

Cadmium in the California Current system: Tracer of past and present upwelling

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Abstract. Over 100 samples were collected off the west coast of North America during 1991–1993 to determine the relation between wind-driven upwelling and nearshore concentrations of dissolved silicate (Si), phosphate (P), and cadmium (Cd). Highly enriched in deep water offshore, these constituents are sensitive indicators of upwelling. Coastal water was sampled from the shore in January and June 1992 at 12 sites distributed between 36° and 48°N latitude. In January the composition of nearshore water along this transect was fairly uniform: 5–15 $\mu\text{mol/kg}$ for Si, 0.5 to 1.0 $\mu\text{mol/kg}$ for P, and 0.1–0.3 nmol/kg for Cd. In June, elevated concentrations of Si (30 $\mu\text{mol/kg}$), P (2.0 $\mu\text{mol/kg}$), and Cd (0.6 nmol/kg) revealed a region of intense upwelling between 38° and 40°N. The pattern is broadly consistent with meridional gradients in coastal upwelling calculated from the long-term mean of alongshore winds compiled from ship reports. Nearshore water was also collected biweekly to monthly at two sites 3 km apart near San Francisco Bay (37.5°N) during 1991–1993. The variability seen in the time series suggests that the composition of nearshore water integrates the effect of alongshore winds over timescales of several weeks. Seasonal variations in Si (5–50 $\mu\text{mol/kg}$), P (0.5–2.5 $\mu\text{mol/kg}$), and Cd (0.1–0.8 nmol/kg) concentrations were consistent with upwelling during spring and summer. Maximum Si, P, and Cd concentrations reached in May 1991 were consistent with advection to the very nearshore region from a depth of about 300 m relative to a vertical profile at a distance of 200 km from the coast. Nearshore Si, P, and Cd concentrations were reduced relative to 1991 in 1992 and, to a lesser extent, in 1993 due to weaker upwelling linked to the warm phase of the El Niño–Southern Oscillation. During periods of weaker upwelling or downwelling, variations in P, Si, and Cd concentrations became uncoupled. There is a good correlation between the coastal Cd time series near San Francisco Bay (37.5°N) and a second order polynomial function of the upwelling index of Bakun [1975] at 36°N, filtered with a 30-day running mean ($r^2 = 0.71$, $n=39$). The index is a daily estimate of coastal upwelling calculated from 6-hourly mean atmospheric pressure distributions at 36°N. From this function and a record of daily upwelling indices we infer a range of annually averaged coastal Cd concentrations of at least 0.3–0.5 nmol/kg since 1967. Cd/Ca ratios in shells of foraminifera from San Francisco Bay suggest that average coastal Cd concentrations 3500–4500 years ago were at the upper end of this range.

Introduction

Nutrient-rich waters of major eastern boundary currents such as the California, Canary, and Peru/Humboldt systems sustain highly productive food webs [Wooster and Reid, 1963; Walsh, 1977; Smith; 1981, 1992]. The origin of these nutrient enrichments is not entirely understood because the relative importance of different nutrient input mechanisms has been hard to establish [Hood *et al.*, 1991]. For the California Current, explanations proposed in the past include shoaling of isopycnal surfaces linked to anticyclonic circulation of the North Pacific gyre [Reid, 1962], wind-driven coastal and

offshore upwelling [Bakun, 1973; Bakun and Nelson, 1991], and southward advection of nutrient-rich water from the southern margin of the Alaskan gyre [Chelton *et al.*, 1982]. Recent multidisciplinary studies of the California Current have shown that the offshore supply of nutrients also depends on a complex pattern of cross-shelf circulation involving the formation of offshore-directed jets and eddies perhaps associated with prominent coastline features [Mooers and Robinson, 1984; Rienecker *et al.*, 1985; Chavez *et al.*, 1991]. Despite a number of unanswered questions, nutrient enrichments in eastern boundary currents can be largely attributed to upwelling driven by strong equatorward winds during spring and summer.

The overall wind pattern over eastern boundary current systems is a reflection of the difference in heat capacity between land masses and the surface layer of the ocean

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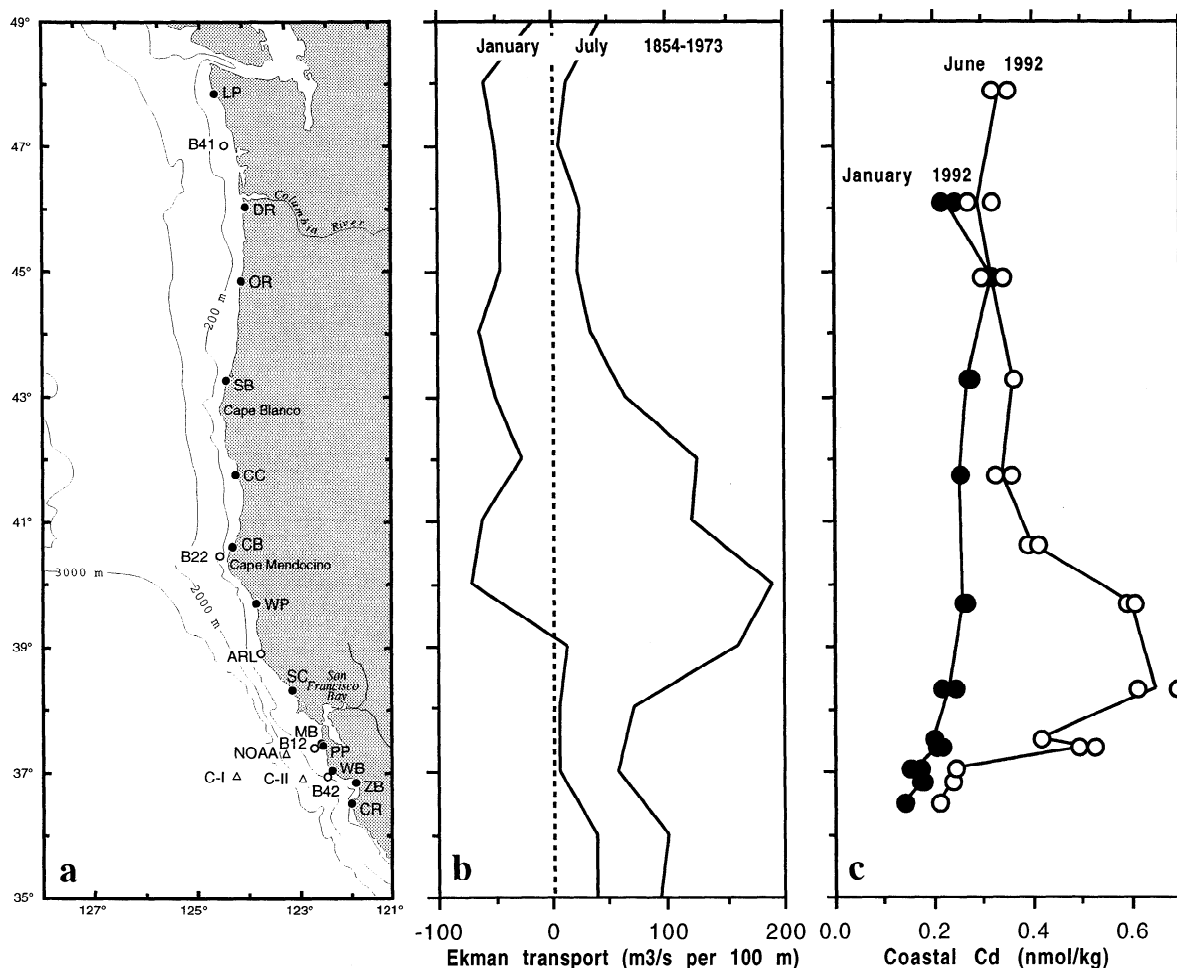


Figure 1. Water composition along nearshore transects. (a) Map of the north American west coast showing the shore-based sampling locations with the following abbreviations: LP, Lapush; DR, Del Ray Beach; OR, Otter Rock, SB, Sunset Beach; CC, Crescent City; CB, Centerville Beach; WP, Westport; SC, Schoolhouse Beach; MB, Moss Beach; PP, Pillar Point; WB, Waddell Beach; ZB, Zmudowski Beach; and CR, Carmel River Beach. Open circles show the location of wind measurements at buoys B42, B22, and B41 and the Point Arena lighthouse (ARL). Triangles show the location of Cd profiles C-I and C-II of *Bruland* [1980] and the NOAA station. (b) Cross-shelf Ekman transport calculated by *Huyer* [1983] from long-term mean winds within 100 km of the coast compiled by *Nelson* [1977]. 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). Determinations for replicate samples are shown by individual circles. (d) Salinity along nearshore the transects, with same symbols as in Figure 1c. (e) Phosphate and (f) silicate concentrations along the nearshore transect. The dashed and dotted lines show phosphate and silicate concentrations predicted from Cd in Figure 1c and the depth relations in Figures 4a and 4c, respectively.

[*Crowley and North, 1991*]. In the case of the California Current, strong zonal atmospheric pressure gradients during spring and summer are due to greater warming of air masses over western North America relative to the North Pacific [*Huyer, 1983*]. The implication is that the supply of nutrients to eastern boundary currents is linked to climate. Because air temperatures over land are more sensitive to climate warming than temperatures over the ocean, *Bakun* [1990] suggested that rising concentrations of greenhouse gases in the atmosphere could lead to intensified coastal upwelling in the future. Large scale changes in ocean-atmosphere circulation could affect not only the biology of eastern boundary currents, but also moisture and heat exchange with the adjacent continents [*Cayan and Peterson, 1989*]. The geological record provides one of the few ways to test models predicting the climate response to changes in the Earth's radiation balance. Because the greater sensitivity of land masses to solar heating

determines the large-scale wind pattern over the California Current system, modeling constraints may be obtained by quantifying upwelling conditions during the last climatic optimum 9000 years ago, when summer insolation was 8% higher than today [*Crowley and North, 1991*]. Summer insolation in the northern hemisphere has decreased steadily since then due to precession of the equinoxes.

