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Quantifying the flux of CaCO₃ and organic carbon from the surface ocean using in situ measurements of O₂, N₂, pCO₂, and pH

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Ocean acidification from anthropogenic CO₂ has focused our attention on the importance of understanding the rates and mechanisms of CaCO₃ formation so that changes can be monitored and feedbacks predicted. We present a method for determining the rate of CaCO₃ production using in situ measurements of fCO₂ and pH in surface waters of the eastern subarctic Pacific Ocean. These quantities were determined on a surface mooring every 3 h for a period of about 9 months in 2007 at Ocean Station Papa (50°N, 145°W). We use the data in a simple surface ocean, mass balance model of dissolved inorganic carbon (DIC) and alkalinity (Alk) to constrain the CaCO₃: organic carbon (OC) production ratio to be approximately 0.5. A CaCO₃ production rate of 8 mmol CaCO₃ m⁻² d⁻¹ in the summer of 2007 (1.2 mol m⁻² yr⁻¹) is derived by combining the CaCO₃: OC ratio with the net organic carbon production rate (2.5 mol C m⁻² yr⁻¹) determined from in situ measurements of oxygen and nitrogen gas concentrations measured on the same mooring (Emerson and Stump, 2010). Carbonate chemistry data from a meridional hydrographic section in this area in 2008 indicate that isopycnal surfaces that outcrop in the winter in the subarctic Pacific and deepen southward into the subtropics are a much stronger source for alkalinity than vertical mixing. This pathway has a high enough Alk:DIC ratio to support the CaCO₃:OC production rate implied by the fCO₂ and pH data.


1. Introduction

[2] The CaCO₃: organic carbon (OC) mix of the particulate and dissolved material that exits the surface ocean strongly influences the effect of the biological pump on the fCO₂ of the atmosphere [e.g., Broecker and Peng, 1982; Sarmiento and Gruber, 2007; Emerson and Hedges, 2008]. This mixture also helps determine the depth at which the exported particulate organic matter degrades [Klaas and Archer, 2002; Armstrong et al., 2002], which greatly influences the effectiveness of the marine carbon pump on atmospheric fCO₂ and deep ocean oxygen concentration [Yamanaka and Tajika, 1996; Kwon et al., 2009]. Thus, changes in the formation rate of CaCO₃-containing algae in response to anthropogenic CO₂ addition to the atmosphere will cause a carbon cycle feedback that is presently difficult to predict.

[3] Global estimates of the formation rate of CaCO₃ in ocean surface waters are based primarily on interpretation of climatological distributions of alkalinity (Alk) and dissolved inorganic carbon (DIC) using seasonal changes in mixed-layer alkalinity [Lee, 2001] and calculation of vertical fluxes based on gradients in subsurface waters [Sarmiento et al., 2002; Moore et al., 2002; Jin et al., 2006]. In addition, Balch et al. [2007] have interpreted satellite measurement of reflectance and color in terms of CaCO₃ standing stocks. Global CaCO₃ export rates derived from these methods range from 0.5 to 1.6 Gt C yr⁻¹ (see Jin et al. [2006] and Berelson et al. [2007] for reviews). The fate of particulate CaCO₃ after it leaves the upper ocean has been determined by distinguishing the fraction of the measured water column alkalinity that can be attributed to CaCO₃ dissolution, TA* [Feely et al., 2002], by sediment trap experiments [e.g., Honjo et al., 1995; Wong et al., 1999] and by sediment-water dissolution and burial measurements [Hales and Emerson, 1997; Jahnke et al., 1994; Berelson et al., 2007]. This paper presents the results of the first successful long-term (9 month) autonomous in situ measurements of

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Figure 1. Changes in (a) temperature and (b) the degree of supersaturation of oxygen and nitrogen in the surface waters at Stn P (50°N and 145°W). Notice the evolution of the difference between O2 and N2 supersaturation between summer and winter. These data were used in a simple upper ocean model to determine the net biological O2 production in a companion paper [Emerson and Stump, 2010].

both fCO2 and pH in open ocean surface waters, and its interpretation in terms of the ratio of CaCO3: OC production. We believe that this general method could be used to ground truth the rates of CaCO3 production derived from GCMs and satellites. The work presented here is the companion to another paper [Emerson and Stump, 2010] in which in situ measurements of O2 and N2 from the same mooring deployment were interpreted in terms of net community production (NCP) of oxygen and organic matter. By combining these results with simultaneous measurements of fCO2 and pH we constrain the CaCO3: OC formation ratio to be about 0.5 and the CaCO3 production rate to be ~8 mmol m−2 d−1 in the summer of 2007 in the subarctic Pacific Ocean. We show that the likely transport pathway for resupplying alkalinity removed from North Pacific surface waters is along isopycnal surfaces that plunge into deeper waters to the south rather than by vertical processes assumed in the earlier studies.

