Abstract

Uncertainty in the air-sea CO₂ exchange (CO₂ flux) in coastal upwelling zones is attributed to high temporal variability, which is caused by changes in ocean currents. Upwelling transports heterotrophic, CO₂ enriched water to the surface and releases CO₂ to the atmosphere, whereas the presence of nutrient-rich water at the surface supports high primary production and atmospheric CO₂ uptake. To quantify the effects of upwelling on CO₂ fluxes, we measured CO₂ flux at a coastal upwelling site off of Bodega Bay, California, during the summer of 2007 and the fall of 2008 using the eddy covariance technique and the bulk method with pCO₂ measurements from November 2010 to July 2011. Variations in sea surface temperatures (SST) and alongshore wind speeds suggest that the measurement period in 2007 coincided with a typical early-summer upwelling period and the measurement period in 2008 was during a typical fall relaxation period. A strong source of CO₂ (\(\sim 1.5 \pm 7\) SD (standard deviation) g C m\(^{-2}\) day\(^{-1}\)) from the ocean to the atmosphere during the upwelling period was concurrent with high salinity, low SST, and low chlorophyll density. In contrast, a weak source of CO₂ flux (\(\sim 0.2 \pm 3\) SD g C m\(^{-2}\) day\(^{-1}\)) was observed with low salinity, high SST and high chlorophyll density during the relaxation period. Similarly, the sink and source balance of CO₂ flux was highly related to salinity and SST during the \(pCO₂\) measurement periods; high salinity and low SST corresponded to high \(pCO₂\), and vice versa. We estimated that the coastal area off Bodega Bay was likely a source of CO₂ to the atmosphere based on the following conclusions: (1) the overall CO₂ flux estimated from both eddy covariance and \(pCO₂\) measurements showed a source of CO₂; (2) although the relaxation period during the 2008 measurements were favorable to CO₂ uptake, CO₂ flux during this period was still a slight source, (3) salinity and SST were found to be good predictors of the CO₂ flux for both eddy covariance and \(pCO₂\) measurements, and historical data of daily averaged SST and salinity between 1988 to 2011 show that 99% of the data falls within the range of our observation in May–June 2007, August–September 2008 and November 2010–July 2011 indicating that our data set was representative of the
annual variations in the sea state. Based on the developed relationship between $p\text{CO}_2$ and SST and salinity, the average annual $\text{CO}_2$ flux between 1988 and 2011 was estimated to be $\sim 35 \text{ mol C m}^{-2} \text{ yr}^{-1}$. The peak monthly $\text{CO}_2$ flux of $\sim 7 \text{ mol C m}^{-2} \text{ month}^{-1}$ accounted for about 30% of the dissolved inorganic carbon in the surface mixed-layer.

1 Introduction

Intensive efforts have been underway over the last few decades to better understand and quantify global air-sea $\text{CO}_2$ exchange. These investigations reveal that the oceans absorb approximately one-third of the global anthropogenic $\text{CO}_2$ emissions (Gruber et al., 2009; Takahashi et al., 2009), and have accumulated 118 ($\pm$19) Pg C of carbon emitted by fossil fuel combustion, land use change, and cement production between 1800 and 1994 (Sabine et al., 2004). However, current estimates of the global ocean $\text{CO}_2$ uptake still contain considerable uncertainty, and more observations are necessary to better understand this critical carbon reservoir (Doney et al., 2009). One of the largest uncertainties in the global carbon cycle is the role of coastal seas, which potentially account for 30% of the net global sink of $\text{CO}_2$ from the atmosphere to the ocean (Chen and Borges, 2009). Current global estimates do not account for the variability of the coastal ocean due to the difficulties of quantifying coastal $\text{CO}_2$ fluxes (Takahashi et al., 2009). In order to better understand the dynamics of coastal $\text{CO}_2$ fluxes, we must understand the physical and biological processes unique to coastal waters that control these fluxes.

Coastal upwelling is an important process that conflates the physical and biological influences on the coastal carbon cycle (Dugdale et al., 2006; Gattuso et al., 1998). Upwelling conveys deep nutrient-rich water to the surface and supports diverse coastal ecosystems. Although the surface of coastal upwelling zones covers only 1% of the global ocean, these areas support approximately 50% of the fishery industry because of their high primary productivity (Gattuso et al., 1998). Observational studies indicate that upwelling along the California coast has increased over the past 30 yr (Garcia-Reyes and Largier, 2010). This intensification of upwelling is likely related to increasing greenhouse gases, as the increasing temperature difference between land and sea accelerates coastal upwelling (Bakun, 1990; Diffenbaugh et al., 2004).

The sign of the effects of coastal upwelling on $\text{CO}_2$ fluxes has been debated. Upwelling provides a source of $\text{CO}_2$ from the ocean to the atmosphere because deep water is enriched with respired $\text{CO}_2$. At the same time, upwelling carries nutrients to the surface that enhance the biological uptake of $\text{CO}_2$ (Borges and Frankignoulle, 2002). Thus, the net $\text{CO}_2$ flux in upwelling zones averaged for inter-seasonal scales can be a sink of $\text{CO}_2$ from the atmosphere to the ocean (Evans et al., 2011; Gago et al., 2003; Hales et al., 2005; Ianson and Allen, 2002). The source and sink pulses of $\text{CO}_2$ flux reported in past studies range from $\sim 10$ to $30 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Copin-Montegut and Raimbault, 1994; Friederich et al., 2002; Goyet et al., 1998; Hales et al., 2005; Ianson and Allen, 2002; Ianson et al., 2009; Kelley and Hood, 1971; Lendt et al., 2003; Simpson and Zirino, 1980; Torres et al., 1999), using the sign convention of positive fluxes into the atmosphere from the ocean, and they are frequent two orders magnitude greater than the global average net $\text{CO}_2$ flux of approximately $0.4 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Takahashi et al., 2009). This emphasizes the importance of understanding $\text{CO}_2$ fluxes in the complex coastal zones where upwelling occurs. Despite its importance, uncertainty in determining the net $\text{CO}_2$ flux in upwelling zones remains due to the spatial and temporal sparsity of the available measurements.