The Cd data presented here provide a quantitative basis for reconstructing upwelling and zonal atmospheric pressure gradients for the California Current system since the last climatic optimum. Recently, *van Geen et al.* [1992] showed that the past intensity of upwelling in the California Current system can be reconstructed from the chemical composition of foraminifera shells deposited in estuarine sediments. This type of reconstruction relies on two key properties of the trace element Cd in the ocean. First, Cd is a sensitive hydrographic indicator of upwelling because the distribution of this trace

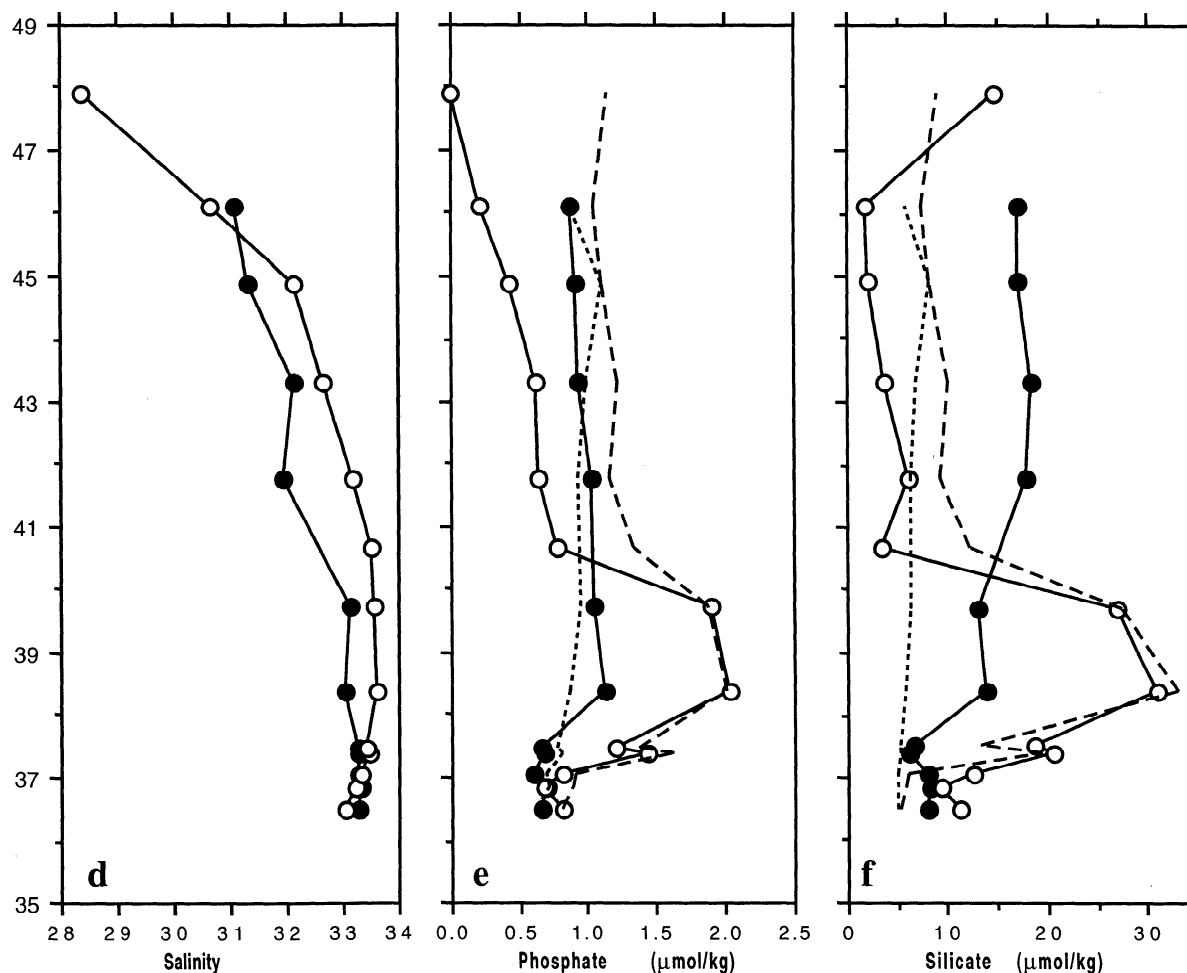


Figure 1. (continued)

element in the water column closely mirrors that of the nutrient phosphate [Martin *et al.*, 1976; Boyle *et al.*, 1976; Bruland *et al.*, 1978; Bruland, 1980; Boyle, 1988]. Second, Cd is incorporated in the calcite shell produced by certain benthic microorganisms in proportion to dissolved Cd levels in ambient seawater during their lifetime. This was first demonstrated by Hester and Boyle [1982] for deep ocean benthic foraminifera and has become an important tool to determine past changes in deep ocean circulation [Boyle, 1988; 1992]. The estuarine and coastal species *Elphidiella hannai* also responds to ambient dissolved Cd [van Geen *et al.*, 1992]. In this paper, we further document the relation between upwelling and variations in nearshore Cd today on the basis of over 100 seawater samples collected from beaches of California, Oregon, and Washington during 1991-1993. The data include alongshore transects collected in January and June 1992 between 36° and 48°N latitude and a 3-year time series at two locations near 37.5°N.

Methods

Nearshore Water Sampling and Analysis

Coastal water was sampled from the surfzone near Pillar Point and Moss Beach (Figure 1a) at biweekly to monthly intervals from February 1991 to December 1993. Trace metal samples were collected in acid-washed polyethylene bottles attached to a plexiglas holder at the end of a 3-m-long

fiberglass pole. Salinity and nutrient samples were taken simultaneously from a separate bottle attached to the pole. On most occasions, time series samples were collected in the morning. Replicate trace element samples were taken at the same location within a few minutes of each other. The same procedure was followed to collect nearshore water in January and June 1992 over a distance of 1700 km along the Washington, Oregon, and California coast (Figure 1a). Time series and transect samples were stored in the dark until filtration at the end of each sampling day.

Trace element samples were filtered through an acid-washed 0.4 μm Nuclepore filter with a Nalgene polysulfone filtration system adapted for vacuum filtration and equipped with a teflon O-ring. After filtration, 0.5 mL of 12 N Ultrex II HCl (Baker) per 250 mL of seawater was added to the samples. Cd, Cu, Ni, and Zn contributions from this acid were not significant. Trace metals 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]. Low trace element water ($\text{Zn} < 0.1 \text{ nmol/kg}$) used to clean bottles, filters, and the filter rig was obtained from a combined Milli-RO/Milli-Q Plus system (Millipore). Table 1 lists the reproducibility of trace metal determinations for spiked and unspiked consistency standards run with each batch of 10 samples. Mean recoveries of the trace metal spikes were indistinguishable from 100%.

Nutrient samples were filtered through disposable 0.45 μm Durapore filters and acidified with 60 μL of 12 N Ultrex II HCl

Table 1. Trace Metal Spike Recovery From Preconcentrations

	Unspiked	Standard Deviation	Spike	Standard Deviation	Recovery, %
Cd	0.001	±0.001	0.436	±0.015	101±4
Cu	0.5	±0.1	11.7	±0.6	98±6
Ni	2.7	±0.3	18.8	±0.3	98±4
Zn	0.1	±0.1	15.2	±1.2	94±8

Unspiked sample was collected 2 km off Maui, Hawaii. Concentrations are listed in nmol/kg. Means and standard deviations from 15 analyses.

per 60 mL of seawater. Dissolved silicate (Si) and phosphate (P) were measured spectrophotometrically with a QuickChemAE system (Lachat Instruments). Si and P procedures prescribed by the manufacturer are adaptations for flow-injection analysis of standard colorimetric methods described by *Strickland and Parsons* [1968]. There was a significant crossover effect proportional to the Si concentration into the P channel of the instrument, probably because because molybdate blue is used in both methods. The artifact was corrected for by analyzing Si and P standards in artificial seawater separately and measuring absorption in both channels. The correction due to the cross-over amounted to a downward adjustment of $\leq 10\%$ in P concentrations for all samples. A reduction in reaction temperature for the P channel from 65 to 37 °C now recommended by the manufacturer largely eliminates this interference. Si and P blank corrections, determined by including Sargasso Sea surface water with each batch of samples, averaged 0.5 and 0.1 $\mu\text{mol/kg}$, respectively. Reproducibility of nutrient measurements for replicate injections was typically better than $\pm 5\%$. A nutrient profile in the Santa Barbara Basin determined with the same instrument is entirely consistent with published data [*van Geen et al.*, 1995]. Salinity was measured on samples stored in glass with a Guildline Autosol salinometer standardized with International Association for Physical Sciences of the Ocean (IAPSO) water.

Wind Data and Upwelling Indices

We compare nutrient and dissolved Cd distributions in the California Current system to wind data from three different sources to evaluate the relation between atmospheric circulation 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. More recently, *Bakun and Nelson* [1991] recomputed mean wind stress data and calculated the wind-stress curl which drives oceanic upwelling on a grid that extends about 1000 km offshore.

The second source of wind data are meteorological buoys of the National Data Buoy Office at 36.8°N (B42), 37.4°N (B12), 40.7°N (B22), and 47.4°N latitude (B41) and an additional shore-based station at the Point Arena lighthouse (39.0°N, Figure 1a). The distance of the buoys from the coast ranges between 11 and 24 km. Wind speed and direction were averaged daily. The principal axes of the wind vectors were rotated counterclockwise by 30° at B42 (36.8°N), B12 (37.4°N), and Point Arena (39.0°N) to calculate the alongshore

component. North of these stations, the coast runs approximately north-south.

The third indicator of upwelling used in this paper is an upwelling index derived from synoptic surface pressure fields provided by the Fleet Numerical Oceanography Center. 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 \mathbf{M} is determined from the longshore component of the calculated wind speed $\mathbf{M} = 1/f \cdot d_a \cdot C_d \cdot |\mathbf{V}| \cdot \mathbf{V}$ where f is the latitude-dependent Coriolis parameter, d_a is the density of air, C_d is a constant empirical drag coefficient, and \mathbf{V} is the estimated wind vector of magnitude $|\mathbf{V}|$. A drag coefficient of 0.0013 is used to calculate the daily upwelling index, hereafter referred to as the daily Bakun index, calculated from 6-hourly atmospheric pressure fields. Monthly Bakun indices are based on monthly averaged pressure data and a larger drag coefficient of 0.0026 [*Bakun*, 1973]. The larger drag coefficient partially compensates for underestimating upwelling from monthly averaged data caused by the squared dependence of wind stress on velocity. Bakun indices are routinely available from the Pacific Fisheries Environmental Group. Records of daily and monthly Bakun indices starting in 1967 and 1946, respectively, have been reconstructed [*Bakun*, 1973, 1975].

