



# Inorganic carbon dynamics during northern California coastal upwelling

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## ARTICLE INFO

### Article history:

Received 17 May 2010

Received in revised form

14 March 2011

Accepted 19 April 2011

Available online 3 May 2011

### Keywords:

Carbon

Upwelling

Acidification

California

Continental shelf

Phytoplankton

## ABSTRACT

Coastal upwelling events in the California Current System can transport subsurface waters with high levels of carbon dioxide (CO<sub>2</sub>) to the sea surface near shore. As these waters age and are advected offshore, CO<sub>2</sub> levels decrease dramatically, falling well below the atmospheric concentration beyond the continental shelf break. In May 2007 we observed an upwelling event off the coast of northern California. During the upwelling event subsurface respiration along the upwelling path added ~35 μmol kg<sup>-1</sup> of dissolved inorganic carbon (DIC) to the water as it transited toward shore causing the waters to become undersaturated with respect to Aragonite. Within the mixed layer, pCO<sub>2</sub> levels were reduced by the biological uptake of DIC (up to 70%), gas exchange (up to 44%), and the addition of total alkalinity through CaCO<sub>3</sub> dissolution in the undersaturated waters (up to 23%). The percentage contribution of each of these processes was dependent on distance from shore. At the time of measurement, a phytoplankton bloom was just beginning to develop over the continental shelf. A box model was used to project the evolution of the water chemistry as the bloom developed. The biological utilization of available nitrate resulted in a DIC decrease of ~200 μmol kg<sup>-1</sup>, sea surface pCO<sub>2</sub> near ~200 ppm, and an aragonite saturation state of ~3. These results suggest that respiration processes along the upwelling path generally increase the acidification of the waters that are being upwelled, but once the waters reach the surface biological productivity and gas exchange reduce that acidification over time.

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## 1. Introduction

Seasonal upwelling in the California Current System (CCS) brings dense water with high partial pressures of carbon dioxide (pCO<sub>2</sub> > 600 ppm) to the sea surface and into contact with the atmosphere near shore (Hales et al., 2005a; van Geen et al., 2000; Feely et al., 2008). The large gradient in pCO<sub>2</sub> (ΔpCO<sub>2</sub> > 200 ppm) between the upwelled waters and the atmosphere results in the exchange of CO<sub>2</sub> across the air–sea interface causing these near shore upwelling regions to be local sources of CO<sub>2</sub> to the atmosphere (Hales et al., 2005b). As upwelled waters age and are advected offshore sea surface pCO<sub>2</sub> drops dramatically, reaching levels significantly lower than the atmospheric concentration seaward of the shelf break (Hales et al., 2005b; van Geen et al., 2000; Feely et al., 2008). Hence, this water transitions from a near shore regional source to an offshore regional sink for atmospheric CO<sub>2</sub>. Processes that may be important in this transition and

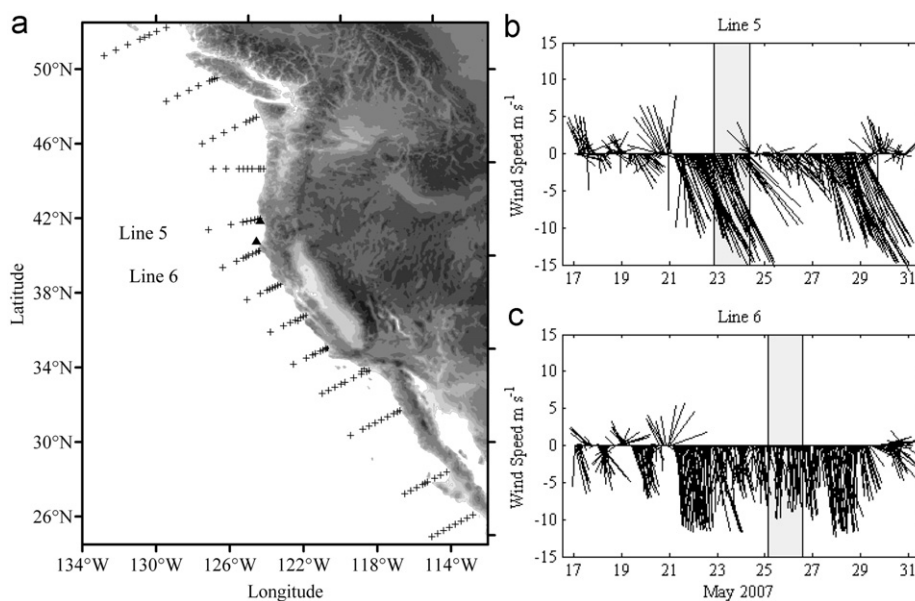
influence the carbon characteristics of upwelled water include biological productivity/respiration, calcium carbonate dissolution/precipitation, and air–sea gas exchange. Here we use observations from an upwelling event off the coast of northern California in May, 2007, to determine the importance of each of these processes in transforming the carbon characteristics of the upwelled water during various stages of the upwelling process.

