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$\Delta^{14}\text{C}$ AND $\delta^{13}\text{C}$ OF SEAWATER DIC AS TRACERS OF COASTAL UPWELLING: A 5-YEAR TIME SERIES FROM SOUTHERN CALIFORNIA

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ABSTRACT. Marine radiocarbon (^{14}C) is a widely used tracer of past ocean circulation, but very few high-resolution records have been obtained. Here, we report a time series of carbon isotope abundances of dissolved inorganic carbon (DIC) in surface seawater collected from the Newport Beach pier in Orange County, within the Southern California Bight, from 2005 to 2010. Surface seawater was collected bimonthly and analyzed for $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and salinity. Results from May 2005 to November 2010 show no long-term changes in $\delta^{13}\text{C}$ DIC values and no consistent variability that can be attributed to upwelling. $\Delta^{14}\text{C}$ DIC values have lowered from ~34‰ to about ~16‰, an 18‰ decrease from the beginning of this project in 2005, and is consistent with the overall ^{14}C depletion from the atmospheric thermonuclear bomb pulse at the end of the 1950s. $\Delta^{14}\text{C}$ DIC values, paired with salinity, do appear to be suitable indicators of upwelling strength with periods of upwelling characterized by more saline and lower DIC $\Delta^{14}\text{C}$ values. However, a similar signal was not observed during the strong upwelling event of 2010. These results were obtained in the Southern California Bight where upwelling is fairly weak and there is a complex oceanographic circulation in comparison with the remaining western USA coastline. It is therefore likely that the link between DIC $\Delta^{14}\text{C}$, salinity, and upwelling would be even stronger at other sites. These data represent the longest time series of $\Delta^{14}\text{C}$ data from a coastal Southern California site performed to date.

INTRODUCTION

Along the west coast of North America, an eastern boundary current (known as the California Current) flows south from Vancouver Island to Baja California, resulting in cool sea surface temperatures (SSTs) (Hickey 1979). Further cooling is caused by seasonal offshore winds that force seawater away from the coast, resulting in upwelling of cold, deep waters (Lynn and Simpson 1987; Legaard and Thomas 2006). This strong, seasonal upwelling is characteristic of the entire western coastline of North America and affects primary productivity by supplying cold, nutrient-rich water to the ocean surface close to the coastline. The timing and intensity of seasonal upwelling varies on decadal (Chhak and Di Lorenzo 2007) and shorter timescales (Legaard and Thomas 2007), and substantial changes (such as timing, intensity, or duration of upwelling) can interfere with the entire marine ecosystem in this region (Brodeur et al. 2006; Bograd et al. 2009). Recently, strong El Niño events have led to significantly decreased upwelling, decreased wind-driven mixing, and a weakening of the California Current (Lynn et al. 1995; Bograd and Lynn 2001), in conjunction with increased rainfall in California and significant negative impacts on marine ecosystems (Chavez et al. 2002). Our understanding of the relationships between California Current strength, upwelling, rainfall, and ENSO, and how these might change due to anthropogenic influences, is currently limited by the short duration of instrumental records. It would therefore be of significant interest if a proxy of seasonal upwelling intensity could be identified that would allow the extension of upwelling records into the past. For this to be achieved, we have investigated whether aspects of seawater geochemistry allow the quantitative reconstruction of seasonal upwelling intensity along the western coastline of North America.

Upwelling seawater is colder and more saline than surface seawater, but these properties do not unambiguously allow the reconstruction of upwelling intensity because other controls exist for these variables at the sea surface, such as evaporation-precipitation balance. In addition, upwelled seawater contains dissolved inorganic carbon (DIC) with isotopic signals different from surface seawater.