Results

Transects

Figure 1 compares nearshore Cd, P, and Si distributions along the Washington, Oregon, and California coast in January and June 1992 with the long-term meridional distribution of coastal upwelling during these two months [*Huyer*, 1983]. It is important to note that Cd concentrations for replicate samples collected a few minutes apart and shown individually in Figure 1c are analytically indistinguishable. Gradual variations in nearshore water composition along the transects also suggest that Cd, P, and Si do not merely reflect local processes. In January 1992, concentrations of Cd, P, and Si were fairly uniform between 37°N and 47°N: ~0.2 nmol/kg, 1 $\mu\text{mol/kg}$, and 15 $\mu\text{mol/kg}$, respectively (Table 2 and Figures 1c, 1e, and 1f). Even though the mean wind pattern suggests onshore Ekman transport during this period, i.e. downwelling (Figure 1b), nearshore Cd, Si, and P concentrations were somewhat higher than typical for surface waters ~100 km from the coast: 0.06-0.16 nmol/kg, 0.3-0.6 $\mu\text{mol/kg}$, and 3-9 $\mu\text{mol/kg}$, respectively [*Bruland*, 1980; *Jones and Murray*, 1984]. The summer distribution of upwelling tracers was very different. Figure 1b shows that strong equatorward winds typically prevail between 38° and 43°N latitude during spring and summer. The area of strongest long-term upwelling overlaps with elevated nearshore Cd, P, and Si concentrations observed in June 1992 between Centerville Beach (40.6°N) and Schoolhouse Beach (38.4°N): 0.6 nmol/kg, 2 $\mu\text{mol/kg}$, and 30 $\mu\text{mol/kg}$, respectively (Figures 1c, 1e, and 1f). Comparison of the winter and late spring transects suggests that large-scale variations in upwelling off California, Oregon, and Washington determine Cd, P, and Si concentrations near the coast.

Table 2. Composition of Nearshore Water During 1992 Transects

Location	Date	Salinity	Si	P	Cd	Ni
Del Ray Beach	Jan. 16	31.110	17.2	0.88	0.231	4.6
Otter Rock	Jan. 16	31.356	17.1	0.92	0.318	5.0
Sunset Beach	Jan. 18	32.156	18.5	0.93	0.274	6.3
Crescent City	Jan. 19	31.969	18.0	1.03	0.255	10.9
Westport	Jan. 19	33.150	13.1	1.05	0.262	4.8
Schoolhouse Beach	Jan. 19	33.051	13.9	1.14	0.231	5.7
Moss Beach	Jan. 23	33.301	6.7	0.66	0.199	6.4
Pillar Point	Jan. 23	33.303	6.1	0.68	0.211	8.3
Waddell Beach	Jan. 23	33.264	8.1	0.61	0.163	5.2
Zmudowski Beach	Jan. 23	33.325	8.2	0.70	0.177	5.6
Carmel River Beach	Jan. 23	33.286	8.1	0.66	0.139	4.0
Lapush	June 13	28.372	14.7	0.00	0.335	4.6
Del Ray Beach	June 14	30.685	2.0	0.21	0.295	4.8
Otter Rock	June 15	32.158	2.2	0.42	0.320	5.8
Sunset Beach	June 15	32.667	3.7	0.63	0.363	5.2
Crescent City	June 15	33.196	6.2	0.64	0.343	7.2
Centerville Beach	June 16	33.514	3.6	0.79	0.403	6.4
Westport	June 16	33.577	27.0	1.89	0.600	4.9
Schoolhouse Beach	June 16	33.626	31.0	2.04	0.652	5.8
Moss Beach	June 18	33.411	18.8	1.22	0.397	4.5
Pillar Point	June 18	33.458	22.7	1.45	0.509	6.5
Waddell Beach	June 4	33.310	12.6	0.82	0.246	5.0
Zmudowski Beach	June 4	33.261	9.3	0.69	0.239	5.4
Carmel River Beach	June 4	33.039	11.2	0.82	0.211	3.9

Si and P concentrations listed in $\mu\text{mol/kg}$, Cd and Ni in nmol/kg .

Time Series

Samples collected during 1991-1993 at Pillar Point and Moss Beach (37.5°N) confirm that upwelling largely determines temporal variations in nearshore Cd, P, and Si concentrations. The following two measures of wind forcing are shown in Figures 2a and 2b for comparison with changes in nearshore water composition: (1) the daily Bakun index at 36°N , together with a 30-day running mean applied to the same record, and (2) daily alongshore winds measured at B42 (36.8°N), about 75 km south of Pillar Point, with a 30-day running mean as well. The filtered Bakun index and wind records share many common features. Both show that upwelling prevailed over most of the 3-year period, with extended periods of downwelling restricted to the months of November through February. There are also significant differences between the two measures of wind forcing. Buoy winds indicate that the maximum intensity of upwelling-favorable winds was comparable from year to year at B42 (36.8°N), whereas the Bakun index suggests stronger upwelling in 1991 relative to 1992 and 1993. Daily buoy winds also show greater variability than the daily Bakun index, including more days of downwelling during spring and summer (Figures 2a and 2b).

Nearshore Cd, P, and Si concentrations rapidly responded to strengthening of upwelling-favorable winds during the spring transitions of 1991 and 1993 (Figure 2). Response to the spring transition of 1992 was more muted, particularly for the nutrients P and Si. Maximum P and Si concentrations reached in 1992 (1.4 and 23 $\mu\text{mol/kg}$, respectively) were about half the highest levels reached in 1991 (2.4 and 48 $\mu\text{mol/kg}$). The very similar P and Si records at Pillar Point and Moss Beach (37.5°N , correlation coefficient $r^2=0.90$, number of samples $n=38$) and the lack of any systematic differences between the two sites show that variability in the composition of coastal water sampled from the beach is limited on spatial scales of a

few kilometers. Figure 2c shows Cd concentrations determined on all samples collected at Pillar Point and Moss Beach (37.5°N) with each data point showing the mean of determinations on two separate bottles. Maximum Cd concentrations reached in 1991, 1992, and 1993 were 0.8, 0.5, and 0.7 nmol/kg , respectively (Figure 2c). Cd concentrations during periods of persistent downwelling were about 0.2 nmol/kg . Comparison of variations in nearshore Cd, P, and Si concentrations during 1991-1993 with the highly variable record of daily upwelling proxies suggests that the composition of coastal water sampled from the beach integrates daily fluctuations in wind forcing over several weeks. Visually, seasonal variations in nearshore Cd concentrations resemble the filtered records of wind forcing more closely than variations in P and Si (Figure 2).

Before examining the Cd data more closely, certain artifacts attributable to nearshore sampling are discussed. In contrast to nearly all samples from Pillar Point, many samples collected at Moss Beach showed strong Ni enrichments relative to ~ 5 nmol/kg concentrations measured in California Current waters offshore [Bruland, 1980]. Filters used for the trace metal samples also showed that nearshore waters at Moss Beach often contained more suspended material than at Pillar Point, suggesting local sediment input, perhaps from eroding cliffs. A second reason for the difference between the two sites may be that a rocky promontory near Pillar Point facilitates sampling a few meters from the beach. A link between local runoff and Ni enrichments is suggested by negative salinity excursions that coincide on some occasions (e.g., February 1992 and April 1993), as well as by more frequent elevated Ni concentrations observed in 1992 and 1993 relative to the dry year of 1991 (Table 3). Dissolved Cu and Zn concentrations (not shown) were also systematically higher in Ni-enriched samples than in California Current water offshore sampled by Bruland [1980]. The salinity of anomalously enriched samples allows us to rule out any significant contribution of low-salinity, metal-enriched water from San Francisco Bay at Pillar Point and Moss Beach [Flegal et al., 1991; van Geen and Luoma, 1993]. On the basis of these observations, samples affected by local inputs and therefore not representative of the composition of coastal water were flagged by the following criteria: (1) whenever Cd concentrations at Pillar Point and Moss Beach differed by more than 20% and (2) the Ni concentration was greater than 10 nmol/kg at one of the sites, the enriched sample was rejected from the mean shown in Figure 2c. Out of a total of 40 sampling occasions, Moss Beach Cd data were not included in the mean nine times and Pillar Point data, two times. The data were rejected from both sites on only one occasion, February 18, 1992 (Table 3). The overall pattern of Cd fluctuations at Pillar Point and Moss Beach (37.5°N) during 1991-1993 is not strongly altered by this selection (Figure 2c).

Discussion

We first determine to what extent the various seawater constituents measured at the beach can be relied on as indicators of upwelling intensity. The Cd time series at Pillar Point (37.5°N) is then compared to four different measures of wind forcing and found to be most closely correlated to the Bakun index at 36°N . The discussion concludes with a comparison of coastal Cd variability over the past 25 years estimated from the Bakun index with a long-term trend over

