Reconstructing Ocean History

A Window into the Future

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PAST AND PRESENT COASTAL UPWELLING ALONG THE WESTERN AMERICAS

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ABSTRACT

Every year, increasing insolation during spring and summer sets up a broad pattern of equatorward winds along the western shores of North and South America. These winds are responsible for large-scale advection of nutrient-rich waters to the surface and, therefore, the elevated productivity of the California and Peru/Humboldt eastern boundary current systems. Because the Earth's radiation balance is involved, eastern boundary currents probably responded to past changes in summer insolation and could be sensitive to future changes in greenhouse gas concentrations. The hydrography of the nutrient-like trace element Cd and its incorporation into the geologic record provide a unique way to quantify the sensitivity of coastal upwelling to climate change, using the effect of orbital changes in insolation during the Holocene as a test case.

In California, we have used the Cd content of carefully cleaned shells of the benthic foraminifer *Elphidiella hannai* to infer changes in estuarine dissolved Cd concentrations that are directly linked to coastal upwelling. Shells of *E. hannai* have been recovered from sediment sections that span much of the Holocene from several California estuaries. We report here that mean Cd/Ca ratios in shells of *E. hannai* from San Francisco Bay dated 7.5ka are considerably higher (402 ± 54 nmol/mol, n = 9) than in tests dated 900–1900 AD (274 ± 15 nmol/mol, n = 19). Based on a comparison of wind forcing with an 8-year time series of nearshore Cd, this suggests that mean wind stress during the upwelling season was about twice as high during the early Holocene than it is today. Further interpretation, however, will require a better understanding of the origin of an increase in variance of replicate Cd/Ca determinations in downcore intervals. The modern hydrography of Cd also shows that an inter-hemispheric comparison of upwelling records will be necessary to distinguish changes due to variations in solar forcing from changes due to the evolution of the El Niño/Southern Oscillation through the Holocene.

1. INTRODUCTION

Contours of the annual temperature range at the Earth's surface clearly mark the boundary of continents because seasonal temperature variations are much greater over land than over the ocean (Monin, 1975, as reproduced in Crowley and North, 1991). The contrast is a reflection of the ~60-fold lower effective heat capacity of land surfaces compared to the ocean. Heating of air masses over the continents during spring and summer causes an intensification of the subtropical high-pressure systems over the major ocean basins. Equatorward winds responding to this atmospheric pressure gradient force an offshore Ekman transport of surface water off North and South America, Europe, and Africa during spring and summer (Bakun and Nelson, 1991). The resulting divergence causes coastal upwelling of cold and nutrient-rich subsurface water. The effect of upwelling on the nutrient content of nearshore waters is pronounced along the western margin of North and South America because subsurface source waters are particularly enriched (Broecker and Peng, 1982). The intimate connection between atmospheric and oceanic circulation is largely responsible for the very high biological productivity of eastern boundary currents such as the California and Peru/Humboldt systems. It is therefore important to determine how such systems will respond to changes in the radiation balance of the Earth as the concentration of greenhouse gases in the atmosphere continues to increase. Bakun (1990) argued, for instance, that coastal upwelling along major eastern boundary currents will intensify as a consequence of greenhouse warming because temperatures are likely to increase faster over land.

Coastal upwelling prevails in April August off California and Oregon, and in October February along the coast of Chile (Fig. 1). The evolution of this seasonal pattern in response to different boundary conditions is difficult to model from first principles because of the different feedbacks that come into play. One important feedback is cloud cover because it has a large effect on the surface radiation balance of both landmasses and the ocean. Because modeling of feedbacks is difficult, it is important to test model predictions of large-scale wind patterns under different boundary conditions. The geologic record provides one of the few ways available to do this. The past 9 kyr of the Holocene provide an interesting test-case because precession of the equinoxes has gradually decreased northern hemisphere insolation by 35 W/m^2 (i.e., ~8%) at mid-latitudes and increased southern hemisphere January insolation by a comparable amount (Kutzbach and Guetter, 1986). This is a large perturbation considering that a 1% change in the solar constant or a doubling of atmospheric CO_2 is equivalent to about a 4 W/m^2 change in radiation (Crowley and North, 1991). Other boundary conditions such as ice volume, dust loading, or atmospheric CO_2 did not change appreciably during the Holocene. A simple argument based on the heating contrast between land and sea would suggest that coastal upwelling decreased during the Holocene along the California Current, while the intensity of upwelling increased in the Peru/Humboldt system over the same period. The pattern is confirmed by a series of modeling results, some of which were most recently presented by Kutzbach *et al.* (1998). The NCAR Climate Community Model version 1 (CCM1) predicts that May September wind stress at 37.8°N off San Francisco was 40% higher than today at 6 ka when summer insolation was 6% higher than today (Fig. 2). Conversely, the model predicts that November March wind stress off Valparaiso is nearly 50% higher today than it was earlier during Holocene. Unlike its predecessor CCM0, CCM1 includes interactive components such as soil moisture, snow hydrology, sea-ice, and mixed-layer ocean temperature and runs for a full seasonal cycle of insolation. It is worth noting that the prediction by the same model that maximum

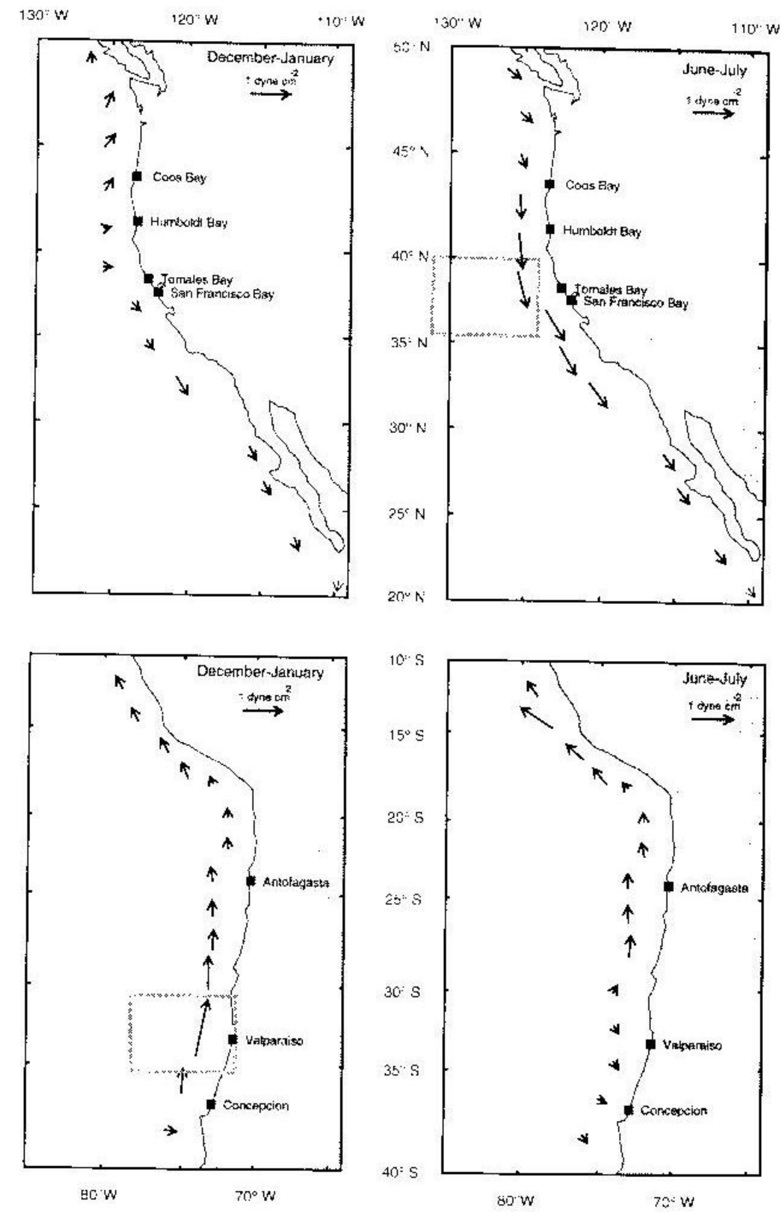

Figure 1. Mean seasonal wind stress along the western Americas based on long-term ship observations. Redrawn from Bakun and Nelson (1991). CCM1 grid boxes for predictions shown in Fig. 2 are indicated. Locations where either surfzone time series or sediment material have been collected to reconstruct past upwelling are also shown.

