Seasonal cycle of surface ocean pCO_2 on the Oregon shelf

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[1] Previous work has shown that the Oregon shelf is a sink for atmospheric carbon dioxide (CO_2) during the upwelling season; however, until now, summertime variability in CO_2 exchange and sign of the flux for the rest of the year were unknown. Observations of the partial pressure of CO_2 (pCO_2) in surface waters from August 2007 to May 2010 from ships and a buoy were used with historical data to produce a composite seasonal cycle for the central Oregon midshelf. These data indicate that the region is highly variable, at times being either a sink or strong source for atmospheric CO_2. Interannual wind variability was an important determining factor in shaping the sink/source nature of this system. Late summer and early autumn was most variable relative to the rest of the year. Winter pCO_2 was near or slightly below atmospheric levels. Strong shelf-wide undersaturated conditions were first observed in early spring and lasted until the upwelling season became developed. Peak upwelling season pCO_2 ranged from <200 μatm to >1000 μatm. In July 2008, ship and buoy data revealed previously unobserved high-pCO_2 waters (~1000 μatm) at the surface. These conditions persisted for nearly 2 months and drove this system to be only a weak net annual atmospheric CO_2 sink of -0.3 ± 6.8 mol m^{-2} yr^{-1}. These data showed, for the first time, the seasonal cycle of surface ocean pCO_2 on the central Oregon midshelf and the impact of heretofore undocumented pCO_2 levels on an estimate of sea-air CO_2 flux for this region.

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1. Introduction

[2] It is well known that the open ocean plays a key role in the exchange of CO_2 with the atmosphere, taking up nearly 2 Pg (1 Pg = 10^{15} g) C yr^{-1} [*Takahashi et al.*, 2009]. Recent syntheses have focused on the role of the coastal ocean in sea-air CO_2 flux because this is an important and poorly understood region of carbon exchange between the terrestrial environment, the open ocean and the atmosphere [e.g., *Chavez and Takahashi*, 2007; *Hales et al.*, 2008; *Liu et al.*, 2010]. The coastal ocean dominates in terms of per unit area rates of primary production [*Behrenfeld and Falkowski*, 1997] and export production [*Muller-Karger et al.*, 2005] and may be an important conduit of carbon into the deep sea by advection off the shelf (defined as inshore of 200 m) in bottom-boundary layer currents [*Hales et al.*, 2006]. Large uncertainty in coastal ocean carbon flux estimates persists, owing to extreme variability observed on short temporal and small spatial scales relative to the open ocean. In addition to high localized variability, there is also large variability across regions. It has been stated that low-latitude coastal areas are generally thought to be sources of atmospheric CO_2 while high-latitude coastal margins act as sinks [*Cai et al.*, 2006; *Chavez and Takahashi*, 2007]. This broad generalization is poorly constrained because seasonal and interannual variability has only been characterized in a limited number of coastal regions. There is a general lack of observations to resolve even the seasonal cycle in most coastal locations, and the coastal margin of the U.S. Pacific Northwest is no exception.

[3] The Oregon coast is within the Cascadian margin, stretching from approximately Cape Mendocino, California, to the northern end of Vancouver Island, Canada. This represents the northern portion of the California Current System along the west coast of North America. In this region, equatorward winds that drive the Ekman transport of surface water offshore and subsequent upwelling of cold nutrient- and CO_2-rich water from depth, nominally begin in April and last until October. These upwelling-favorable winds drive a southward mean current on the shelf during the summer months, that reverses direction with the change to northward and downwelling-favorable winds during winter [*Huyer and Smith*, 1978]. The large-scale seasonal change in physical forcing is accompanied by significant changes in water column structure and water property distributions. Winter months are characterized by large freshwater inputs [e.g., *Wetz et al.*, 2006; *Chase et al.*, 2007] and strong storms [*Strub et al.*, 1987]. In summer, freshwater fluxes from land are greatly reduced relative to winter [*Colbert and McManus*, 2003] and water property distributions are driven by upwelling [*Barth and Wheeler*, 2005].

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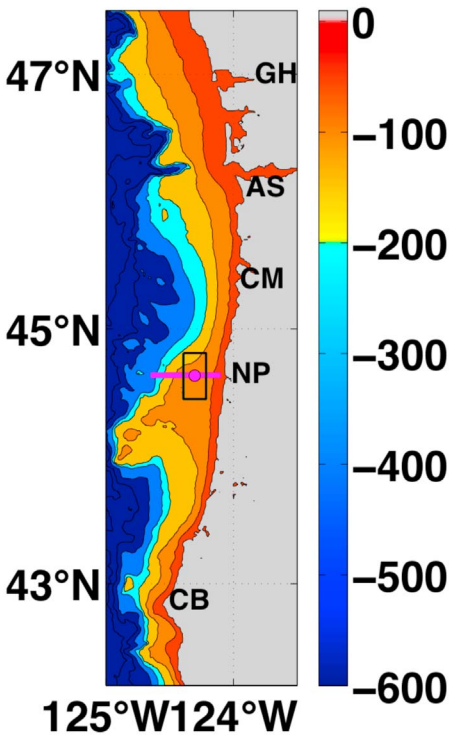

Figure 1. ETOPO1 1–Arc Minute Global Relief Model bathymetry for Oregon highlighting the shelf (0–200 m). Circle near Newport, Oregon, is the position of the NH10 buoy, the platform for our moored system. The east-west bar is the Newport Hydrographic line (NH line) extending from shore out past the shelf break (25 nm). The region where data are selected for construction of a composite year of pCO_2 (box, dimensions are 44.45°N–44.81°N and 124.3925°W–124.2155°W) is inshore of the 200 m isobath, centered on the NH10 buoy position (44.633°N, 124.304°W), extends ~20 nm in the north-south direction and ~10 nm in the east-west direction, and represents the central Oregon mid-shelf. Bathymetry data are provided by the National Geophysical Data Center (http://www.ngdc.noaa.gov/mgg/global/global.html.). Coastal locations mentioned in the text are shown: GH, Grays Harbor, Washington; AS, Astoria, Oregon; CM, Cape Meares, Oregon; NP, Newport, Oregon; CB, Cape Blanco, Oregon.