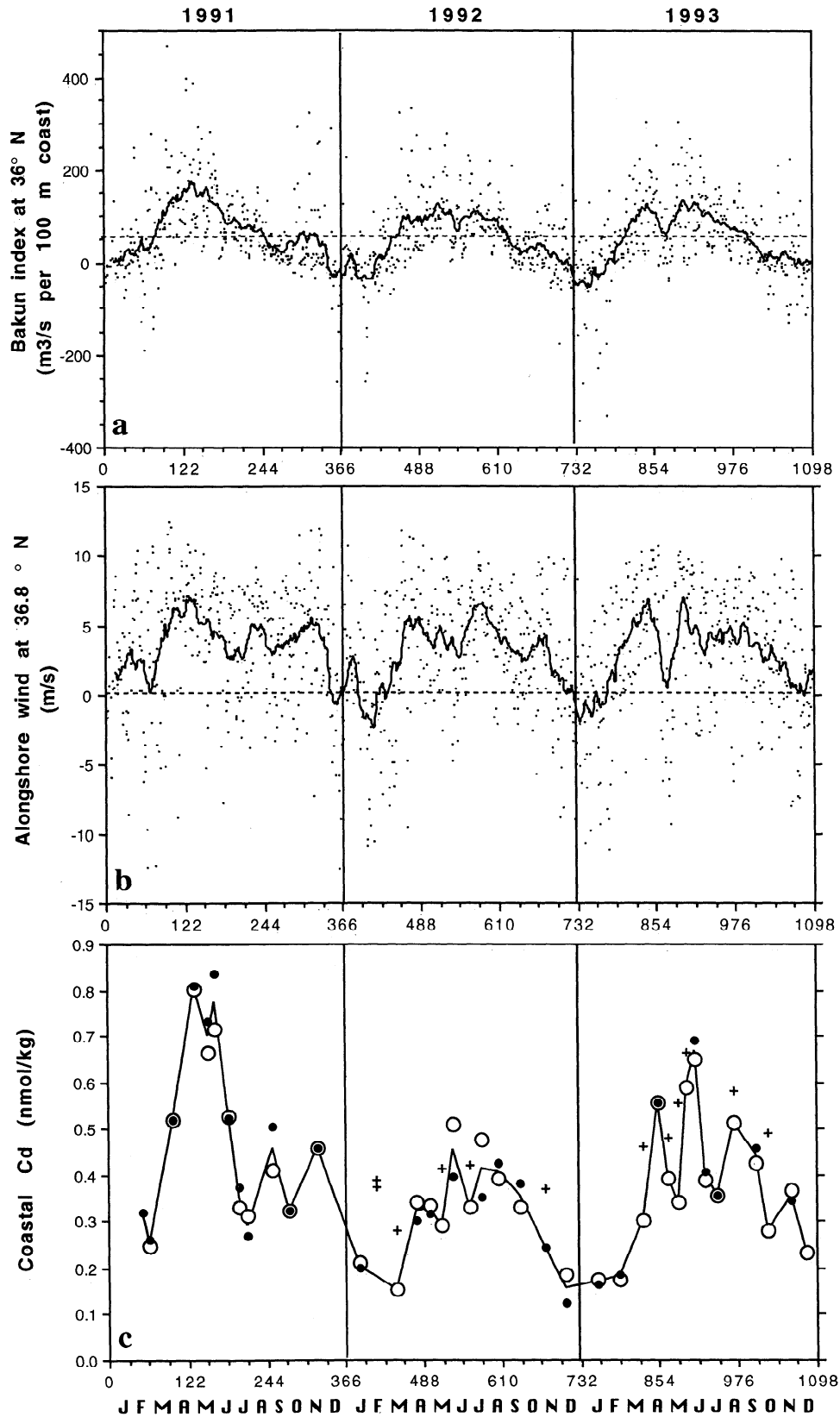


Figure 2. Wind forcing and upwelling at Pillar Point (37.5°N), 1991-1993. (a) Daily upwelling index of *Bakun* [1975] at 36°N latitude. Solid line is a 30-day running mean. Day 1 on horizontal axis corresponds to January 1, 1991. (b) Daily alongshore winds (positive equatorward) at meteorological B42 (36.8°N) calculated relative to 330°T. Solid line is a 30-day running mean. (c) Dissolved Cd concentrations at Pillar Point (open circles) and Moss Beach (solid circles) (37.5°N). Crosses indicate samples not included to calculate the representative mean shown by the solid line. (d) Salinity, (e) dissolved phosphate, and (f) dissolved silicate at Pillar Point and Moss Beach, with same symbols as in Figure 2c. Dashed lines indicate salinity, P, and Si concentrations predicted from average Cd concentrations in Figure 2c and the depth relations in Figure 4.

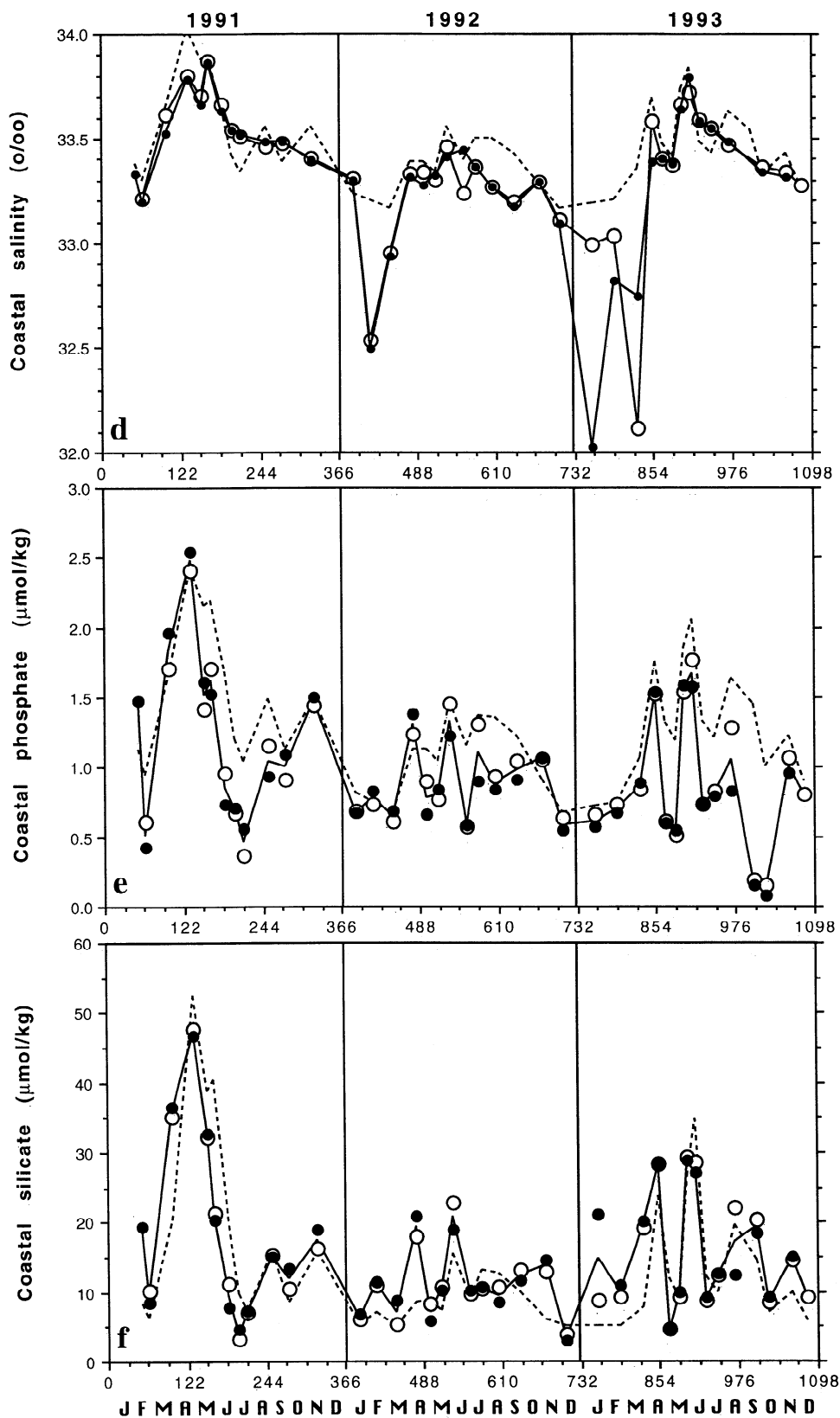


Figure 2. (continued)

the past 4500 years derived from the Cd content of foraminiferal shells.

Comparison Between Upwelling Tracers

The internal consistency of variations in upwelling tracer concentrations is tested by comparing the composition of

nearshore samples with published offshore water column profiles. Cd profiles for the California Current have been determined on at least five occasions within a distance of 200 km from Pillar Point and Moss Beach: in April 1977 [Bruland *et al.*, 1978], March 1978 [Bruland, 1980], July 1978 [Bruland, 1980], December 1978 [Knauer and Martin, 1981],

Table 3. Composition of Nearshore Water at Time Series Stations During 1991-1993

Sampling Date	Day 1991	Pillar Point					Moss Beach					Mean Cd
		Salinity	Si	P	Cd	Ni	Salinity	Si	P	Cd	Ni	
Feb. 20, 1991	51						33.334	19.4	1.47	0.319	7.2	0.319
March 9, 1991	68	33.208	10.2	0.60	0.246	7.8	33.195	8.5	0.42	0.263	7.5	0.255
April 9, 1991	99	33.615	35.0	1.71	0.520	8.7	33.522	36.6	1.96	0.520	7.1	0.520
May 14, 1991	134	33.802	47.6	2.41	0.803	7.4	33.784	46.8	2.54	0.809	10.3	0.806
June 3, 1991	154	33.701	32.1	1.42	0.665	5.7	33.665	32.7	1.61	0.734	13.6	0.700
June 13, 1991	164	33.867	21.3	1.71	0.714	7.0	33.866	20.4	1.52	0.834	9.9	0.774
July 3, 1991	184	33.663	11.2	0.96	0.528	6.7	33.630	7.8	0.73	0.523	6.6	0.525
July 21, 1991	202	33.541	3.1	0.67	0.330	4.5	33.540	4.7	0.70	0.372	5.6	0.351
Aug. 2, 1991	214	33.509	7.0	0.36	0.311	6.8	33.520	7.2	0.56	0.268	6.0	0.290
Sept. 11, 1991	254	33.458	15.3	1.15	0.410	6.7	33.483	14.9	0.93	0.504	8.6	0.457
Oct. 4, 1991	277	33.476	10.4	0.91	0.323	5.7	33.482	13.3	1.09	0.322	6.2	0.322
Nov. 20, 1991	324	33.404	16.1	1.44	0.459	9.3	33.399	18.8	1.50	0.456	8.8	0.458
Jan. 23, 1992	388	33.303	6.1	0.68	0.211	8.3	33.301	6.7	0.66	0.199	6.4	0.205
Feb. 18, 1992	414	32.533	11.0	0.73	0.374	19.8	32.492	11.4	0.82	0.388	15.3	
March 20, 1992	445	32.950	5.4	0.60	0.153	6.2	32.937	8.8	0.68	0.281	12.7	0.153
April 20, 1992	476	33.334	18.0	1.23	0.342	7.1	33.311	20.8	1.38	0.303	5.2	0.322
May 11, 1992	497	33.337	8.2	0.90	0.334	6.1	33.276	5.7	0.65	0.316	7.0	0.325
May 31, 1992	517	33.298	10.6	0.76	0.290	7.1	33.326	10.2	0.83	0.412	10.9	0.290
June 18, 1992	535	33.458	22.7	1.45	0.509	6.5	33.411	18.8	1.22	0.397	4.5	0.453
July 14, 1992	561	33.235	9.6	0.57	0.332	8.0	33.447	10.2	0.58	0.422	13.1	0.332
July 31, 1992	578	33.366	10.3	1.31	0.477	8.1	33.366	10.6	0.90	0.352	6.7	0.415
Aug. 27, 1992	605	33.270	10.6	0.93	0.393	7.9	33.266	8.4	0.83	0.424	11.3	0.408
Sept. 29, 1992	638	33.192	13.0	1.04	0.331	6.6	33.167	11.7	0.91	0.381	8.5	0.356
Nov. 9, 1992	679	33.294	12.9	1.05	0.371	12.7	33.293	14.5	1.07	0.244	5.3	0.244
Dec. 9, 1992	709	33.101	3.8	0.63	0.184	8.5	33.088	2.8	0.54	0.125	5.6	0.155
Jan. 28, 1993	759	32.995	8.6	0.65	0.174	8.0	32.023	21.0	0.57	0.164	6.9	0.169
March 4, 1993	794	33.033	9.1	0.72	0.175	7.9	32.811	10.9	0.66	0.185	10.5	0.180
April 8, 1993	829	32.112	19.1	0.83	0.301	7.4	32.739	20.1	0.88	0.460	16.9	0.301
May 1, 1993	852	33.578	28.2	1.52	0.557	7.3	33.388	28.3	1.54	0.557	7.1	0.557
May 18, 1993	869	33.407	4.5	0.60	0.393	6.2	33.404	4.6	0.59	0.478	15.2	0.393
June 2, 1993	884	33.375	9.2	0.51	0.341	9.2	33.381	9.8	0.54	0.554	21.1	0.341
June 15, 1993	897	33.664	29.3	1.54	0.589	7.6	33.638	28.7	1.58	0.665	11.9	0.589
June 29, 1993	911	33.719	28.6	1.77	0.649	10.0	33.790	27.1	1.57	0.688	11.8	0.668
July 14, 1993	926	33.589	8.6	0.72	0.388	6.4	33.584	9.1	0.73	0.407	9.8	0.398
Aug. 2, 1993	945	33.548	12.3	0.82	0.355	5.8	33.548	12.6	0.79	0.355	5.9	0.355
Aug. 27, 1993	970	33.469	22.1	1.28	0.510	6.8	33.481	12.3	0.82	0.579	12.0	0.510
Sept. 29, 1993	1003		20.3	0.18	0.426	6.0		18.4	0.14	0.456	9.3	0.441
Oct. 18, 1993	1022	33.359	8.4	0.15	0.280	6.6	33.336	9.1	0.07	0.490	15.3	0.280
Nov. 24, 1993	1059	33.335	14.6	1.06	0.365	7.6	33.312	15.1	0.96	0.346	7.5	0.356
Dec. 17, 1993	1082	33.275	9.3	0.80	0.234	6.3						0.234