2. Setting and Methods

2.1. Station Papa

[5] The subarctic Pacific Ocean at Ocean Station Papa (hereafter Stn. P, located at 50°N, 145°W) is a region where precipitation and fresh water runoff from the continents exceeds evaporation leading to a layer of low-salinity water that caps a permanent halocline. There is a strong seasonality in temperature in surface waters (Figure 1a). In winter the Aleutian low is positioned in the Gulf of Alaska and brings winds that average 12 m s−1 which combine with cold temperatures (<6°C) to mix the surface layer to depths of the halocline at about 110 m. In summer the Aleutian low moves northward and wind speeds drop to an average of 7–8 m s−1 allowing the formation of a shallower thermocline and the mixed layer decreases to 25–30 m as the waters warm. Geostrophically driven surface currents in the subarctic region north of 42°N are characterized by cyclonic circulation in which the flow west of 140°W and south of 55°N is to the east [Favorie et al., 1976], with a surface Ekman flow in the vicinity of Stn P to the southeast. In a classic interpretation of the hydrographic data from weather ships during the period of the 1950s and 1960s, Tabata [1961] showed that the salt balance in the region constrains upward advection across the halocline to an annually averaged value of 10–20 m yr−1. This work and more recent studies [Large et al., 1986; Archer et al., 1993; Large et al., 1994] demonstrated that a one dimensional heat and nutrient budget is pretty well closed in summer, but in the fall and winter horizontal fluxes become an important component of the transport.

[6] The macronutrients dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphates (DIP) are above detection limits by traditional methods in surface waters of the high-latitude North Pacific Ocean year-round. Wong et al. [2002] demonstrated using 2 years of surface water sampling from container ships that NO3 levels drop from values of about 17 μmol kg−1 in winter to about 8 μmol kg−1 in August and September. These changes were interpreted along with Redfield stoichiometry (ΔC: ΔN = 6.6) to indicate a summertime carbon export from the mixed layer of ~19 mmol C m−2 d−1. This result is very similar to that determined based on oxygen mass balance (17 mmol C m−2 d−1) using in situ O2 and N2 measurements [Emerson and Stump, 2010]. The latter result was determined from a simple upper ocean model and in situ measurements of the degree of supersaturation of oxygen and nitrogen (see Figure 1b). Net biological oxygen production determined from these data is proportional to the difference in supersaturation between oxygen and nitrogen gas (ΔO2 − ΔN2), which is very large during summer and effectively non existent in winter. We used these data to suggest that almost all of the net biological carbon production in this area was in summer [Emerson and Stump, 2010], and our interpretation of the fCO2 and pH data in this paper will also focus in the period of June-October 2007.

[7] A convenient aspect of studying the carbonate chemistry in the northeast subarctic Pacific is that Sta P has been the site of intensive studies of particle fluxes [Wong et al., 1999; D. Timothy et al., The climatology and nature of settling particles in the subarctic northeast Pacific is that Sta P has been included a Gill sonic anemometer that made a 2 min average of wind speed and direction measurements every 10 min.
Surface ocean temperature and salinity were measured at 10 min intervals at 1 m, 5 m, 8 m, 10 m, 35 m, 45 m, and 5 more depths down to 200 m, and at hourly intervals at 20 m. An hourly time series of the mixed-layer depth was computed by determining the depth at which the density was 0.2 kg m$^{-3}$ larger than the 1 m surface value. Currents were measured every 20 min at 5 m and 35 m depths using Sontek acoustic Doppler current meters. Data from this project can be found on the Web at http://www.pmel.noaa.gov/stnP/.

Measurements of oxygen and total gas tension at two meters depth were used to determine the concentrations of O$_2$ and N$_2$. These methods and data have been presented and interpreted previously [Emerson and Stump, 2010]. Here we focus on describing the utility of fCO$_2$ and pH measurements in determining the contribution of CaCO$_3$ formation to the local carbon cycle. (See Cullison Gray et al. [2011] for a more general evaluation of calculating inorganic carbon species from pH and fCO$_2$ measurements.)

The mole fraction of carbon dioxide was measured at a depth of about one meter and in the atmosphere every 3 h using the NOAA/PMEL-built MAPCO$_2$ system. This system uses an automated bubble equilibrator-based gas collection system with an infrared gas analyzer (Li-820, Li-Cor Biogeosciences, Incorporated, Lincoln, Nebraska). The equilibrator is based on the design of Friederich et al. [1995]. Calibration is performed immediately prior to the atmospheric and surface ocean measurements using a CO$_2$ calibration span gas that has been compared to standards from NOAA/ESRL which are traceable to World Metrological Organization (WMO) references. System accuracy is estimated to be 1–2 ppm based on laboratory calibrations, field comparisons with underway CO$_2$ systems, and international intercomparison exercises. Data and diagnostic information are transmitted from the system to PMEL daily and posted on the Web in near-real time (http://www.pmel.noaa.gov/co2/moorings/papa/papa_main.htm).

pH measurements were made every 3 h with a Sunburst Sensors automated pH sensor that was attached to the mooring bridle at a depth of about 2 m. Hydrogen ion concentrations are determined with this instrument spectrophotometrically using a sulphonephthalein indicator that develops a pH-dependent color [Martz et al., 2003; Seidel et al., 2008]. Because small samples are used and a rather short path length is necessary, the effect of the reagent addition on the in situ pH is determined by using a dye dilution curve and extrapolating the measured absorption readings to the values for zero added reagent. The method is precise to better than ±0.001 pH unit and accurate to ±0.002 pH units based on laboratory tests in which results of the in situ instrument were compared with those determined by hand on a laboratory spectrophotometer. Data from the instrument was recorded internally and downloaded when it was retrieved during buoy replacement (once each year).