Another uncertainty in the $\text{CO}_2$ flux of coastal upwelling zones is attributed to the fact that a standard measurement technique for air-sea $\text{CO}_2$ flux is still under development. Quantifications of the spatial and temporal variations of $\text{CO}_2$ flux in upwelling zones were made, for example, by Friederich et al. (2002) for the California coast and Evans et al. (2011) for the Oregon coast. However, these past studies estimated the $\text{CO}_2$ flux using the bulk method based on the partial pressure of $\text{CO}_2$ ($p\text{CO}_2$) measured in surface waters. Currently, the gas transfer coefficient required for the bulk method is determined solely by empirical relationships between gas transfer coefficients and wind speed, which were developed in the open ocean where wind speeds are generally...
much higher than coastal areas (Ho et al., 2006; Wanninkhof and McGillis, 1999). Under lower wind speeds, the effects of factors such as surface films and rain may be important as well for determining gas transfer properties (Frew et al., 2004; Jähne et al., 1987), and the effects of breaking waves and bubbles may be especially influential in coastal seas (Keeling, 1993).

The eddy covariance technique utilized in this study is considered to be the most direct CO₂ flux measurement method available. The application of the technique to ocean fluxes is still challenging due to the fact that data processing introduces high uncertainty to the measurement of smaller fluxes (less than 1 gC m⁻² day⁻¹) and the sensors are sensitive to contamination in marine environments (Else et al., 2011; Iwata et al., 2005; Prytherch et al., 2010). However, frequent maintenance and the expected large magnitude of the CO₂ fluxes from coastal upwelling zones enabled us to employ the open path eddy covariance technique.

The objective of this study was to quantify the CO₂ flux from the wind-driven upwelling zone near Bodega Bay, California, and evaluate the physical and biological effects of upwelling on the observed near-shore CO₂ flux. We hypothesized that the sink or source characteristics of the coastal region are determined by a balance between the transports of CO₂ enriched water to the surface and high primary productivity. To test this hypothesis, we measured CO₂ fluxes using the eddy covariance technique and the bulk transfer method with pCO₂ measurements and compared the observed CO₂ fluxes with environmental variables related to upwelling events (e.g. wind speed, salinity, sea temperature) and primary production (e.g. light and nutrient availability and chlorophyll density).

2 Methods

2.1 Site descriptions

The study site was located at the intertidal zone in the vicinity of the Bodega Bay Marine Laboratory (BML) in Northern California (Fig. 1). The coastal sea of Northern California is classically characterized by northerly winds in the summer due to the lateral pressure gradient (Dorman et al., 2000) established by the Pacific High offshore. The predominant alongshore wind causes Ekman transport along with lateral shear vorticity, which generates positive curl in the surface stress, resulting in strong coastal upwelling. Spatial distributions of water temperature indicated that our study area was particularly favorable for wind-driven upwelling events (Day and Faloona, 2009). The region’s wind-driven upwelling cycle, nutrient availability and subsequent primary production have been described in CoOP WEST (Wind Events and Shelf Transport) studies (Dugdale et al., 2006; Largier et al., 2006; Wilkerson et al., 2006). The region’s typically strong winds are periodically interrupted by a period with weaker winds known as a relaxation period, which lasts for ~3–7 days. The repeating cycles of upwelling and relaxation create a unique biological system. Upwelling carries deep water that is relatively cold and nutrient-rich to the surface, but increased turbidity (Day and Faloona, 2009) and lateral exports of nutrients inhibit production, while nutrients brought up to the surface are consumed during the subsequent relaxation period (Largier et al., 2006; Wilkerson et al., 2006).

The year of 2007 and 2008, when the eddy covariance measurements operated, were neutral to El Niño-Southern Oscillation. The winter of 2010, when pCO₂ measurements were operated, was characterized as a moderate El Niño condition.
2.2 Eddy covariance measurements

2.2.1 Data collection

Eddy covariance CO$_2$ flux measurements were recorded from 28 May to 5 June in 2007 and from 31 August to 25 September in 2008. A three-dimensional sonic anemometer (C-SAT3, Campbell Scientific, USA) and an open path infrared gas analyzer (ATDD, NOAA, USA in 2007 (Auble and Meyers, 1992) and LI-7500, Li-Cor, USA in 2008) were mounted on a 13 m tower within an intertidal zone (38°18′58″N, 123°04′20″W). The density of CO$_2$ and H$_2$O, three dimensional wind components, and sonic temperature were recorded at 10 Hz. The data were stored in a compact flash memory card in a datalogger (CR1000; Campbell) and manually collected.

2.2.2 CO$_2$ flux calculations

Mixing ratios of CO$_2$ and H$_2$O to dry air were computed for each 10 Hz data point based on the ideal gas law; air temperature at each 10 Hz data point was computed from the sonic temperature and the vapor pressure calculated from the H$_2$O density, and the dry air pressure at each 10 Hz data point was computed from the vapor pressure and atmospheric pressure. High frequency data were not available for atmospheric pressure, so standard atmospheric pressure was used.