Si and P concentrations listed in $\mu\text{mol/kg}$, Cd and Ni in nmol/kg . Day 1991 refers to time axis used in Figures 2 and 7. Mean Cd at Pillar Point and Moss Beach was calculated from data selected by criteria discussed in text.

and September 1980 [Bruland *et al.*, 1985]. At ~1000 m depth, Cd concentrations reported for these stations are indistinguishable within the analytical precision of the different methods used, 1.05 ± 0.05 nmol/kg (Figure 3). Perhaps more surprising is the fact that even at 200 m depth, offshore Cd concentrations are restricted to a narrow range of 0.65-0.75 nmol/kg . Cd and P are taken up by plankton causing a strong depletion in surface water, while sinking and decomposition of biogenic matter returns Cd and P to the water column at depth [Martin *et al.*, 1976; Boyle *et al.*, 1976; Bruland *et al.*, 1978; Bruland, 1980; Boyle, 1988]. Parallel increases of P and Cd concentrations with depth show that uptake and release processes within the water column are closely linked for these constituents (Figure 4a). Unlike the global compilation of Boyle [1988] which exhibits a change in slope of the Cd-P relation, the Cd-P relation is linear in the California Current system throughout the upper 1000 m of the water column, with a P intercept of 0.2 $\mu\text{mol/kg}$ at zero Cd (Figure 4a).

A general linear relation between Cd and salinity in the available California Current profiles suggests that vertical

gradients in these properties are due in part to mixing of two end members (Figure 4b). Isopycnal maps of P distributions for the North Pacific indicate that the nutrient-enriched end-member at depth is an extension of oxygen-depleted waters from the eastern equatorial Pacific [Reid, 1965; Lynn and Simpson, 1987]. Cd and nutrient-depleted surface water contains fresher subarctic waters entrained with the California Current from the north. It is difficult to separate the relative contributions of local uptake and release versus large-scale advection to the vertical profiles of Cd and P in the California Current from the available data.

The relation between Si and Cd in California Current profiles is not linear, indicating that Si and Cd regeneration deep in the water column are uncoupled (Figure 4c). Similar patterns have been observed throughout the ocean and attributed to deeper remineralization of opaline hard parts relative to labile plankton tissue rich in P and Cd [Broecker and Peng, 1982]. The relation between Si and Cd in the California Current region can be described by a second order polynomial. The parameterization has no mechanistic implication and serves only to calculate an expected Si

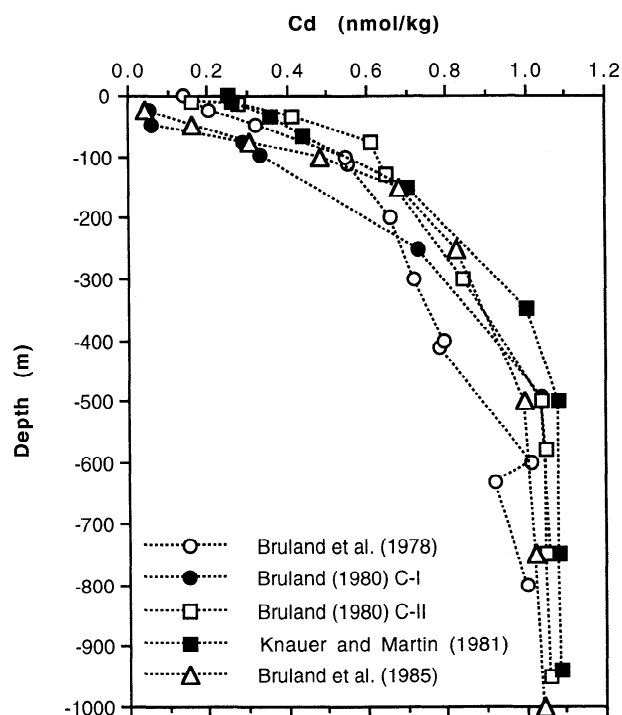


Figure 3. Upper 1000 m of published Cd profiles off California 1977-1980, with profile at station 64 of *Bruland et al.* [1978] collected in April 1977, profile at station C-I of *Bruland* [1980] collected March 1978, profile at station C-II of *Bruland* [1980] collected July 1978, profile of *Knauer and Martin* [1981] collected December 1978, profile of *Bruland et al.* [1985] collected September 1980. All profiles were collected in the region of stations C-I and C-II of *Bruland* [1980] shown in Figure 1a.

concentration from the measured Cd concentration, assuming conservative mixing.

During periods of strong upwelling ($Cd \geq 0.5$ nmol/kg) in May 1991, June 1992, and April and June 1993, P and Si concentrations predicted from Cd agree rather well with corresponding nutrient concentrations measured offshore at depth (Figure 2). In June 1992, measured P and Si concentrations also agreed closely with Cd-predicted values over a 350 km distance along the coast between Westport (39.7°N) and Carmel River Beach (36.5°N) (Figures 1e and 1f). These observations suggest that Cd, P, and Si are advected conservatively to the coastal region from deep waters offshore during periods of strong upwelling. There is no detectable input of Cd, P, and Si to coastal waters by sediment diagenesis and/or rivers during these periods [*van Geen and Luoma, 1993*]. Assuming Cd, P, and Si were advected conservatively at Pillar Point (37.5°N) in May 1991 when upwelling was particularly strong, a maximum depth of origin of nearshore water relative to profiles C-I and C-II of *Bruland* [1980] can be estimated independently from these tracers. Table 4a lists the data of *Bruland* [1980] used to obtain depths of origin from Cd, P, and Si by linear interpolation as a function of depth. The calculated depths of origin shown in Table 4b range between 309-327 m and 235-269 m relative to stations C-I and C-II, respectively, located 200 km and 100 km west of Pillar Point (Figure 1a).

In principle, differences in Cd, P, and Si concentrations reached during the upwelling season from one year to the other

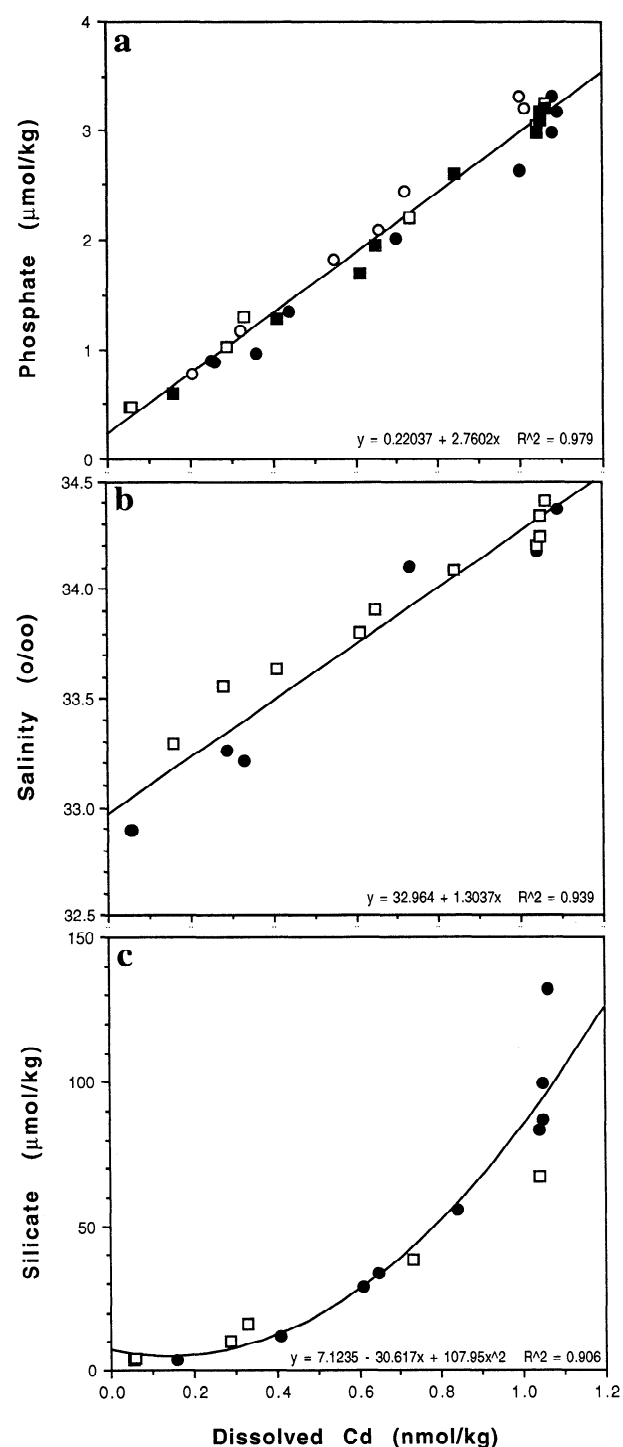


Figure 4. Relations between upwelling tracers at depth in the California Current showing regressions of (a) phosphate, (b) salinity, and (c) silicate as a function of Cd concentrations in the upper 1000 of the water column, based on published data from references in Figure 3. See legend in Figure 3 for symbols.