2.3. Seawater Hydrography and Carbonate Chemistry

We also present carbonate chemistry and hydrographic data from a University of Washington Student Cruise on the R. V. Thompson between Ocean Station P and Hawaii in August/September 2008 (TN224). The cruise track headed south from Stn P (145°W, 50°N) to 38°N, then jogged north to 45°N and 152°W where it again turned south and followed the meridional transect occupied previously by CLIVAR P16 along 152°W. (See Howard et al. [2010] for more information about the cruise.) Hydrographic stations were occupied every 2 degrees with sampling to depths of 1000–2000 m. Dissolved inorganic carbon (DIC) was analyzed by coulometry [Johnson et al., 1998] and alkalinity by open-cell potentiometric titration [Millero et al., 1998; Dickson et al., 2003]. Certified reference materials [Dickson et al., 2003] were used to validate accuracy of both methods. Duplicate analysis of reference materials and samples indicate a precision of ±2 μmol kg$^{-1}$ and ±4 μeq kg$^{-1}$ for DIC and Alk, respectively.

3. Results

3.1. Surface Ocean fCO$_2$ and pH Time Series

Data from June 2007 to February 2008 (Figure 2) indicate seasonal changes of ~55 ppm for fCO$_2$ and ~0.04 pH units. Scatter around the daily averaged trends presented in Figure 2 is on the order of the errors reported above. The fCO$_2$ values are near atmospheric equilibrium (375–390) with slight supersaturation in summer and undersaturation in winter, which is similar to earlier seasonal fCO$_2$ data from this time series location [Wong and Chan, 1991]. The pH measurements follow a trend opposite to that of fCO$_2$. Data associated with each measurement indicated that the linearity in the trend of pH absorbance versus volume of added reagent during the dye dilution curves began to deteriorate (dropped below $r^2 = 0.99$) after November 2007 (~day 330). We do not interpret the pH data after this time because of uncertain accuracy. There is not a third measurement of the carbonate system from the same location and time for an independent check on the accuracy of these measurements. We will show, however, that the formation rate of CaCO$_3$ depends mainly on the observed changes in pH and fCO$_2$ rather than absolute values. Thus, small inaccuracies that could exist will not affect our conclusions. Drift in the pH data due to biofouling, however, could be a problem, and in
current field studies we are determining Alk and DIC at each opportunity to empirically determine stability.

3.2. Hydrographic Data From TN224

A section of the hydrographic data from the Student Cruise in 2008 is presented in Figure 3. Meridional trends along 152°W are shown as a function of depth and density. The low-salinity waters of the surface subarctic Pacific contrast the high-salinity waters in the subtropics (Figure 3a). Meridional trends in surface water alkalinity follow those of salinity much more closely than do DIC changes (Figures 3b and 3c) indicating the more conservative behavior of alkalinity [Lee et al., 2006]. The carbonate ion concentration (Figure 3d) was calculated from DIC and Alkalinity using the apparent constants for the carbonate equilibria presented by Lueker et al. [2000]. The dashed line in Figure 3d indicates the saturation horizon for aragonite (aragonite is supersaturated above and undersaturated below) using the aragonite solubility product presented by Mucci [1983] and assuming calcium is a conservative ion in seawater and varies only with salinity. The saturation horizon follows $\sigma_\theta \approx 26.5$ which plunges from depths just below the euphotic zone at 50°N to between 400 and 500 m in the subtropics.

4. Discussion

4.1. Carbonate Equilibrium

[15] Changes in the pH and $fCO_2$ of surface seawater depend on temperature, salinity and reactions that alter dissolved inorganic carbon and total alkalinity. We demonstrate these effects on the data by calculating the carbonate ion concentration (Figure 4 and equation (1)) from measured pH and $fCO_2$. Chemical equilibrium constants used in the calculation are: the Henry’s Law coefficient for CO$_2$ solubility in seawater ($K_{H}$, Weiss [1974]), and the values reported by Lueker et al. [2000] for the hydration of CO$_2$ to HCO$_3^-$ ($K_1^\prime$) and the equilibrium between HCO$_3^-$ and CO$_3^{2-}$ ($K_2^\prime$). Lueker et al. [2000] demonstrated that the dissociation constants determined by Mehrbach et al. [1973] interpreted on the “total hydrogen scale” give internally consistent results when combined with highly precise measurements of Alk, DIC and $fCO_2$ values below 500 micro atmospheres.

$$[CO_3^{2-}] = \frac{K_H K_1^\prime fCO_2}{[H^+]}$$  \hspace{1cm} (1)$$

Individual points in Figure 4 are carbonate ion concentrations determined from $fCO_2$, pH, T and S data. The line is the expected $[CO_3^{2-}]$ change for constant values of DIC and Alk but varying T and S. The observed increase in $[CO_3^{2-}]$ by 5–15 $\mu$mol kg$^{-1}$ cannot be due to surface water temperature and salinity changes alone—it requires some combination of biological processes and gas exchange that alter dissolved inorganic carbon (and possibly alkalinity).

Figure 3. Sections of (a) salinity (color scale is in, ppt), (b) Alk (color scale is in, $\mu$eq kg$^{-1}$), (c) DIC (color scale is in $\mu$mol kg$^{-1}$) and (d) $[CO_3^{2-}]$ (color scale, $\mu$mol kg$^{-1}$) as a function of depth (m) along 152°W from Thompson cruise TN224 (August/September 2008). Constant density surfaces are indicated by the white contour intervals. The dark, dashed line in Figure 3d is the depth of the aragonite saturation horizon ($\Omega_{arag.} = 1$).