Each 10 Hz measurement of the mixing ratios of CO$_2$ and H$_2$O, 3-D wind velocity, and sonic temperature were filtered by a de-spiking algorithm to remove outliers when a datum was greater or less than the median of the 20 adjacent data points ±6× their standard deviation (Burba and Anderson, 2010). About 0.02% of the 10 Hz data points were filtered out and interpolated.

The data stream was divided into 30-min intervals, with the validity of the 30-min averaging period tested using an Ogive function (Foken and Wichura, 1996). The first and second axis-rotation schemes were applied on the three dimensional wind speeds (Bal-docchi et al., 1988) for each 30-min data set. The first axis-rotation calculates a wind vector along a mean wind direction, and the second axis-rotation computes 3-D wind vectors to align the mean vertical wind speed to zero. After the axis rotation, the time lag between the infrared gas analyzer and the sonic anemometer was estimated individually for every 30 min period. Within a –2.0 to +2.0 s range, the lag was chosen to maximize the covariance between the CO$_2$ mixing ratio and the vertical wind speed. On average, the CO$_2$ mixing ratio measurement had to be advanced by 0.6 s to maximize the correlation with the vertical wind speed measurement. The CO$_2$ flux was calculated as the covariance between the CO$_2$ mixing ratio and the vertical wind speed every 30 min (Webb et al., 1980).

2.2.3 Corrections

The effects of the sensor-heating correction (Burba et al., 2008) and cross-sensitivity correction were evaluated. Since the temperature of the infrared gas analyzer detector cell is maintained above the ambient temperature and radiant heating can also increase the temperature of the sensor, the surface of the analyzer can be warmer than its surroundings. Fluctuations of air temperature caused by the hot surface of the analyzer can cause a negative correlation between CO$_2$ density and the vertical wind speed, resulting in a false sink of CO$_2$ flux (Burba et al., 2008). The sensor-heating correction (method (4) described in Burba et al., 2008) was applied to all data. Some uncertainties in applying the correction are as follows: (1) the sensor was oriented nearly vertically but not perfectly, whereas the correction method developed by Burba et al. (2008) assumes that the sensor is exactly vertical; (2) we did not measure the temperature of the sensor surface, and it had to be estimated by empirical equations (method (4) in Burba et al., 2008); (3) the NOAA gas analyzer was used for the measurement in 2007 instead of the LI-7500 gas analyzer, and an appropriate correction for the NOAA gas analyzer is most probably different from that for the LI-7500 gas analyzer. Regardless of these uncertainties, we used the same correction as for the LI-7500 to be consistent. The relationship between CO$_2$ flux with heat correction and CO$_2$ flux without the heat...
correction was as follow.

\[ F_{cc} (\text{g C m}^{-2} \text{day}^{-1}) = 1.03 \times F_{cw} + 0.76 \quad (R^2 = 0.99) \]  
for the NOAA gas analyzer, and

\[ F_{cc} (\text{g C m}^{-2} \text{day}^{-1}) = 0.97 \times F_{cw} + 0.89 \quad (R^2 = 0.92) \]  
for the LI-7500 gas analyzer. \( F_{cc} \) is CO\textsubscript{2} flux with heat correction and \( F_{cw} \) is CO\textsubscript{2} flux without heat correction.

Contamination, especially by sea spray, on the mirror surface of the infrared gas analyzer can potentially cause a false negative correlation between CO\textsubscript{2} density and relative humidity (Prytherch et al., 2010). Prytherch et al. (2010) attributed the high magnitude of the CO\textsubscript{2} flux often observed by the eddy covariance technique over the ocean to this cross-sensitivity, and suggested an algorithm to estimate the uncontaminated slope of the CO\textsubscript{2} mixing ratio to humidity. However, our sensors were cleaned at least every 3 days, and the sensitivity of the CO\textsubscript{2} mixing ratio to humidity in our data (~0.0025 (mmol CO\textsubscript{2} mol\textsubscript{air}^{-1} (% humid 100^{-1})) was much less than that reported in Prytherch et al. (2010) (~0.07 (mmol CO\textsubscript{2} mol\textsubscript{air}^{-1} (% humid 100^{-1})). Else et al. (2011) reported that the application of the cross-sensitivity correction lead to large scatter in the data. We also encountered the same problem, (CO\textsubscript{2} flux with cross-sensitivity correction) = 0.63\times(CO\textsubscript{2} flux without the correction) + 0.80, (R\textsuperscript{2} = 0.15). Consequently the correction was not applied to our study.

### 2.2.4 Quality controls

Data quality was assessed using diagnostic values provided by the infrared gas analyzer and the sonic anemometer (9 %: numbers in parentheses indicate the data amount filtered out by each process). After the sonic anemometer data was filtered using the diagnostic value, data during offshore winds, wind directions of 310°–160° (where a wind direction of 0° indicates a northerly winds and the degree increases clockwise), were filtered out (39 %). The double-differenced time series using the median of absolute deviation about the median was then used to filter out outliers (10 %) (Sachs, 1996), with the parameter \( z \) in the outlier detector set as 4 (Papale et al., 2006). Finally, apparent outliers (larger than 30 g C m\textsuperscript{-2} day\textsuperscript{-1} or lower than −30 g C m\textsuperscript{-2} day\textsuperscript{-1}) were also filtered out (1 %). After all data filtering processes were complete, 48 % of the CO\textsubscript{2} fluxes remained for further analysis.