[4] Upwelling source waters along this coast have very high pCO_2 values, approaching or exceeding 1000 μatm [*Hales et al.*, 2005a; *Feely et al.*, 2008]. Outcrops of this water in nearshore settings off the Oregon coast have been observed with pCO_2 values near 700 μatm [*van Geen et al.*, 2000; *Hales et al.*, 2005a]. This water is then advected offshore and along shore, and because of its high preformed nutrient concentration [*Hales et al.*, 2005b], a lack of micronutrient limitation [*Chase et al.*, 2007], and fast-growing coastal phytoplankton assemblages [*Dugdale et al.*, 1990, 2006; *Wetz and Wheeler*, 2003], the pCO_2 is rapidly drawn down to levels far below equilibrium with the atmosphere (~200 μatm or less). The net result is that on average the Oregon shelf appears to act as a sink for atmospheric CO_2 during the upwelling season [*Hales et al.*, 2005a]. Following the upwelling season, the winds reverse to become dominantly poleward and downwelling-favorable by about October and large storms impact the Oregon coast until about April.

[5] To date programs studying pCO_2 variability on the Oregon shelf have focused on the upwelling season. No published data exist for fall, winter or spring conditions. Here we present the seasonal cycle of surface ocean pCO_2 on the Oregon shelf, and describe the physical and biological processes that influence the observed variability.

2. Methods

[6] To build a data set capable of resolving pCO_2 variability along the coast, we equipped a mooring (position shown in Figure 1) and numerous vessels of opportunity with instruments to measure sea surface temperature (SST), salinity, pCO_2, dissolved oxygen, chlorophyll and colored dissolved organic matter (CDOM) fluorescence and turbidity. Sections 2.1–2.3 describe the ship and mooring measurement systems and the data processing for each.

2.1. Ship Measurements

[7] We equipped vessels of opportunity with a new underway pCO_2 measurement system. This system, modified from that described by *Hales et al.* [2004], uses a LI-COR LI-840 infrared (IR) CO_2 sensor with a miniature membrane contactor (Liqui-Cel 1 × 5.5) as an equilibrator to achieve a faster analytical response than traditional systems using showerhead equilibrators. Prefiltration was achieved using a custom tangential flow filtration system with an 8 μm filter element, in which 1–10% of the main flow was directed tangentially to the primary flow and across the filter to the membrane contactor. Sample liquid flow through the contactor was typically ~300 ml min^{-1}, while the atmospheric air carrier flow rate was fixed at 30 ml min^{-1}. Data were collected at 1 Hz, and standard sequences using gases of known CO_2 mixing ratio (xCO_2, ppm) were run every two hours and used to correct for IR analyzer inaccuracy. Calibrated xCO_2 data were adjusted to pCO_2 using the measured total pressure in the equilibrator. The calibrated atmospheric xCO_2 data were converted to pCO_2 using atmospheric pressure measured in the LI-COR cell. Measurement-temperature pCO_2 was then corrected to pCO_2 at SST using the difference between ship intake and equilibrator temperatures, after accounting for the flow-based lag time (usually ~50 s) between those two temperature sensor locations, and the relationship for the temperature effect on isochemical seawater described by *Takahashi et al.* [1993].

[8] The pCO_2 system was integrated with a Seabird SBE45 for temperature and salinity, a Seabird SBE43 for dissolved oxygen, a chlorophyll fluorometer (WETLabs WetStar; excitation/emission wavelengths of 460/695 nm), CDOM fluorometer (WETLabs WetStar; excitation/emission wavelengths of 370/460 nm), and a beam transmissometer (WETLabs C-Star, wavelength 660 nm). Seawater flow rate was also monitored downstream of the pCO_2 equilibrator and used for data quality control; data from all measurements were removed during periods of low flow delivery to the equilibrator. All ancillary measurements are made at 1 Hz coincident with the pCO_2 measurement. The intake depth for the seawater flow-through system on most ships was typically 3 m. Optical instruments were kept clean during

Table 1. Dates of Cruise Observations Spanning August 2007 to September 2008[a]

Ship	Date
OSU R/V *Wecoma*	14–31 August 2007
OSU R/V *Elakha*	12 October 2007
OSU R/V *Wecoma*	1–19 November 2007
OSU R/V *Elakha*	20 November 2007
OSU R/V *Elakha*	11 February 2008
OSU R/V *Elakha*	14 February 2008
OSU R/V *Elakha*	17 February 2008
OSU R/V *Wecoma*	20–21 February 2008
OSU R/V *Elakha*	4 March 2008
OSU R/V *Wecoma*	18–21 March 2008
OSU R/V *Elakha*	24–25 March 2008
OSU R/V *Wecoma*	10–17 April 2008
NOAA *McArthur II*	20–27 April 2008
OSU R/V *Elakha*	5–6 May 2008
NOAA ship *Miller Freeman*	21–23 May 2008
OSU R/V *Wecoma*	28 May to 7 June 2008
OSU R/V *Elakha*	1 July 2008
OSU R/V *Elakha*	2–3 July 2008
NOAA ship *McArthur II*	12–21 July 2008
OSU R/V *Elakha*	22 August 2008
OSU R/V *Wecoma*	13–24 September 2008

[a]OSU, Oregon State University.

each cruise. Owing to a computer theft, we were unable to calibrate our fluorometer with bottle samples collected during all cruises. The chlorophyll calibration was done using surface Niskin bottle samples collected during the July 2008 cruise aboard the NOAA ship *McArthur II*. These data, although limited in time, cover a substantial portion of the dynamic range of chlorophyll concentrations encountered in this region (0–20 mg m^{-3}). Observations of CDOM will be presented elsewhere.

2.2. Moored Measurements

[9] Moored pCO_2 measurements were made using a Submersible Autonomous Moored Instrument CO_2 sensor (SAMI-CO_2) [*DeGrandpre et al.*, 1995] produced by Sunburst Sensors which was deployed immediately under the surface float on the Oregon State University (OSU) NH10 buoy (Figure 1). The NH10 buoy is located at the 80 m isobath, about 20 km from shore nearly due west of Newport, Oregon. This location was chosen by the Oregon Coastal Ocean Observing System (OrCOOS; http://agate.coas.oregonstate.edu/index.html.) because it is almost exactly halfway between the shore and the shelf break. The SAMI was factory calibrated prior to each deployment. Buoy measurements agree well (typically within ±5 μatm) with ship data collected during close ship track passes to service and check the buoy throughout the deployments. In addition to the pCO_2 sensor, the mooring hosted a Seabird SBE16plus that measured and logged temperature and salinity and captured and logged the signals from a SBE43 sensor for dissolved oxygen and a WETLabs C-star transmissometer (660 nm) for optical beam transmission. Additional optics sensors deployed on the buoy include a WETLabs combination chlorophyll fluorometer and turbidity sensor (FLNTUSB which uses excitation/emission wavelengths of 470/695 nm for chlorophyll and backscatter at 700 nm for turbidity) and CDOM fluorometer (FLCDSB; excitation/emission of 370/460 nm). All sensors were positioned at approximately 1 m depth in the bridle of the buoy, and measurements were recorded hourly. Copper tape, faceplates and shutters were used to achieve a 4 month nonfouled record from our moored optical sensors. Optics data were first passed through a standard deviation filter to remove aberrant measurements caused by biofouling (by removing data outside of one standard deviation from the mean or the raw counts). All measurements were subsequently smoothed with a Loess filter with a 6 h filter span. The chlorophyll fluorometer was calibrated using data collected during the NOAA ship *McArthur II* July 2008 cruise.