Figure 4. Carbonate ion concentrations ($x$) as a function of time in the surface ocean calculated from $fCO_2$, pH, T, and S using carbonate equilibria (see section 4.1). The line is the value calculated from carbonate equilibrium for constant Alk and DIC and the measured temperature and salinity. (Initial values are $T = 7.04^\circ$C, $S = 32.58$, Alk = 2.373 meq kg$^{-1}$, and DIC = 2.204 mmol kg$^{-1}$).
Pacific has been observed previously to be about 80 µmol kg⁻¹ [Wong et al., 2002]. If this change were due only to organic carbon production, with the resulting increase of 12 µeq kg⁻¹ in alkalinity, it would result in an increase of the carbonate ion concentration of 58 µmol kg⁻¹, which is much greater than the observations in Figure 4.

During CaCO₃ formation Alk decreases at twice the rate of DIC indicating that CaCO₃ precipitation alone would cause [CO₃²⁻] to decrease with time in surface waters. Qualitatively, fCO₂ and pH changes that result in the small, ~10 µmol kg⁻¹, [CO₃²⁻] increase during summer require formation of calcium carbonate and organic matter. In the following discussion we use a simple mass balance model to constrain the rates of CaCO₃ and organic matter formation.

### 4.2. The Rates of Organic Carbon and CaCO₃ Production

Emerson and Stump [2010] determined net community organic carbon production during the summer of 2007 at Stn P using oxygen and nitrogen data along with a mixed-layer model. The model assumed a well-mixed surface layer of water that is open to gas exchange at the air-water interface and water exchange along and across isopycnals via advection and mixing (Figure 5). Since a detailed description of the model was presented previously, we review it only briefly here. The time rate of change of solute concentration, [C] (mol m⁻³), in a mixed layer of depth h (m) is equal to the sum of air-water exchange, mixing and biological production.

\[
\frac{d[C]}{dt} = F_{A-W} + E + A_v + A_z + M_z + M_\sigma + J_C
\]  

Terms on the right hand side are: air-water gas exchange, \(F_{A-W}\) (mol m⁻² d⁻¹); entrainment due to mixed layer deepening, E; horizontal advection in the mixed layer, \(A_v\); vertical exchange, either by upwelling, \(A_z\), or mixing along and across density surfaces, \(M_z\) and \(M_\sigma\), respectively; and finally biological production, \(J_C\). Each term for the physical processes is the product of a mass transfer coefficient or
Changes and air vertical advection and diffusion had minor influence. Local transport across the base of the mixed layer in summer by TN224 data are available from the authors. 2008). The Clivar P16 data are available online, and the DICN (S = 35), in the northeast Pacific Ocean along 152°W. Alkalinity, AlkN (S = 35), and dissolved inorganic carbon, \( \text{DICN} \) are presented for a winter cruise (P16, March, 2007) and a summer Thompson cruise (TN224, August/September 2008). The Clivar P16 data are available online, and the TN224 data are available from the authors.

Figure 6. Surface concentrations of salinity-normalized alkalinity, AlkN (S = 35), and dissolved inorganic carbon, DICN (S = 35), in the northeast Pacific Ocean along 152°W. Data are presented for a winter cruise (P16, March, 2007) and a summer Thompson cruise (TN224, August/September 2008). The Clivar P16 data are available online, and the TN224 data are available from the authors.

Mixing term and measured concentration or concentration gradients. The mass transfer coefficients and mixing terms are identified in Figure 5 and in the following equations. These quantities must be either measured or estimated from previous studies of physical processes in this region to determine the net biological carbon production, \( J_c \).

We solve equation (3) for DIC and Alk using \( O_2 \) and \( N_2 \) determined organic carbon production rates and a range of \( \text{CaCO}_3 \); OC production ratios. The terms of equation (3) that were most influential in controlling the summertime mass balance of \( O_2 \) and \( N_2 \) [Emerson and Stump, 2010] were the time rate of change and air-water gas transfer. Transport across the base of the mixed layer in summer by vertical advection and diffusion had minor influence. Local changes and air-water gas exchange are most important in the \( O_2 \) and \( N_2 \) mass balance because residence times of these gases with respect to air-sea exchange are relatively short: on the order of a few weeks to a month. This is not the case for dissolved inorganic carbon because the \([\text{CO}_2]\) gas is only a small component of the DIC in the mixed layer, and its residence time with respect to gas exchange is about 10 times that for oxygen and nitrogen. Local concentrations of dissolved inorganic carbon and alkalinity are more influenced by mixing and advection than are \( O_2 \) and \( N_2 \), thus processes occurring in the greater subarctic north Pacific have more influence in the DIC and Alk mass balances. In the following paragraphs we briefly describe how each of the terms on the right side of equation (3) and the coefficients in Figure 5 were evaluated.

