_{pico}$	
Subarctic (45°N–50°N)	25.8 ± 4.6 [9.3]	-4.1 ± 0.9 [3.1]	-1.7 ± 0.3	0.8	0.82	-0.81	0.10	0.89	-0.17	0.50	0.17	0.15	2.8
Transition (32°N–45°N)	11.8 ± 3.2 [1.8]	0.2 ± 0.0 [4.0]	1.5 ± 1.3	0.3	0.85	-0.75	0.87	0.85	0.84	0.89	0.83	0.58	2.4
Northern (40°N–45°N)	17.1 ± 4.4 [13.7]	-2.1 ± 0.5 [4.0]	1.1 ± 1.0	0.4	0.83	-0.78	0.94	0.84	0.95	0.73	0.07	-0.16	2.9
Southern (32°N–40°N)	5.4 ± 1.8 [2.3]	3.0 ± 0.5 [0.7]	2.6 ± 1.8	0.1	0.54	0.21	0.18	-0.57	0.08*	0.75	0.05	-0.14	-1.6
Subtropics (22°N–32°N)	8.1 ± 2.1 [2.6]	0.1 ± 0.0 [1.3]	0.8 ± 0.1	0.1	0.86	-0.17	-0.50	0.34	-0.50	0.12	-0.21	0.32	0.7
All data										0.08	-0.28	0.19	
Bloom region (30°N–31.2°N)	12.3	0.5	-	0.1	0.97	-0.69	-0.79	0.71	-0.79	0.74	-0.26	0.50	3.3
										-0.11	-0.57	0.52	

<sup>a</sup>Values for  $NCP$  and  $CO_2 flux$  are mean ± error of 1  $\sigma$  (regional s.d. is in brackets). Negative  $CO_2 flux$  represents oceanic  $CO_2$  uptake. Correlation coefficient ( $r$ ) is shown between two parameters listed at top of each column. All correlations were significant ( $P < 0.001$  for all cells except cell marked with an asterisk,  $P < 0.02$ ). Micro, microphytoplankton; nano, nanophytoplankton; pico, picophytoplankton;  $f_{micro}$ ,  $f_{nano}$  and  $f_{pico}$  are the respective fractions of total cell count made up by these phytoplankton classes.

<sup>b</sup>Climatological  $CO_2 flux$  is presented for comparison, aligned with climatological boxes that most closely correspond to it: subarctic, 46°N–50°N; transition, 30°N–46°N; northern transition, 38°N–46°N; southern transition, 30°N–38°N; subtropics, 22°N–30°N.





**Figure 4.** Continuous estimates of  $NCP$  and  $CO_2$  flux and flow cytometry-derived concentrations of microphytoplankton ( $10\text{--}60\ \mu\text{m}$ ), nanophytoplankton ( $2\text{--}10\ \mu\text{m}$ ) and picophytoplankton ( $1\text{--}2\ \mu\text{m}$ ) along legs of cruise track. Units of  $NCP$  and  $CO_2$  flux are  $\text{mmol C m}^{-2}\ \text{d}^{-1}$ ; negative  $CO_2$  flux represents oceanic  $CO_2$  uptake. Picophytoplankton represent *Synechococcus* north of the TZCF and *Prochlorococcus* south of it. Blue and magenta lines bound SAFZ and STFZ, respectively. Dotted vertical lines, position of TZCF (colors refer to cruise legs; see key). Transition zone is highlighted in gray.

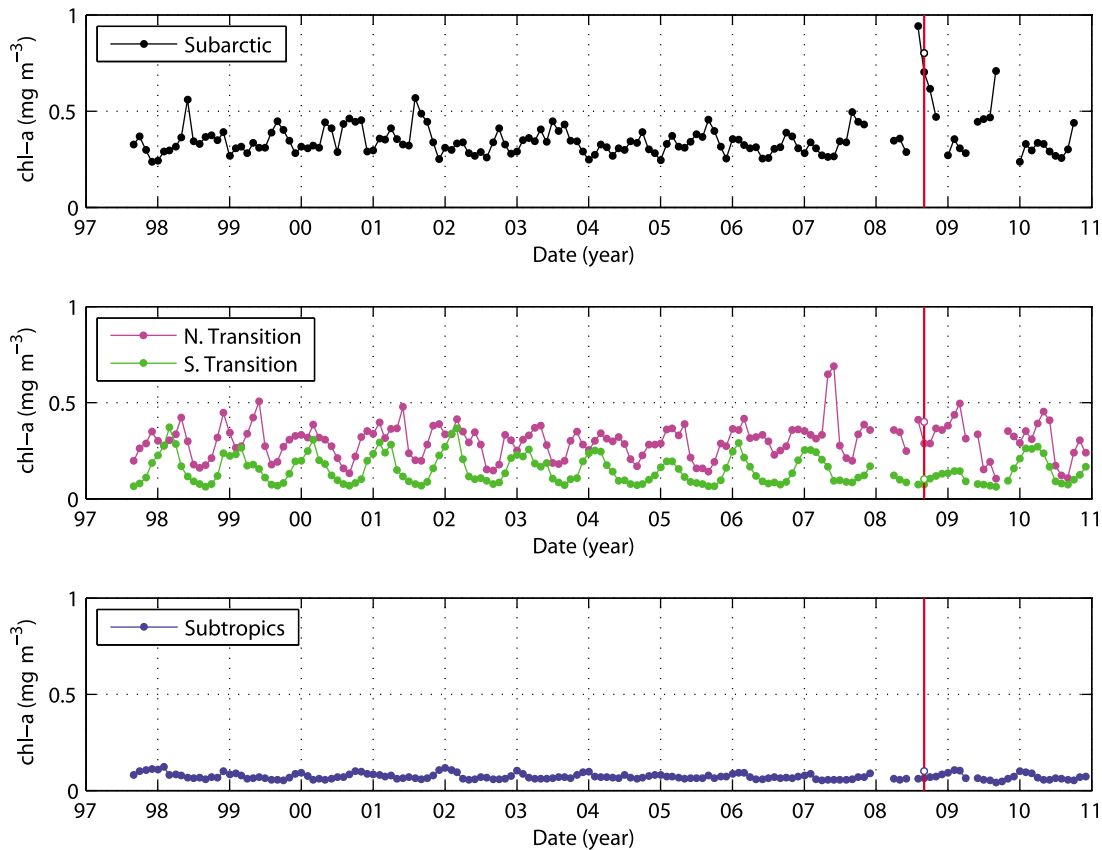
[38] The high  $NCP$  and  $CO_2$  influx in the subarctic estimated during our cruise were consistent with bloom conditions, although there is evidence that we sampled during a declining stage of this bloom. SeaWiFS *chl-a* in our cruise region declined from August to September and onward (Figure 5). At OSP, our  $O_2/Ar$ -based  $NCP$  on 30 August ( $30\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ) was lower than  $O_2/Ar$ -based  $NCP$  ( $43\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ) estimated on 21 August [Hamme *et al.*, 2010].

[39] In the subtropics, mean  $NCP$  ( $8.1 \pm 2.1\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ) was very similar to that previously observed at ALOHA ( $8 \pm 4\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ; Table 1), indicating that observations at this station are generally representative of the NE Pacific subtropical region.  $CO_2$  flux showed a weak efflux ( $0.1 \pm 0.0\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ),  $\sim 8\times$  lower than climatological September  $CO_2$  efflux (Table 2). *Chl-a* in the subtropics ( $0.1\ \text{mg m}^{-3}$ ) was similar to typical September values from the SeaWiFS time series (Figure 5).