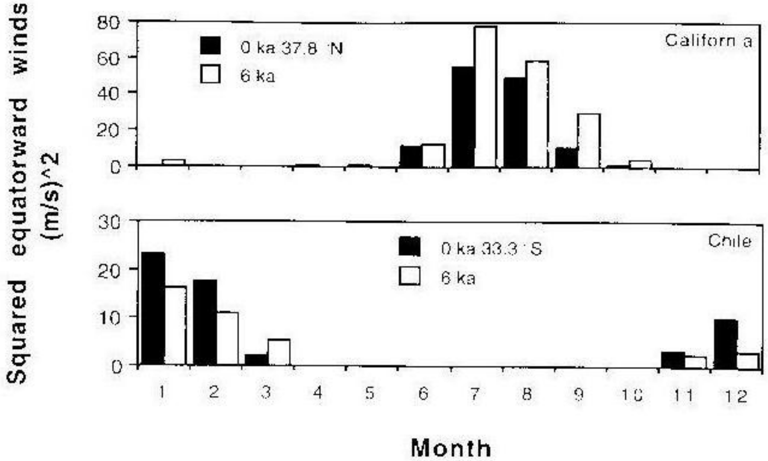

Figure 2. Model calculation of upwelling-favorable winds off California and Chile at 0 and 6 ka. Data from CCM1 described by Kutzbach *et al.* (1998). For an empirical drag coefficient of 0.0013 and a density air of 0.00122 g/cm^3 (Bakun and Nelson, 1991), the maximum value of squared wind scales of 80 and 20 m^2/s^2 in the northern and southern hemispheres, respectively, are equivalent to wind stress levels of 1.27 and 0.31 dyne/cm^2.

wind stress off California is considerably higher than along the Chilean coast today is not supported by the observations (Fig. 1). This discrepancy may, however, be partly due to the relatively coarse resolution of 4° latitude by 7.5° longitude of CCM1.

Changes in nearshore water composition coupled to coastal upwelling provide the opportunity to reconstruct past changes in wind patterns in response to changes in insolation during the Holocene. One requirement for monitoring coastal upwelling on the basis of coastal water chemistry is that the composition of source waters be markedly different from that of surface waters during non-upwelling conditions. This is certainly the case along the western Americas where the combination of reduced ventilation and elevated-productivity sets a steep vertical gradient in concentrations of nutrients and the nutrient-like trace metal Cd. Two profiles analyzed by Bruland (1980) off the coast of California show an order of magnitude increase in Cd concentrations in the upper 500 m of the water column (Fig. 3). Regular monitoring of nearshore water composition off California and Oregon has shown that dissolved Cd concentrations increase up to five-fold during the upwelling season (van Geen *et al.*, 1992; van Geen and Luoma, 1993; van Geen and Husby, 1996). From a paleoceanographic perspective, the geochemistry of Cd has an additional important characteristic, i.e. the substitution of Cd for Ca in the lattice of biogenic carbonate in proportion to dissolved Cd in ambient seawater. This was first demonstrated by Boyle (1981, 1988) for foraminifera and required devising a cleaning procedure that effectively removes potentially contaminating material such as organic matter and Fe/Mn oxides. More recently, van Geen *et al.* (1992) demonstrated that the Cd/Ca ratio of the benthic foraminifer *Elphidiella hannai* living in shallow coastal waters and US west coast estuaries also reflects the average Cd content of overlying water.

In this paper, we present new dissolved Cd data demonstrating that the expression of coastal upwelling is particularly pronounced in a nearshore region that extends only a few kilometers offshore from the surfzone. We augment a previously published set of surfzone transects along the coasts of California, Oregon, and Washington with new data

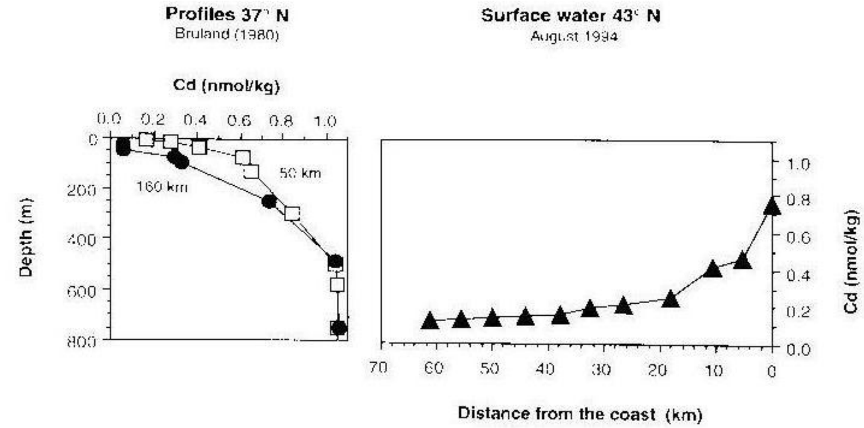

Figure 3. Cd distribution in the water column off California and Oregon. Left panel shows Cd profiles offshore of California reported by Bruland (1980). Right panel shows surface water Cd concentrations for a transect perpendicular to the Oregon coast at 43.2°N collected August 24–September 5, 1994. Sample at 0 km was collected from the surfzone at the same latitude after the cruise on September 5, 1994.

confirming that the nearshore chemical expression of coastal upwelling follows a broad, recurrent, pattern that is consistent with large-scale forcing rather than local processes. We extend a time series of surfzone Cd outside San Francisco Bay to the period 1991–1998 to demonstrate that interannual variability of the seasonal Cd cycle at this location is modulated by processes related to the El Niño/Southern Oscillation (ENSO). We proceed by re-examining a previously published Cd/Ca calibration for *E. hannai* (van Geen *et al.*, 1992) in light of updated time series of dissolved Cd and a consideration of the life cycle of shallow-water species. We then briefly discuss a previously published foraminiferal Cd/Ca record from San Francisco Bay that spans the past 1,100 years and includes a response to anthropogenic inputs over the past several decades (van Geen and Luoma, 1999a). We provide a preliminary interpretation of a limited set of data for shells of *E. hannai* formed in San Francisco Bay 7.5 kyr ago that contain significantly higher Cd levels than more recent pre-industrial shells. We conclude by pointing out that separating the importance of changes in insolation vs. ENSO on the composition of nearshore water along the western Americas will require an interhemispheric comparison of Holocene trends in upwelling.