2.3. Sea-Air CO_2 Flux Estimate

[10] The mooring data were used to calculate the first annual estimate of sea-air CO_2 flux for this region. The sea-air CO_2 flux (F) was calculated using

$$F = k_{CO2} K_{CO2} \Delta pCO_2, \quad (1)$$

where k_{CO2} is the gas transfer velocity (m d^{-1}), K_{CO2} is the solubility of CO_2 (mol m^{-3} atm^{-1}), and ΔpCO_2 is the seawater pCO_2 minus the atmospheric pCO_2 (atm). The atmospheric pCO_2 was taken here to be an average measured during fall, spring and summer cruises (392 μatm). All input parameters were hourly values (wind magnitude, SST, salinity, and surface water pCO_2). The k_{CO2} was calculated with the parameterization by *Ho et al.* [2006] using wind speeds from the NOAA C-Man station in Newport, Oregon. The k_{CO2} were corrected to SST using the relationship for the Schmidt number dependence of gas transfer velocity described by *Wanninkhof* [1992]. A salinity correction of k_{CO2} was not conducted here because the difference between k_{CO2} at SST in freshwater versus saltwater (S = 35) is on the order of a few percent. Note that we used shore-based winds because the NOAA and NH10 buoy wind records had large gaps during the wintertime. C-Man winds have a strong diurnal signal, and are typically weaker than offshore winds (nearshore wind magnitude ~75% of offshore magnitude over this study period; data not shown), therefore, for a given delta pCO_2, our flux estimate using these winds is lower than a calculation based on offshore winds.

3. Results

[11] This data set has captured pCO_2 variability across all seasons on the Oregon shelf for the first time. Between August 2007 and May 2010, 21 cruises (104 days of total ship time; Table 1) and 4 mooring deployments (572 days of total data) were completed. Ship-based measurements were collected between August 2007 and September 2008, and coverage over the shelf varied by month, with cruises during 6 out of 10 months surveying much of the coast between Grays Harbor, Washington, and Newport, Oregon. During October 2007 and February, March, and August 2008, ship coverage was limited to the NH Line (our most intensely sampled transect; shown in Figure 1). No ship data were available for December and January. The first mooring time series took place from 13 August 2007 to 8 November 2007. A mooring time series was attempted in winter 2007–2008 but a storm broke the buoy from its anchor shortly after deployment. Subsequent mooring time series were from 10 April 2008 to 15 September 2008; 20 March 2009 to 25 May 2009; and 25 August 2009 to 11 May 2010,

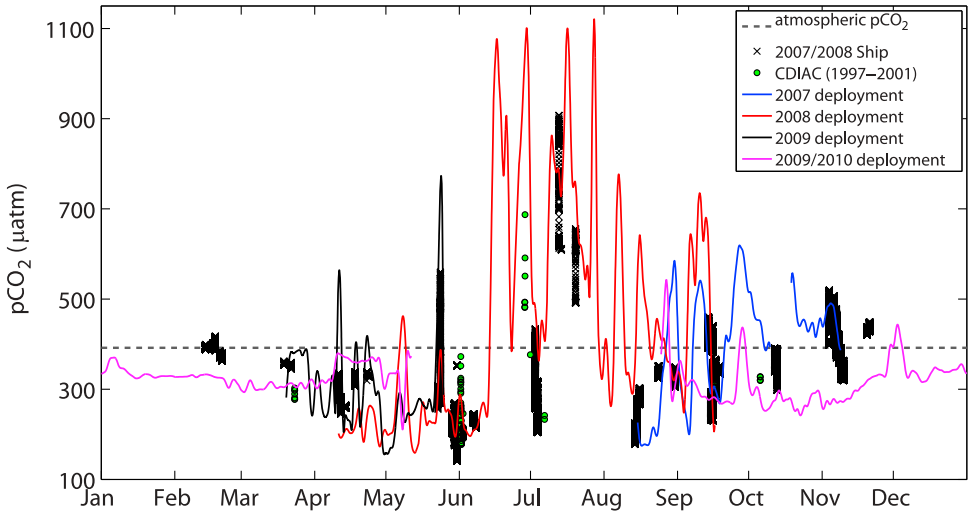

Figure 2. Composite seasonal cycle of pCO_2 (μatm) collected from ships (within the box region defined in Figure 1) and moorings near the NH10 station position off Newport, Oregon.

respectively. To compare our buoy data to ship measurements we have defined an area around the buoy position for selecting ship-based observations (Figure 1), with dimensions ~10 nm east–west and ~20 nm north–south (44.45°N to 44.81°N and 124.3925°W to 124.2155°W). This area was chosen to capture ship data in the vicinity of the buoy and it should be noted that the dimensions are large compared to the scales of variability we observe, which can result in an imperfect agreement between buoy and ship data. Historical Carbon Dioxide Information and Analysis Center (CDIAC) pCO_2 data and ship-based observations made during this study were selected from this region and used for the construction of a composite year of pCO_2 for the central Oregon midshelf.

[12] CDIAC pCO_2 data for the central Oregon shelf from within our defined region near the NH10 buoy are nonexistent for the winter season (December–February) [*Hales et al.*, 2005a]. However, CDIAC pCO_2 data do exist for the remainder of the year. Using both historical data and data collected during this project for a region representing the central Oregon midshelf (Figure 1), we have constructed a seasonal cycle of pCO_2 (Figure 2). Currently our winter ship observations are very limited (5 cruises), but the existing data suggest that pCO_2 conditions are at most near equilibrium with the atmosphere during this season. Data from our 2009–2010 buoy deployment demonstrate that pCO_2 levels may be slightly undersaturated with respect to the atmosphere over a majority of the winter. The pCO_2 on the shelf trends toward strongly undersaturated conditions in the spring (March–May), punctuated by brief periods of elevated values during early upwelling season southward wind events (Figure 3). Summer (June–August) values show the highest pCO_2 variability on the shelf, with values ranging from <200 to >1000 μatm. The pCO_2 variability is decreased in the autumn