[40] Although  $NCP$  in the subtropics was  $\sim 3\times$  lower than in the subarctic during our cruise, we observed a peak in

$NCP$  at  $30^\circ\text{N}\text{--}31^\circ\text{N}$ ,  $152^\circ\text{W}$  (Figure 4) associated with the late summer bloom that has been previously observed in this region ( $\sim 30^\circ\text{N}$ ,  $130^\circ\text{W}\text{--}160^\circ\text{W}$ ) and that can last up to 3–4 months [Wilson *et al.*, 2008]. This recurrent bloom has been attributed both to  $N_2$  fixation by unicellular cyanobacteria and endosymbionts, and to *Rhizosolenia* diatom mats that can vertically migrate into the nitracline through ballasting [Wilson, 2003; Wilson *et al.*, 2008].  $NCP$  estimates at  $30^\circ\text{N}\text{--}31^\circ\text{N}$  peaked at  $19\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ , approximately twice the mean subtropical rate.

[41] The transition zone ( $32^\circ\text{N}\text{--}45^\circ\text{N}$ ) had mean  $NCP$  intermediate between the subarctic and subtropics ( $11.8 \pm 3.2\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ; Table 2), and within the range of previous  $NCP$  estimates in both the subarctic and transition zone (Table 1). Notably,  $NCP$  in the transition zone had much higher spatial variability than in the subarctic or subtropics, with regional s.d. of 11.8, equivalent to the mean (Table 2). It had mean  $CO_2$  efflux ( $0.2 \pm 0.0\ \text{mmol C m}^{-2}\ \text{d}^{-1}$ ) that was  $\sim 7\times$  lower than September climatological efflux (Table 2).



**Figure 5.** Time series of monthly satellite-based SeaWiFS 9-km *chl-a* (1997–2010) averaged over cruise regions (longitude 145°W–155°W, latitudes 45°N–50°N for subarctic, 40°N–45°N for northern transition, 32°N–40°N for southern transition, 22°N–30°N for subtropics). Grid lines mark beginning of each year. Red line marks month of cruise and open circles show mean *chl-a* measured on cruise. Figure made using data from NASA Giovanni.

[42] In the northern transition zone, mean *NCP* ( $17.1 \pm 4.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) was similar to a previous estimate in this region (Table 1) and on the high end of previous summertime *NCP* estimates in the subarctic. Both meridional and zonal (145°W–152°W) *NCP* variability were high in this region (regional s.d. = 13.7, Table 2).  $\text{CO}_2$  influx ( $2.1 \pm 0.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ ) here was greater than climatological September estimates, which show a mean efflux of  $1.1 \pm 1.0 \text{ mmol C m}^{-2} \text{ d}^{-1}$  (Table 2); this discrepancy could be attributable to the anomalous bloom conditions in the subarctic, or to interannual variability in the frontal dynamics of the transition region. Based on the SeaWiFS time series (Figure 5) *chl-a* was not anomalously high during our cruise in either of these regions, as it was in the subarctic. In the southern transition zone, *NCP* at  $5.4 \pm 1.8 \text{ mmol C m}^{-2} \text{ d}^{-1}$  was similar to previous estimates at ALOHA, and mean  $\text{CO}_2$  efflux was  $3.0 \pm 0.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$ , similar to the September climatological value in this region (Table 2).

[43] Compared with a wealth of *NCP* estimates at OSP in the subarctic and ALOHA in the subtropics, we have only a few snapshots of *NCP* in the transition zone. Based on our results and previous studies, *NCP* in the northern transition zone resembles the subarctic, with comparably high summertime daily *NCP* rates (Table 1) and a strong link between

*NCP* and  $\text{CO}_2$  uptake. We observed the highest spatial variability in *NCP* and  $\text{CO}_2$  flux in this region, and it has high interannual variability in satellite *chl-a* (Figure 5). Frontal dynamics in this region likely play a role in this temporal and spatial biological patchiness, as we discuss further below. In contrast, the southern transition zone resembles the subtropical gyre, with lower daily *NCP* rates that peak in spring, lower spatial variability and a summertime  $\text{CO}_2$  efflux.

## 5.2. Impact of *NCP* on $\text{CO}_2$ Uptake

[44] Through the high spatial resolution of our measurements, we observed several regions in which *NCP* and  $\text{CO}_2$  influx were highly coupled, demonstrating a link between the biological pump and atmospheric  $\text{CO}_2$  uptake on a ~2-week timescale. In the subarctic, we observed this high correlation during the decline of the anomalous bloom (including micro- and nanophytoplankton) described above, most likely stimulated by volcanic deposition of iron. This could be characteristic of the “event-driven, mass sedimentation carbon pump” described by Karl *et al.* [2003] in which perturbations such as pulsed delivery of iron lead to blooms and aggregation of large phytoplankton like diatoms, resulting in rapid, efficient export events. These

results indicate that intermittent iron supply in this region (through volcanic events, eddy transport from the continental shelf or atmospheric deposition) would lead to a stronger carbon sink on short-term (seasonal) timescales.

[45] Throughout the transition zone, we observed similarly high correlation between *NCP* and  $\text{CO}_2$  influx. *NCP* was highly correlated with concentrations of micro- and nanoplankton, which were abundant in the northern transition zone, and was highly correlated with the fraction of total cell count comprising microphytoplankton. The SAFZ, STFZ and TZCF have been found to be associated with high *PP*, *NCP* and abundance of microphytoplankton by other researchers [Leonard et al., 2001; Juranek, 2007; Howard et al., 2010; Juranek et al., 2012].

[46] Frontal dynamics may play a role in the biological patchiness observed in the transition zone due to (i) meso-scale perturbations associated with frontal zones, leading to dynamic upwelling [Roden, 1991; Olson et al., 1994] that can bring nutrients to the surface and stimulate phytoplankton growth [Strass, 1992; Denman and Gargett, 1995]; (ii) variations in Ekman convergence and resulting nutrient supply at the TZCF [Ayers and Lozier, 2010]; and (iii) convergence of biomass (phytoplankton) at the TZCF [Polovina et al., 2001], as has been observed at similar convergent fronts [Mann and Lazier, 2006; Franks, 1992; Olson et al., 1994].

[47] In the subtropics, phytoplankton abundance (*chl-a*) and  $\%O_{2bio}$  were highly correlated as in the subarctic (Figure 3), but there was a much lower correlation between *NCP* and  $\text{CO}_2$  influx (Table 2;  $r = 0.20$  versus  $r = 0.89$  in the subarctic). This probably results from the strong influence of temperature on the summertime  $\text{CO}_2$  flux in this region, yielding a weaker link between *NCP* and  $\text{CO}_2$  uptake. The dominance of picophytoplankton over nano- and microphytoplankton in the subtropics (Figure 3) may also lead to less efficient export.

[48] We observed a peak in *NCP* at  $\sim 30^\circ\text{N}$ ,  $130^\circ\text{W}$ – $160^\circ\text{W}$ , where recurrent late summer phytoplankton blooms have been observed. In this region ( $30^\circ\text{N}$ – $31.2^\circ\text{N}$ ), *NCP* was highly correlated with *chl-a* and  $\text{CO}_2$  influx, and the slope of this correlation was similar to that observed in the subarctic and transition zone (Table 2). At this location, microphytoplankton and picophytoplankton (*Prochlorococcus*) dominated, and their abundances were highly correlated with *NCP* ( $r = 0.70$  and  $0.45$ , respectively).