2. METHODS

2.1. Surfzone and Surface Water Samples

Perhaps the most surprising conclusion from our studies so far has been the demonstration that variations in dissolved Cd concentrations in the surfzone along the coasts of California and Oregon are determined primarily by large-scale wind forcing. Procedures followed to collect and process surfzone water have not changed substantially since the first time series was initiated in 1991 outside San Francisco Bay (van Geen and Luoma, 1993; van Geen *et al.*, 1992; van Geen and Husby, 1996). For surfzone collection, acid-washed polyethylene bottles are attached to a plexiglas holder at the end of a 3-m-long fiberglass pole. Salinity and nutrient samples are taken simultaneously from a separate bottle attached to the pole. A duplicate trace element sample is always taken within a few minutes at the same location. All samples are stored in the dark until filtration before the end of the day. To reduce the risk of contamination, the samples are acidified only after the bottles have been returned to our laboratory. Irreversible adsorption of Cd on the bottle walls does not appear to be a problem.

Samples collected between 1991 and 1994 were preconcentrated from 18 to 1 mL by metal-ligand adsorption onto a resin column with the automated device of van Geen and Boyle (1990), as modified by van Geen and Luoma (1993). This method has since then been modified for Cd preconcentration of a smaller sample volume (0.5 mL) on a smaller column (75 µL) placed in-line with the autosampler of a Hitachi Z8200 atomic absorption spectrophotometer. In this procedure, the autosampler is disconnected from the Hitachi instrument and the syringe pump, autosampler arm, and sample tray are moved by a programmable stepping-motor controller. A buffered sample (pH ~ 8) containing the ligand is slowly taken up through the resin column and then returned to the same cup. An acidic solution is then taken up to release the bound Cd and elute it directly into the graphite tube heated at ~150°C. After elution, Cd is quantified by atomic absorption. More recently, the in-line pre-concentration method was simplified by replacing the hydrophobic ligand-resin combination with an even smaller column (5 µL) of the 8-hydroxyquinoline resin of Landing *et al.* (1986) to reduce matrix interference (Takesue and van Geen, in preparation).

Ancillary parameters are always measured in the surfzone samples to provide a context for the Cd results. Nutrient samples are filtered through disposable syringe filters and acidified in the field. Dissolved silicate and phosphate concentrations are measured spectrophotometrically using methods described by Strickland and Parsons (1968). Salinity is measured on samples stored in glass with a standardized Guildline Autosal salinometer.

The new data presented in this paper include a transect of surface samples collected on board ship across the Oregon continental shelf in August 1994. These samples were pumped on-board from a towed device that consists of a bathythermograph towed horizontally, ~1 m below the surface and ~3 m from the side of the ship, and a Teflon-lined polyethylene tube (3/8" ID) projecting ~2 cm forward of the bathythermograph (Boyle *et al.*, 1982). The other end of this tube is directed to the shipboard laboratory and connected to an acid-cleaned plexiglas vessel placed in a Class-100 laminar flow bench. To prime the pumping device, a vacuum is created in this vessel with a rotary pump. Since the sampling vessel is located upstream of the pump, the sample cannot be contaminated by the pump. Although these samples were not filtered, they were otherwise treated and analyzed like the surfzone samples.

2.2. Wind Forcing

Wind data from two different sources are used to establish the relation between climatology and nearshore water composition. The first data set is the long-term (1854–1972) mean of wind measurements from ship reports compiled by Nelson (1977) at 1° by 1° (~100 km) resolution. Huyer (1983) used these results to compute offshore Ekman transport for 1° squares nearest to the coast. The second indicator of upwelling is an upwelling index derived from synoptic surface pressure fields. For calculation of the upwelling index, the atmospheric pressure field is interpolated on a 3° by 3° (~300 km) grid and the geostrophic wind calculated from finite difference derivatives (Bakun, 1975). The wind at the sea surface is estimated by rotating the geostrophic wind vector by 15° to the left and reducing it by 30% to approximate frictional effects. The cross-shelf Ekman transport in the surface layer M is determined from the alongshore component of the calculated wind speed $M = 1/f \cdot d_a \cdot C_d \cdot |V| \cdot V$ where f is the latitude-dependent Coriolis parameter, d_a is the density of air, C_d is a constant empirical drag coefficient, and V is the estimated wind vector of magnitude |V|. Surface pressure measurements are collected every 6 hours to provide a daily upwelling index, hereafter referred to as the daily Bakun index. Bakun indices are routinely calculated by the Pacific Fisheries Environmental Group (http://upwell.pfeg.noaa.gov/).

2.3. Foraminiferal Cd/Ca Analyses

The reconstructions of the past Cd content of nearshore water is based on the demonstration by Boyle (1981, 1988) that the amount of Cd substituted for Ca in the calcite lattice of certain benthic foraminifera (expressed as their Cd/Ca ratio) living near the sediment-water interface is proportional to the dissolved Cd content of overlying water. Cd/Ca ratios were measured for batches of 10–20 shells of *E. hannai* (~0.5 mg of calcite) that were cleaned of organic matter with hydrogen peroxide. Fe and Mn oxide coatings were removed with a reducing hydrazine solution. Reagent concentration and cleaning times have been reduced relative to the revised procedure of Boyle and Keigwin (1985/86) because tests of *E. hannai* appear to dissolve more rapidly than deep ocean benthic foraminifera. Further modifications of the procedure are described in Lynch-Stieglitz *et al.* (1996). Our reproducibility for Cd/Ca determinations obtained by measuring Cd and Ca in foram solutions by graphite-furnace and flame-atomic absorption, respectively, is on the order of ±5% for a consistency standard similar in composition to that of a solution of dissolved foraminifera.

3. RESULTS AND DISCUSSION

3.1. Modern Hydrography of Cd in the Surfzone

A cross-shelf surface transect collected during upwelling conditions in August 1994 off the coast of Oregon shows that the chemical expression of upwelling becomes stronger as the distance to the coast decreases. Previously, Bruland (1980) observed that surface Cd concentrations increase from about 0.1 nmol/kg 160 km offshore to 0.2 nmol/kg 50 km offshore. However, detailed mapping of the very nearshore region shows that the most dramatic effect of coastal upwelling is observed within the innermost 50 km. Surface water shows an increase from ~0.1 nmol/kg 60 km offshore to nearly 0.8 nmol/kg at the coast (Fig. 3). Much of this increase occurs within 15 km of the coast, and a surfzone sample collected at the same latitude a few days after the cruise shows that the highest concentrations of upwelling tracers are found in surfzone waters. Although riverine and sedimentary sources can elevate Cd concentrations in coastal waters, parallel changes in other water properties such as temperature, salinity, and nutrient concentrations across the same transect suggest a primarily advective origin for the Cd enrichment along the eastern margin of the California Curent (Table 1). A narrow shelf (~15 km) and rapid cross-shelf exchange (~2 days for 10 cm/s offshore transport) in this region probably minimize potential enrichments of Cd due to the recycling of remineralized plankton (van Geen and Luoma, 1993; van Geen *et al.*, in press, Takesue and van Geen, in preparation).