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The $\delta^{13}\text{C}$ value of deep ocean water DIC is expected to be lower than that of surface ocean water DIC due to the oxidation of ^{13}C -depleted organic matter sinking from the surface. Increased upwelling should therefore lower the $\delta^{13}\text{C}$ of surface water DIC. Changes in upwelling intensity can also be tracked by the magnitude of the ^{14}C depletion in surface water DIC with respect to atmospheric $^{14}\text{CO}_2$ (e.g. the difference between pre-bomb $\Delta^{14}\text{C}$ of surface waters and that of subsurface waters, which are older due to isolation from the atmosphere and radiodecay of ^{14}C). In the past, interannual DIC $\Delta^{14}\text{C}$ variability has been used to detect upwelling in a coastal region in the northeast Pacific (Robinson 1981). The work of Robinson (1981) in Half Moon Bay shows large seasonal changes ($\sim 100\%$) that were attributed to the enhanced upwelling in this coastal region and to the larger ^{14}C gradient between atmosphere and surface ocean waters during the period of sample collection (1978–1979).

Recently, Hinger et al. (2010) demonstrated that DIC $\Delta^{14}\text{C}$ in seawater can be correlated with the onset and duration of recent coastal upwelling at a site in the Southern California Bight (SCB), when combined with other proxies, such as salinity and the Bakun upwelling index. This index is an estimate of the volume of seawater upwelled along the coast due to geostrophic winds and is constructed using surface atmospheric pressure fields (Bakun 1973). However, Hinger's record extended across only 2 periods of upwelling between 2005–2007. To examine whether the relationships between salinity, DIC $\Delta^{14}\text{C}$, and upwelling are consistent in the longer term, we continued to study the salinity, temperature, and carbon isotope abundances of DIC in surface seawater collected biweekly at a coastal site off Southern California within the Southern California Bight (SCB) from 2008–2010. Here, we show the complete time series of carbon isotope abundances of DIC from 2005–2010, including data from Hinger et al. (2010). This represents a unique time series of coastal data against which new proxies can be calibrated, so that we can understand the influence of upwelling on coastal seawater geochemistry over longer timescales.

SAMPLING LOCATION AND PROCESSING

Surface seawater was sampled biweekly within the Southern California Bight (SCB) ($33^{\circ}36'21''\text{N}$, $117^{\circ}55'52''\text{W}$) from the Newport Beach pier, which is located about 2 miles south of the mouth of the Santa Ana River, Orange County, California (Figure 1). Sample location and long-term sample collection started in 2005 and is continuous except for a short interval from April to October 2009. The DIC CO_2 extraction procedure, graphite sample production to undergo accelerator mass spectrometry (AMS) measurements, and high-precision $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements, background corrections, and error calculation methods are provided in detail in Hinger et al. (2010). Briefly, seawater collected for DIC $\Delta^{14}\text{C}$ analysis was acidified to produce CO_2 following an established protocol (McNichol et al. 1994). The CO_2 was then converted to graphite by the hydrogen reduction method (Santos et al. 2004) and analyzed for ^{14}C using AMS techniques at the Keck Carbon Cycle Accelerator Mass Spectrometer Facility, UC Irvine, USA (Santos et al. 2007). DIC $\Delta^{14}\text{C}$ background corrections were determined by measuring the mass and the ^{14}C -AMS signature of several procedural blank samples produced along with the DIC seawater targets. Small aliquots of CO_2 were taken to undergo stable isotope ratio mass spectrometer (IRMS) measurements, using a Delta Plus CFIRMS interfaced with a Gasbench II tray. Water temperature was taken *in situ* during seawater collection. Non-poisoned seawater samples were measured for salinity at the Scripps Oceanographic Institution Data Facility. Salinity was identified in Hinger et al. (2010) as a key characteristic of seawater, which can aid in the identification of upwelling events in the SCB. However, salinity is also useful for screening samples that are influenced by freshwater from the Santa Ana River after rare rain events, which causes lower DIC $\delta^{13}\text{C}$ and DIC $\Delta^{14}\text{C}$ (Hinger et al. 2010).