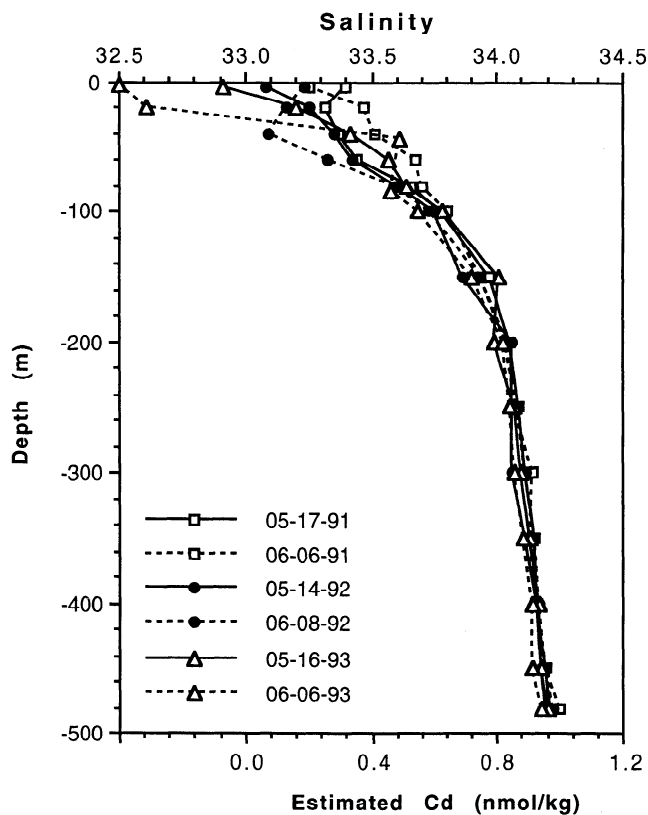
could be due to either a change in wind forcing or a change in the composition of source waters at depth. The latter mechanism prevails in the eastern equatorial Pacific where surface water Cd and nutrient concentrations vary in response to the El Niño-Southern Oscillation cycle [*Shen et al., 1987, 1992*]. Comparable variations in water column structure do not seem to take place in the California Current system. The

Table 4a. Nearshore Water and Profiles of *Bruland* [1980]

	Salinity	P, μmol/kg	Si, μmol/kg	Cd, nmol/kg
Nearshore May 14, 1991	33.793	2.47	47.2	0.806
C-I 98 m	33.210	1.30	16.2	0.33
250 m	34.107	2.20	38.5	0.73
490 m	34.181	3.04	66.9	1.04
C-II 35 m	33.365	1.29	12.0	0.41
75 m	33.807	1.70	28.7	0.61
130 m	33.904	1.95	33.5	0.65
300 m	34.089	2.60	55.6	0.84

Table 4b. Maximum Depth of Origin of Nearshore Water

Intrapolated from:	Interpolated From			
	Salinity	P	Si	Cd
Depth/C-I	197 m	323 m	327 m	309 m
Depth/C-II	49 m	266 m	235 m	269 m

**Figure 5.** Salinity profiles off Pillar Point during upwelling season, 1991-1993, including results from two CTD casts each year at the NOAA station in Figure 1a. Approximate Cd scale (bottom) was determined from the salinity-Cd relation in Figure 4b.

invariant Cd concentration at depth for five profiles collected between 1977 and 1980 was noted earlier. Because offshore Cd profiles are not available for 1991-1993, salinity is used here as an indicator of source water composition based on the assumption that the Cd-salinity relation at depth did not change over this period. Figure 5 shows that salinity variations west of San Francisco Bay during the upwelling seasons of 1991, 1992, and 1993 were ≤ 0.05 below 200 m depth. From the relations in Figure 4 we infer that the composition of source waters remained constant within ± 0.1 $\mu\text{mol/kg}$, ± 3 $\mu\text{mol/kg}$, and ± 0.03 nmol/kg for P, Si, and Cd, respectively. Regional wind forcing, not variations in source water composition, determines nearshore water composition in the California Current system during the upwelling season.

The salinity of nearshore samples can also be compared to variations predicted from the Cd-salinity relation offshore (Figure 4b). The north-south salinity gradient along the transects is largely unrelated to upwelling and reflects southward advection of subarctic water and/or freshwater input from the Strait of Juan de Fuca, the Columbia River, and other rivers along the coast (Figure 1d). A seasonal reduction in runoff between January and June 1992 is suggested by the broad increase in coastal water salinity along the transect. Salinity variations measured at Pillar Point and Moss Beach (37.5°N) during 1991-1993 show some relation to upwelling, with the exception of negative excursions during winter 1992 and 1993 due to high rainfall (Figure 2d). Salinity maxima of 33.9 (1991), 33.5 (1992), and 33.8 (1993) correspond to periods of strongest upwelling as indicated by Cd, P, and Si. Excluding the heavy rainfall periods, the seasonal salinity range of about 0.8 (Figure 2d) corresponds roughly to the range predicted by nearshore Cd concentrations and the Cd-salinity relation with depth offshore (Figure 4b). Beyond this, salinity is clearly not a quantitative indicator of the origin of nearshore water. Table 4a and 4b show that salinity measured at the beach in May 1991 corresponds to a depth of origin of ~ 200 m and ~ 50 m relative to profiles C-I and C-II of *Bruland* [1980]. This is much shallower than indicated independently by Cd, P, and Si and demonstrates that dilution by runoff remains significant during periods of intense upwelling. Figure 2d suggests that without dilution, coastal salinity could have reached a value of ~ 34.0 . *Lentz* [1987] reports that during the spring transitions of 1981 and 1982, shoaling of isopycnals near the coast in the Coastal Ocean Dynamics Experiment (CODE) area was sufficient to bring 34.0 salinity water well onto the continental shelf. The maximum depths of origin calculated in Table 4 are therefore not unreasonable. The limited use of salinity as a quantitative upwelling tracer in nearshore waters is also shown by surface salinity surveys west of San Francisco Bay during 1991, 1992, and 1993 (Figure 6). The region under the immediate influence of discharge from San Francisco Bay is not included in these maps. Comparison of the different upwelling seasons shows that surface salinities were higher in 1991 than in 1992 over a broad region west of Pillar Point (37.5°N), in agreement with the nearshore measurements (Figure 2d). In 1993, however, offshore surface salinities were depressed throughout the region by about 1.0 relative to 1992, despite stronger upwelling. The difference is most likely related to stronger than average precipitation over western North America in early 1993 [*Halpert et al.*, 1994].

There are also a number of systematic discrepancies between measured P and Si concentrations predicted from Cd,

particularly during periods of reduced upwelling or downwelling. Figure 1f shows that nearshore water was enriched in Si by $\sim 10 \mu\text{mol/kg}$ relative to the Cd-derived concentration in January 1992 between Del Ray Beach (46.1°N) and Pillar Point (37.4°N). The time series data show pronounced Si excesses at Pillar Point and Moss Beach during two periods of elevated runoff in February-March 1992 and January-April 1993 (Figure 2f). Because Si concentrations in rivers typically range between 200 and $300 \mu\text{mol/kg}$ [Martin and Meybeck, 1979; Flegal et al., 1991], these enrichments are attributed to continental runoff.

Discrepancies between measured P concentrations and Cd-derived values seem to be caused by a different mechanism. In June 1992, P concentrations measured between Del Ray Beach (46.1°N) and Centerville Beach (40.6°N) were consistently $\sim 0.5 \mu\text{mol/kg}$ lower than the Cd-derived value (Figure 1e). The time series data in Figure 2e show comparable deficits in June-August 1991, 1992, and 1993 following the season of strongest upwelling at Pillar Point and Moss Beach (37.5°N). We believe these P deficits relative to Cd reflect plankton (mostly diatom) uptake in nearshore waters at a low Cd-P ratio relative to the ratio in upwelling source waters [Bruland et al., 1978]. This was recently confirmed by incubation experiments on deck of recently upwelled water collected off the coast of Oregon (A.v.G., unpublished data). Alternatively, deviations from the offshore Cd-P relation at depth could be caused by Cd input to coastal water from sediment diagenesis. This possibility cannot be ruled out from the available data but seems unlikely because other trace elements such as Cu and Zn would probably have been affected as well. Cu and Zn concentrations in samples collected from the beach are comparable to the composition of California Current surface water offshore [van Geen and Luoma, 1993].

In summary, this extensive data set shows that (1) the composition of nearshore water integrates the effect of alongshore winds over timescales of weeks to months; (2) maximum Cd, P, and Si concentrations reached during the upwelling season can differ by a factor of 2 from one year to the other; (3) Cd, P, and Si concentrations during periods of strong upwelling are consistent with advection from $\sim 300 \text{ m}$ depth at a distance of 200 km from the coast; and (4) during periods of weaker upwelling or downwelling, variations in Cd, Si, and P concentrations are decoupled from the offshore relations at depth. The data suggest that Cd is a sensitive tracer of upwelling that is less affected by continental runoff than Si and salinity. Cd also seems less sensitive to uptake by nearshore plankton than P. Further discussion of the relation between upwelling tracers and wind forcing focuses on Cd.