Cospectra of CO\textsubscript{2} and temperature with the vertical wind speed were evaluated to assess data quality (Fig. 2). Based on surface layer similarity theory, within the inertial subrange the logarithmic cospectra of scalar and vertical wind speed follows a \(-4/3\) slope against normalized frequency (Kaimal et al., 1972). Although the theoretical characteristics became obscure under less stationary conditions, the overall structure resembled the ideal curve (Fig. 2). The cospectra did not vary noticeably with atmospheric stability, based on analysis of \( z/L \), where \( z \) is measurement height and \( L \) is the Monin-Obukhov length.

Footprint analysis (Schuepp et al., 1990) performed on the quality-controlled fluxes indicated that 90 % of the fluxes originated from within 3 km of the coast. The 30 m of land between the tower base and the ocean accounted for less than 0.01 % of the flux footprint, even under conditions with the smallest flux.

### 2.3 Environmental data and the Bodega Ocean Observing Node (BOON)

Wind speed and wind direction were measured with the same sonic anemometer used for the eddy covariance measurements. Datasets of air temperature, wind speed, wind direction, Photosynthetic Photon Flux Density (PPFD), sea surface temperature (SST), salinity, and chlorophyll density were obtained from the Bodega Ocean Observing Node (BOON, http://www.bml.ucdavis.edu/). Air temperature, wind speed, wind direction, and PPFD had been recorded every hour at a meteorological tower located 30 m inland from the intertidal zone (38°19′ N, 123°04′ W) since 1988, and SST, salinity, and chlorophyll density had been measured on a buoy (BML buoy) located 1.3 km offshore (38°18′ N, 123°04′ W) of our study site. SST and salinity had been measured
since 1988, and chlorophyll data was available only from 2005 to 2008. The $p$CO$_2$ was measured every hour by a SAMI-pCO$_2$ (Sun-Burst Sensors, USA) colorimetric sensor mounted on the buoy from November 2010 to July 2011. The measurement was temporarily halted due to a system malfunction in December 2010 through February 2011. The sensor was calibrated by the factory within the range 150–700 µatm. All the data used in this study are summarized in Table 1.

2.4 CO$_2$ flux estimation with $p$CO$_2$ and atmospheric CO$_2$

CO$_2$ flux ($F_c$) was calculated from $p$CO$_2$ ($C_{pw}$), SST, salinity, and atmospheric CO$_2$ pressure ($C_{pa}$) with the bulk method for each $p$CO$_2$ measurement based on the following equation (e.g. Wanninkhof and McGillis, 1999).

$$F_c = k[C_{pa} - C_{pw}]$$

The solubility, $\alpha$, was computed by SST and salinity based on Weiss (1974); the gas transfer coefficient, $k$, was determined to be the average value calculated following Wanninkhof and McGillis (1999) (hereafter, W&M99), Wanninkhof (1992) (hereafter, W92), Ho et al. (2006) (hereafter, Ho06), Nightingale et al. (2000) (hereafter, N00), and Sweeney et al. (2007) (hereafter, Sw07). The equations for $k$ (md$^{-1}$) are as follows:

[W&M99]
$$k = 0.0068u^3 \times (Sc/660)^{0.5}, \quad (4)$$

[W92]
$$k = 0.074u^2 \times (Sc/660)^{0.5}, \quad (5)$$

[Ho06]
$$k = 0.061u^2 \times (Sc/660)^{0.5}, \quad (6)$$

[N00]
$$k = [0.053u^2 + 0.024u] \times (Sc/660)^{0.5}, \quad (7)$$

[Sw07]
$$k = 0.065u^2 \times (Sc/660)^{0.5}, \quad (8)$$

where, $u$ is wind speed and $Sc$ is Schmidt number (Wanninkhof, 1992).

Data collected monthly by the NOAA/ESRL Carbon Cycle Greenhouse Gases (CCGG) group’s aircraft program were used to estimate $C_{pa}$. The nearest routine sampling location is offshore near Trinidad Head, CA, which is located about 300 km north of Bodega Bay (~41°10’N, 124°20’W). The lowest altitude data (near 300 m a.s.l.) from each month since September 2003 were used to estimate the average monthly atmospheric CO$_2$ concentration in the marine boundary layer throughout the region. The CO$_2$ concentration was converted to the pressure, $C_{pa}$ under the standard atmosphere.

2.5 Effective upwelling and National Data Buoy Center 46013 data

The National Data Buoy Center (NDBC) 46013 buoy is located off of Bodega Bay, California (38°14’N, 123°18’W). The Effective Upwelling Index (EUI) was introduced by Garcia-Reyes (2011) as a proxy for the cumulative NO$_3$. It is estimated using the sea surface temperature measured at the NDBC 46013 buoy ($SST_{N13}$) from the National
Data Buoy Center (http://www.ndbc.noaa.gov). To identify upwelling periods, NO3 concentrations were estimated based on the NO3-SST relation (Garcia-Reyes, 2011).

EUI was then calculated as a summation of a temporal differential of NO3 estimated while the daily averaged alongshore wind speed (AWS) was greater than 5 ms\(^{-1}\). EUI was set back to zero when daily AWS was less than 5 ms\(^{-1}\) for over 3 days.