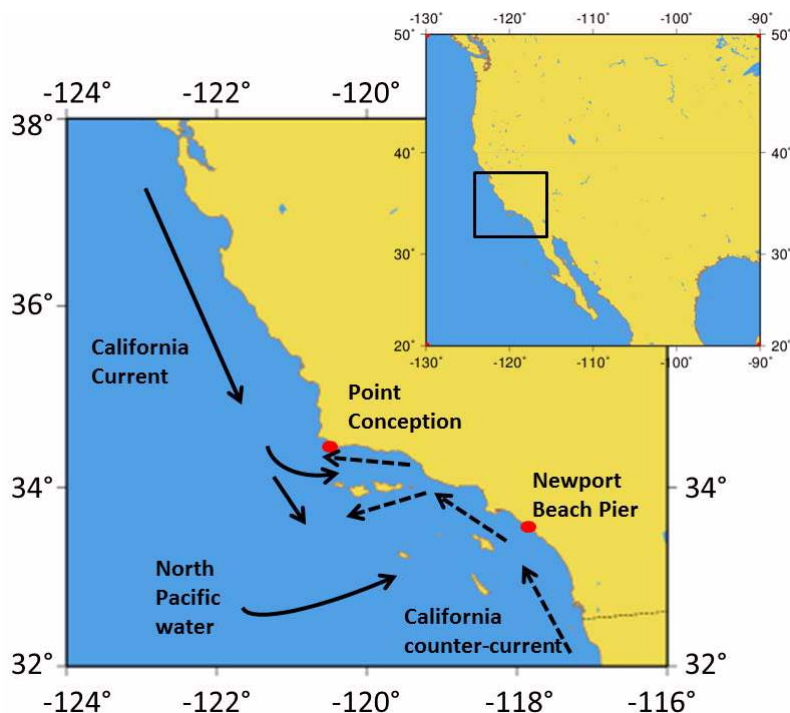


Figure 1 Oceanography of the Southern California Bight with the Newport Beach sampling site and Point Conception (an oceanographic discontinuity) labeled.

RESULTS AND DISCUSSION

Figure 2 shows the complete Newport Beach pier time series of SST, salinity, DIC $\delta^{13}\text{C}$, and DIC $\Delta^{14}\text{C}$ from 2005 to November 2010, combined with data from Hinger et al. (2010). The data set from 2008–2010 is presented in Table 1. The standard deviations of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements for the period 2005 to early 2009 are $\pm 2.0\text{‰}$ and $\pm 0.2\text{‰}$ ($\pm 1 \sigma$), respectively (based on a pooled standard deviation calculation of the sets of replicated measurements; McNaught and Wilkinson 1997). These errors are greater than the individual measurement error (shown in Table 1). Consequently, they reflect the procedural error introduced during the processing of DIC for isotope analysis (Hinger et al. 2010). For the period June 2009 through 2010, a similar error calculation was based on 11 $\Delta^{14}\text{C}$ and 8 $\delta^{13}\text{C}$ replicates yielding standard deviations of $\pm 2.23\text{‰}$ and $\pm 0.4\text{‰}$ ($\pm 1 \sigma$), respectively. We were concerned about the increased pooled standard deviation calculation associated with the $\delta^{13}\text{C}$ replicates from this period. After a careful screening to identify and exclude any analytical instrument problems, no points from that time period could be rejected (Figure 2a). Also shown in Figure 2 (c,d) are salinity measurements and fortnightly averages of daily water temperature made at 3 m depth from Newport Beach pier by the Newport City Lifeguards (data available from http://shorestation.ucsd.edu/active/index_active.html#newportstation). To obtain a record of upwelling to allow comparison with seawater geochemistry, the Bakun upwelling index (at 33°N and 119°W) is also plotted in Figure 2e (data available for download from the Pacific Fisheries Environmental Laboratory at <http://www.pfel.noaa.gov/products/PFEL/modeled/indices/upwelling/NA>).