### 5.3. Impact of *NCP* on $\text{CO}_2$ Uptake Over Annual Cycle

[49] Our snapshot observations demonstrate the strong link between *NCP* and  $\text{CO}_2$  uptake in the subarctic and transition zone. However, our larger goal is to put these estimates in the context of determining the impact of *NCP* on annual  $\text{CO}_2$  uptake in the North Pacific. To do this, we made two box model calculations to examine the seasonal cycle of  $p\text{CO}_2$  and *DIC* in our cruise region using a climatological surface  $p\text{CO}_2$  data set in boxes of  $4^\circ$  latitude  $\times$   $5^\circ$  longitude [Takahashi et al., 2009, section 3.5]. We first examined the seasonal cycle of  $p\text{CO}_2$  in a simplified “abiotic” system in which only temperature and gas exchange influence  $p\text{CO}_2$  and  $\text{CO}_2$  flux. Second, we used a simplified *DIC* mass balance approach to compare the annual climatological  $\text{CO}_2$  flux with the contribution of *NCP* and physical input of *DIC*.

#### 5.3.1. Abiotic $p\text{CO}_2$ Model

[50] A simplified mass balance of *DIC* in the mixed layer can be written as:

$$\frac{dDIC}{dt} = \frac{1}{h} FCO_{2(in)} + J_{\text{phys}} + J_{\text{nep}} \quad (4)$$

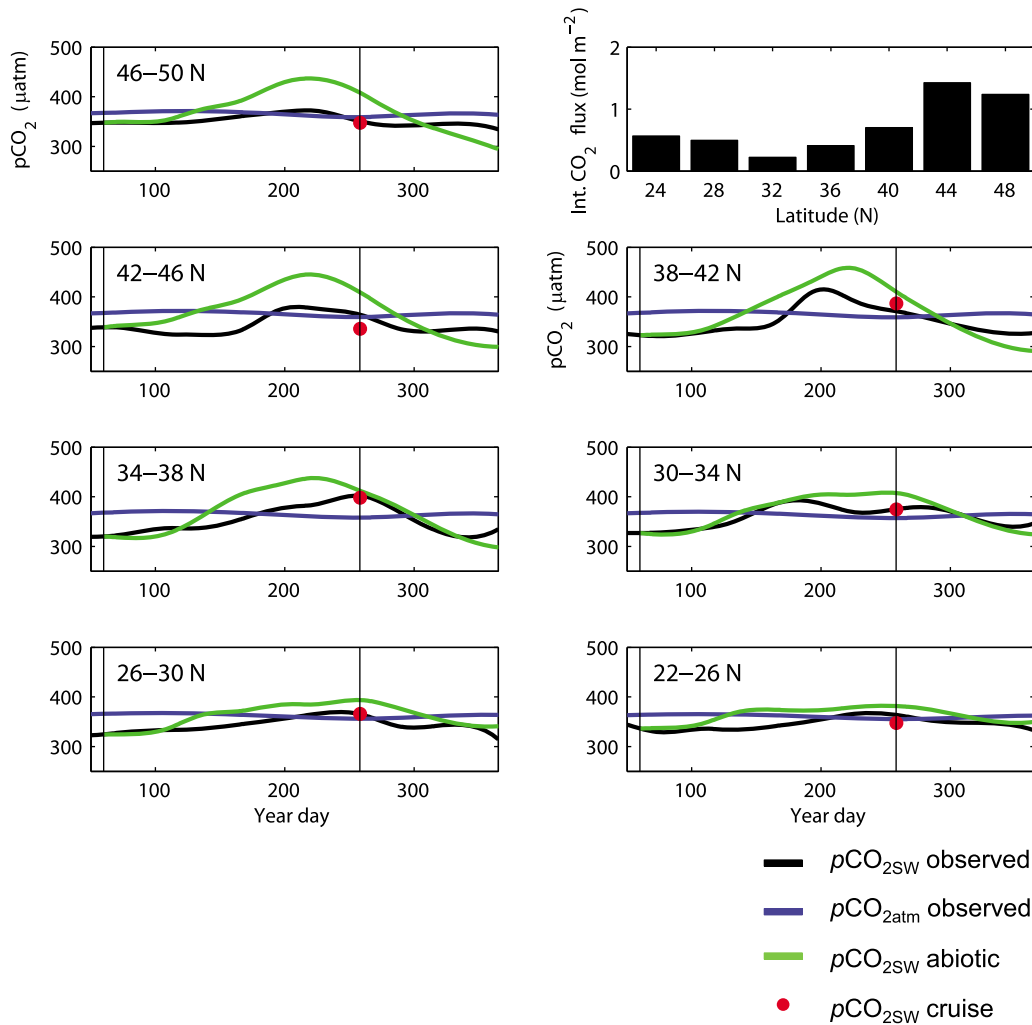
where  $FCO_{2(in)}$  is the sea-air flux of  $\text{CO}_2$  ( $k\text{CO}_2 * k_H(p\text{CO}_{2\text{atm}} - p\text{CO}_{2\text{SW}})$ ), with positive  $FCO_{2(in)}$  defined as into the ocean (note this is the opposite of the sign convention in equation (3) and our results),  $h$  is the mixed layer depth,  $J_{\text{phys}}$  is the physical input of *DIC* due to advection, diffusion and entrainment (with supply of *DIC* defined as positive and removal as negative), and  $J_{\text{nep}}$  is the export of carbon due to *NCP* (with respiratory source of *DIC* defined as positive and biological uptake of *DIC* as negative). The annual cycle of  $FCO_{2(in)}$  is mainly controlled by seasonal changes in surface ocean  $p\text{CO}_2$  with a secondary effect of variation in  $k\text{CO}_2$  due to seasonal wind speed variation.

[51] To separate the influence of temperature on  $p\text{CO}_2$  from the biological and physical effects, we described seasonal changes in  $p\text{CO}_2$  in an “abiotic” ocean in which only warming or cooling and air-sea gas exchange influenced seasonal changes in *DIC* and  $p\text{CO}_2$ . In this case, the *DIC* mass balance simplifies to:

$$\frac{dDIC}{dt} = \frac{1}{h} FCO_{2(in)} = \frac{1}{h} k\text{CO}_2 k_H (p\text{CO}_{2\text{atm}} - p\text{CO}_{2\text{SW}}) \quad (5)$$

[52] We initialized this abiotic model with the 1 March climatological  $p\text{CO}_{2\text{SW}}$  and *DIC*. We calculated the initial  $FCO_{2(in)}$  based on the 1 March climatological  $p\text{CO}_{2\text{SW}}$ ,  $p\text{CO}_{2\text{atm}}$ ,  $k_H$  and  $k\text{CO}_2$ . We distributed this  $FCO_{2(in)}$  over a daily time step and recalculated  $dDIC/dt$  and  $p\text{CO}_{2\text{SW}}$  based on thermodynamic equilibrium (using climatological daily interpolated values of  $h$ , alkalinity,  $p\text{CO}_{2\text{atm}}$ , temperature, salinity,  $k_H$  and  $k\text{CO}_2$ ; see Methods for details), and repeated the process for each subsequent daily time step. In the region of our study, the mixed layer generally begins to shoal in March, and therefore we assume that any influence of entrainment on *DIC* is negligible until late summer or early fall, when the mixed layer begins to deepen again.