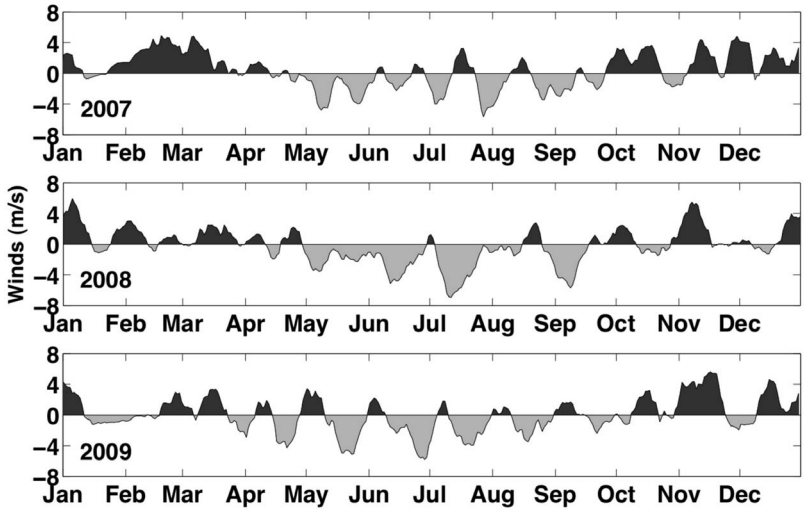

Figure 3. The 10 day running averaged daily median N-S wind magnitude for (top) 2007, (middle) 2008, and (lower) 2009, observed at the NOAA C-Man station in Newport, Oregon. Dark is northward (downwelling favorable), and light is southward (upwelling favorable).

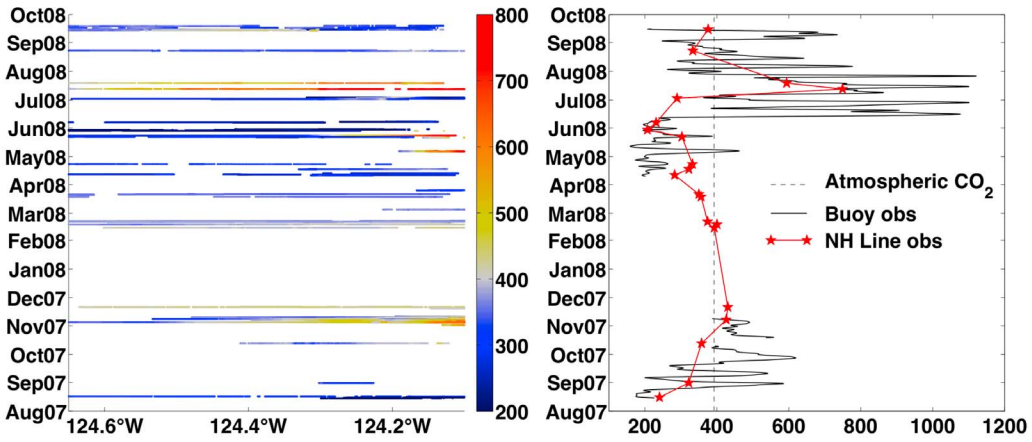

Figure 4. (left) The pCO_2 (μatm) from all cruise data collected over the shelf along the NH line (shown in Figure 1). (right) Buoy and ship (averaged for the central Oregon midshelf region defined in Figure 1) pCO_2 (μatm) data plotted with the average atmospheric pCO_2 measured during this study (392 μatm).

(September–November) relative to summer, with the range of values trending toward equilibrium with the atmosphere as wind conditions seasonally reverse from upwelling to downwelling favorable and net photosynthetic productivity decreases over the Oregon shelf.

3.1. Winter

[13] Although ship-based winter sampling was temporally and spatially limited, pCO_2 on the shelf was near equilibrium with the atmosphere during all cruises in 2008. Surface water with SSTs ~8°C and salinity ~28 was adjacent to the coast. Chlorophyll concentrations were observed to be low during this time of year, and winds were persistently downwelling favorable (Figure 3). Data from our winter 2009–2010 buoy deployment show that during at least some years the shelf can maintain a state of undersaturated pCO_2 (~340 μatm) with respect to the atmosphere for the entire season. By March, pCO_2 had fallen well below atmospheric equilibrium and chlorophyll increased to 3 mg m^{-3}, consistent with the general timing of the spring bloom on the Oregon shelf [*Huyer et al.*, 2007].

3.2. Spring

[14] The month of April is nominally when the spring transition from downwelling to upwelling conditions occurs on the Oregon shelf (e.g., http://www.cbr.washington.edu/data/trans.html.), and during this month in 2008 the shelf had transitioned from winter pCO_2 values near equilibrium with respect to the atmosphere to a strong sink for atmospheric CO_2. Buoy data showed pCO_2 values undersaturated with respect to the atmosphere by over 150 μatm, and pCO_2 observed from the ship showed similarly undersaturated conditions over the entire Oregon shelf off Newport (Figure 4).

[15] Spring SSTs were between 9°C and 10°C and freshwater originating from the Columbia River mouth was observed over the shelf both north and south of Astoria, Oregon (46.2°N; Figure 1). Chlorophyll was generally ~5 mg m^{-3} throughout the survey region, with the highest concentrations observed within and near the Columbia River (>10 mg m^{-3}). Moderate Resolution Imaging Spectroradiometer (MODIS) chlorophyll shows the bulk of phytoplankton biomass along the Oregon coast in the vicinity of the Columbia River at this time (Figure 5).

[16] In late spring (May), SSTs were warmer by 2–3°C from the values observed in early spring 2008 and low-salinity water was only observed south of the Columbia River mouth. The occurrence of plume water south of the Columbia River is indicative of the change in circulation along the Washington and Oregon coasts from winter-downwelling conditions to summer-upwelling conditions [*Hickey*, 1989], although this pattern is sensitive to the intensity and duration of upwelling-favorable winds [*Hickey and Banas*, 2008]. The change to upwelling conditions is reflected in the change to a positive upwelling index for the Oregon coast (45°N) beginning in April (http://www.pfeg.noaa.gov/products/PFEL/modeled/indices/upwelling/NA/upwell_menu_NA.html.), and is also evident in the pattern of SST and salinity on the southern portion of our ship survey during this time. In the region near Newport, Oregon, SST was 10°C and salinity was 32, substantially cooler and saltier compared with the surface water properties over the shelf on the northern portion of our ship survey. Widespread undersaturation with respect to atmospheric CO_2 was evident on the shelf and extending out into the North Pacific. Buoy and ship pCO_2 observations were the lowest in our record during this time (Figure 4). Chlorophyll was between 3 and 5 mg m^{-3} on the shelf north of Newport, Oregon, but exceeded 10 mg m^{-3} in the region of active upwelling near and south of Newport, Oregon. Satellite chlorophyll (Figure 5) and moored chlorophyll measurements (Figure 6) show that this was the first period within the 2008 upwelling season where substantial primary production (indicated by increased chlorophyll) was observed in the vicinity of Newport, Oregon.