The air water exchange term is normally separated into a diffusive flux, \( G \) (mol m\(^{-2}\) d\(^{-1}\)) and a bubble flux, \( B \). The first is characterized by the mass transfer coefficient for gas exchange, \( k_c \) (m d\(^{-1}\)), multiplied by the difference in concentration of the gas in the mixed layer and that at saturation equilibrium with the atmosphere, \([\text{C}^\text{sat}]/[\text{C}^\text{sat}]+k_c \text{CO}_2\) F + B = k_c \{[\text{CO}_2] - [\text{CO}_2]^\text{sat}\} + V_{inj} X_c \tag{4}

The air injection mechanism of bubble processes is parameterized by a mass transfer coefficient, \( V_{inj} \), and the mole fraction of gas C in the atmosphere, \( X_c \) [e.g., Hamme and Emerson, 2006]. While bubble processes have a large influence on the gas exchange of insoluble gases like \( O_2 \) and \( N_2 \), they are not very important for the more soluble \( \text{CO}_2 \), and they are ignored here. The concentrations of dissolved \( \text{CO}_2 \) in the mixed layer and the value in equilibrium with the atmosphere ([\( \text{CO}_2 \)] and \([\text{CO}_2]^\text{sat}\)) are calculated from the ocean and atmosphere /\text{CO}_2 data in Figure 2 using the solubility of \( \text{CO}_2 \) in seawater. The mass transfer coefficient, \( k_c \), is dependent on the physical properties of the gas and solute via the Schmidt number, \( S_C = (\nu/D) \), where \( \nu \) (cm\(^2\) s\(^{-1}\)) is the kinematic viscosity of the liquid and \( D \) (cm\(^2\) s\(^{-1}\)) the molecular diffusion coefficient of the gas (see Emerson and Hedges [2008, chap. 9] for more details). The mass transfer coefficient has been correlated with wind speed in surface ocean purposeful tracer release experiments. We determine the mass transfer coefficient normalized to \( k_{\text{CO}_2} \) at 20°C and \( S = 35 \) using the relationship to wind speed presented by Nightingale et al. [2000].

Entrainment is active only when the mixed layer deepens in the fall and winter. Since we interpret the data only through September, this term is of little importance till the very latter part of the period of interest when concentrations below the mixed layer are incorporated while the mixed layer deepens.

Ekman transport is assumed to dominate the advective flow in the mixed layer, \( h \), which is about 30 m deep during most of the summer.

\[ A_v = u \left( \frac{d[C]}{dx} \right) h + v \left( \frac{d[C]}{dy} \right) h \tag{5} \]

Here, \( u \) and \( v \) (m d\(^{-1}\)) are the zonal and meridional components of surface currents. Ekman transport at Stn P is greater in winter than summer because of the variability in wind speed [Roden, 1977; Ayers and Lozier, 2010]. Winds are mainly to the east resulting in a southward vector of velocity that reaches values of \( \sim 0.1 \) m s\(^{-1}\) in the wintertime. (See results from the global ocean data assimilation System, http://ferret.pmel.noaa.gov/NVODS). We consider the southward component of the surface transport to be the most important because both meridional currents and concentration gradients are strongest. Both atmospheric wind and surface ocean current velocities were measured on the mooring in 2007 (data not presented). The southward component of the surface currents during the period of June to October 2007 was variable and small averaging essentially zero from 5 m depth measurements and 0.01 m s\(^{-1}\) from Ekman transport calculations. We use advection velocities that incorporate this range of measurements in the sensitivity analysis described below.

Mixed layer concentration gradients of salinity-normalized alkalinity and dissolved inorganic carbon, AlkN and DICN, from both TN224 and CLIVAR P16 (Figure 6) indicate essentially no meridional gradient in AlkN north of
the subarctic-subtropical boundary, but a strong gradient in DIC which decreases to the south. Because curvature in the horizontal gradient is difficult to quantify from this data, we assume two extreme cases for horizontal advection of DIC. The minimum influence of meridional advection is represented by no divergence of flux at 50°N; the advective flux from the north equals that to the south. In the other extreme we assume no horizontal gradient north of 50°N so that from the north equals that to the south. In the other extreme isopycnal mixing does not play a role in the summertime mass balance of the mixed layer because it is isolated by thermal stratification. However, as we shall see, it is an important process balancing biological removal of CaCO3 on an annual basis.

[25] Vertical advection across the base of the summer mixed layer is described by:

\[ A_x = w \left( \frac{d[C]}{dz} \right) \Delta z \]  

where \( w (m d^{-1}) \) is the upwelling velocity, and \( \Delta z \) represents the depth scale for vertical transport which we take to be the mixed layer depth. The high end of the range of vertical advection velocities calculated previously for this region is on the order of 1 × 10^{-6} m s^{-1} (Tabata [1961] and Sasai and Ikeda [2003], \( w \approx 0.1 m d^{-1} \)). These values are dominated by winter time upwelling and the value we determine from satellite wind stress curl patterns during the summer of 2007 is 100 times smaller and negligible in the transport balance.

[26] Vertical mixing across the base of the mixed layer is depicted as:

\[ M_z = K_z \left( \frac{d[C]}{dz} \right) \]  

where \( K_z (m^2 s^{-1}) \) is the vertical eddy diffusion coefficient (see Figure 5). Diapycnal mixing processes are difficult to evaluate, but are potentially important because of the strong gradient in DIC between the surface mixed layer and the region below. (From the data in Figure 3, the DIC difference between 25 and 75 m depth in August of 2008 was ~50 \( \mu \)mol kg^{-1}, whereas the gradient in Alk was negligible.) A minimum value for the vertical eddy diffusion coefficient is that estimated within the thermocline by microstructure measurements [Gregg, 1989] and measured by tracer release experiments [e.g., Ledwell et al., 1998], 0.1–0.2 × 10^{-4} m^2 s^{-1}. However, Large et al. [1986] showed that during storms, diffusive mixing across the base of the mixed layer at Stn P can be characterized by eddy diffusion coefficients up to one hundred times this value over short periods of time. We assume \( K_z = 0.1 \times 10^{-4} m^2 s^{-1} \) is a lower limit and solve for values that are three times and ten times greater to determine the sensitivity to diapycnal mixing.