[53] The observed (climatological)  $p\text{CO}_2$  peaks in summer in all boxes in our cruise region along  $152^\circ\text{W}$ , yielding a summertime  $\text{CO}_2$  efflux in all regions (Figure 6). In the abiotic model, however, the estimated summertime increase in  $p\text{CO}_2$  (and thus  $\text{CO}_2$  efflux) is greater than the observed  $p\text{CO}_2$  in all boxes. Biological ( $J_{\text{nep}}$ ) and physical ( $J_{\text{phys}}$ ; equation (4)) input or removal of *DIC* must be responsible for the difference in annual cycles of the predicted abiotic and observed  $p\text{CO}_2$ . In spring and summer in the subarctic and transition zone, when the mixed layer is shoaling or stable and wind speeds are low, removal of *DIC* by  $J_{\text{nep}}$  is much greater than net removal by  $J_{\text{phys}}$  [Ayers and Lozier, 2012], and is the dominant cause of the observed  $p\text{CO}_2$  ( $p\text{CO}_{2\text{SW}}$ ) being less than the abiotic  $p\text{CO}_2$  ( $p\text{CO}_{2\text{abio}}$ ). In the subtropics in spring and summer, based on studies at ALOHA,  $J_{\text{nep}}$  is the only term removing *DIC*, because  $J_{\text{phys}}$  is a net *DIC* source [Keeling et al., 2004; Quay and Stutsman, 2003]. In contrast, in fall and winter, when the mixed layer is deepening, addition of *DIC* through positive  $J_{\text{phys}}$  outweighs removal of *DIC* by  $J_{\text{nep}}$  in the subarctic, transition zone and subtropics [Ayers and Lozier, 2012];



**Figure 6.** Abiotic model of annual  $p\text{CO}_2$  cycle in cruise region along  $152^\circ\text{W}$ . Observed (climatological) ocean and atmosphere  $p\text{CO}_2$ , black and blue lines, respectively. Modeled abiotic  $p\text{CO}_2$ , green line. Red dot,  $p\text{CO}_2$  measured on cruise in this study (September) normalized to year 2000  $p\text{CO}_2$  for consistency with climatological data [Takahashi *et al.*, 2009]. Black vertical lines bound spring-summer period (1 March–15 September). Top right graph, integrated  $\text{CO}_2$  flux due to difference between abiotic and observed  $p\text{CO}_2$  (for period when abiotic  $p\text{CO}_2$  is greater than observed  $p\text{CO}_2$  in each box).

Keeling *et al.*, 2004], and causes  $p\text{CO}_{2\text{SW}}$  to be greater than  $p\text{CO}_{2\text{abio}}$ .

[54] We calculated the integrated  $\text{CO}_2$  flux resulting from the difference between  $p\text{CO}_{2\text{abio}}$  and  $p\text{CO}_{2\text{SW}}$  by summing daily  $\text{CO}_2$  flux =  $k_{\text{CO}_2} k_{\text{H}} (p\text{CO}_{2\text{abio}} - p\text{CO}_{2\text{SW}})$  for the period in each box when  $p\text{CO}_{2\text{abio}}$  is greater than  $p\text{CO}_{2\text{SW}}$ , typically March–September. The trends in this integrated flux along the cruise track largely correspond to the trends in  $NCP$  and  $FCO_{2(\text{in})}$  we observed on our cruise (Figure 6). The integrated flux is greatest in the subarctic ( $46^\circ\text{N}$ – $50^\circ\text{N}$ ) and northern transition zone ( $38^\circ\text{N}$ – $46^\circ\text{N}$ ), implying high summer drawdown of  $p\text{CO}_2$  by  $NCP$  (assuming  $J_{\text{phys}}$  is small), in agreement with our cruise observations of high  $NCP$  and strong coupling of  $NCP$  and  $\text{CO}_2$  uptake in these regions. The integrated flux is lower in the southern transition zone ( $30^\circ\text{N}$ – $38^\circ\text{N}$ ) and subtropics ( $22^\circ\text{N}$ – $30^\circ\text{N}$ ), in agreement with our cruise observations in these regions of lower  $NCP$ ,  $\text{CO}_2$  efflux, and little coupling between  $NCP$  and  $FCO_{2(\text{in})}$ .  $p\text{CO}_{2\text{SW}}$  is lower than  $p\text{CO}_{2\text{abio}}$  for the longest interval

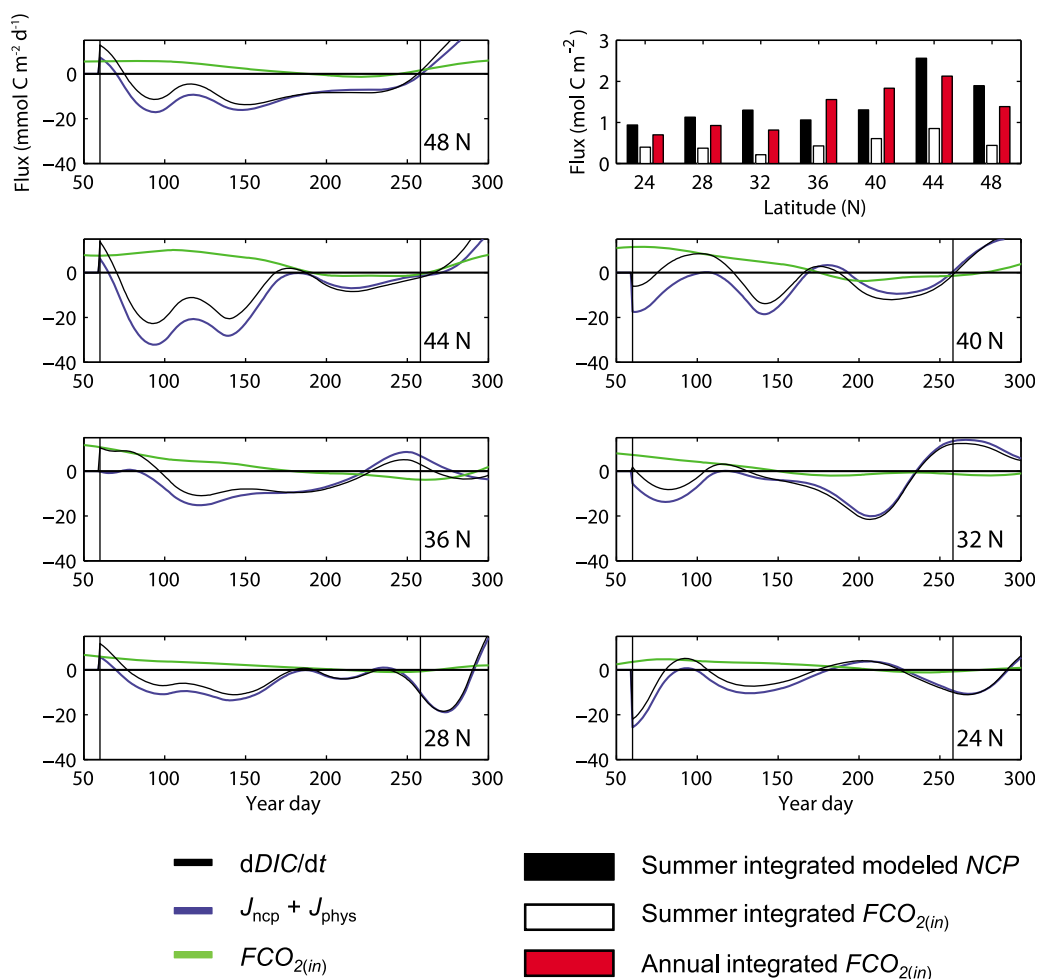
(>240 days) in the subtropics, as a result of a long growing season, and in the subarctic and northern transition zone (which has both a spring and a fall bloom [Longhurst, 2007]).