The California Current System (CCS) is an eastern boundary current (EBC) system that flows along the west coast of the U.S. and southern Canada (Hickey, 1979; Hickey and Banas, 2008). Throughout the spring and summer seasons the mean winds are directed equatorward along the coast resulting in offshore Ekman transport at the coastline (Allen et al., 1995; Huyer et al., 1979; Huyer, 1983; Lentz, 1992; Strub et al., 1987a, b). To compensate for the offshore surface flow, nutrient and carbon rich, subsurface, coastal water is upwelled onto the continental shelf. During periods of strong equatorward wind stress this subsurface water can be upwelled into the euphotic zone (upwelling events) providing the nutrients necessary to stimulate phytoplankton blooms (Maclsaac et al., 1985).

The primary productivity that is stimulated by seasonal upwelling in EBC systems is what makes these regions some of the most productive areas in the world's ocean, accounting for

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**Fig. 1.** (a) The NACP West Coast Cruise study region with plus signs representing station locations. The two triangles near shore, by Lines 5 and 6, indicate the locations of the National Data Buoy Center (NDBC) (<http://www.ndbc.noaa.gov/>) buoys where wind data were collected. (b) 10 m wind speeds from NDBC buoy #46027 near Line 5 and (c) from NDBC buoy #46022 near Line 6 are shown. Negative (positive) wind speeds indicate upwelling (downwelling) favorable conditions. The shaded region in each figure indicates when the line was occupied during the cruise.

~10–15% of the global ocean new production (Chavez and Toggweiler, 1995). In most EBC systems, the nutrients that fuel primary productivity during upwelling events are generally the byproducts of organic matter decomposition. In the CCS, ~1/3 of the upwelled nutrients are preformed; these are the nutrients that were present when the water was last at the sea surface (Hales et al., 2005b). These preformed nutrients are what allow phytoplankton to reduce sea surface  $p\text{CO}_2$  to levels significantly below atmospheric concentrations in the CCS (Hales et al., 2005b; van Geen et al., 2000).

In addition to nutrients, primary producers are sensitive to the carbon characteristics of upwelled waters, yet few studies in the CCS have included rigorous carbonate chemistry analysis (Hales et al., 2005b; Ianson et al., 2003). In the May and the June of 2007 the North American Carbon Program West Coast Cruise was conducted to document the carbon and nutrient characteristics of coastal water along the continental shelf of western North America during the upwelling season. Thirteen cross-shelf transects between Queen Charlotte Sound, Canada, and San Gregorio Baja California Sur, Mexico, were sampled for water mass characteristics (Fig. 1a). During the cruise an upwelling event off the coast of northern California brought waters undersaturated with respect to aragonite to the sea surface (Feely et al., 2008). Here we evaluate how biological productivity/respiration, calcium carbonate dissolution/precipitation, and gas exchange were influencing the carbon characteristics of these waters as they were transported toward shore, upwelling into the mixed layer, and advected offshore over time.

## 2. Measurements and methods

At each station, conductivity, temperature, and pressure measurements were made over the full water column and discrete water samples were collected from 12-l Niskin-type bottles for dissolved inorganic carbon (DIC), Total Alkalinity (TA), oxygen, and nutrient analysis. DIC was analyzed by gas extraction and coulometry using a modified Single-Operator Multi-Metabolic Analyzer (SOMMA) system with a precision of  $\pm 1.5 \mu\text{mol kg}^{-1}$

(Johnson et al., 1985, 1987, 1993; Johnson, 1992; Wilke et al., 1993). Seawater TA was measured using the method of acidimetric titration described by Dickson et al. (2003), at a precision of  $\pm 2 \mu\text{mol kg}^{-1}$ . Oxygen concentrations were determined with a precision of  $\pm 0.2 \mu\text{mol kg}^{-1}$  using the whole-bottle titration technique of Carpenter (1965) with modifications by Culbertson and Knapp (1991). Titrations were completed using an MBARI-designed automated oxygen titrator and the MBARI oxygen program written by Gernot Friedrich (MBARI). Nutrient samples were analyzed with a continuous flow analyzer using the WOCE hydrographic program protocols (Gordon et al., 1992) at a precision of  $0.2 \mu\text{mol kg}^{-1}$  for nitrate,  $0.03 \mu\text{mol kg}^{-1}$  for phosphate, and  $0.2 \mu\text{mol kg}^{-1}$  for silicic acid.

## 3. Calculations

### 3.1. Mixed layer depth criterion

To define a mixed layer depth criterion that could be used at each station in the northern California region various ranges in potential density difference ( $\Delta\sigma_\theta$ ) between the sea surface and the underlying water were evaluated. For each  $\Delta\sigma_\theta$  criterion the standard deviation of the resulting mixed layer depths was compared to the mean mixed layer depth. Any  $\Delta\sigma_\theta$  criterion resulting in a standard deviation value that was less than the mean mixed layer depth was considered appropriate (Lentz, 1992). From the range of appropriate  $\Delta\sigma_\theta$  criteria that were determined, 0.035 had the smallest standard deviation and is used here.

### 3.2. Carbon transformations during water transit

In order to isolate changes in DIC mediated from biological processes, on each transect, we determined the change in concentration of non-conservative properties ( $\text{NO}_3^-$  and TA) along density surfaces relative to an offshore source or reference station (e.g.  $\Delta\text{NO}_3^- = \text{NO}_3^-_{\text{station}} - \text{NO}_3^-_{\text{source}}$ ). Before making these calculations, the DIC,  $\text{NO}_3^-$ , and TA data were salinity normalized to the

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