[27] Transport along density surfaces in the subarctic Pacific is also a vertical exchange because the depth of the density horizons representing the base of the winter mixed layer at Stn P (50°N) (\( \sigma_0 \approx 26.2 \)) plunges to ~200 m at 40°N and ~400 m at 30°N. Mixing along isopycnal surfaces is described by the diffusion equation:

\[ M_{\sigma} = K_{\sigma} \left( \frac{d[C]}{dl} \right) \]  

where \( l \) is the distance along the isopycnal surface and \( K_{\sigma} (m^2 s^{-1}) \) is the isopycnal eddy diffusion coefficient. This process connects the mixed layer in winter and water below the mixed layer in summer with deeper thermocline waters to the south. Isopycnal mixing does not play a role in the summertime mass balance of the mixed layer because it is isolated by thermal stratification. However, as we shall see, it is an important process balancing biological removal of CaCO3 on an annual basis.

[28] We calculate the change in Alk and DIC in the mixed layer at Stn P using the same mass transfer coefficients employed to constrain the O2 and N2 mass balance [Emerson and Stump, 2010]. The value of the net biological oxygen production was transformed to net organic carbon production and DIC decrease using a \( \Delta C/\Delta O_2 \) ratio of ~1.45 [Hedges et al., 2002]. Initial alkalinity and DIC in the mixed layer are given values near those measured at 152°N (Figure 3) but adjusted to exactly match the fCO2 and pH measured at Stn P in June 2007. Equation (3) is stepped forward in time and the fCO2 and pH are recalculated by the chemical equilibrium equations after each time step. The process is completed for ratios of calcium carbonate to organic carbon export rates of, CaCO3: OC = 0.0, 0.5 and 1.0, and for the range of advection and diapycnal eddy diffusion discussed above. Net biologic carbon production rates determined from O2 and N2 mass balance are relatively insensitive (±20%) to this range of mixing parameters.

[29] Results of the calculations are presented in Figure 7 and Table 1. The top three panels of Figure 7 are solutions for a diapycnal eddy diffusion coefficient of 0.1 × 10^{-4} m^2 s^{-1}. The bottom three solutions are the changes derived for an eddy diffusion coefficient three times this value. In order to match the observed fCO2 and pH with low \( K_z \) (Figure 7, Case I), it is necessary to have a CaCO3: OC ratio of at least 0.5. No production of CaCO3 results in fCO2 and pH trends less than those observed and a value of CaCO3: OC = 1.0 creates trends in the correct sense but too extreme. Increasing the vertical eddy diffusion coefficient (Figure 7, Case II) makes it possible to match the fCO2 and pH data using a CaCO3: OC = 0.0, but we show in the following paragraph describing the results in Table 1 that this case violates other constraints.

[30] The sensitivity analysis in Table 1 compares results from different model runs with observed changes in summertime fCO2 and pH (as in Figure 7) and also with expected changes in Alk and DIC. Expected alkalinity changes are determined from carbonate equilibrium with fCO2 and pH. Because calculated alkalinity is susceptible to small errors in these measurements, we assume a wide range of acceptable alkalinity change in the row labeled “Measured Values” of Table 1. The constraint for summertime change in DIC is taken from previous measurements during the summertime in the eastern subarctic Pacific of ~80 \( \mu \)mol kg^{-1} over a period of 2 years (1995-1997 [Wong et al., 2002]) from container ship crossings from Asia to Western North America. Because these data are from an earlier time, we assume an acceptable value for 2007 to be somewhere in the range of \( \Delta DIC = (50-100) \mu \)mol kg^{-1}.

[31] The sensitivity analysis was carried out for a southward component of advection in the surface layer of 0 and 0.01 m s^{-1}; however, only the results for \( v = 0.01 m s^{-1} \) are presented in Figure 7 and Table 1 because horizontal advection of this magnitude made little difference in the predicted changes. Bold values of the “Model Results” in
Figure 7. Comparison of model predictions and observations of $fCO_2$ and pH as a function of month in 2007. Thin lines are the model estimates, and solid symbols represent the data. Model solutions are for an advective velocity, $v$, of 0.01 m s$^{-1}$ and CaCO$_3$:OC values of 0.0, 0.5, and 1.0. The top three panels (CASE I) are solutions in which the vertical eddy diffusion coefficient is the minimum value of $K_z = 0.1 \times 10^{-4}$ m$^2$ s$^{-1}$. The bottom three panels (CASE II) are solutions in which the vertical eddy diffusion coefficient is $K_z = 0.3 \times 10^{-4}$ m$^2$ s$^{-1}$.