Upwelling tracer measurements in repeated transects along the California and Oregon coast collected during the downwelling (January) and upwelling (June) seasons of 1992 (van Geen and Husby, 1996), shown again in Fig. 4, are supplemented with new data

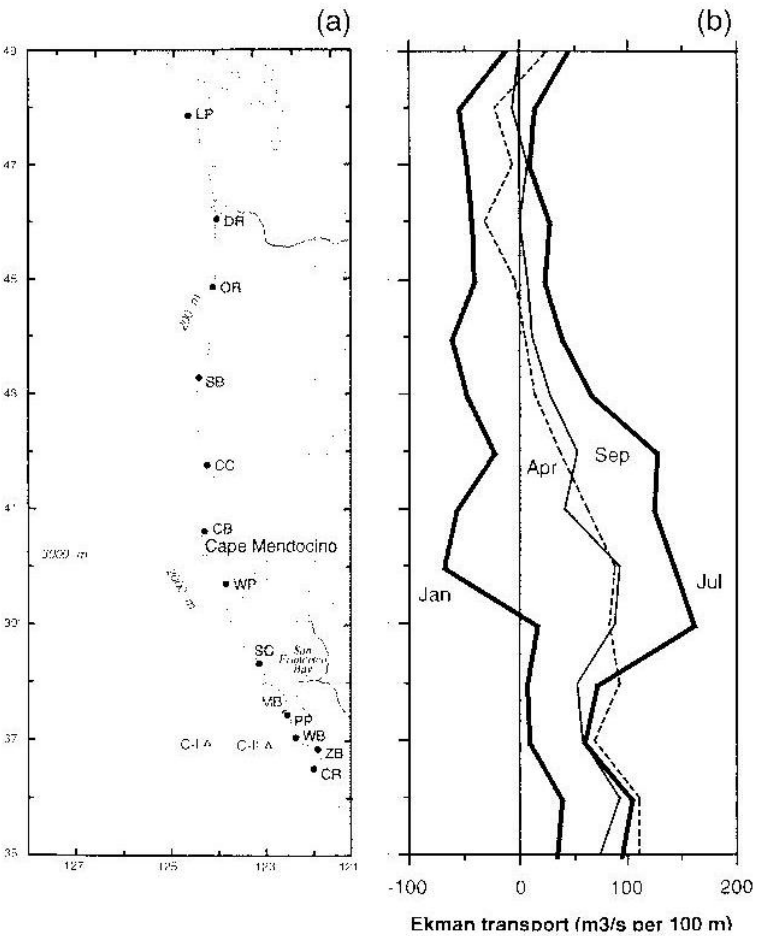

Figure 4. Surfzone Cd along nearshore transects. (a) Map of the north American west coast showing the shore-based sampling locations with the following abbreviations: LP, LaPush; DR, Del Rey Beach, OR, Otter Rock, SB: Sunset Beach; CC, Crescent City; CB, Centerville Beach; WP, Westport; SC, Schoolhouse Beach, MB, Moss Beach; PP, Pillar Point; WB, Waddell Beach; ZB, Zmudowski Beach, and CR, Carmel River Beach. Triangles show the location of Cd profiles C-I and C-II of Bruland (1980). (b) Cross-shelf Ekman transport calculated by Huyer (1983) from long-term mean winds within 100 km of the coast. Positive Ekman transport corresponds to upwelling. (c) Nearshore Cd concentrations along the transect on January 16–23 (solid circles) and June 4–18, 1994 (open circles) and March 22–26 (filled triangles) and August 22–September 8 (open triangles), 1994. Determinations for replicate samples are shown by individual symbols.

Table 1. Surface water composition off the Oregon coast of at 43.2°N in August 1994

Longitude (°W)	Distance to coast (km)	Bottom depth (m)	Temperature (°C)	Salinity	Silicate (μmol/kg)	Phosphate (μmol/kg)	Cadmium (nmol/kg)
124.380	0	0		33.525	39.0	1.930	0.758
124.448	5	40	10.00	33.092	20.4	0.780	0.457
124.515	11	65	12.90	32.843	14.6	0.690	0.423
124.613	18	105	13.70	32.465	7.6	0.360	0.246
124.720	26	200		31.992	3.6	0.100	0.209
124.797	32	370	17.16	32.001	3.2	0.100	0.188
124.868	38	370	17.74	32.006	2.8	0.110	0.156
124.948	44	880	18.42	31.978			0.148
125.023	50	1,110	18.65	31.875	3.3	0.110	0.144
125.093	55	1,450	18.40	31.885	3.4	0.060	0.131
125.167	61	1,600	18.30	31.945	3.3	0.090	0.124

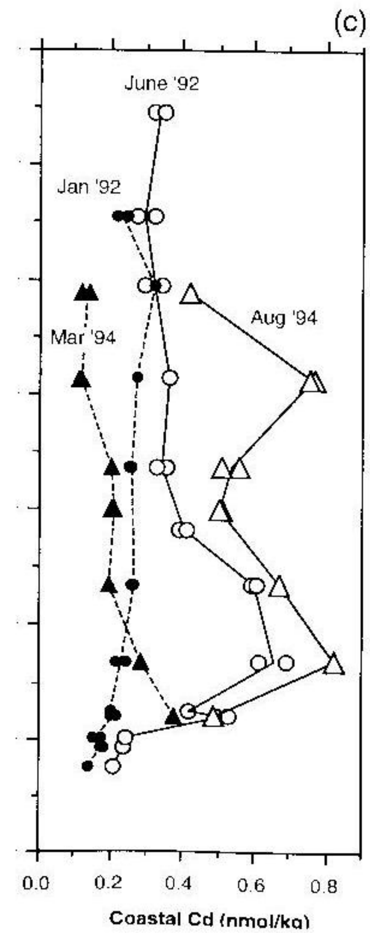

Figure 4. *Continued*

Table 2. Composition of surfzone water during 1994 transects

Location	Latitude (°N)	Salinity 3-94	Salinity 8-94	Phosphate (µmol/kg) 3-94	Phosphate (µmol/kg) 8-94	Cadmium (nmol/kg) 3-94	Cadmium (nmol/kg) 8-94
Otter Rock	44.750	31.743	33.021	0.43	0.47	0.131	0.417
Coos Bay	43.240	31.967	33.525	0.51	1.93	0.119	0.758
Crescent City	41.750	31.997	33.319	0.54	0.90	0.200	0.535
Trinidad Head	41.020	32.472	33.559	0.55	1.28	0.206	0.503
Westport	39.700	33.028	33.649	0.69	1.53	0.194	0.673
Schoolhouse Beach	38.350	32.358	33.724	1.07	1.85	0.289	0.823
Pillar Point	37.400	32.738	33.610	0.96	1.19	0.375	0.490

for March and August 1994. Data for ancillary tracers are included in Table 2. The spatial and temporal patterns of Cd along the California and Oregon coasts suggest that large-scale atmospheric circulation, as opposed to local and variable wind forcing or local inputs, determines the composition of surfzone water. Large-scale spatial variations of Cd concentrations along the transects are fairly gradual and progress in time with the evolution of the seasonal wind field. This is shown by comparing long-term average coastal upwelling calculated for January, April, July, and September (Huyer, 1983) (Fig. 4b) with the 1992 and 1994 transect data (Fig. 4c). During winter months when downwelling conditions prevail (January 1992, March 1994), surfzone Cd concentrations are below 0.3 nmol/kg throughout much of the region. Higher Cd levels at the southern end of the March 1994 transect mark the onset of the upwelling season. As the spring transition moves northward and upwelling intensifies later in the season (Strub *et al.*, 1987), Cd concentrations increase to 0.6–0.8 nmol/kg in a broad region centered near 39°N. This 400 km-long section of coastline showing elevated Cd levels is slightly to the south of the region where the climatology suggests that upwelling peaks in July (Fig. 4).