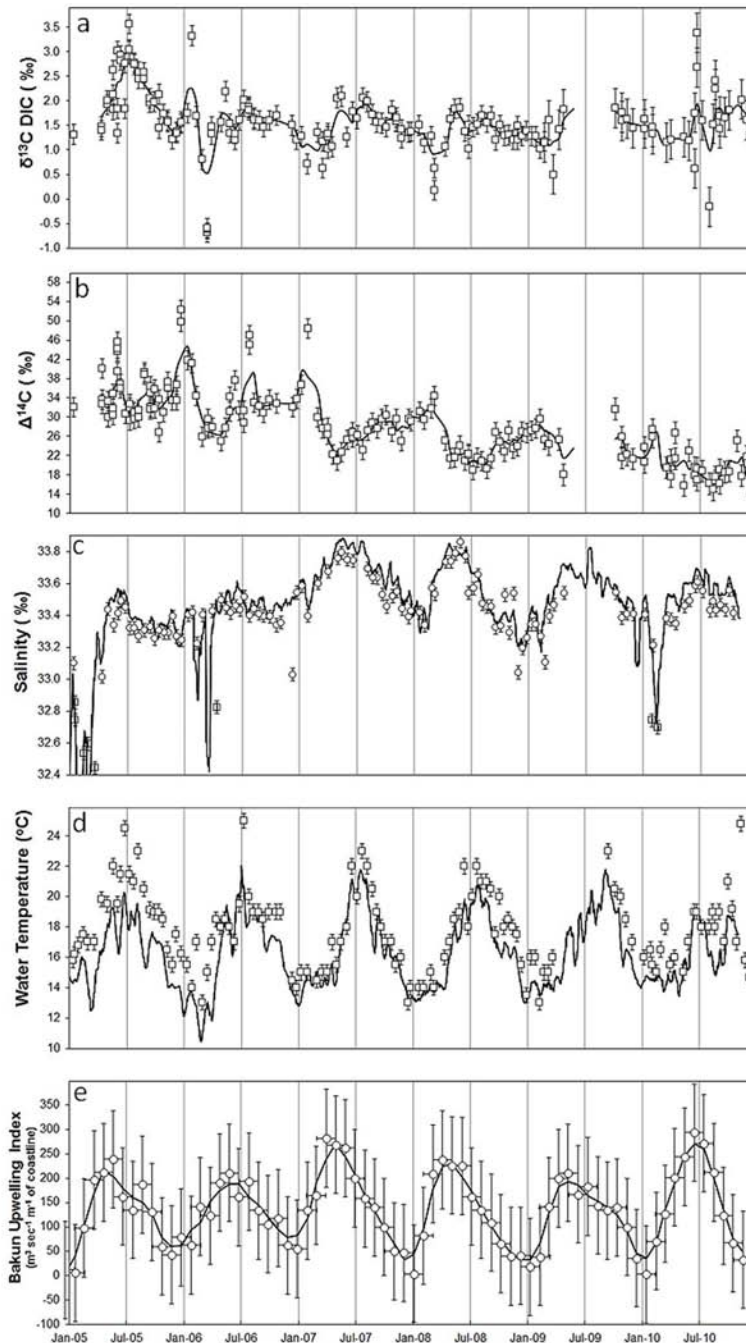


Figure 2 Results: (a) DIC $\delta^{13}\text{C}$, (b) DIC $\Delta^{14}\text{C}$, (c) salinity, (d) sea surface temperature (SST), and (e) Bakun upwelling index. Solid lines in parts (a), (b), and (e) are 3-point moving averages. Solid lines in parts c) and d) represent biweekly average salinity and temperature measured at 3 m depth from Newport Beach pier. Salinity values that are <33.00 psu (shown by open square symbols) are likely a result of mixed water masses due to high precipitation and runoff from the Santa Ana River. Those results are represented here to illustrate those rare rain events. The DIC $\delta^{13}\text{C}$ and DIC $\Delta^{14}\text{C}$ associated with those lower salinity values are not shown or discussed. The standard deviation of $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ measurements shown here is based on a pooled standard deviation calculation of the sets of replicated measurements (McNaught and Wilkinson 1997), as described in text.

Table 1 Complete temperature, salinity, DIC $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ values from surface seawater samples collected from sites off the coast of Southern California from 2008–2010. The ^{14}C results are reported as age-corrected $\Delta^{14}\text{C}$ (‰), as defined by Stuiver and Polach (1977). The $\Delta^{14}\text{C}$ uncertainties shown here are the statistical propagated errors from individual measurements.