### 5.3.2. DIC Mass Balance

[55] We next used a simplified version of the  $\text{DIC}$  mass balance approach of Lee [2001] to compare the annual climatological  $FCO_{2(\text{in})}$  with the contribution of  $NCP$ . Rearranging the  $\text{DIC}$  mass balance (equation (4)), the magnitude of  $\text{DIC}$  drawdown plus  $\text{CO}_2$  invasion must be the net result of  $NCP$  plus physical supply:

$$J_{\text{nep}} + J_{\text{phys}} = \frac{d\text{DIC}}{dt} - \frac{1}{h} FCO_{2(\text{in})}. \quad (6)$$

[56] We again initialized the model with the 1 March value of  $p\text{CO}_2$  and climatological  $\text{DIC}$ . We calculated daily  $FCO_{2(\text{in})}$  and salinity-normalized  $d\text{DIC}/dt$  using daily interpolated data described above and solved for  $J_{\text{nep}} + J_{\text{phys}}$ . Initially, we assumed  $J_{\text{phys}} = 0$  during the well-stratified



**Figure 7.** Model of climatological  $p\text{CO}_2$  and  $\text{DIC}$  seasonal cycle, distinguishing influence of  $\text{FCO}_{2(\text{in})}$  and  $\text{NCP}$  plus physical inputs ( $J_{\text{nep}} + J_{\text{phys}}$ ) on seasonal changes in  $\text{DIC}$  ( $d\text{DIC}/dt$ ). Black vertical lines bound spring-summer period (1 March–15 September) over which summer  $\text{NCP}$  and  $\text{FCO}_{2(\text{in})}$  (top right) were integrated.

spring-summer season (when observed  $p\text{CO}_2$  is less than abiotic  $p\text{CO}_2$ , typically March–September) to obtain an estimate of  $J_{\text{nep}}$ . This would result in an upper-boundary estimate for  $\text{NCP}$  in the transition zone (where  $J_{\text{phys}}$  removes a small amount of  $\text{DIC}$  in spring-summer; Ayers and Lozier, 2012) and a minimum estimate of  $\text{NCP}$  in the subtropics (where  $J_{\text{phys}}$  is positive in spring-summer [Keeling et al., 2004]). We integrated this estimate of summer  $\text{NCP}$  by integrating the values of  $J_{\text{nep}} + J_{\text{phys}}$  for the period 1 March–15 September (Figure 7).

[57] To obtain the observed summertime  $p\text{CO}_2$  decrease (if  $J_{\text{phys}} = 0$ ) requires mean daily  $\text{NCP}$  in the subarctic and northern transition zone of 10 and 13  $\text{mmol C m}^{-2} \text{d}^{-1}$ , respectively (Table 3). These values are slightly lower but within the range of uncertainty of previous field estimates for these regions (Table 1). Our cruise-based  $\text{NCP}$  estimate was more than  $2\times$  than the model estimate in the subarctic (26  $\text{mmol C m}^{-2} \text{d}^{-1}$ ), likely reflecting the anomalous conditions there during our cruise, and 31% greater in the northern transition zone.

[58] In the southern transition zone and subtropics, modeled summer  $\text{NCP}$  was about half that in the subarctic and

northern transition zone, at 5–6  $\text{mmol C m}^{-2} \text{d}^{-1}$ , similar to our cruise estimates of 5–8  $\text{mmol C m}^{-2} \text{d}^{-1}$  and within the uncertainty of previous field estimates of  $\text{NCP}$  in these regions (Tables 1 and 3). The  $\sim 2\times$  lower summer  $\text{NCP}$  in the subtropics compared to the northern transition zone is similar to the meridional trends in  $\text{NCP}$  estimated from our cruise observations. This suggests that our  $\text{O}_2/\text{Ar}$ -based  $\text{NCP}$  in the transition zone and subtropics during September 2008 may be representative of the climatological  $\text{NCP}$  during the spring-summer growing season. Modeled  $\text{NCP}$  in the subtropics (5  $\text{mmol C m}^{-2} \text{d}^{-1}$  versus our cruise-based estimate of 8  $\text{mmol C m}^{-2} \text{d}^{-1}$ ) is probably underestimated because physical supply of  $\text{DIC}$  in the subtropics is positive during the summer, as has been shown at ALOHA [Keeling et al., 2004; Quay and Stutsman, 2003]. In support of this, the stability ( $\Delta\sigma/\Delta z$ ) in the upper water column in the subtropics and southern transition zone was much less than that in the subarctic during our late summer cruise (Figure 2).

[59] Integrated annual climatological  $\text{FCO}_{2(\text{in})}$  was similar in magnitude to modeled summer-integrated  $\text{NCP}$  along the cruise track, peaking in the northern transition zone at

**Table 3.** Results of Model of Climatological  $p\text{CO}_2$  and  $\text{DIC}$  Seasonal Cycle

Latitude (N) Along 152°W	Summer-Integrated Modeled $NCP^a$ (mol C m <sup>-2</sup> )	Daily Average Summer Modeled $NCP$ (mmol m <sup>-2</sup> d <sup>-1</sup> )	Summer-Integrated $FCO_{2(in)}^a$ (mol C m <sup>-2</sup> )	Annual-Integrated $FCO_{2(in)}$ (mol C m <sup>-2</sup> yr <sup>-1</sup> )	Summer-Integrated Modeled $NCP$ /Annual-Integrated $FCO_{2(in)}$
46°–50°	1.9	9.5	0.4	1.4	1.4
42°–46°	2.6	13.1	0.9	2.1	1.2
38°–42°	1.3	6.5	0.6	1.8	0.7
34°–38°	1.1	5.5	0.4	1.6	0.7
30°–34°	1.3	6.5	0.2	0.8	1.6
24°–30°	1.1	5.5	0.4	0.9	1.2
22°–24°	0.9	4.5	0.4	0.7	1.3
Subarctic	1.9	9.5	0.4	1.4	1.4
N. Transition	2.0	10.1	0.8	2.0	1.0
S. Transition	1.2	6.0	0.3	1.2	1.2
Subtropics	1.0	5.0	0.4	0.8	1.3

<sup>a</sup>Summer-integrated modeled  $NCP$  and  $FCO_{2(in)}$  are integrated for the period 1 March–15 September. In model, positive  $FCO_{2(in)}$  represents influx into ocean. Regions were defined as described in Table 2.

2.0 mol C m<sup>-2</sup> yr<sup>-1</sup>, slightly lower in the subarctic and southern transition zone (1.2–1.4 mol C m<sup>-2</sup> yr<sup>-1</sup>), and lowest in the subtropics at 0.8 mol C m<sup>-2</sup> yr<sup>-1</sup> (Figure 7 and Table 3). On average, the magnitude of summer-integrated  $NCP$  balances annual-integrated  $FCO_{2(in)}$  across the cruise track, with ratios of summer  $NCP$  to annual  $FCO_{2(in)}$  of 0.7–1.4 across all regions (Table 3). Some carbon exported through  $NCP$  during summer could be remineralized and returned to the mixed layer in winter, as has been observed in the North Atlantic [Körtzinger *et al.*, 2008]; this would lower O<sub>2</sub>/Ar-based  $NCP$  and CO<sub>2</sub> uptake. However, winter mixed layer depths in the NE Pacific are much lower than in the North Atlantic, so the effect may not be as pronounced there.

[60] We conclude that  $NCP$  exerts a significant control on the high CO<sub>2</sub> uptake in the NE Pacific, with the remainder of annual CO<sub>2</sub> uptake impacted by surface cooling and physical processes. It is difficult to directly estimate the contribution of  $NCP$  to annual CO<sub>2</sub> uptake, because the response time of CO<sub>2</sub> gas exchange with respect to changes in temperature and DIC is relatively sluggish (~1 year) [Broecker and Peng, 1982]. Therefore,  $NCP$  that takes place in summer likely drives uptake of CO<sub>2</sub> in fall or winter.