We use the longest available time series from Pillar Point, California, to show that not only the seasonal upwelling cycle, but also the interannual variability of wind forcing is reflected in surfzone chemistry. Data collected during 1991–1993 outside San Francisco Bay were used by van Geen and Husby (1996) to derive a quadratic relation between surfzone Cd concentrations and wind forcing: Cd (nmol/kg) = 0.22 [±0.03] − 1.2 [±0.7] 10^{-3} (Index) + 1.2 [±0.5] 10^{-5} $(\text{Index})^2$, where the "Index" is the Bakun index at 36°N, filtered with a 30-day running mean, 14 days prior to the day nearshore water is sampled, and the values in brackets indicate the standard errors for the model parameters calculated from the covariance matrix of the least squares regression. Considerable day-to-day variability in the Bakun index is removed by the 30-day filter (Fig. 5a). The 1994 and 1995 surfzone data in Fig. 5b are taken from van Geen and Luoma (1999a). The 1996–1998 data are shown here for the first time. The relation between the filtered Bakun index and surfzone Cd for the period 1991–1993 is extrapolated through 1998 (Fig. 5b). The correspondence between observed and predicted changes in surfzone chemistry over a broad range of time scales supports a causal relation between large-scale wind forcing and nearshore Cd. Values predicted from the Bakun index match reductions in wind forcing lasting about two weeks during the upwelling seasons of 1993 and 1995, for instance. Interannual variability in the Bakun index, such as the relatively weak upwelling seasons of 1992, 1995, and 1998, are also closely reproduced in surfzone Cd time series. Comparison with the NINO3 index of surface water temperatures anomalies in the eastern

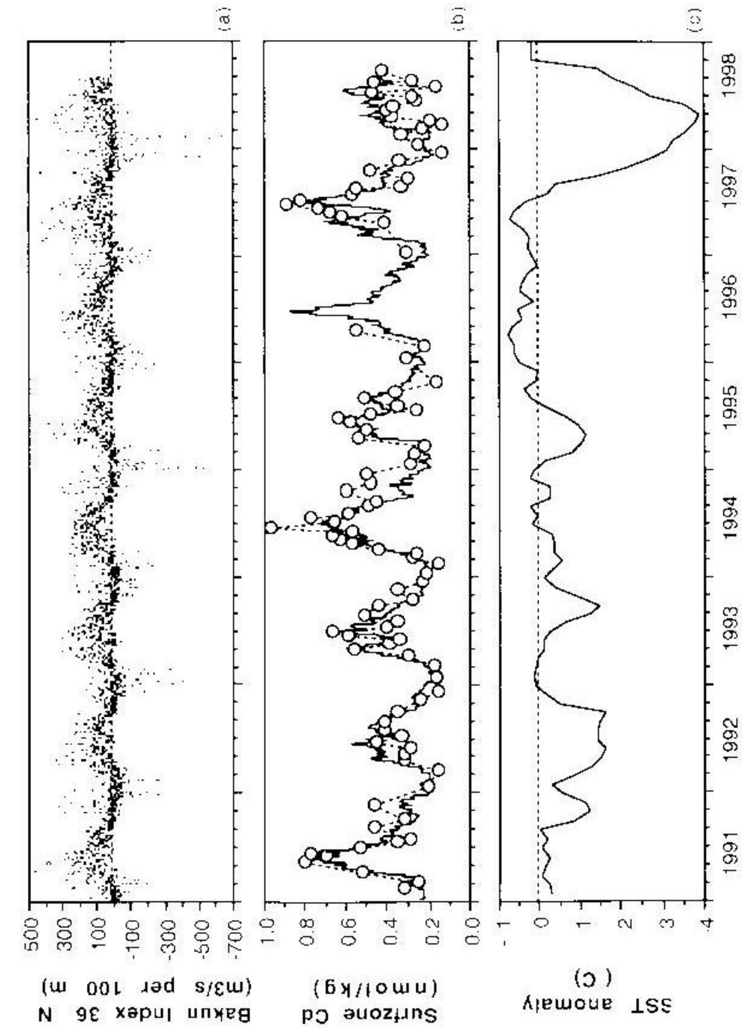

Figure 5. Comparison of surfzone Cd time series outside San Francisco Bay with wind forcing. (a) Small dots are daily values of Bakun upwelling index at 36°N. Positive values correspond to offshore transport at the surface driven by equator-ward wind stress. (b) Surfzone Cd concentrations at Pillar Point, California (open circles) and variations in surfzone Cd predicted by quadratic relation to 30-day filtered Bakun index based on 1991–1993 data (solid line). (c) NINO3 monthly-averaged sea surface temperature anomaly in the eastern equatorial Pacific obtained from a blend of ship, buoy, and bias-corrected satellite data from the Integrated Global Ocean Services System web page (http://ingrid.ldgo.columbia.edu/SOURCES/.Indices/ensomonitor.html). Positive anomalies correspond to El Niño years. Note inverted temperature scale.

tropical Pacific suggest that the reduced amplitude of Cd variations in 1992–1993 and 1998 are probably linked to the El Niño-Southern Oscillation (Fig. 5c). Surfzone Cd concentrations reached during the upwelling seasons of 1994 and 1997 are nearly twice as high as during El Niño years 1992 and 1998 when Cd levels appear to be suppressed. Although there are some notable discrepancies, the overall relation between large-scale wind forcing and surfzone Cd remains quite remarkable.

Why wind forcing is so closely reflected in the Cd content of surfzone water remains a bit of a puzzle. Physical observations of coastal upwelling combined with synchronized shipboard and surfzone sampling off the coast of Oregon provide some hints of what might be happening. Vertical nutrient profiles across the continental shelf collected at the location of the cross-shelf transect but one year later (August 1995) show that the composition of surfzone water at this location was consistent with conservative advection of nutrient-enriched bottom water from the edge of the continental shelf into the surfzone (van Geen *et al.*, in press). This intrusion of bottom water far onto the shelf agrees with advection patterns observed with current moorings deployed nearshore and with model predictions (Huyer, 1983; Lentz, 1994; Allen *et al.*, 1995). Such observations support the notion of efficient exchange of bottom and surfzone water. There is also evidence that the composition of source waters over the shelf during upwelling is rather uniform over alongshore distances on the order of ~100 km (Hermann *et al.*, 1989). The strong alongshore currents and intense mixing in the bottom boundary layer (Lentz and Trowbridge, 1991) probably contribute to maintaining a consistent composition of source waters at depth. If the proposed dynamic link between the surfzone and shelf water at depth indeed exists, this connection could explain why spatial and temporal changes in surfzone composition appear to be tied to large-scale wind patterns rather than local forcing.

3.2. Paleo-upwelling and Foraminiferal Cd/Ca

In previous interpretations of foraminiferal Cd/Ca records from San Francisco Bay (van Geen *et al.*, 1992; van Geen and Husby, 1996; van Geen and Luoma, 1999a), the assumption has been that the shell of *E. hannai* is formed throughout the year. Before questioning this assumption, we review the available water column and foraminiferal calibration data. In order to calculate a representative annual average for Pillar Point, the updated surfzone time series was collapsed into a single year and binned in 2-month intervals. Average Cd concentrations for these two-month intervals show a 3-fold seasonal range (Fig. 6). The annually averaged surfzone Cd concentrations at this location during 1991–1998 calculated from the six binned intervals is 0.39 nmol/kg. The same procedure applied to a 1991–1995 Cd time series within central San Francisco Bay near the location where sediment cores containing *E. hannai* were collected yields a mean Cd concentration of 0.52 nmol/kg (van Geen and Luoma, 1999a). Over the past century, this estuary has experienced rapid industrial development and therefore contains a whole suite of contaminants, including an excess of Cd in the water column. While the seasonal cycle in dissolved Cd within San Francisco Bay is driven largely by variations in nearshore water composition outside, there is a distinct anthropogenic overprint at this location (van Geen and Luoma, 1999a).