Nearshore Cadmium and Wind Forcing

The Cd time series is compared with the following four different estimates of offshore transport: Bakun upwelling indices at (1) 36° and (2) 39°N and daily alongshore winds squared (sign preserved) at (3) B42 (36.8°N) and (4) the Point Arena lighthouse (39.0°N). The use of the square of daily alongshore winds is dictated by the dependence of Ekman transport on wind stress. The 1991-1993 record at B12 (37.4°N) is not discussed here because it is incomplete. The four records of wind forcing, all filtered with a 30-day running mean, are shown in Figure 7. In regressing nearshore Cd concentrations as a function of the different upwelling proxies, leads and lags of up to 20 days between the time series were tested. Results from these regressions are

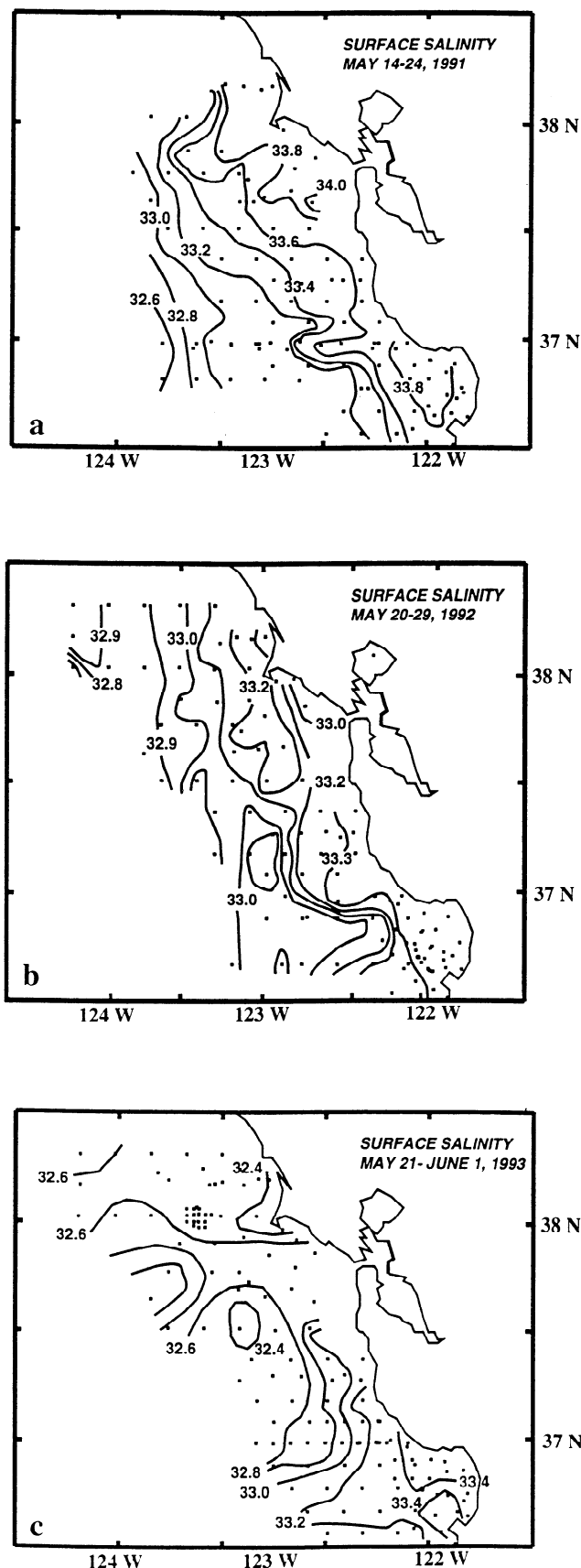


Figure 6. Surface salinity distributions west of San Francisco Bay, (a) 1991, (b), 1992, and (c) 1993. The data were collected during the upwelling season by cruises of the National Marine Fisheries Service. Dots indicate stations used to draw contours.

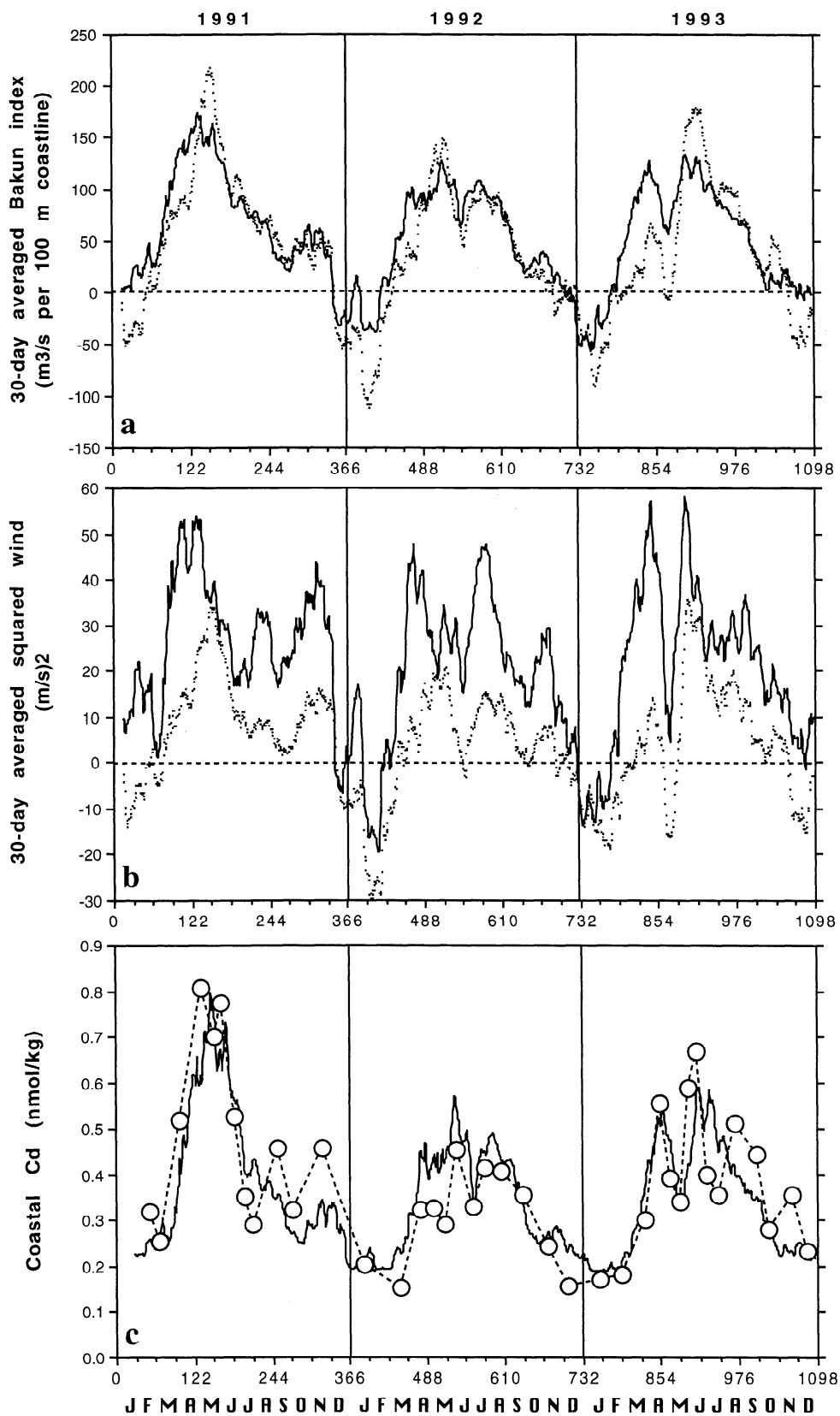


Figure 7. Comparison of variations in cadmium concentrations off Pillar Point (37.5° N) with different measures of wind forcing. (a) Daily Bakun indices at 36° N (solid line) and 39° N (dotted line), filtered with 30-day running mean. (b) Daily alongshore winds (squared with sign conserved and positive equatorward) at buoy B42 (36.8° N, solid line) and the Point Arena lighthouse (39.0° N, dotted line), filtered with a 30-day running mean. (c) Comparison of mean coastal Cd concentrations at Pillar Point (open circles) with prediction from regression of filtered daily Bakun index at 36° N (Figure 9a).

summarized in Figure 8. All correlation coefficients were calculated for the same total of 39 mean coastal Cd values (Table 3). Variations in coastal Cd are equally well described by a second order polynomial function of the Bakun index at 36°N ($r^2=0.71$), with the Cd response lagged by 7 or 14 days relative to wind forcing (Figure 8a). On the basis of unpublished coastal Cd data for 1994, the function calculated for a 14-day lag is used hereafter (Figure 9a). The correlation between mean P at Pillar Point and Moss Beach (37.5°N) and the Bakun index with a lag of 14 days was much lower than for Cd ($r^2=0.28$). A simple linear relation between Cd and the Bakun index significantly underestimates coastal Cd concentrations during periods of strong upwelling ($r^2=0.66$). A detailed physical interpretation of the relation between coastal Cd and the Bakun index at 36°N is beyond the scope of this paper. In order to obtain comparable correlation coefficients, the coastal Cd time series was also fitted with a second order polynomial to the three other measures of wind forcing. Figure 8 shows that the correlation between the Cd time series and wind forcing was lower for squared winds measured at Point Arena (39.0°N, $r^2=0.64$), followed by the Bakun index at 39°N ($r^2=0.60$) and squared winds measured at B42 (36.8°N, $r^2=0.59$). Coastal Cd concentrations and these three measures of wind forcing offset by the optimal number of days are shown in Figures 9b, 9c, and 9d. Phase differences between the time series at the highest correlation show a consistent geographical pattern (Figure 8). The Bakun index at 36°N and buoy winds at B42 (36.8°N) determined south of Pillar Point (37.5°N) lead variations in coastal Cd by about 14 days. The apparent delay in the response of coastal Cd to wind forcing may be due the inertia of cross-shelf circulation. The Bakun index at 39°N and winds at Point Arena (39.0°N) both lead Cd measured at Pillar Point (37.5°N) by about 2 days. The smaller lag relative to wind forcing determined north of Pillar Point (37.5°N) is consistent with the northward propagation of the spring transition [Strub *et al.*, 1987].