Sample ID (dates in month/day/year)	Measured sea surface temperature (°C)	Measured salinity (‰)	Lab nr (UCIAMS-)	^{14}C (‰)	±	$\delta^{13}\text{C}$ (‰)
2/15/2008	14.0	33.34	61025	29.5	1.8	1.1
3/9/2008	15.0	33.57	85157	31.8	1.3	1.3
3/18/2008	14.0	33.53	61026	34.3	1.9	0.6
4/22/2008	16.0	33.73	61027	25.1	1.8	1.1
5/7/2008	17.0	33.74	61028	21.4	1.8	1.6
5/21/2008	18.5	33.79	61029	21.6	1.7	1.8
6/6/2008	19.0	33.86	61030	24.0	1.8	1.9
6/23/2008	22.0	33.77	61031	21.0	1.8	1.4
7/3/2008	18.0	33.54	61032	22.1	1.9	1.0
			85154	22.3	1.5	1.5
7/18/2008	20.0	33.57	61033	19.0	2.0	1.5
8/1/2008	22.0	33.65	61034	21.6	1.9	1.5
8/14/2008	21.0	33.47	61035	20.8	1.8	1.7
8/29/2008	21.0	33.45	61036	19.3	1.8	1.6
9/12/2008	20.5	33.46	61037	21.5	2.0	1.7
9/26/2008	17.5	33.32	61038	26.7	1.8	1.2
10/10/2008	20.0	33.33	61039	24.9	1.9	1.5
10/24/2008	18.0	33.53	61040	22.8	1.9	1.3
11/7/2008	18.5	33.29	61041	27.2	2.1	1.3
11/21/2008	18.0	33.54	61042	23.4	1.9	1.2
12/5/2008	17.5	33.04	61043	23.9	1.9	1.5
12/19/2008	15.5	33.19	61044	27.0	1.7	1.3
1/2/2009	13.5	33.26	61045	26.7	2.0	1.4
1/16/2009	16.0	33.34	61046	27.1	1.9	1.3
1/30/2009	16.0	33.34	61047	27.5	1.9	1.3
2/13/2009	13.0	33.27	61048	29.6	2.0	1.0
2/27/2009	15.0	33.11	61049	25.2	1.9	1.2
3/13/2009	15.0	33.39	85155	24.3	1.6	1.6
4/14/2009			85153	25.3	1.3	1.4
4/28/2009		33.54	92366	18.0	1.5	1.8
10/7/2009	20.5	33.54	92367	31.7	1.6	1.9
10/27/2009	20.0	33.38	92368	25.8	1.6	1.6
			85144	21.5	1.3	1.8
11/12/2009	18.5	33.41	92369	22.2	1.6	1.6
12/1/2009	17.0	33.41	92370	21.3	1.6	1.4
1/7/2010	16.0	33.40	85145	23.7	1.3	1.4
			92371	20.6	1.8	1.6
1/29/2010			92372	25.8	1.6	1.2
2/2/2010	15.5	33.21	92373	27.4	1.5	1.5
			85143	25.9	1.3	1.3
2/16/2010	15.0	32.70	92374	32.9	1.5	1.7
3/2/2010	16.5	31.90	92375	24.4	1.5	0.8
			85147	21.1	1.3	
3/16/2010	18.0	33.38	92376	19.5	1.5	1.2

Table 1 Complete temperature, salinity, DIC $\Delta^{14}\text{C}$, and $\delta^{13}\text{C}$ values from surface seawater samples collected from sites off the coast of Southern California from 2008–2010. The ^{14}C results are reported as age-corrected $\Delta^{14}\text{C}$ (‰), as defined by Stuiver and Polach (1977). The $\Delta^{14}\text{C}$ uncertainties shown here are the statistical propagated errors from individual measurements. (*Continued*)