How do the water column observations at these two sites compare to the foraminiferal results? Calibration data for shells of *E. hannai* collected inside and outside San Francisco Bay presented by van Geen *et al.* (1992) are replotted in Fig. 7. Individual foraminiferal Cd/Ca determinations for batches of 10–15 shells are shown as a function of updated annual mean Cd/Ca ratios measured in local water. Distribution

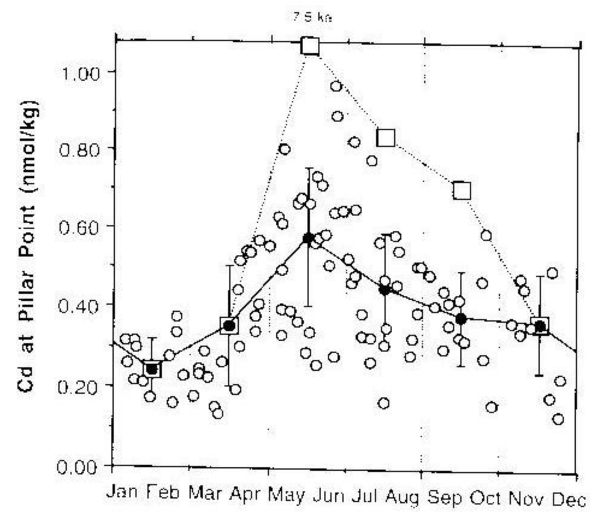

Figure 6. Seasonal variations in surfzone Cd outside San Francisco Bay. All data collected during 1991–1998 are shown by open circles. The solid line is the mean for 2-month intervals. Error bars are the standard deviation of Cd concentrations for each interval. The dotted line and squares show a possible scenario under stronger upwelling conditions of 7.5 ka.

coefficients $K_d = (Cd/Ca)_{shell}/(Cd/Ca)_{water}$ for Cd in the shell of *E. hannai* can be calculated from independent observations inside and outside the estuary. A K_d of 5.7 ± 0.3 is calculated from the mean composition of coastal water during 1991–1998 (Ca 9.7 10^{-3} mol/kg) and the composition of tests collected in rocky tidal pools at Pillar Point in 1991 and 1992 (Cd/Ca 228 ± 13 nmol/mol, n = 25, van Geen *et al.*, 1992; van Geen and Luoma, 1999a). This distribution coefficient is indistinguishable from a K_d of 6.3 ± 0.5

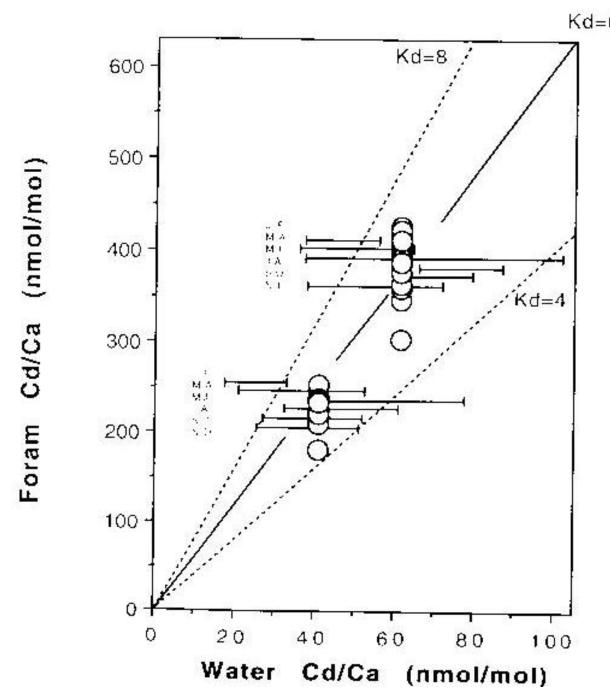

Figure 7. Calibration of *E. hannai* based on dissolved Cd and foraminiferal Cd/Ca ratios inside and outside San Francisco Bay. Each circle represents a foraminiferal Cd/Ca determination on a batch of 10–15 shells. These determinations are plotted as function of the mean water column Cd/Ca measured inside and outside San Francisco Bay. Variations in water column Cd/Ca through the year are decomposed in two-month intervals indicated by error bars. These error bar show the standard deviation of water Cd/Ca ratios over two months and are centered on mean Cd/Ca for the same period. Also indicated is the expected relation between shells and foraminifera for three different distribution coefficients.

for Richardson Bay calculated for tests in the upper 30 cm of the box core and the mean composition of Central Bay water in 1991 1995 (Cd/Ca 386 ± 33 nmol/mol, Ca 8.5 10^{-3} mol/kg). The agreement between distribution coefficients in- and outside the bay suggests that differences in salinity or sediment type between the two environments have no major effect on the incorporation of Cd into the shell of *E. hannai*. A solid line corresponding to a mean Kd of 6.0 was drawn in Fig. 6 starting from the origin based on the assumption that no Cd is incorporated in the shell of *E. hannai* if there is no Cd in the water.

Although the life history of *E. hannai* has, to our knowledge, not been studied in detail, observations of the life cycle of other shallow-water benthic foraminifera indicate that the assumption of constant growth throughout the year needs to be reconsidered. Classic studies of the life cycle of related elphidids such as *Ephidium crispum* (*Polystomella crispa*, Lister, 1903; Jebbs, 1956) and *Ammonia beccarii* (*Streblus beccarii*, Bradshaw, 1957) have demonstrated that shallow-water benthic foraminifera observed in their natural environment produce chambers much more rapidly at certain times of the year than others. In temperate waters of the English Channel, for instance, *E. crispum* undergoes asexual reproduction during the first spring and sexual reproduction during the second, while in warmer waters of the Indian Ocean the same cycle takes place within a single year (Jebbs, 1956). In laboratory cultures of *A. beccarii*, Bradshaw (1957) was able to observe the addition of a chamber every two days under optimal conditions (30 °C). Juveniles reached reproductive maturity in as little as 15 days, after which they died. The timing of reproduction may also be related to the availability of food, often diatoms (Lee *et al.*, 1991). These observations combined with the fact that the California Current experiences seasonal variations in overlying water temperature, food supply, and Cd concentrations indicate that the ecology of this organisms must be understood to determine which phase of the seasonal cycle is predominantly recorded in the shell.

To estimate the potential seasonal bias introduced by non-uniform shell growth throughout the year, we return to the mean seasonal variations in water column Cd inside and outside San Francisco Bay. The mean and standard deviation of water column Cd for 2-month intervals for the locations inside and outside San Francisco Bay is shown in Fig. 7. The variance associated with each interval is due to month-to-month variability in surfzone composition in a single year, as well as interannual variability. The data available suggest that if the shell of *E. hannai* is formed within 2 months or less, the observations could conceivably indicate a Kd ~8 if the shell is formed mostly during non-upwelling months, or a K_d ~4 if the shell is formed during the upwelling months (Fig. 7). In the absence of the culturing experiments for *E. hannai* in seawater of known Cd content, this issue cannot be addressed directly the way it has been for planktonic foraminifera (Mashiotta *et al.*, 1997).

Keeping a potential seasonal bias in mind, we re-examine a well-dated Cd/Ca record for *E. hannai* in San Francisco Bay that spans the past 1,000 years (Fig. 8, van Geen and Luoma, 1999a). The Cd/Ca data are shown as a function of depth together with the estimated ages of different sediment horizons determined from a suite of radioisotopes which includes ^{137}Cs, ^{210}Pb, and ^{14}C (Fuller *et al.*, 1999; van Geen *et al.*, 1999). Cd/Ca determinations for batches of 10 15 shells average 274 ± 15 nmol/mol (n = 19) in the section deposited well before industrialization of the basin. The reproducibility of ±5% for this interval is about as good as can be expected considering the propagation of errors of individual Cd and Ca determinations by graphite-furnace and flame atomic absorption, respectively, assuming that the population of *E. hannai* is homogeneous in composition. Comparison with a value of 228 ± 13 nmol/mol (n = 25) reported by van Geen *et al.* (1992) for *E. hannai* from Pillar Point outside San Francisco Bay suggests that mean pre-industrial Cd levels inside the mouth of San Francisco Bay were at most 20% higher than in nearshore coastal water. For reasons that are presently not understood, other sediment sections from San Francisco Bay containing *E. hannai* show considerably greater variance in Cd/Ca that cannot be explained analytically if the population of *E. hannai* is homogeneous in composition. One example is the upper 60 cm of the San Francisco Bay cores containing bomb-produced ^{137}Cs. Cd/Ca determinations for this interval average 386 ± 33 nmol/mol (n = 19). This increase in the variance could reflect the rapid changes in overlying water Cd caused by industrialization of the basin combined with imperfect mixing of shells with a different Cd content (van Geen and Luoma, 1999b).