3.3. Summer

[17] The greatest interannual and intraseasonal variability in surface water pCO_2 occurs in summer over the central Oregon shelf (Figure 2). June and July 2008 marked a sharp transition in the functioning of the coast from being a sink for atmospheric CO_2 to a source. We lack ship-based measurements for June, but it is clear from our mooring observations that the Oregon shelf transitioned radically from

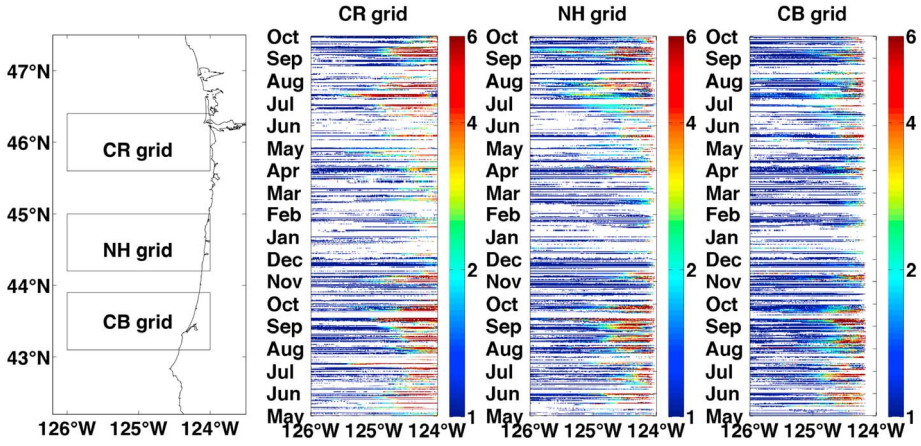

Figure 5. Moderate Resolution Imaging Spectroradiometer (MODIS) Level 2 chlorophyll (mg m^{-3}) from individual satellite passes (usually two per day) from May 2007 to October 2008 for select regions off the Columbia River (CR grid), Newport, Oregon (NH grid), and Coos Bay, Oregon (CB grid). Data are plotted in log scale.

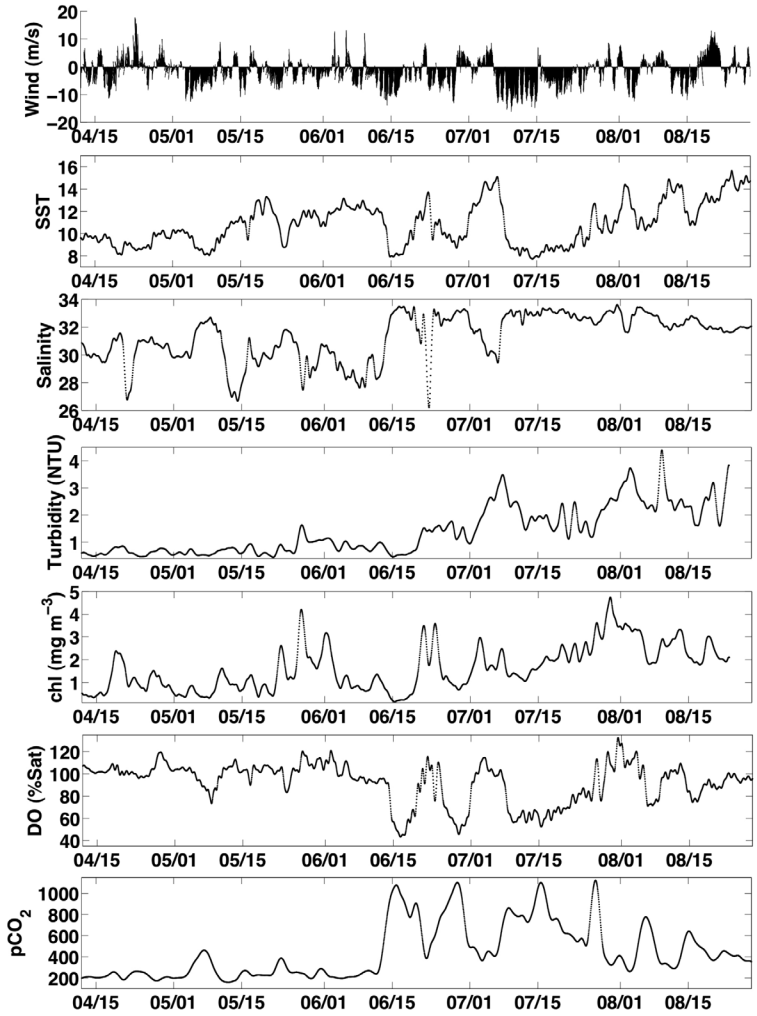

Figure 6. Hourly vector winds (m s^{-1}) from the NOAA C-Man station in Newport, Oregon, and SST (°C), salinity, turbidity (nephelometric turbidity units, NTU), chlorophyll (mg m^{-3}), dissolved oxygen (percent saturation), and pCO_2 (μatm) from the NH10 buoy for the time period 12 April to 28 August 2008.

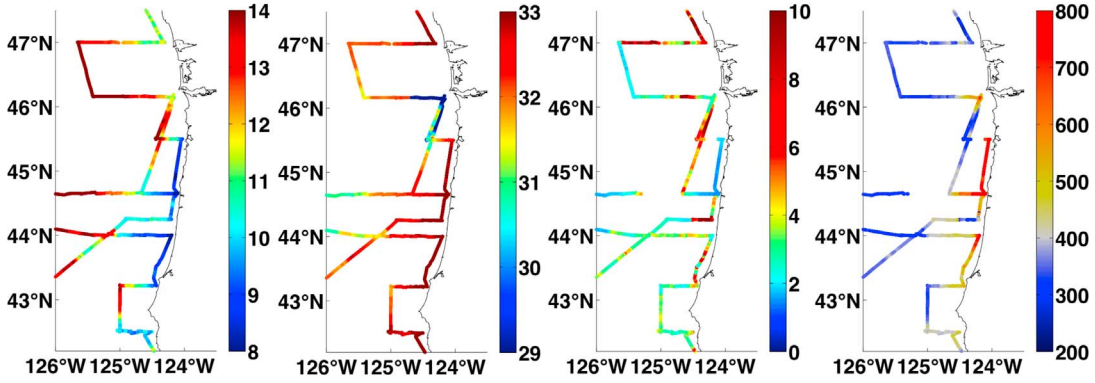

Figure 7. Underway SST (°C), salinity, chlorophyll (mg m^{-3}), and pCO_2 (μatm) from cruises during July 2008.

pCO_2 near ~200 μatm, increasing to ~1000 μatm over the course of a <10 day period with the onset of continuous and strong (>10 m s^{-1}) upwelling-favorable winds around 10 June (Figure 6). The mooring data reveal a significant drop in oxygen percent saturation, a 4°C decrease in SST, and a low standing stock of phytoplankton biomass that persisted for the entire ~15 day upwelling event in June 2008. A brief increase in chlorophyll and oxygen saturation, and a decrease in pCO_2 were observed at NH10 during two periods of reduced upwelling-favorable winds before an intense, prolonged upwelling event began, spanning most of July 2008.