## 6. Conclusions

[61] Mean  $NCP$  and CO<sub>2</sub> influx along our cruise track were greatest in the subarctic ( $25.8 \pm 4.6$  and  $4.1 \pm 0.9$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively) and the northern transition zone ( $17.1 \pm 4.4$  and  $2.1 \pm 0.5$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively). In the subarctic, our observations of  $NCP$  were ~2× the mean of previous summer observations, reflecting the influence of an anomalous phytoplankton bloom. In the transition zone, we detected high zonal and meridional variability in  $NCP$  and CO<sub>2</sub> flux at <5-km scales, suggesting the impact of frontal dynamics on biogeochemical fluxes in this region, and the need for observations throughout the year to determine its mean annual state. In the southern transition zone and subtropics,  $NCP$  ( $5.4 \pm 1.8$  and  $8.1 \pm 2.1$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively) was about 2–3× lower than in the subarctic and northern transition zone, and CO<sub>2</sub> had mean efflux ( $3.0 \pm 0.5$  and  $0.1 \pm 0.0$  mmol C m<sup>-2</sup> d<sup>-1</sup>, respectively).

[62]  $NCP$  and CO<sub>2</sub> influx were highly correlated in the subarctic and transition zone with a slope of 2 to 3, indicating the strong coupling between biological uptake and CO<sub>2</sub> influx during summertime in these regions.  $NCP$  in these regions was also highly correlated with concentrations of microphytoplankton. In contrast,  $NCP$  and CO<sub>2</sub> influx were not strongly coupled in the subtropics, suggesting that the temperature effect on solubility dominates CO<sub>2</sub> flux during summertime there. In the subtropics,  $NCP$  was uncorrelated with microphytoplankton and weakly correlated with picophytoplankton, potentially indicating the lower efficiency of a picophytoplankton-dominated biological pump.

[63] Our analysis and modeling of the climatological  $\text{DIC}$  and  $p\text{CO}_2$  cycles in the transition zone and subtropics yielded a similar meridional pattern in integrated summertime  $NCP$  and CO<sub>2</sub> flux as we found during our cruise in September 2008.  $NCP$  in the northern transition zone was ~2–3× that in the southern transition zone and subtropics, suggesting that our snapshot estimates in these regions are representative of the seasonal influence of  $NCP$  on CO<sub>2</sub> influx. Based on our model of the climatological seasonal  $\text{DIC}$  and  $p\text{CO}_2$  cycle in the Northeast Pacific, we conclude that summertime  $NCP$  is similar in magnitude to the annual atmospheric CO<sub>2</sub> uptake in the NE Pacific, indicating that  $NCP$  has a significant impact on CO<sub>2</sub> uptake in this region. More continuous observations of the temporal and spatial variability of the biological pump in this region and more sophisticated physical modeling would improve our ability to distinguish the magnitude of the influences of temperature, biological uptake, and physical dynamics in this region of high CO<sub>2</sub> uptake.

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## References

Ayers, J. M., and M. S. Lozier (2010), Physical controls on the seasonal migration of the North Pacific transition zone chlorophyll front, *J. Geophys. Res.*, 115, C05001, doi:10.1029/2009JC005596.