Table 1 are those that fall within the range of “Measured Values” at the top. We evaluate acceptable ratios of CaCO$_3$:OC by a process of elimination: (a) The high value for the eddy diffusion coefficient of $1.0 \times 10^{-4}$ m$^2$ s$^{-1}$ creates both $fCO_2$ and pH changes that are much too extreme for all CaCO$_3$:OC ratios indicating that the diapycnal diffusion rate is strongly constrained by the steep depth gradient of DIC accompanied by almost no gradient in alkalinity. (b) Another clear incompatibility between model and measurements is that the CaCO$_3$:OC ratio = 1 and $K_z = 0.3 \times 10^{-4}$ m$^2$ s$^{-1}$ produces an $fCO_2$ change that is too large. (c) At the other extreme the combination of CaCO$_3$:OC = 0 and

<table>
<thead>
<tr>
<th>$K_z \times 10^4$ (m$^2$ s$^{-1}$)</th>
<th>CaCO$_3$/OC</th>
<th>$\Delta pH$</th>
<th>$\Delta fCO_2$ (ppm)</th>
<th>$\Delta$DIC (µmol kg$^{-1}$)</th>
<th>$\Delta$Alk (µeq kg$^{-1}$)</th>
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<tr>
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<td>Model Results</td>
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<td>(50–100)</td>
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<td>–47</td>
<td>–77</td>
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</tbody>
</table>

OC discussed in the text. “Model values” given in bold font are within the range of the “measured values.”
K_z = 0.1 × 10^{-4} creates f/CO_2 and pH changes in the opposite sense to those measured.

[32] We have now eliminated all but the 2–5th rows in Table 1. All these scenarios are within or close to the acceptable range of f/CO_2 and pH change. Only the case for CaCO_3: OC = 0 and K_z = 0.3 × 10^{-4} m^2 s^{-1} clearly violates acceptable trends in DIC and Alk. The predicted alkalinity change for this scenario is positive, which is in dramatic contrast to the change required for chemical equilibrium with f/CO_2 and pH (−25 to −100 μeq kg^{-1}). Also, the calculated ∆DIC of −23 μmol kg^{-1} is much smaller for this case than previously measured summertime changes of (50–100) μmol kg^{-1}.

[33] In order to meet the constraints of the temporal changes of the carbonate system as determined by time series measurements of f/CO_2, pH and previous measurements of DIC change in summer our model suggests that the CaCO_3: OC ratio must be on the order of 0.5. Acceptable values are between 0.5 and 1.0 for K_z = 0.1 × 10^{-4} m^2 s^{-1} and <0.5 for K_z = 0.3 × 10^{-4} m^2 s^{-1}. Combining the CaCO_3: OC ratio with the organic carbon production rate of 17 mmol m^{-2} d^{-1} results in a flux of CaCO_3 from the surface ocean in this region of ~8 mmol m^{-2} d^{-1}.

4.3. Alkalinity Mass Balance for the Upper Ocean in the Subtropical Pacific

[34] If the CaCO_3 is being produced at a rate that is about half of that of organic carbon in the subtropical Pacific in summer, what are the processes that supply alkalinity to the surface waters? Horizontal fluxes via surface water transport are negligible in this area of the subtropical Pacific because of small gradients both meridionally (Figure 6) and zonally (data not shown). Vertical transport of DIC and Alk and nitrate concentrations, Alk + [NO_3], which normalizes the observed alkalinity for changes due to organic matter degradation.) A plot of this type for the upper 200 m in the subtropical Pacific Ocean indicates very little vertical gradient in alkalinity across the depth of the winter mixed layer, 120m, resulting in a ∆AlkPN/∆DICN ratio of only ~0.1 (Figure 8a). In a one dimensional steady state system a ratio of 0.1 will accommodate a CaCO_3: OC rain ratio of ~0.13, which is consistent with the results of Sarmiento et al. [2002] and Jin et al. [2006], but not with our derived CaCO_3: OC rain ratio.

[35] Another potential transport mechanism to subtropical Pacific surface waters is transport along constant density surfaces. Density horizons that outcrop in the subtropical Pacific in winter (σ_θ = 26.0–26.4) plunge into the subtropical thermocline to the south (Figure 3). A plot of AlkPN versus DICN along these isopycnal surfaces (Figure 8b) yields a ∆AlkPN/∆DICN ratio of about 0.4 rather than 0.1. If the pathway for exchange of carbonate parameters between the surface waters in the subtropical ocean and deeper waters is along isopycnal surfaces, the source of alkalinity for CaCO_3 formation is much greater.

[36] The alkalinity gradient along an isopycnal surface that crops out in the subtropical Pacific in winter necessary to supply the CaCO_3 fluxes reported here by along-isopycnal eddy diffusion can be determined from equation (8):

\[ F_{\text{alk}} = K_z (\Delta \text{Alk}/\Delta z) \]

Using a distance, \( \Delta l \), of 20° latitude (50°N and 30°N; \( \Delta l = 2.22 \times 10^6 \) m), an along-isopycnal eddy diffusion coefficient
CO2 and pH data from the same period to constrain the surrounding Stn P (0.9 ± 0.1 mol C m⁻³ time series measurements of oxygen and nitrogen gas mass changes (Figure 3) are many times this value indicating the potential of this source, even if it operates only for a very brief time each year when the isopycnals crop out in the winter mixed layer.

5. Conclusions

Organic carbon export from surface waters in the eastern subarctic Pacific at Stn P is estimated to be 17 mmol C m⁻² d⁻¹ in the summer of 2007 based on in situ, time series measurements of oxygen and nitrogen gas mass balance (2.5 mol C m⁻² yr⁻¹ assuming 150 days of productivity [Emerson and Stump, 2010]). Here we use in situ fCO2 and pH data from the same period to constrain the CaCO₃:OC production ratio to be about 0.5. Together these results suggest a CaCO₃ production of ~8 mmol m⁻² d⁻¹ in summer with very little production in winter, which results in an annual flux of 1.2 mol CaCO₃ m⁻² yr⁻¹. The CaCO₃ production rate is rate is similar to that determined using estimates of seasonal change of DIC and Alk from regressions to T and NO₃ [Lee, 2001] for the four grid points surrounding Stn P (0.9 ± 0.1 mol C m⁻² yr⁻¹, Kitack Lee, personal communication, 2009). It is also within the range of values determined in this area during the summer using in vitro methods [Lipsen et al., 2007].