2.6 Statistic analysis

2.6.1 For the eddy covariance data set

A t-test was used to test the significance of differences between the 2007 and 2008 CO2 fluxes and environmental parameters (i.e. SST, salinity, PPFD, wind speeds, AWS, friction velocity, chlorophyll density).

2.6.2 For the pCO2 data set

Linear correlation analysis was used to investigate relationships between environmental parameters (i.e. SST, salinity, PPFD, wind speeds and AWS) and pCO2 and CO2 fluxes calculated from pCO2. Since diurnal variations in pCO2 were minimal (less than 10 % of the total variations), these data were averaged for 24-h periods.

2.7 Estimates of dissolved inorganic carbon (DIC) and cumulative monthly CO2 flux and net primary production (NPP)

To evaluate the monthly net CO2 exchange between the air-water interface and the monthly net primary production (NPP) and to compare them with the dissolved inorganic carbon (DIC) pool, monthly CO2 fluxes and NPP were estimated and compared with estimated DIC per unit area within the surface mixed layer.

Since daily averaged pCO2 was most correlated with SST and salinity, as will be demonstrated later, daily pCO2 from 1988 to 2011 was estimated based on the SST and salinity data collected from the BML buoy with the following equation:

\[
C_{pw} = -142S_T + 115S_s - 1473 \tag{9}
\]

where, \(S_T\) is SST and \(S_s\) is salinity. CO2 fluxes were calculated in the same manner as explained above. DIC (\(C_{dic}\)) was computed based on the estimated pCO2, SST, salinity and pH (pp 324–325 in Sarmiento and Gruber, 2006):

\[
C_{dic} = C_{pw}K_0[1 + K_1[H^+]^{-1} + K_2[H^+]^{-2}] \tag{10}
\]

where, \(K_0\) is the solubility of CO2 (mol kg\(^{-1}\) atm\(^{-1}\)), \(K_1\) and \(K_2\) are dissociation constants of inorganic carbon species (mol kg\(^{-1}\)) determined from temperature and salinity, and [H\(^+\)] is hydrogen ion concentration (mol kg\(^{-1}\)) and equal to 10\(^{-pH}\). Hauri et al. (2012) reported seasonal cycles of pH off the Central California coast, and based on these results we approximated the pH seasonal cycle with a sine curve. The influence of the seasonal variation of pH on the DIC calculation was minimal (less than 3 %). Similarly, the NPP off Central California reported in Kahru and Mitchell (2002) was approximated by a sine curve. The surface mixed-layer depth was approximated by wind stress estimated from wind speeds (Lentz, 1992).

3 Results and discussions

High CO2 efflux to the atmosphere was observed during the measurement period in 2007. The average CO2 flux during this period was 1.5 (±7 SD) g C m\(^{-2}\) day\(^{-1}\) with high variability (Fig. 3a, Table 2). Although a relatively strong sink of CO2 was observed with high wind speeds on 7–12 September 2008, the overall CO2 flux measured in 2008 was a slight source of CO2, with a magnitude of 0.2 (±3 SD) g C m\(^{-2}\) day\(^{-1}\) (Fig. 4a, Table 2), and the average CO2 flux during the 2008 measurement season was not statistically different from zero (Table 2).
Contrasting differences were found in SST, salinity, and chlorophyll density between
the 2007 and 2008 measurement seasons (Table 2). No difference in AWS between
the 2007 and 2008 measurement periods was apparent. However, AWS on longer
time scales strengthened in late spring to early summer corresponding with a drop
in sea surface temperatures (Fig. 5a, b). The AWS then weakened in fall leading to
an increase in sea surface temperature (Garcia-Reyes, 2011). A high EUI (\(-20 \mu\text{M}\))
was still observed during fall 2008, but a negative AWS (\(\sim -5 \text{m}^2\text{s}^{-1}\)) was frequently
observed, creating conditions favorable to relaxation (Fig. 5a, c). The relatively lower
SSTs ranging from 10 to 12°C in May–June and higher SSTs ranging from 15 to 18°C
in August–September shown in Fig. 5b are compatible with the typical seasonal vari-
ations in SST, where upwelling intensifies in early summer and relaxes in fall (Garcia-
Reyes, 2011). The upwelling season is also characterized by high temporal variations
in CO\(_2\) flux, which was also observed in the 2007 measurements, due to the highly
dynamic shifts of water chemistry caused by upwelled water with high CO\(_2\) and sub-
sequent CO\(_2\) uptake by primary production (Dugdale et al., 2006; Evans et al., 2011;
Gago et al., 2003).

Relaxation periods are favorable to stratification of the upper water column, which
was reflected in lower salinity (\(\sim 32\text{psu}\)) and higher SST (\(\sim 17\text{°C}\)) during the 2008
measurement period. Stratification further enhances nutrient depletion on the surface
and increases primary production, resulting in higher chlorophyll density. Interestingly,
an increasing trend of chlorophyll density was observed during the 2008 measurement
period (Fig. 4d). A sink of CO\(_2\) (\(2\text{gCm}^{-2}\text{day}^{-1}\)) was consistently observed on 15
September 2008 when chlorophyll density approached the maximum of 2.3\text{mgm}^{-3}.
The measurement period in 2008 fell directly between high upwelling events with the
peaks of EUI in mid-July and October 2008 (Fig. 5c). Therefore, high nutrient levels
were brought to the surface by the preceding upwelling event, increasing the chloro-
phyll density until the nutrients were depleted. Kahru and Mitchell (2002) reported high
NPP of 2.4 \text{gCm}^{-2}\text{day}^{-1} (ca. 5 \times 10^{12}\text{gCmonth}^{-1} for the area of 6.2 \times 10^{6}\text{km}^2) in sum-
mer when nutrient availability was high near our study site. However, the overall CO\(_2\)
flux was near zero or a slight source during the 2008 measurement period despite
the favorable conditions for CO\(_2\) uptake. This was because the period preceded a high
upwelling period that stimulated higher chlorophyll density and probable relaxation con-
ditions, as inferred from the negative AWS.