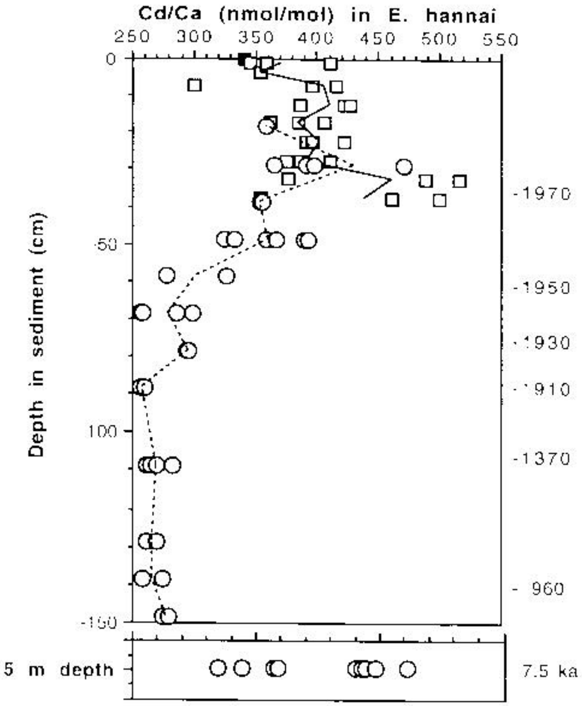

Figure 8. Cd/Ca record for *E. hannai* in a box core (open squares) and a gravity core from San Francisco Bay (van Geen and Luoma, 1999a). Also shown are Cd/Ca data for *E. hannai* from a deeper Holocene interval in the same area (lower panel). The earliest date of deposition of different sediment intervals is indicated on the right margin. The age of the older sediment horizons at 7.5 ka, 960 AD, and 1370 AD was determined from ^{14}C-dated mollusk shells. A sediment mixing/accumulation model for the period starting after 1910 was constructed on the basis of ^{137}Cs, ^{210}Pb, and ^{228}Th data (Fuller *et al.*, 1999).

From a paleoceanographic perspective, deeper sediment sections from San Francisco Bay that were collected more recently in the same location and showed high Cd/Ca variance are cause for greater concern. The problem is illustrated with a suite of Cd/Ca determinations for an early mid-Holocene interval at 15 m-depth below the sediment-water interface (Fig. 8). A few shallower intervals that were analyzed from the same core showed similar results. The bottom of this core (17-m depth) was radiocarbon-dated at 7.5 ka, but shells of *E. hannai* were not present in sufficient quantity for replicate analyses by GFAA. Mollusk shells from several shallower intervals in this core were also radiocarbon-dated and showed a remarkably consistent sedimentation rate of 2 m/kyr at this location (van Geen, in preparation). Nine Cd/Ca determinations for batches of

20–30 shells from the 15-m interval average 402 ± 54 nmol/mol with a range of 320–470 nmol/mol (Fig. 8). At this point, it is difficult to interpret such a wide range because the origin of the increased variance is not understood. We do not believe the increased variance for replicate Cd/Ca determinations in downcore intervals is due to diagenesis. One reason is that analysis of 2–4 m.y.-old shells of *E. hannai* from the uplifted coastal Merced formation south of San Francisco provided by J. Ingle (Stanford U.) show Cd/Ca and Mn/Ca ratios very similar to shells collected in the surfzone (unpubl. results). Another reason is that the increased variance downcore could reflect an actual increase in the variability of individual shell Cd/Ca values due to a seasonal bias introduced when mean annual Cd concentrations were higher than today. Before exploring this possibility with a simple numerical experiment, we reconstruct mean upwelling conditions of San Francisco Bay at 7.5 ka by taking the available data at face value.

The uncertainty in mean Cd/Ca for pre-industrial and early Holocene conditions in San Francisco Bay is reduced by the square root of the number of determinations: (274 ± 0.8% and 402 ± 4.5% nmol/mol for intervals 900–1800 AD and 7500 BP. Based on present mean surfzone Cd of 0.4 nmol/kg, the foraminiferal data therefore suggest a mean surfzone value of 0.6 nmol/kg for the early Holocene with an uncertainty of about ±5%. A change of that magnitude in the mean annual value is not unreasonable since annual means ranging 0.30–0.50 nmol/kg were measured outside San Francisco Bay during 1991–98 (Fig. 5). Stronger upwelling conditions during the early Holocene, suggested by higher mean Cd/Ca values, are consistent with model predictions of the effect of higher summer insolation (Kutzbach *et al.*, 1998). Stronger upwelling is also consistent with observations of lower mid-Holocene intertidal water temperatures off southern California recorded by the oxygen isotopic composition of *Mytilus californianus* (Glassow *et al.*, 1994). What increase in summer wind-stress would be required to raise mean nearshore Cd concentrations by 50%? To a first approximation this can be estimated from the quadratic relation between the Bakun index and nearshore Cd during the upwelling season. Under today's conditions, the annually averaged Cd concentration of 0.4 nmol/kg is the mean of ~0.3 and 0.5 nmol/kg corresponding to the downwelling and upwelling seasons, respectively (Fig. 6). In the same fashion, a mean of 0.6 nmol/kg at 7.5 ka can be decomposed into values of 0.3 and 0.9 nmol/kg. According to the empirical relation between nearshore Cd and the Bakun index, mean Cd values of 0.5 and 0.9 nmol/kg for the 6-month duration of the upwelling season translate into mean upwelling index values of about 100 and 190 m^3/s per 100 m coast at 0 and 7.5 ka, respectively. Everything else being equal, the empirical relation suggests that 50% higher mean coastal Cd concentrations would require about twice the current mean wind stress during the upwelling season. CCM1 (Kutzbach *et al.*, 1997) predicts 40% higher mean wind stress during June-October at 37.5°N under 6 ka insolation conditions (Fig. 2). Clearly, both the origin of increased Cd/Ca variance downcore and results from higher-resolution models will have to be examined before such a discrepancy can be interpreted. The main point of this calculation is to show that Cd-based reconstructions should be sensitive enough to detect such changes.