Sample ID (dates in month/day/year)	Measured sea surface temperature (°C)	Measured salinity (‰)	Lab nr (UCIAMS-)	^{14}C (‰)	\pm	$\delta^{13}\text{C}$ (‰)
3/30/2010	15.5	33.37	92377	17.6	1.6	1.2
			85146	21.1	1.3	
4/13/2010	16.0	33.30	85148	26.7	1.3	
			85158	21.4	1.3	
5/11/2010	15.0	33.46	92378	15.7	1.7	1.3
5/27/2010	17.0	33.49	92379	23.0	1.7	1.2
6/15/2010	19.0	33.58	92380	17.9	1.7	1.8
			85149	19.5	1.3	0.6
6/22/2010	19.0	33.61	92381	16.9	1.5	3.4
			85151	19.3	1.3	2.7
7/8/2010	18.0	33.55	92382	18.7	1.7	1.6
7/30/2010	18.0	33.43	92383	16.1	1.5	-0.2
8/10/2010	19.0	33.49	92384	14.9	1.6	1.5
8/18/2010	18.0	33.43	92385	16.8	1.8	2.2
			92386	17.5	1.5	2.4
9/1/2010	19.0	33.47	92387	16.2	1.7	1.7
			85159	19.1	1.3	1.4
9/17/2010	17.0	33.43	92388	18.5	1.7	1.7
9/29/2010	21.0	33.56	92389	18.7	1.6	1.8
10/26/2010	17.0		92390	25.1	1.7	
11/9/2010	24.8		92391	17.8	1.9	2.0
11/23/2010	15.8		92392	21.8	1.7	1.6
12/7/2010	14.7		92393	13.9	1.7	1.5

At Newport Beach pier, weekly average water temperatures from 2005–2010 measured at 3 m depth from an automated shore station ranged from 11 to 22 °C. Our measurements of sea surface temperature taken at the time of water sampling correspond well, but are often slightly higher than the weekly average record because they are individual measurements and because they were made in surface seawater during the day. SSTs during spring and summer of 2010 were unusually low (Figure 2d). These unusually low temperatures can be seen in many automated shore station SST records from the Southern California region in 2010 and are associated with a strengthened North Pacific High that intensified the flow of cold air and water from the north (Bjorkstedt et al. 2010).

Over the period 2005–2010, there is interannual variability in seawater salinity but no clear seasonal trend. Periods of higher salinity (~33.8 psu compared to an average of ~33.5 psu) can be seen in the spring of 2007 and 2008 at the same time as peaks in upwelling intensity (Figure 2e). The seawater samples associated with the DIC $\delta^{13}\text{C}$ and DIC $\Delta^{14}\text{C}$ shown in Figure 2(a,b) are screened for salinity, and samples of 33 psu or less are discarded because the geochemistry of these samples are likely to be influenced by freshwater from the nearby Santa Ana River (Hinger et al. 2010).

The $\delta^{13}\text{C}$ values of DIC in upwelled water is normally lower than that in surface water because of the presence of ^{13}C -depleted DIC from the remineralization of organic matter. Thus, $\delta^{13}\text{C}$ of DIC is often used as a tracer of upwelling strength (Sheu et al. 1996). However, our $\delta^{13}\text{C}$ values show a

complex pattern of variability ranging from -0.8 to 3.5‰ with no clear decrease during upwelling periods (Figure 2a) as might have been expected. This is a somewhat surprising result, and may be because the signal at this site is complicated by aspects of ocean circulation in this region, e.g. standing eddies (DiGiacomo and Holt 2001). A clearer signal may be observable at sites with stronger upwelling and simpler circulation patterns north of Point Conception (Figure 1) or along Baja California. It is interesting to note that the 2 periods of largest $\delta^{13}\text{C}$ variability were in the spring of 2006 and 2010, both following unusually wet periods in Southern California. Those results are not due to input of river water that usually contains low $\delta^{13}\text{C}$ of DIC values (Hinger et al. 2010). Note that our DIC $\delta^{13}\text{C}$ and DIC $\Delta^{14}\text{C}$ associated with lower salinity values in Figure 2c are not shown or discussed in Figure 2a,b, and therefore cannot be evoked to explain the variability observed. We suspect that the Southern California Bight eddies, generally smaller in size (DiGiacomo and Holt 2001), had increased during these wet periods, complicating even further the circulation pattern in this region.

DIC $\Delta^{14}\text{C}$ values range from 14‰ and 52‰ between 2005 and 2010. A clear decrease of about 16‰ is seen from a mean of $\sim 34\text{‰}$ in 2005 to the current average value of 18‰ in 2010. This decrease is consistent with the overall ^{14}C depletion from the atmospheric thermonuclear bomb pulse at the end of 1950s. Superimposed on this overall trend are interannual changes due to upwelling and mixing of surface with deeper waters in the region. Shifts of $8\text{--}14\text{‰}$ (indicating the presence of older seawater) occurred during the springs of 2006, 2007, and 2008. Occasional high $\Delta^{14}\text{C}$ values occurred periodically (every 6–7 months) in the early part of the record but are not observed in subsequent years. This may be due to the presence of open water eddies at our coastal site (Massiello et al. 1998; Hinger et al. 2010).