- Ayers, J. M., and M. S. Lozier (2012), Unraveling dynamical controls on the North Pacific carbon sink, *J. Geophys. Res.*, *117*, C01017, doi:10.1029/2011JC007368.
- Benitez-Nelson, C., et al. (2001), A time-series study of particulate matter export in the North Pacific Subtropical Gyre based on  $^{234}\text{Th}$ :  $^{238}\text{U}$  disequilibrium, *Deep Sea Res., Part I*, *48*, 2595–2611, doi:10.1016/S0967-0637(01)00032-2.
- Boyd, P. W., and T. W. Trull (2007), Understanding the export of biogenic particles in oceanic waters: Is there consensus?, *Prog. Oceanogr.*, *72*, 276–312, doi:10.1016/j.pocean.2006.10.007.
- Boyd, P. W., et al. (1996), *In vitro* iron enrichment experiments in the NE subarctic Pacific, *Mar. Ecol. Prog. Ser.*, *136*, 179–193, doi:10.3354/meps136179.
- Broecker, W. S., and T.-H. Peng (1982), *Tracers in the Sea*, pp. 154–156, Lamont-Doherty Geol. Obs., Palisades, N. Y.
- Cassar, N., et al. (2009), Continuous high-frequency dissolved  $\text{O}_2/\text{Ar}$  measurements by equilibrator inlet mass spectrometry, *Anal. Chem.*, *81*, 1855–1864, doi:10.1021/ac802300u.
- Cassar, N., et al. (2011), The influence of iron and light on net community production in the subtropical and polar frontal zones, *Biogeochemistry*, *8*, 227–237, doi:10.5194/bg-8-227-2011.
- Charette, M. A., S. B. Moran, and J. K. B. Bishop (1999),  $^{234}\text{Th}$  as a tracer of particulate organic carbon export in the subarctic northeast Pacific Ocean, *Deep Sea Res., Part II*, *46*, 2833–2861, doi:10.1016/S0967-0645(99)00085-5.
- Craig, H., and T. Hayward (1987), Oxygen supersaturation in the ocean: Biological versus physical contributions, *Science*, *235*(4785), 199–202, doi:10.1126/science.235.4785.199.
- Denman, K. L., and A. E. Gargett (1995), Biological-physical interactions in the upper ocean: The role of vertical and small scale transport processes, *Annu. Rev. Fluid Mech.*, *27*, 225–256, doi:10.1146/annurev.fl.27.010195.001301.
- Emerson, S. (1987), Seasonal oxygen cycles and biological new production in surface waters of the subarctic Pacific ocean, *J. Geophys. Res.*, *92*, 6535–6544, doi:10.1029/JC092iC06p06535.
- Emerson, S. R., and J. I. Hedges (2008), *Chemical Oceanography and the Marine Carbon Cycle*, 375 pp., Cambridge Univ. Press, Cambridge, U. K., doi:10.1017/CBO9780511793202.
- Emerson, S., and C. Stump (2010), Net biological oxygen production in the ocean—II: Remote *in situ* measurements of  $\text{O}_2$  and  $\text{N}_2$  in subarctic Pacific surface waters, *Deep Sea Res., Part I*, *57*, 1255–1265, doi:10.1016/j.dsr.2010.06.001.
- Emerson, S., et al. (1991),  $\text{O}_2$ , Ar,  $\text{N}_2$ , and Rn in surface waters of the subarctic ocean: Net biological  $\text{O}_2$  production, *Global Biogeochem. Cycles*, *5*, 49–69, doi:10.1029/90GB02656.
- Emerson, S., et al. (1995), Chemical tracers of productivity and respiration in the subtropical Pacific Ocean, *J. Geophys. Res.*, *100*, 15,873–15,887, doi:10.1029/95JC01333.
- Emerson, S., et al. (1997), Experimental determination of the organic carbon flux from open-ocean surface waters, *Nature*, *389*, 951–954, doi:10.1038/40111.
- Emerson, S., C. Stump, and D. Nicholson (2008), Net biological oxygen production in the ocean: Remote *in situ* measurements of  $\text{O}_2$  and  $\text{N}_2$  in surface waters, *Global Biogeochem. Cycles*, *22*, GB3023, doi:10.1029/2007GB003095.
- Feely, R. A., et al. (1998), A new automated underway system for making high precision  $p\text{CO}_2$  measurements onboard research ships, *Anal. Chim. Acta*, *377*, 185–191, doi:10.1016/S0003-2670(98)00388-2.
- Franks, P. J. S. (1992), Sink or swim: Accumulation of biomass at fronts, *Mar. Ecol. Prog. Ser.*, *82*, 1–12, doi:10.3354/meps082001.
- García, H. E., and L. I. Gordon (1992), Oxygen solubility in seawater: Better fitting equations, *Limnol. Oceanogr.*, *37*, 1307–1312, doi:10.4319/lo.1992.37.6.1307.
- Guéguen, C., and P. Tortell (2008), High-resolution measurement of Southern Ocean  $\text{CO}_2$  and  $\text{O}_2/\text{Ar}$  by membrane inlet mass spectrometry, *Mar. Chem.*, *108*, 184–194, doi:10.1016/j.marchem.2007.11.007.
- Hamme, R., and S. Emerson (2004), The solubility of neon, nitrogen and argon in distilled water and seawater, *Deep Sea Res., Part I*, *51*(11), 1517–1528.
- Hamme, R., and S. Emerson (2006), Constraining bubble dynamics and mixing with dissolved gases: Implications for productivity measurements by oxygen mass balance, *J. Mar. Res.*, *64*, 73–95, doi:10.1357/00224006776412322.
- Hamme, R. C., et al. (2010), Volcanic ash fuels anomalous plankton bloom in subarctic northeast Pacific, *Geophys. Res. Lett.*, *37*, L19604, doi:10.1029/2010GL044629.
- Harrison, P. J., P. W. Boyd, D. E. Varela, S. Takeda, A. Shiimoto, and T. Odate (1999), Comparison of factors controlling phytoplankton productivity in the NE and NW subarctic Pacific gyres, *Prog. Oceanogr.*, *43*, 205–234, doi:10.1016/S0079-6611(99)00015-4.
- Harrison, P. J., F. A. Whitney, A. Tsuda, H. Saito, and K. Tadokoro (2004), Nutrient and plankton dynamics in the NE and NW gyres of the Subarctic Pacific Ocean, *J. Oceanogr.*, *60*, 93–117, doi:10.1023/B:JOCE.0000038321.57391.2a.
- Ho, D. T., C. S. Law, M. J. Smith, P. Schlosser, M. Harvey, and P. Hill (2006), Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations, *Geophys. Res. Lett.*, *33*, L16611, doi:10.1029/2006GL026817.
- Ho, D. T., R. Wanninkhof, P. Schlosser, D. S. Ullman, D. Hebert, and K. F. Sullivan (2011), Toward a universal relationship between wind speed and gas exchange: Gas transfer velocities measured with  $^3\text{He}/\text{SF}_6$  during the Southern Ocean Gas Exchange Experiment, *J. Geophys. Res.*, *116*, C00F04, doi:10.1029/2010JC006854.
- Howard, E., S. Emerson, S. Bushinsky, and C. Stump (2010), The role of net community production in air-sea carbon fluxes at the North Pacific subarctic-subtropical boundary region, *Limnol. Oceanogr.*, *55*(6), 2585–2596, doi:10.4319/lo.2010.55.6.2585.
- Intergovernmental Oceanography Commission (1994), *Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements, IOC Manuals and Guides 29*, UNESCO, Paris.
- Juranek, L. W. (2007), Assessment of Pacific Ocean organic carbon production and export using measurements of dissolved oxygen isotopes and oxygen/argon gas ratios, PhD diss., School of Oceanogr., Univ. of Washington, Seattle.
- Juranek, L. W., and P. D. Quay (2005), *In vitro* and *in situ* gross primary and net community production rates in the North Pacific Subtropical Gyre using labeled and natural abundance isotopes of dissolved  $\text{O}_2$ , *Global Biogeochem. Cycles*, *19*, GB3009, doi:10.1029/2004GB002384.
- Juranek, L. W., et al. (2012), Biological production in the NE Pacific and its influence on air-sea  $\text{CO}_2$  flux: Evidence from dissolved oxygen isotopes and  $\text{O}_2/\text{Ar}$ , *J. Geophys. Res.*, *117*, C05022, doi:10.1029/2011JC007450.
- Kaiser, J., et al. (2005), Marine productivity estimates from continuous  $\text{O}_2/\text{Ar}$  ratio measurements by membrane inlet mass spectrometry, *Geophys. Res. Lett.*, *32*, L19605, doi:10.1029/2005GL023459.
- Karl, D. M. (1999), A sea of change: Biogeochemical variability in the North Pacific Subtropical Gyre, *Ecosystems (N. Y.)*, *2*, 181–214, doi:10.1007/s100219900068.
- Karl, D., et al. (1997), The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean, *Nature*, *388*, 533–538, doi:10.1038/41474.
- Karl, D., R. R. Bidigare, and R. M. Letelier (2001), Long-term changes in plankton community structure and productivity in the North Pacific Subtropical Gyre: The domain shift hypothesis, *Deep Sea Res., Part II*, *48*, 1449–1470, doi:10.1016/S0967-0645(00)00149-1.
- Karl, D. M. et al. (2003), Temporal studies of biogeochemical processes determined from ocean time series observations during the JGOFS era, in *Ocean Biogeochemistry: The Role of the Ocean Carbon Cycle in Global Change*, edited by M. J. R. Fasham, pp. 239–267, Springer, Berlin, doi:10.1007/978-3-642-55844-3\_11.
- Keeling, C. D., H. Brix, and N. Gruber (2004), Seasonal and long-term dynamics of the upper ocean carbon cycle at Station ALOHA near Hawaii, *Global Biogeochem. Cycles*, *18*, GB4006, doi:10.1029/2004GB002227.
- Körtzinger, A., U. Send, R. S. Lampitt, S. Hartman, D. W. R. Wallace, J. Karstensen, M. G. Villagarica, O. Llinás, and M. D. DeGrandpre (2008), The seasonal  $p\text{CO}_2$  cycle at 49°N/16.5°W in the northeastern Atlantic Ocean and what it tells us about biological productivity, *J. Geophys. Res.*, *113*, C04020, doi:10.1029/2007JC004347.
- Langmann, B., K. Zaksek, M. Hort, and S. Duggen (2010), Volcanic ash as fertiliser for the surface ocean, *Atmos. Chem. Phys.*, *10*, 3891–3899, doi:10.5194/acp-10-3891-2010.
- Laws, E. A. (1991), Photosynthetic quotients, new production and net community production in the open ocean, *Deep Sea Res.*, *38*, 143–167, doi:10.1016/0198-0149(91)90059-0.
- Lee, K. (2001), Global net community production estimated from the annual cycle of surface water total dissolved inorganic carbon, *Limnol. Oceanogr.*, *46*, 1287–1297, doi:10.4319/lo.2001.46.6.1287.
- Lee, K., et al. (2006), Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophys. Res. Lett.*, *33*, L19605, doi:10.1029/2006GL027207.
- Leonard, C., R. R. Bidigare, M. P. Seki, and J. J. Polovina (2001), Inter-annual mesoscale physical and biological variability in the North Pacific Central Gyre, *Prog. Oceanogr.*, *49*, 227–244, doi:10.1016/S0079-6611(01)00024-6.
- Lewis, E., and D. W. R. Wallace (1998), *Program developed for  $\text{CO}_2$  system calculations, ORNL/CDIAC-105*, 21 pp., Carbon Dioxide Inf.