The overall CO\(_2\) flux estimated from \(\Delta p\text{CO}_2\) was also a source of 0.4
\((\pm 0.6 \text{SD}) \text{gCm}^{-2}\text{day}^{-1}\) from November 2010 to July 2011 (Fig. 6f). The \(p\text{CO}_2\) data
were often out of the calibration range (150–700 \mu\text{atm}), and therefore the data may
not have been accurate at higher \(p\text{CO}_2\) values (Fig. 6e). However, \(p\text{CO}_2\) higher than
1000 \mu\text{atm} is likely in our study area (personal communication with John Largier of Uni-
versity of California, Davis, 2007). Correlation analysis showed that \(p\text{CO}_2\) was most
 correlated with SST \((R = -0.54, p < 0.001)\) followed by salinity \((R = 0.50, p < 0.001)\),
and CO\(_2\) flux was strongly correlated to wind speeds \((R = 0.58, p < 0.001)\) and AWS
\((R = 0.51, p < 0.001)\) followed by SST \((R = -0.40, p < 0.001)\) and salinity \((R = 0.34,
p < 0.001)\). Similar to the flux data obtained by the eddy covariance technique, higher
salinity and lower SST corresponded with higher \(p\text{CO}_2\) and a source of CO\(_2\) (Fig. 7).
Salinity and SST buoy data from 1988–2011 showed that salinity reached its maximum
level and SST reached its minimum level concurrently, as AWS peaked during the up-
welling season in late spring and early summer (Fig. 8). Therefore, although AWS did
not reflect the CO\(_2\) flux on short time scales (\(\sim 1\text{h}\)), it likely reflected the CO\(_2\) fluxes on
a seasonal scale. Interestingly, the seasonal change of the atmospheric CO\(_2\) showed
a very similar pattern to AWS, (Fig. 8a) with a higher peak during a high upwelling
season in late spring to early summer; however, because the atmospheric changes in
CO\(_2\) concentration were so much smaller than those induced in the surface ocean this
periodicity did not influence the overall flux significantly.

The CO\(_2\) flux estimated from the eddy covariance technique and from the bulk
method both showed that positive CO\(_2\) fluxes were larger than negative fluxes, and
that this balance was tightly reflected in salinity and SST. Considering the fact that
99% of the historical data set of salinity and SST fell within the range of our observ-
vations, supporting the notion that the data is representative of the region in general,
our data indicates that the overall exchange of CO$_2$ in this area is likely a net source of CO$_2$ to the atmosphere. Table 3 lists our CO$_2$ flux data together with the CO$_2$ flux in upwelling zones reported in past studies. Although the annual net CO$_2$ flux in some upwelling zones (e.g. North Pacific and Galician coast) show a sink of CO$_2$ and high primary production (Evans et al., 2011), particularly in strong downwelling conditions (Lanson et al., 2009), other studies conducted in North-Central California (Feely et al., 2008; Friederich et al., 2002; Wilkerson et al., 2006) further support our conclusion that the upwelling zone off of Bodega Bay is an overall source of CO$_2$ to the atmosphere. Despite the high chlorophyll density of 11 mgm$^{-3}$ observed in the early summer of 2000 by Wilkerson et al. (2006), their pCO$_2$ measurements still indicated that the area was a source of CO$_2$ to the atmosphere (Table 3). Their study also showed that the magnitude of high pCO$_2$ was similar over the cross-shelf distance of at least 50 km offshore (Wilkerson et al., 2006).

The estimation of CO$_2$ flux and DIC based on the relationship of pCO$_2$ with SST and salinity revealed that the monthly CO$_2$ flux reached its maximum in May ($\sim$ 7 molC m$^{-2}$ month$^{-1}$), which is equal to about 30% of DIC within the surface mixed-layer (hDIC) (Fig. 9). The annual CO$_2$ flux was estimated to be about 35 molC m$^{-2}$ yr$^{-1}$. The fraction of monthly NPP to hDIC became highest ($\sim$ 50%) in late summer, and the annual NPP was estimated to be about 40 molC m$^{-2}$ yr$^{-1}$. This simple estimation suggested that CO$_2$ flux and NPP were about the same magnitude and together accounted for significant flux compared to the stock of DIC.