Sediment trap collections at 200 m at Sta P have a CaCO₃:OC molar ratio of between 0.25 and 0.5 in summer [Wong et al., 1999; Timothy et al., submitted manuscript, 2011]; however, the sediment trap absolute fluxes of both OC and CaCO₃ are far less than those predicted here. Mean values for summertime sediment trap fluxes at 200 m over many years of observations were ~2.5 and ~0.8 mmol m⁻² d⁻¹ compared to our estimates of 17 and 8 mmol C m⁻² d⁻¹. Part of this difference can be attributed to the rapid decrease in particle flux between the mixed layer and 200 m. Three short-term deployments of free-floating sediment traps in 1987, 88 and 93 [Wong et al., 1999] resulted in decreases between 50 and 200 m in organic and inorganic carbon fluxes of ~3 times and 1.5 times, respectively. Thus, extrapolating the climatological sediment trap fluxes at 200 m to shallower depths approaches organic carbon fluxes that are about half of the values determined here, but the 50 m CaCO₃ flux is still ~7 times lower than our suggested value. It is not unusual for sediment trap fluxes to under estimate particle fluxes particularly during high flux events [Benitez-Nelson et al., 2001], which would be associated with CaCO₃ formation. It is also possible that we cannot assume the earlier trap fluxes are representative of the conditions of our observations, particularly since CaCO₃ production appears to be much more of an irregular process than net organic carbon export. Wong et al. [2002] observed that DIC summertime drawdown in the north Pacific was a regular and repeatable while alkalinity changes show no consistent seasonal change.

A CaCO₃:OC production ratio of 0.5 suggested here is about 5 times the value determined for this area by Sarmiento et al. [2002] and Jin et al. [2006] based on vertical gradients of Alk and DIC. Part of this difference may be that our measurements span a period of only one season and are local while estimates derived from climatological data are annual averages and more basin-wide in scale. We also demonstrate that transport along isopycnal surfaces that

Kᵣ = 1000 m² s⁻¹ [Ledwell et al., 1998; Gnanadesikan et al., 2002] and an alkalinity flux necessary to maintain a CaCO₃ flux of 8 mmol m⁻² d⁻¹ (Fₚ₀₂ = 16 meq m⁻² d⁻¹) results in an alkalinity increase of only about one micro-equivalent over a distance of 20 degrees latitude. Measured results in an alkalinity increase of only about one micro-equivalent over a distance of 20 degrees latitude. Measured changes (Figure 3) are many times this value indicating the potential of this source, even if it operates only for a very brief time each year when the isopycnals crop out in the winter mixed layer.
outcrop in the north Pacific is the most important flux pathway supplying alkalinity to the euphotic zone to accommodate CaCO₃ export determined from our in situ measurements. Interpreting vertical gradients of Alk and DIC can give misleading results about the importance of CaCO₃ export locally.

[30] Using the fluxes reported here we construct a regional carbon flux balance (Figure 9) that assumes a steady state over a period of at least several years. The net biological organic matter production of 17 mol m⁻² d⁻¹ (2.5 mol C m⁻² yr⁻¹) determined from the in situ O₂ and N₂ measurements combined with a CaCO₃:OC ratio of 0.5 require an alkalinity export of ~8 meq m⁻² d⁻¹ (1.2 mol CaCO₃ m⁻² yr⁻¹). The alkalinity that leaves the euphotic zone by biological processes must be balanced by an isopycnal flux because of the very small gradients in normalized potential alkalinity in both surface waters (Figure 6) and vertically (Figure 8a). A flux of 8 meq m⁻² d⁻¹ of alkalinity to the upper ocean along isopycnal surfaces with an AlkNP: DIC ratio of 0.4 implies an additional source of DIC of ~20 mmol m⁻² d⁻¹. The DIC mass balance is closed by a net export of 3 mmol m⁻² d⁻¹ out of the subarctic upper ocean via the combined fluxes across the air-water interface and surface water transport to the subtropical ocean.

[41] The importance of gas exchange in the carbon cycle in the northeast subarctic Pacific is determined using equation (4) and the fCO₂ data (Figure 2). To a first approximation surface waters were slightly supersaturated in the summer of 2007, and undersaturated by an average of 15 ppm in winter. Using mean gas exchange mass transfer coefficients for CO₂ in summer and winter of 3 and 6 mmol m⁻² d⁻¹, respectively [see Emerson and Stump, 2010] along with the fCO₂ data results in a mean annual flux from the atmosphere to the ocean of ~3 mmol m⁻² d⁻¹. This additional source to the subarctic mixed layer means that the flux of DIC to the south via surface ocean advection must be about 6 mmol C m⁻² d⁻¹ (Sasai and Ikeda [2003] modeled the observed DIC distribution in the North Pacific Ocean using an ocean GCM and climatological distributions of DIC. Their biological organic carbon export values were about half those suggested here and the Ekman transport to the subtopics was less, but the same fluxes dominated the balance.

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