[18] The ship data for July show distributions of SST and salinity typical of coastal upwelling, but variability in surface pCO_2 not observed before for this region (Figure 7). Ship surveys show that cold SST (~8°C), high-salinity (≥33) water spanned the coast from Cape Meares, Oregon (45.5°N), south to Cape Blanco, Oregon (42.8°N). The pCO_2 in the upwelled water reached values broadly in excess of 800 μatm, and >1000 μatm at the NH10 mooring site (Figure 4). This high-pCO_2 water extended out past the shelf break (25 nm off Newport; Figure 7) within the upwelling plume. Previous observations show that surface expressions of recently upwelled water off Oregon approach 700 μatm [*van Geen et al.*, 2000]. Subsurface upwelling source waters over the shelf can have a pCO_2 approaching 1000 μatm early in the upwelling season, and significantly exceeding those levels by the end of the summer growing season [*Hales et al.*, 2006]. These observations of >1000 μatm pCO_2 at the surface are the highest values yet observed, and represent close coupling between the nearshore-midshelf surface waters and deep upwelling source waters. The frequency and persistence of these events would have a significant impact on the net annual sea-air CO_2 flux for this region.

[19] August 2007 was the warmest month sampled by ships in our record, and SSTs over the shelf mostly exceeded 14°C, except off Newport, Oregon, where cold, recently upwelled waters were evident. Low-salinity water (<30) originating from the Columbia River was present on the shelf from Grays Harbor, Washington (47°N), to Cape Meares, Oregon (45.5°N), but only resulted in an elevated pCO_2 signal near the Columbia River mouth. The entire shelf was undersaturated with respect to atmospheric CO_2, and therefore functioned as an atmospheric CO_2 sink. The pCO_2 levels observed at the NH10 buoy just following deployment in August 2007 were <200 μatm, and track well the levels across the midshelf (Figure 4). The standing stock of chlorophyll was high over the entire shelf (>7 mg m^{-3}), presumably the result of net photosynthetic uptake of inorganic carbon that drove the large-scale CO_2 undersaturation observed during this time.

3.4. Autumn

[20] September and October 2007 both experienced periods of upwelling-favorable winds (Figure 3) and coincident elevated pCO_2 conditions at NH10 (Figure 4), but limited ship data for October indicate that this high-pCO_2 water was confined to inshore of NH10 and pCO_2 over the midshelf to outer shelf was below equilibrium with respect to the atmosphere. Autumn on the Oregon shelf marks the transition from summer-upwelling to winter-downwelling conditions. During the first portion of our November survey, SSTs had decreased by more than 3°C from those observed in October. Surface water pCO_2 had risen to approach atmospheric equilibrium, but with a significant degree of spatial variability. pCO_2 was still undersaturated in the region between the Columbia River and Newport, Oregon, but was oversaturated with respect to atmospheric CO_2 on the southern end of the survey; a pattern that resulted from late-season upwelling that caused cooler SSTs (10°C) and higher salinity (33) in the southern portion of our survey, and chlorophyll concentrations near 5 mg m^{-3} in the region of active upwelling. During the second portion of this cruise the wind conditions changed from upwelling favorable to strongly downwelling over the course of two days as the first winter storm impacted the coast. This drove a rapid change in seawater pCO_2. The variability observed during the first portion of the cruise was eliminated and the shelf pCO_2 transitioned to being homogenously distributed just slightly above equilibrium with the atmosphere. Chlorophyll also showed a similar response to the arrival of winter storm conditions, with variable concentrations prior to the change in the weather and then driven to <1 mg m^{-3} as the standing stocks of phytoplankton were diluted by storm generated mixing.

4. Discussion

4.1. Composite Seasonal Cycle and Interannual pCO_2 Variability

[21] It is important to note that our composite year includes a continuous record of summer surface pCO_2 values

that reached previously unobserved levels in excess of 1000 μatm. During our sample period the Oregon shelf transitioned from being a sink for atmospheric CO_2 in the 2008 spring to early summer, to a strong source for nearly a 2 month period in the late summer (June/July). There is likely large interannual variability driving the sink/source function of the coast, and this variability is demonstrated by our buoy time series spanning multiple years. The buoy records captured autumn conditions during 3 years in September 2007, 2008, and 2009. The differences in pCO_2 observed between these three autumns (Figure 2) are likely due to interannual variability in the wind forcing (Figure 3).

[22] Winds were more persistent and strongly upwelling favorable in September 2008 compared to September 2007 and 2009 (Figure 3), and that resulted in large differences in pCO_2 between these time periods (Figure 2). At the start of August 2008, there was a nearly month long relaxation in N-S winds (Figure 3), and the shelf experienced a general warming. The pCO_2 dropped to below atmospheric equilibrium by the start of September 2008 (Figure 4). During September 2008 the shelf experienced a period of strong and prolonged equatorward wind with few wind reversals (Figure 3). The pCO_2 at NH10 during this event reached ~700 μatm, but was rapidly drawn down to below equilibrium with the atmosphere by a phytoplankton bloom which followed the wind event (Figures 5). The winds in September 2007 were more weakly upwelling favorable and pCO_2 increased to only ~500 μatm. Winds in September 2009 were very weak and variable (Figure 3), and pCO_2 was ~90 μatm undersaturated with respect to the atmosphere for nearly the entire month.