UPWELLING IN THE SCB FROM 2005–2010; EFFECTS ON SEAWATER GEOCHEMISTRY

The California Current region is extensively monitored annually due to its importance to marine primary productivity. Both chemical and physical parameters obtained during cruises to the north and west of the Newport Beach pier site, along with satellite measurements, showed that upwelling occurred each year between 2005 and 2010, although with significant interannual variability (McClatchie et al. 2009; Bjorkstedt et al. 2010 and references therein). Over this period, the Newport Beach pier time series of seawater geochemistry also shows considerable interannual variability. Hinger et al. (2010) reported that coastal seawater during periods of increased upwelling, such as that of May 2007, is characterized by increased salinity paired with decreased DIC $\Delta^{14}\text{C}$. In the extended record (Figure 2), a second period of upwelling during April/May 2008 is clearly visible, with high salinity and low DIC ^{14}C , coinciding with a peak in Bakun index.

Relatively weak upwelling during 2006, associated with a weak El Niño event, does not appear to result in significantly detectable changes (2σ uncertainty, $\pm 4\text{‰}$) in coastal seawater geochemistry at the Newport Beach site. Surprisingly, there is also no obvious upwelling signal detected in the seawater time series during the strong upwelling that resumed in 2010 (Bjorkstedt et al. 2010). As atmospheric $\Delta^{14}\text{C}$ values decrease, the $\Delta^{14}\text{C}$ difference between surface and deeper waters becomes less significant due to downward mixing of the bomb ^{14}C and the amplitude of changes due to upwelling decreases (Jenkins et al. 2010). However, even at this site, where upwelling is relatively weak and there are complex oceanographic conditions, an upwelling signal is observable in coastal seawater salinity and DIC $\Delta^{14}\text{C}$. Other locations along western North America are likely to experience even stronger seasonal changes in seawater DIC geochemistry as a result of seasonal upwelling (Robinson 1981).

CONCLUSIONS

A 5-year time series of SST, salinity, DIC $\delta^{13}\text{C}$, and DIC $\Delta^{14}\text{C}$ was produced from Newport Beach pier in Southern California, representing the most complete time series of high-precision $\Delta^{14}\text{C}$ data for a coastal site in North America. Apart from allowing investigation of the influence of upwelling on seawater geochemistry, this represents an ideal data set for calibrating new and existing proxies of upwelling in the region.

The seasonal upwelling that characterizes the western coastline of North America influences seawater geochemistry at the site on a seasonal timescale with periods of high salinity and low $\Delta^{14}\text{C}$ indicating the presence of saline, older upwelled waters.

Overall $\Delta^{14}\text{C}$ values range from 14‰ to 52‰ with a constant decreasing trend due to the gradual reduction of atmospheric ^{14}C after the bomb peak. Additional variability can be attributed to periods of increased upwelling. In contrast, DIC $\delta^{13}\text{C}$ shows no clear pattern with upwelling intensity.

No clear relation between $\Delta^{14}\text{C}$ and upwelling was seen until spring 2007, when upwelling within the California Current system strengthened due to the onset of moderately strong La Niña conditions in 2007 (McClatchie et al. 2009). In 2007 and 2008, strong summer upwelling coincides with the most negative $\Delta^{14}\text{C}$ values observed during each year. However, during the strong upwelling period of 2010 no clear shift to lower $\Delta^{14}\text{C}$ values occurred for reasons not currently understood.

Even though this region has complex oceanographic circulation patterns and lower upwelling intensity than areas further north, a seasonal upwelling signal was visible in seawater geochemistry and the DIC $\Delta^{14}\text{C}$ record. When paired with salinity, the $\Delta^{14}\text{C}$ seems to indicate the strength of upwelling. We suspect that the upwelling $\Delta^{14}\text{C}$ signal may be stronger in sites outside of the South California Bight, which are more directly impacted by the California Current.

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