4 Summary

The CO$_2$ flux from the coastal waters of Bodega Bay was measured during a typical upwelling season in 2007 and during a relaxation season in 2008. CO$_2$ flux was also estimated from pCO$_2$, measured from November 2010 to July 2011. Contrasting patterns in CO$_2$ flux and environmental parameters were observed between the two measurement periods in 2007 and 2008. Measurements in 2007 were during a typical upwelling period, as indicated by the seasonal variations of AWS and EUI in early summer, and a source of CO$_2$ to the atmosphere was observed concurrently with low SST, high salinity, and low chlorophyll density. The measurements in 2008 were, on the contrary, made during a relaxation period with high SST and low salinity that likely led to water stratification and high chlorophyll density. A strong upwelling event preceding the measurements in 2008 likely created favourable conditions for CO$_2$ uptake. However, the average CO$_2$ flux over the 2008 measurements was a small source of CO$_2$ overall. The magnitude of the observed sources CO$_2$ to the atmosphere estimated by the bulk method were also much higher than that of sinks of CO$_2$ during the pCO$_2$ measurements. Similar to the fluxes observed by the eddy covariance technique, those estimated by the pCO$_2$ measurements were closely related to salinity and SST. The historical data set of salinity and SST (1988–2011) indicated that 99% of data fell in the range of our observations. Therefore, the area was likely a source of CO$_2$ to the atmosphere annually. Past studies further support the assertion that the overall conditions are favourable to producing a source of CO$_2$ in the coastal upwelling area off of Bodega Bay at least within 50 km of the coast. Although AWS did not reflect pCO$_2$ or CO$_2$ flux on shorter time scales, high AWS together with low SST and high salinity suggests that AWS likely drives the seasonal cycle of CO$_2$ flux. Based on the pCO$_2$ to SST and salinity relationship, the average annual CO$_2$ flux between 1988 and 2011 was estimated to be 35 molC m$^{-2}$ yr$^{-1}$, and the amount of CO$_2$ transferred vertically and consumed by NPP accounted for significant amounts of carbon in comparison to the local dissolved carbon stock.

Acknowledgements. We thank Jackie Sones, Deedee Shideler and logistic supports by Bodega Bay Marine Laboratory, Tessa Hill for pCO$_2$ data retrieval and Joseph Verfaillie for valuable suggestions on data processing and interpretation. Sea surface temperature, wind speed and wind direction for calculating EUI was provided by the National Data Buoy Center. SAMI-pCO$_2$ data were provided by the Bodega Ocean Acidification Research group (NSF OCE # 0927255 to B. Gaylord), and Bodega Ocean Observing Network (BOON) data were provided by John Largier. Atmospheric CO$_2$ data from the NOAA/ESRL Carbon Cycle Greenhouse Gases group were provided by Colm Sweeney.
References


### Table 1. Data summary.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Date range</th>
<th>Location</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Eddy covariance tower</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$ flux</td>
<td>28 May–5 Jun 2007,</td>
<td>Bodega Bay,</td>
<td>38°20’ N,</td>
</tr>
<tr>
<td>Friction velocity</td>
<td>31 Aug–25 Sep 2008,</td>
<td>CA</td>
<td>123°04’ W</td>
</tr>
<tr>
<td>Wind speed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind direction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>BML meteorological tower</strong></td>
<td>1988–2011</td>
<td>Bodega Bay,</td>
<td>38°19’ N,</td>
</tr>
<tr>
<td>Air temperature</td>
<td>CA</td>
<td></td>
<td>123°04’ W</td>
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<tr>
<td>Wind speed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wind direction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>BML buoy</strong></td>
<td>1988–2011</td>
<td>Near Bodega Bay,</td>
<td>38°18’ N,</td>
</tr>
<tr>
<td>Sea surface temperature</td>
<td>CA</td>
<td></td>
<td>123°04’ W</td>
</tr>
<tr>
<td>Salinity</td>
<td>2007–2008</td>
<td>Bay, CA</td>
<td></td>
</tr>
<tr>
<td>Chlorophyll density $p$CO$_2$</td>
<td>Nov 2010–Jul 2011</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>NDBC 40613 buoy</strong></td>
<td>2007–2011</td>
<td>Near Bodega</td>
<td>38°14’ N,</td>
</tr>
<tr>
<td>Wind speed</td>
<td>Bay, CA</td>
<td></td>
<td>123°18’ W</td>
</tr>
<tr>
<td>Wind direction</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Sea surface temperature</strong></td>
<td>Sep 2003–Jan 2012</td>
<td>Near Trinidad</td>
<td>41°05’, 124°17’ W</td>
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<tr>
<td>Aircraft CO$_2$ measurement</td>
<td>Head, CA</td>
<td></td>
<td>(~ 4 km in altitude)</td>
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<tr>
<td>Atmospheric CO$_2$ measurement</td>
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</table>
Table 2. Mean, standard deviation, maximum, and minimum of CO\textsubscript{2} flux ($F_c$) in gCm$^{-2}$ day$^{-1}$, wind speed ($U$) in m s$^{-1}$, friction velocity ($U^*$) in m s$^{-1}$, air temperature ($T_a$) in $^\circ$C, PPFD in $\mu$mol m$^{-2}$ s$^{-1}$, chlorophyll density (CHL) in mg m$^{-3}$, salinity (SS) in psu, sea surface temperature (SST) in $^\circ$C, sea surface temperature measured at the NDBC 46013 buoy (SST\textsubscript{N13}) in $^\circ$C and alongshore wind speeds (AWS) in m s$^{-1}$ from (a) 28 May–4 June 2007 and (b) 30 August–24 September 2008.