[23] The winds are driven by large-scale atmospheric pressure cells that are themselves heavily influenced by interannual variability [*Chavez et al.*, 2003; *Schwing et al.*, 2002], therefore year-to-year differences in pCO_2 conditions should be anticipated. Given the intensity of interannual pCO_2 variability observed in the much longer record from Monterey Bay, California [*Chavez and Takahashi*, 2007; *Friederich et al.*, 2002], it is no surprise that interannual variability is important on the Oregon shelf and this is a significant motivation for producing longer data records. In our record, the largest variability in pCO_2 is during the late summer and early autumn (Figure 2) when strong and persistent winds occur with undersaturated surface water and bottom waters that are highly oversaturated caused in part by the buildup of respired CO_2 from organic matter remineralization over the shelf during the growing season [*Hales et al.*, 2005a, 2006]. Wind conditions during the late summer and early autumn have the potential to expose strongly supersaturated bottom water to the atmosphere, resulting in the massive variability in surface pCO_2 observed during this study; simultaneously, rapid photosynthetic response to abundant upwelled nutrients has the potential to draw surface pCO_2 to levels far below atmospheric saturation. Winter and early spring surface water pCO_2 does not show this degree of variability (Figure 2) because winds during this time are predominantly downwelling favorable (Figure 3), driving offshore waters toward the coast and not exposing deep high-pCO_2 water to the atmosphere. Upwelling conditions show a transition, with low pCO_2 persisting through the early part of the upwelling season, and high and highly variable values seen later in the summer. Measurements of bottom water pCO_2 show that they are near 1000 μatm in May, but significantly exceed that level by August [*Hales et al.*, 2005a]. If these waters are exposed during early upwelling season southward wind events, the elevated CO_2 levels will be lower than seen later in the summer. Ventilation of this high-pCO_2 water in late summer and early autumn has the potential then to drive the largest fluxes. The period of prolonged outgassing of CO_2 to the atmosphere in the summer of 2008 may not occur every year, but is in part be driven by the co-occurrence of persistent and strong upwelling conditions and typically high late summer upwelling source water pCO_2 concentrations.

4.2. Spring Atmospheric CO_2 Sink

[24] The surface oxygen content was oversaturated with respect to equilibration with the atmosphere over the majority of the April to June 2008 period at NH10 (Figure 6). Oxygen oversaturation has been consistently observed over the Oregon shelf during the growing season [*Hales et al.*, 2006] and maintenance of these conditions in the face of gas exchange suggests high rates of net primary production. This is also indicated by the persistent undersaturated pCO_2 conditions relative to the atmosphere over this period (Figure 6). Note that these spring CO_2 sink conditions seem to be more consistent between years than are the late summer and early autumn conditions discussed above (Figure 2). Satellite chlorophyll data (Figure 5) and buoy data (Figure 6) show, however, that phytoplankton biomass was highest in spring near the Columbia River and generally low along the entire coast relative to the summer. The chemical signals of primary productivity occurring without the optical signals of phytoplankton standing stocks suggests one of two things; that the water mass at the mooring site in spring experienced high productivity elsewhere along the coast, not at our mooring site, or that the system was experiencing high net productivity without a concurrent accumulation of biomass.

[25] Given the low salinities observed in tandem with these geochemical signals (Figure 6), the large signals of primary production occurring in the vicinity the Columbia River, and the mean southward flow this time of year, one possibility that must be explored is that this is the result of high net productivity occurring on the shelf near the Columbia River. An estimate of the transit time for a water mass from the Columbia River mouth to Newport is 10 to 27 days, given southward current speeds between 10 and 30 cm s^{-1} [*Huyer*, 1977; *Kosro*, 2005] over the shortest possible transit pathway. As a water mass ages, there is often a lag time between measures of biomass and the chemical signals of primary production [e.g., *Martz et al.*, 2009]. In this setting, primary productivity is often supported by large coastal diatoms [*Wilkerson et al.*, 2000], which are known to have very rapid bloom dynamics [*Dugdale et al.*, 2006]. Rapid growth and nutrient uptake initiates the bloom, and rapid termination of the bloom follows nutrient depletion [*Wetz and Wheeler*, 2003]. The large individual cells and chains sink rapidly, leaving behind the signals of CO_2 depletion and O_2 enrichment, which will be reset toward atmospheric saturation only slowly by gas exchange. The response time for gas exchange is uncertain but can be estimated. Assuming an average wind speed of 10 m s^{-1} (consistent with the high estimated water velocities), the wind speed dependences of *Wanninkhof* [1992] or *Ho et al.* [2006] and a 10 m surface mixed layer

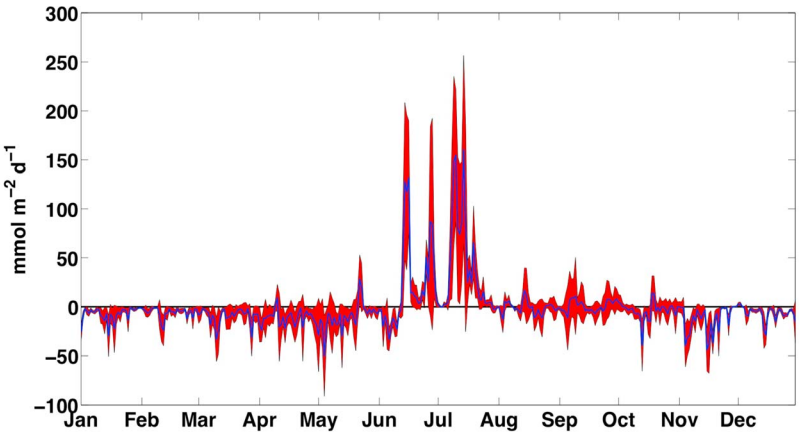

Figure 8. A composite year of sea-air CO_2 flux (mmol m^{-2} d^{-1}) on the central Oregon midshelf calculated from NH10 buoy data. The blue line is the daily mean flux, and the red area represents the standard deviation about the daily means.

(consistent with the plume-associated low-salinity waters), the gas exchange response time will be about 2–3 days for a simple gas like O_2 and approximately 10 times longer for CO_2 [*Sarmiento and Gruber*, 2006]. Therefore, it is possible that the spring/early summer undersaturated pCO_2 conditions on the shelf result from nonlocal productivity associated with the Columbia River system.

[26] Potential problems with this explanation include the following: (1) The shortest-distance transport pathway is simplistic and does not account for the fact that strong upwelling circulation typically pushes the plume offshore of the shelf break. (2) Southward velocities vary across the shelf from ~50 cm s^{-1} in the upwelling jet [*Barth et al.*, 2005] to 0 or even northward nearshore [*Huyer and Smith*, 1978]. (3) The observed close coupling between O_2 oversaturation and pCO_2 undersaturation is not consistent with the transport arguments given above. Oxygen appears oversaturated in our record, when over the time period of our transport argument above it should have reached equilibrium with the atmosphere if the supporting productivity were confined to the mouth of the Columbia River. It is possible that the phytoplankton community was efficiently exported, so we were not able to observe "bloom-like" concentrations of chlorophyll in tandem with the low pCO_2 and high O_2 at the mooring. The winter and spring freshening from Oregon coastal rivers is also likely important and hard to distinguish from Columbia River inputs early in the season from salinity alone. These rivers deliver most of their annual discharge in the winter and early spring [e.g., *Chase et al.*, 2007], and the early season freshening must come at least in part from those sources.