Assuming the above description of early Holocene upwelling off California is correct, the possible effect of seasonal variations in water Cd on the composition of a population of foraminifera can be demonstrated with a simple numerical exercise. This calculation is based on the inferred ~50% higher nearshore Cd concentrations at 7.5 ka and assumes that the increase in the annual mean value was driven largely by conditions during the upwelling season. To estimate the seasonal Cd cycle at 7.5 ka given a mean of 0.6 nmol/kg, an equal portion of the Cd increase was assigned to the three spring and summer 2-month intervals between May and October which correspond roughly to the upwelling season (Fig. 6). Comparison of today's seasonal cycle and the inferred seasonal cycle at 7.5 ka shows that if shell formation takes place in 2 months throughout the year, the Cd content of individual shells formed under late Holocene pre-industrial conditions in San Francisco Bay could span a 3-fold range, while shells formed under early Holocene conditions would span a much wider 5-fold range (Fig. 6). To estimate the variance in Cd/Ca values that could be expected for a population of *E. hannai*, we performed a numerical simulation of two possible life cycles for *E. hannai*: (a) growth within two months throughout the year, and (b) growth over two months in March-April and May-June only. In case (a), groups of 12 shells corresponding to a single Cd/Ca determination were "created" on a spreadsheet using a random integer number generator between 1 and 6 assigned to each of the six 2-month intervals. The composition of each the 12 shells contributing to a single Cd/Ca "determination" was set by the random number which assigns a Cd content based on the mean cycle in nearshore water composition (Fig. 6) and the mean distribution coefficient (Fig. 7). The mean and standard deviation of Cd/Ca obtained for a set of 20 replicate "measurements" on batches of 12 shells was then calculated. The standard deviation of simulated Cd/Ca "determinations" corresponding to present upwelling conditions was ±7%. For hypothetical foraminifera living under the stronger upwelling conditions of 7.5 ka, the standard deviation nearly doubled to ±12%. In case (b), a similar procedure was followed for batches of 12 shells, but there were only two choices for the Cd content each shell corresponding to March-April and May-June conditions at 0 and 7.5 ka. For this set of simulations, the resulting standard deviations for 20 Cd/Ca "determinations" were ±5 and 16% at 0 ka and 7.5 ka, respectively. Although these outcomes should not be taken too literally, the exercise indicates that if most of the calcification of *E. hannai* takes place within a 2-month period, a significant increase in variance Cd/Ca determinations should be expected under stronger upwelling conditions. The increased sensitivity of Inductively-Coupled Plasma Mass Spectrometry (ICP-MS), particularly High Resolution ICP-MS, compared to GFAA has opened up the possibility of testing this hypothesis by analyzing single shells of *E. hannai* (e.g., Lea and Martin, 1996).

What other factor could complicate the translation of nearshore Cd/Ca records into quantitative estimates of summer wind stress along the California Current? One question is whether the Cd content of source waters at depth remained constant during the Holocene. On this time scale, a significant change in ocean or basin-wide Cd inventory that could result in a different Cd to phosphate ratio in upwelling waters seems unlikely (van Geen *et al.*, 1995). This does not rule out, however, a change in the vertical Cd gradient offshore in response to fluctuations in the combination of physical and biogeochemical processes that maintain the present gradient. The sensitivity of the seasonal Cd cycle off Pillar Point to ENSO is one illustration of such variations on relatively short time scale (Fig. 5). The Santa Barbara Basin record of sediment laminations suggests that changes in the composition of upwelling source waters could also have changed in response to changes in ventilation and/or productivity over longer periods (Behl and Kennett, 1996). One constraint is provided, however, by a benthic Cd/Ca record from the depth of the oxygen-minimum zone off California showing that water column Cd concentrations at ~800 m depth remained relatively constant through the Holocene (van Geen *et al.*, 1996). Because the dynamic range of Cd variations at the coast is so wide, a few additional benthic foraminiferal Cd/Ca records from the California margin at 600 and 400 m depth, for instance, should be sufficient to constrain any significant variations in source water composition.

Perhaps a more difficult issue is the nature of the forcing of any changes in nearshore Cd that may be reconstructed in the future for the California coast. The extension of the Pillar Point surfzone time series confirms that the seasonal enrichment in nearshore Cd associated with spring and summer coastal upwelling is suppressed during El Niño years. This observation suggests that variations in the Cd content of biogenic carbonate during the Holocene could have been sensitive to either (1) orbital changes in the intensity of summer insolation or (2) changes in the frequency and/or intensity of the El Niño/Southern Oscillation. One way to address this ambiguity would be to compare paleo-upwelling records from California and Chile. If orbital changes in summer insolation dominated, then opposite changes changed in upwelling intensity should have been recorded by the Cd content of biogenic carbonate in the two hemisphere. On the other hand, a dominant overprint of changes in the frequency and/or intensity of ENSO on changes in nearshore Cd should have been symmetric about the equator.

CONCLUSIONS AND OUTLOOK

Our observations to date show that surfzone Cd is a particularly sensitive and quantitative indicator of the intensity of upwelling-favorable wind forcing along the coast of California and Oregon. The unique hydrography of Cd along the western Americas coupled with its incorporation into biogenic carbonates preserved in the geologic record is the key to using nearshore Cd concentrations for paleoclimate reconstructions. The Cd content of at least one shallow water benthic foraminifer, *Elphidiella hannai*, reflects ambient seawater Cd concentrations, although the possibility of a seasonal bias of foraminiferal Cd/Ca may necessitate single-shell analyses. Alternatively, a different biogenic carbonate phase, such as mollusk shells recovered from archeologic middens, may provide a more reliable record of upwelling changes through the Holocene. Taken at face value, a limited set of results for *E. hannai* from San Francisco Bay suggest that mean annual water column Cd was 50% higher at 7.5 ka than today. This would suggest that summer equatorward wind stress at the coast was twice as high at 7.5 ka, assuming the same relationship between wind forcing and nearshore Cd as today.

As a first step towards an interhemispheric comparison of Cd-based coastal upwelling records, a surfzone sampling program was started in 1997 near Ensenada and La Paz (Mexico) and Antofagasta, Valparaiso, and Concepcion (Chile). This program relies heavily on participation by local scientists and students. Initial results from the expanded surfzone sampling program, are posted at: http://ingrid.ldgo.columbia.edu/SOURCES/.EPCU/.dataset_documentation.html.

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This work started as an attempt to reconstruct Cd contamination in the water column of San Francisco Bay. Sam Luoma of the US Geological Survey provided the critical support and facilities needed to test this idea, and its subsequent expansion into a paleo-upwelling proxy. Numerous colleagues and students listed on our web page have since then contributed to the on-going surfzone time series at various locations. We thank Jack Barth and Bob Smith for letting us collect samples off the coast of Oregon during their 1994 cruise on board RV *Wecoma*. We are grateful to John Lee (City College, New York) for discussions of the life cycle of shallow-water benthic foraminifera. We thank the NOAA Pacific Fisheries Environmental Group (Monterey, California) for providing the upwelling indices and John Kutzbach and his colleagues (U. of Wisconsin, Madison) for making model results available. Mitch Lyle provided a thoughtful review of the manuscript. This is Lamont-Doherty Earth Observatory contribution 5986.

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MAGNETIC SIGNATURE OF RAPID CLIMATIC VARIATIONS IN NORTH ATLANTIC SEDIMENTS

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ABSTRACT

Taking advantage of the continuous high resolution magnetic techniques, we ha studied the magnetic properties of six deep-sea cores located in the Nordic seas and North Atlantic along an E-W transect between 58° to 67°N. The study has been focuss on climatic stage 3 during which these cores exhibit large amplitude short term variatio in the bulk magnetic parameters, in relation with rapid climatic changes. In each co the magnetic mineralogy is uniformly composed of well sorted low Ti-content magneti associated with paramagnetic minerals. This uniformity indicates that short term vari tions in the bulk magnetic parameters only illustrate variations in the amount of ma netic minerals transported by deep currents and deposited at the different sites. The fa climatic changes are thus related to coeval fast changes in the strength of the deep-s circulation. During interstadials the latter took place in the Norwegian sea and tra ported the magnetic particles into the North Atlantic ocean along a path similar to t present day path of the NADW. During stadials and Heinrich events, this deep circu tion was strongly reduced. A tentative comparison of the amount of magnetites tra ported by the deep current and deposited at the studied sites suggests that t Faeroe-Shetland channel and the Denmark strait were the only two active path for t overflow water during climatic stage 3.