<table>
<thead>
<tr>
<th>Location</th>
<th>Time</th>
<th>$F_c$ Mean</th>
<th>$F_c$ Standard deviation</th>
<th>$F_c$ Maximum</th>
<th>$F_c$ Minimum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oregon coastal ocean</td>
<td>May–Aug 2001</td>
<td>0.24 ± 0.25</td>
<td>130 ± 98</td>
<td>20–311</td>
<td>–</td>
</tr>
<tr>
<td>Central California coast</td>
<td>Spring, 1999</td>
<td>1.64 ± 0.02</td>
<td>480 ± 58</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Northern Peru</td>
<td>Spring, 1976</td>
<td>1.64 ± 0.02</td>
<td>480 ± 58</td>
<td>0–33</td>
<td>–</td>
</tr>
<tr>
<td>Vancouver Island, Canada</td>
<td>Typical year</td>
<td>0.35 ± 0.25</td>
<td>220–589</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Galapagos Islands</td>
<td>Spring, 1996</td>
<td>0.34 ± 0.24</td>
<td>315–345</td>
<td>14–36</td>
<td>–</td>
</tr>
<tr>
<td>St. Lawrence Island</td>
<td>Summer, 1996</td>
<td>0.27 ± 0.01</td>
<td>180 ± 18</td>
<td>14–36</td>
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</tr>
<tr>
<td>Peru coast</td>
<td>Aug 1994</td>
<td>0.30 ± 0.22</td>
<td>450–700</td>
<td>14.5–16.5</td>
<td>36–117</td>
</tr>
<tr>
<td>Biological Bay, CA</td>
<td>19–20 May 2001</td>
<td>0.29 ± 0.00</td>
<td>80 ± 10</td>
<td>23.9–33.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Biological Bay, CA</td>
<td>May–Jul 2007</td>
<td>1.94 ± 0.01</td>
<td>439 ± 115</td>
<td>11.5</td>
<td>0.4</td>
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<tr>
<td>Biological Bay, CA</td>
<td>Sep 2009</td>
<td>0.40 ± 0.01</td>
<td>320 ± 10</td>
<td>26.5</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*a* CO\textsubscript{2} flux estimated by reported $p$CO\textsubscript{2} with the bulk method (average of Nightingale et al., 2000 and Wanninkhof 1992).

*b* $dp$CO\textsubscript{2} (atmospheric CO\textsubscript{2} at $p$CO\textsubscript{2}).

*c* Alongshore wind speeds.

Table 3. CO\textsubscript{2} flux, $p$CO\textsubscript{2}, wind speed, sea surface temperature (SST), salinity (SS) and chlorophyll density (CHL) observed in coastal upwelling zones.

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<tr>
<th>Location</th>
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*b* $dp$CO\textsubscript{2} (atmospheric CO\textsubscript{2} at $p$CO\textsubscript{2}).

*c* Alongshore wind speeds.
Fig. 1. Study site with the approximate 90% flux footprint, and the wind rose of daily averaged wind directions and speeds (1990–2008) in Bodega Bay, California (38°18′58″N, 123°04′20″W).

Fig. 2. Normalized cospectra of the vertical wind speed and the CO₂ mixing density, $\langle f_{\text{CO}_2} \rangle$ with $\text{wC}$ (a) and the vertical wind speed and temperature, $\langle f_{\text{CO}_2} \rangle$ with $\text{wT}$ (b). The blue line indicates the average cospectra for $z/L > -0.1$ and the red line indicates the average for $z/L < -0.1$. The white line shows $-4/3$ at log-log scale.
Fig. 3. CO$_2$ flux (a), friction velocity and wind speed (b), SST and PPFD (c), salinity and chlorophyll density (CHL) (d) measured from 28 May to 4 June 2007. All data were plotted every 30 min.

Fig. 4. CO$_2$ flux (a), friction velocity and wind speed (b) SST and PPFD (c), salinity and chlorophyll density (CHL) (d) measured from 30 August to 24 September 2008. All data were plotted every 30 min.
Fig. 5. Alongshore wind speed calculated from wind speed and direction at the NDBC 46013 buoy, with positive AWS (red dots) and negative AWS (blue dots) differentiated by color (a), sea surface temperature at the NDBC 46013 buoy (SST\(_{N13}\)) (b), and effective upwelling index (EUI) (c). All data were averaged daily and plotted. The two boxes indicate the periods when eddy covariance measurements were available.

Fig. 6. Hourly alongshore wind speed (AWS) calculated from wind speed and direction at the NDBC 46013 buoy (black squares), with the 30 point running average (black line) also shown (a), sea surface temperature at the NDBC 46013 buoy (SST\(_{N13}\)) (b), and effective upwelling index (EUI) (c), salinity and SST (d), dpCO\(_2\) (pCO\(_2\)–atmospheric CO\(_2\)) (e) and CO\(_2\) flux estimated by the bulk method (f) from November 2010 to July 2011. (a)–(c) were plotted daily and (d)–(f) were plotted hourly.
Fig. 7. Distribution of daily averaged $p$CO$_2$ in relation to salinity (psu) and seas surface temperature (SST) (°C) measured from November 2010 to July 2011. A multiple linear regression was applied for $p$CO$_2$ against both salinity and SST ($R = 0.57, p < 0.001$).

Fig. 8. Average seasonal variations of atmospheric CO$_2$ concentration between September 2003 to August 2012 obtained near Trinidad Head, CA and alongshore wind speed (AWS) between 1988 to 2011 (a) and average seasonal variations of salinity and sea surface temperature (SST) from 1988 to 2011 obtained from the BML buoy (b). Vertical bars show standard errors (SE). The average and SE for each month were calculated from the monthly averages available for all years.
Fig. 9. Monthly averaged seasonal variations of DIC per unit area within the surface mixed layer (hDIC), monthly CO$_2$ flux ($F_{c,\text{month}}$), and monthly NPP ($\text{NPP}_{\text{month}}$) (a) and the depth of the surface mixed layer depth (b) estimated from 1988–2011 data. The vertical lines indicate standard deviations.