4.3. Summer pCO_2 Variability

[27] Given the magnitude of the effect of the summer upwelling events on the mooring and ship-based pCO_2 observations, one would expect the increase in pCO_2 to be accompanied by the upwelling of nutrients that could fuel photosynthetic CO_2 drawdown [e.g., *Hales et al.*, 2005b]. The ship-based chlorophyll observations reveal only moderately high values north and south of the upwelling plume and off the shelf during July (Figure 7). MODIS satellite chlorophyll data and our mooring observations (Figures 5 and 6) suggest a ~20 day lag between the physical signals of upwelling and the chlorophyll response from the July upwelling event on the shelf, which is long compared to coastal diatom responses [*Dugdale et al.*, 2006]. The MODIS chlorophyll data show that a weak bloom (3 mg m^{-3}) translated offshore during this event, but chlorophyll concentrations did not increase above 5 mg m^{-3} until the bloom moved back onshore when upwelling conditions abated toward the end of July (Figure 6). That is, there was only a minor biological response from this intense upwelling period until the winds decreased and reversed at the end of July 2008, allowing high-pCO_2 surface water to persist on the shelf for nearly a 2 month period. We are currently uncertain why the photosynthetic community did not respond as quickly as expected, but believe there may have been a shift in the community composition compared to those seen early in the season. This issue will be addressed in a future publication.

4.4. Sea-Air CO_2 Fluxes

[28] The fluxes calculated from all buoy data collected at NH10 between August 2007 and May 2010 were averaged for each Julian day to produce a composite year of sea-air CO_2 flux for the central Oregon shelf (Figure 8). From this record the central Oregon midshelf is a small net annual CO_2 sink of -0.3 ± 6.8 mol m^{-2} yr^{-1} (-0.7 ± 18.7 mmol m^{-2} d^{-1}). Our upwelling season estimate is 4.4 ± 24.4 mmol m^{-2} d^{-1} (April to October), which contrasts the previous average estimate of −20 mmol m^{-2} d^{-1} [*Hales et al.*, 2005a]. The composite year of sea-air CO_2 flux shows that the late upwelling season (June to September) is a period when the central Oregon midshelf can be a substantial CO_2 source of 14.3 ± 30.6 mmol m^{-2} d^{-1}. This source period in 2008 was compensated by the mild and strong sink conditions during the winter and spring, respectively. This caused the system to function as only a weak sink on an annual basis. The dynamic nature of sea-air CO_2 fluxes on the central Oregon midshelf is clearly shown in Figure 8, which adds uncertainty to our estimates of average sea-air CO_2 fluxes (reported here as standard deviations). Different years may experience different conditions on the basis of the variable nature of this upwelling system.

[29] It is at this time not clear why the high-pCO_2 water observed in June and July 2008 persisted as long as it did,

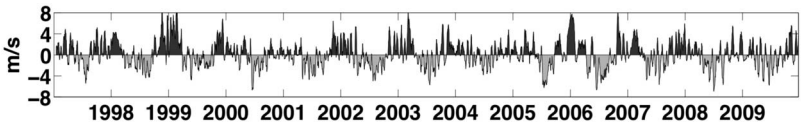

Figure 9. Record of 10 day running averaged daily median N-S wind component (m s^{-1}) from Newport, Oregon, from January 1997 through December 2009. Dark is northward (downwelling favorable), and light is southward (upwelling favorable).

or how representative these conditions are of other years. Until this study, there were no pCO_2 observations during these types of events, although wind records suggest they have probably occurred before. For example, there were periods of persistent, strong, upwelling winds that coincided with the most extreme hypoxic events of 2002 and 2006 [*Grantham et al.*, 2004; *Chan et al.*, 2008]. In 2008 winds were upwelling favorable for the majority of time between May and August, but in June and July there were multiple 10 day or greater periods of 10 day running-averaged southward wind magnitude in excess of 4 m s^{-1} (Figure 3) that coincided with the observed high-pCO_2 water at the surface. Wind events like this might represent a threshold that drives periods of high pCO_2. It is clear that these wind conditions have occurred repeatedly in the past (e.g., 2002, 2005 and 2006; Figure 9), but why high-pCO_2 water persisted on the shelf in 2008 as long as it did is unclear. The co-occurrence of upwelled-source waters that are strongly enriched in CO_2 and nutrient levels with fast-growing coastal diatom phytoplankton communities makes this system inherently tend toward extreme variations. If the productivity response is fast in comparison to supply of upwelled waters, very low surface pCO_2 conditions will be experienced; if the balance is tipped such that upwelled waters are supplied faster than the biology can respond, very high levels of surface pCO_2 will dominate.

[30] Previous work from observations in May and August 2001 has shown that the Oregon coast is a strong sink for atmospheric CO_2 during the upwelling season [*Hales et al.*, 2005a]. There are three important points that help explain the differences in the results between this prior study and ours. First, in 2001 there were no extended periods of uninterrupted, strong upwelling-favorable winds comparable to that seen in mid to late summer of 2008 (Figure 9), suggesting a fundamentally different forcing regime during that time. Second, only two 2 week periods bracketing the upwelling season were sampled during this prior study and we now have continuous measurements through the entire season. Although the wind records of 2001 do not suggest a major event was missed, it is easy to imagine a sparse sampling of the time series record we present here that could yield different net flux estimates. Third, the results of *Hales et al.* [2005a] were strongly influenced by observations over the broad shelf region to the south of the NH line, where the surface pCO_2 levels were more uniformly undersaturated. The sea-air CO_2 flux estimates presented here are from the central Oregon midshelf, and there is likely to be important along- and cross-shelf variability not captured here in our flux estimates. It is clear from the contrasting results between the 2001 work and the present study that spatially and temporally comprehensive and well-resolved pCO_2 observations are needed to diagnose the dynamic nature of sea-air CO_2 fluxes on the Oregon shelf.

5. Conclusions

[31] These data indicate four important features about the Oregon shelf: (1) The net fluxes of the upwelling season are not canceled out by fluxes in the downwelling season, but rather the latter appears to be near-neutral or undersaturated with respect to sea-air exchange. (2) There are strong interannual variations in the system's functioning, particularly during the upwelling season, that can change it from a strong sink in some years to a strong source in others, casting uncertainty on the system's long-term role as source or sink. (3) The balance between the strength/persistence of upwelling-favorable wind-forcing and photosynthetic response to that forcing is critically important in determining the overall function of the Oregon shelf. (4) This region is highly dynamic over a variety of time and space scales and requires near-continuous interannual observation to characterize the variability in pCO_2.

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