- Anal. Cent., Oak Ridge Natl. Lab, Oak Ridge, Tenn., doi:10.2172/639712.
- Longhurst, A. (2007), *Ecological Geography of the Sea*, Acad. Press, San Diego, Calif.
- Mann, K. H., and J. R. N. Lazier (2006), *Dynamics of Marine Systems: Biological-Physical Interactions in the Oceans*, 3rd ed., Blackwell, Malden, Mass.
- Monterey, G., and S. Levitus (1997), *Seasonal Variability of Mixed Layer Depth for the World Ocean. NOAA Atlas NESDIS 14*, 96 pp., U.S. Gov. Print. Off., Washington, D. C.
- Nemcek, N., D. Ianson, and P. D. Tortell (2008), A high-resolution survey of DMS, CO<sub>2</sub>, and O<sub>2</sub>/Ar distributions in productive coastal waters, *Global Biogeochem. Cycles*, 22, GB2009, doi:10.1029/2006GB002879.
- Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), *In situ* evaluation of air-sea exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, 14(1), 373–387, doi:10.1029/1999GB900091.
- Olson, D. B., et al. (1994), Life on the edge: Marine life and fronts, *Oceanography*, 7(2), 52–60.
- Pierrot, D., et al. (2009), Recommendations for autonomous underway pCO<sub>2</sub> measuring systems and data-reduction routines, *Deep Sea Res., Part II*, 56, 512–522, doi:10.1016/j.dsr2.2008.12.005.
- Polovina, J. J., et al. (2001), The transition zone chlorophyll front, a dynamic global feature defining migration and forage habitat for marine resources, *Prog. Oceanogr.*, 49, 469–483, doi:10.1016/S0079-6611(01)00036-2.
- Quay, P. D., and J. Stutsman (2003), Surface layer carbon budget for the subtropical N. Pacific:  $\delta^{13}\text{C}$  constraints at station ALOHA, *Deep Sea Res., Part I*, 50, 1045–1061, doi:10.1016/S0967-0637(03)00116-X.
- Quay, P. D., J. Stutsman, R. A. Feely, and L. W. Juranek (2009), Net community production rates across the subtropical and equatorial Pacific Ocean estimated from air-sea  $\delta^{13}\text{C}$  disequilibrium, *Global Biogeochem. Cycles*, 23, GB2006, doi:10.1029/2008GB003193.
- Quay, P. D., C. Peacock, K. Björkman, and D. M. Karl (2010), Measuring primary production rates in the ocean: Enigmatic results between incubation and non-incubation methods at Station ALOHA, *Global Biogeochem. Cycles*, 24, GB3014, doi:10.1029/2009GB003665.
- Reuer, M. K., et al. (2007), New estimates of Southern Ocean biological production rates from O<sub>2</sub>/Ar ratios and the triple isotope composition of O<sub>2</sub>, *Deep Sea Res., Part I*, 54, 951–974, doi:10.1016/j.dsr.2007.02.007.
- Roden, G. I. (1991), Subarctic-subtropical transition zone of the North Pacific: Large-scale aspects and mesoscale structure, in *Biology, oceanography, and fisheries of the North Pacific Transition Zone and Subarctic Frontal Zone*, NOAA Tech. Rep. NMFS 105, edited by J. A. Wetherall et al., pp. 1–38, Natl. Mar. Fish. Serv., Silver Spring, Md.
- Schlitzer, R. (2000), Applying the adjoint method for global biogeochemical modeling: Export of particulate organic matter in the world ocean, in *Inverse Methods in Global Biogeochemical Cycles*, *Geophys. Monogr. Ser.*, edited by P. Raynor et al., pp. 107–124, AGU, Washington, D. C., doi:10.1029/GM114p0107.
- Schlitzer, R. (2004), Export production in the equatorial and north Pacific derived from dissolved oxygen, nutrient and carbon data, *J. Oceanogr.*, 60, 53–62, doi:10.1023/B:JOCE.0000038318.38916.e6.
- Sherr, E. B., B. F. Sherr, and P. A. Wheeler (2005), Distribution of coccolid cyanobacteria and small eukaryotic phytoplankton in the upwelling ecosystem off the Oregon coast during 2001 and 2002, *Deep Sea Res., Part II*, 52, 317–330, doi:10.1016/j.dsr2.2004.09.020.
- Stanley, R. H. R., J. B. Kirkpatrick, N. Cassar, B. A. Barnett, and M. B. Bender (2010), Net community production and gross primary production rates in the western equatorial Pacific, *Global Biogeochem. Cycles*, 24, GB4001, doi:10.1029/2009GB003651.
- Strass, V. H. (1992), Chlorophyll patchiness caused by mesoscale upwelling at fronts, *Deep Sea Res.*, 39(1), 75–96, doi:10.1016/0198-0149(92)90021-K.
- Strickland, J. D. H., and T. R. Parsons (1972), *A Practical Handbook of Seawater Analysis*, 2nd ed., Fish. Res. Board of Canada, Ottawa.
- Stumm, W., and J. J. Morgan (1996), *Aquatic Chemistry: Chemical Equilibria and Rates in Neutral Waters*, 3rd ed., Wiley, New York.
- Sweeney, C., E. Gloor, A. R. Jacobson, R. M. Key, G. McKinley, J. L. Sarmiento, and R. Wanninkhof (2007), Constraining global air-sea gas exchange for CO<sub>2</sub> with recent bomb 14C measurements, *Global Biogeochem. Cycles*, 21, GB2015, doi:10.1029/2006GB002784.
- Takahashi, T., et al. (2002), Global sea-air CO<sub>2</sub> flux based on climatological surface ocean pCO<sub>2</sub>, and seasonal biological and temperature effects, *Deep Sea Res., Part II*, 49, 1601–1622, doi:10.1016/S0967-0645(02)00003-6.
- Takahashi, T., et al. (2009), Climatological mean and decadal change in surface ocean pCO<sub>2</sub>, and net sea-air CO<sub>2</sub> flux over the global oceans, *Deep Sea Res., Part II*, 56, 554–577, doi:10.1016/j.dsr2.2008.12.009.
- Tortell, P. D. (2005), Dissolved gas measurements in oceanic waters made by membrane inlet mass spectrometry, *Limnol. Oceanogr. Methods*, 3, 24–37, doi:10.4319/lom.2005.3.24.
- Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373–7382, doi:10.1029/92JC00188.
- Wheeler, P. A. (1993), New production in the subarctic Pacific Ocean: Net changes in nitrate concentrations, rates of nitrate assimilation and accumulation of particulate nitrogen, *Prog. Oceanogr.*, 32, 137–161, doi:10.1016/0079-6611(93)90011-2.
- Wilson, C. (2003), Late summer chlorophyll blooms in the oligotrophic North Pacific Subtropical Gyre, *Geophys. Res. Lett.*, 30(18), 1942, doi:10.1029/2003GL017770.
- Wilson, C., et al. (2008), Biological and physical forcings of late summer chlorophyll blooms at 30°N in the oligotrophic Pacific, *J. Mar. Syst.*, 69, 164–176, doi:10.1016/j.jmarsys.2005.09.018.
- Wong, C. S., et al. (2002a), Time-series study of the biogeochemistry of the North East subarctic Pacific: Reconciliation of the Corg/N remineralization and uptake ratios with the Redfield ratios, *Deep Sea Res., Part II*, 49, 5717–5738, doi:10.1016/S0967-0645(02)00211-4.
- Wong, C. S., et al. (2002b), Seasonal cycles of nutrients and dissolved inorganic carbon at high and mid latitudes in the North Pacific Ocean during the Skaugran cruises: Determination of new production and nutrient uptake ratios, *Deep Sea Res., Part II*, 49, 5317–5338, doi:10.1016/S0967-0645(02)00193-5.
- Yuan, X., and L. D. Talley (1996), Characteristics of frontal structure from climatological data and synoptic surveys, *J. Geophys. Res.*, 101, 16,491–16,508, doi:10.1029/96JC01249.