The lower correlation between coastal Cd and measured winds at B42 (36.8°N) compared with the Bakun index at 36°N suggests that large-scale wind forcing rather than local alongshore winds determine nearshore water composition. A noticeable difference between measured winds and the Bakun index at 36°N is that alongshore winds at B42 (36.8°N) were not significantly weaker during the upwelling season of 1992 relative to 1991 and 1993 (Figure 7). The Bakun index and coastal Cd, P, and Si concentrations all show that upwelling was reduced in 1992. The discrepancy between large-scale pressure gradients and local winds measured by meteorological buoys may be specific to the location of B42 (36.8°N) and does not necessarily hold elsewhere. Variations in coastal winds measured at Point Arena (39.0°N), for instance, more closely follow the Bakun index at 39°N, including weakened upwelling in 1992 (Figures 7a and 7b). The three fitting parameters obtained from the regression of nearshore Cd as a function of the Bakun index are used to infer variations in nearshore composition at higher temporal resolution as follows: $Cd \text{ (nmol/kg)} = 0.22 [\pm 0.03] + 1.2 [\pm 0.7] 10^{-3} (\text{Index}) + 1.2 [\pm 0.5] 10^{-5} (\text{Index})^2$. The measure of wind forcing is the Bakun index at 36°N, filtered with a 30-day running mean, 14 days prior to the day nearshore Cd was determined. Standard errors for the model parameters shown in brackets were calculated from the covariance matrix of the least squares regression by estimating the variance of the data from the prediction error [Menke, 1984]. Results from this

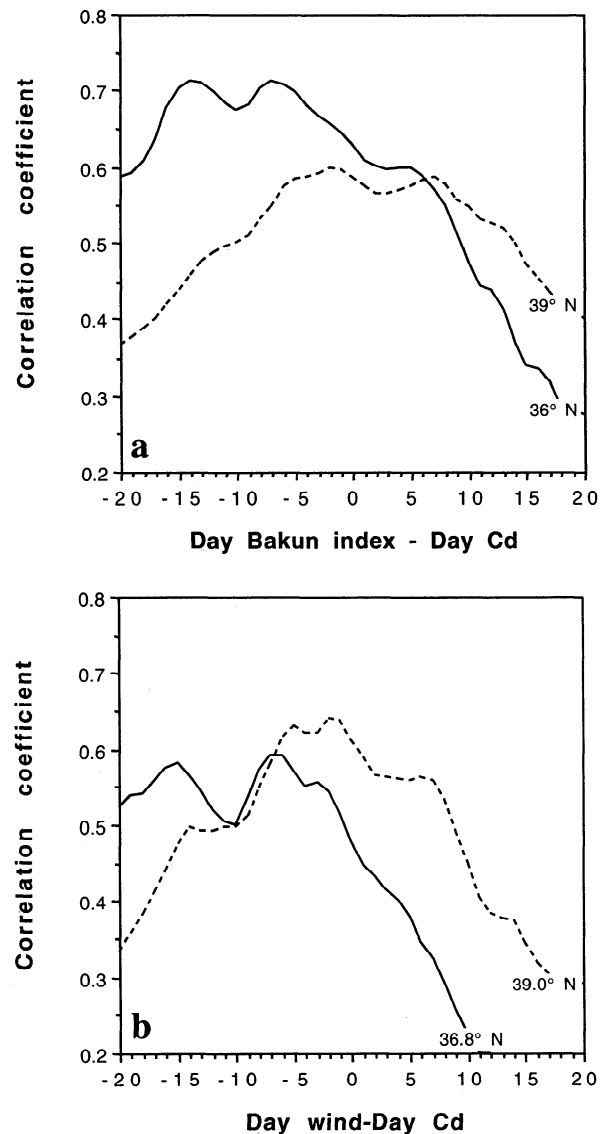


Figure 8. Dependence of correlation on leads and lags between time series. Correlation coefficients for second-order polynomial relation expressing coastal Cd concentrations as a function of 30-day filtered (a) daily Bakun index at 36° and 39°N and (b) squared alongshore winds at B42 (36.8°N) and Point Arena (39.0°N). Horizontal axis indicates leads and lags between the time series expressed as the difference between the day of the value of wind forcing and the day Cd was measured.

expression are compared with measured Cd concentrations in Figure 7c. The correspondence between observed and predicted patterns over the three-year length of the time series supports a causal relation between large-scale wind forcing and nearshore Cd. Values calculated from the Bakun index also match brief reductions in wind forcing that were suggested by only one or two samples during the upwelling seasons of 1992 and 1993 (Figure 7c). The main discrepancies are found during the fall of 1991 and 1993, when measured Cd concentrations were significantly higher than values inferred from the Bakun index at 36°N. Interestingly, alongshore winds measured by B42 (36.8°N) were relatively strong during these periods (Figure 7b). Neither measured winds nor the Bakun index appears to capture all variations in wind forcing that control nearshore Cd concentrations. This is confirmed in the

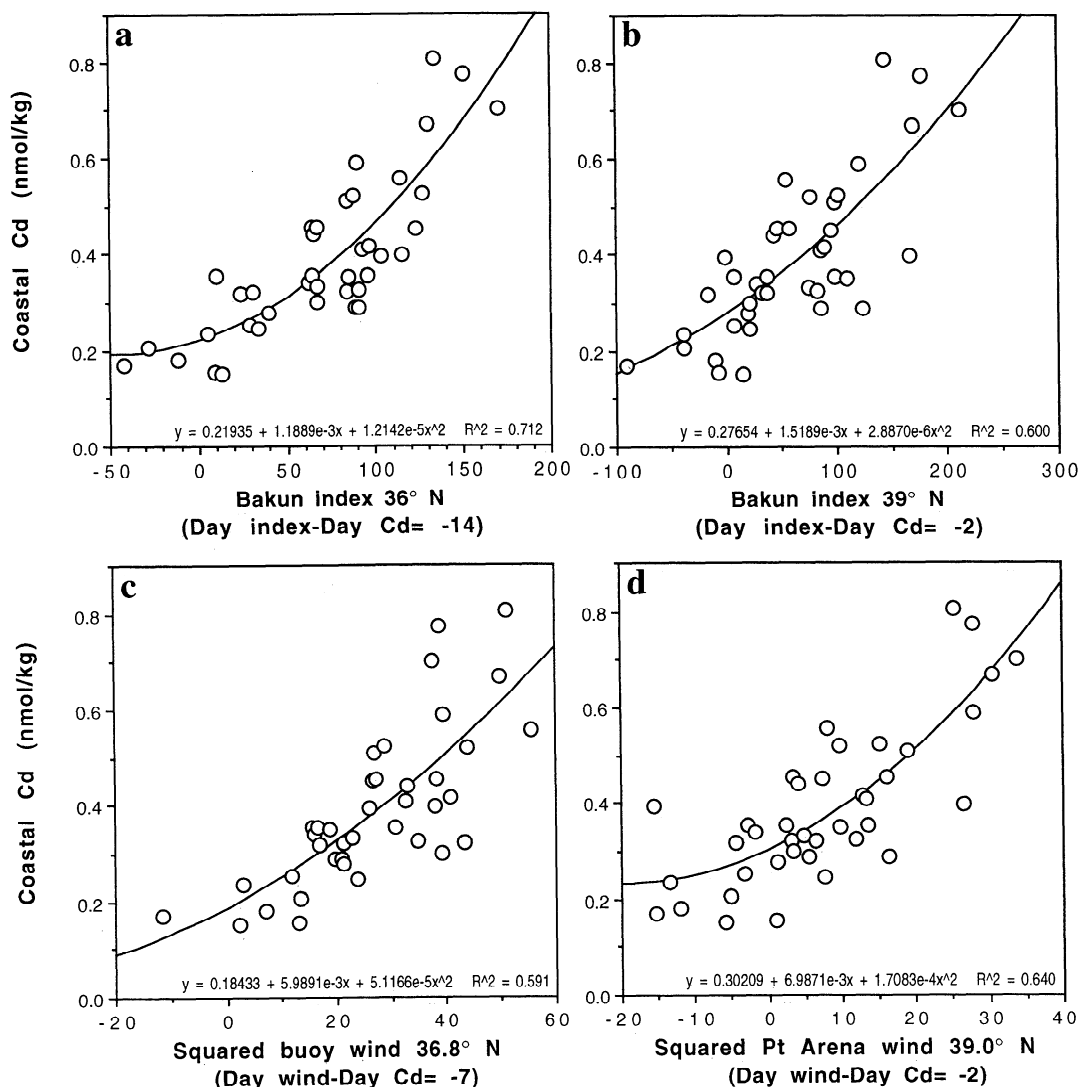


Figure 9. Best fits to the expressions of Cd as a polynomial function of wind forcing. Regression of nearshore Cd as a squared polynomial function of four measures of wind forcing, (a) Bakun index at 36°N, (b) Bakun index at 39°N, (c) buoy wind at 36.8°N, and (d) wind at Point Arena (39.0°N), for lags resulting in highest regression coefficient. Regression parameters shown at bottom.

following sections, where Cd variations along the January and June 1992 transects are compared to Bakun indices and measured winds.

From the onset, *Bakun* [1973, 1975] recognized that atmospheric pressure distributions over the California Current system were poor indicators of meridional gradients in alongshore winds. The maximum in offshore Ekman transport during the upwelling season determined from ship reports is located near Cape Mendocino at 40°N (Figure 1b) and is broadly consistent with coastal Cd distributions in June 1992. The region of maximum upwelling determined from monthly Bakun indices since 1946, however, is located about 750 km farther south at 33°N. This is shown by the mean annual cycle of monthly Bakun indices between 21°N and 60°N (Figure 10a). Figure 11b shows that in June 1992, meridional gradients in daily Bakun indices between 36° and 45°N followed the long-term pattern and thus were inconsistent with the nearshore Cd maximum. *Bakun* [1973] attributes the discrepancy between pressure-derived winds and ship observations to the large distance separating offshore and onshore grid points used to calculate the upwelling index. The Bakun index does not take into account coastal mountain

ranges that reduce the atmospheric pressure gradient at the coast relative to the pressure difference between two grid points 300 km apart.

The pattern of alongshore winds measured near the coast in 1992 does not follow meridional Cd distributions more closely than the Bakun indices. Wind data for the periods December 1991-January 1992 and May-June 1992 from five locations along the transect are shown in Figures 11c and 11d. During the weeks preceding the January transect, alongshore winds were variable and generally downwelling-favorable at Point Arena (39.0°N), B22 (40.7°N), and B41 (47.4°N). Farther south at B42 (36.8°N) and B12 (37.4°N), winds were upwelling-favorable over the same period (Figure 11c). Comparison with the fairly uniform Cd distribution in January 1992 suggests that the composition of nearshore water is not very sensitive to alternating periods of downwelling-favorable and weakly upwelling-favorable winds. In contrast, alongshore winds were stronger and upwelling-favorable at all latitudes in June 1992 (Figure 11d). But there was no clear maximum in mean wind strength corresponding to the region of highest Cd concentrations. Alongshore winds at B42 (36.8°N) and B22 (40.7°N), for instance, were comparable in

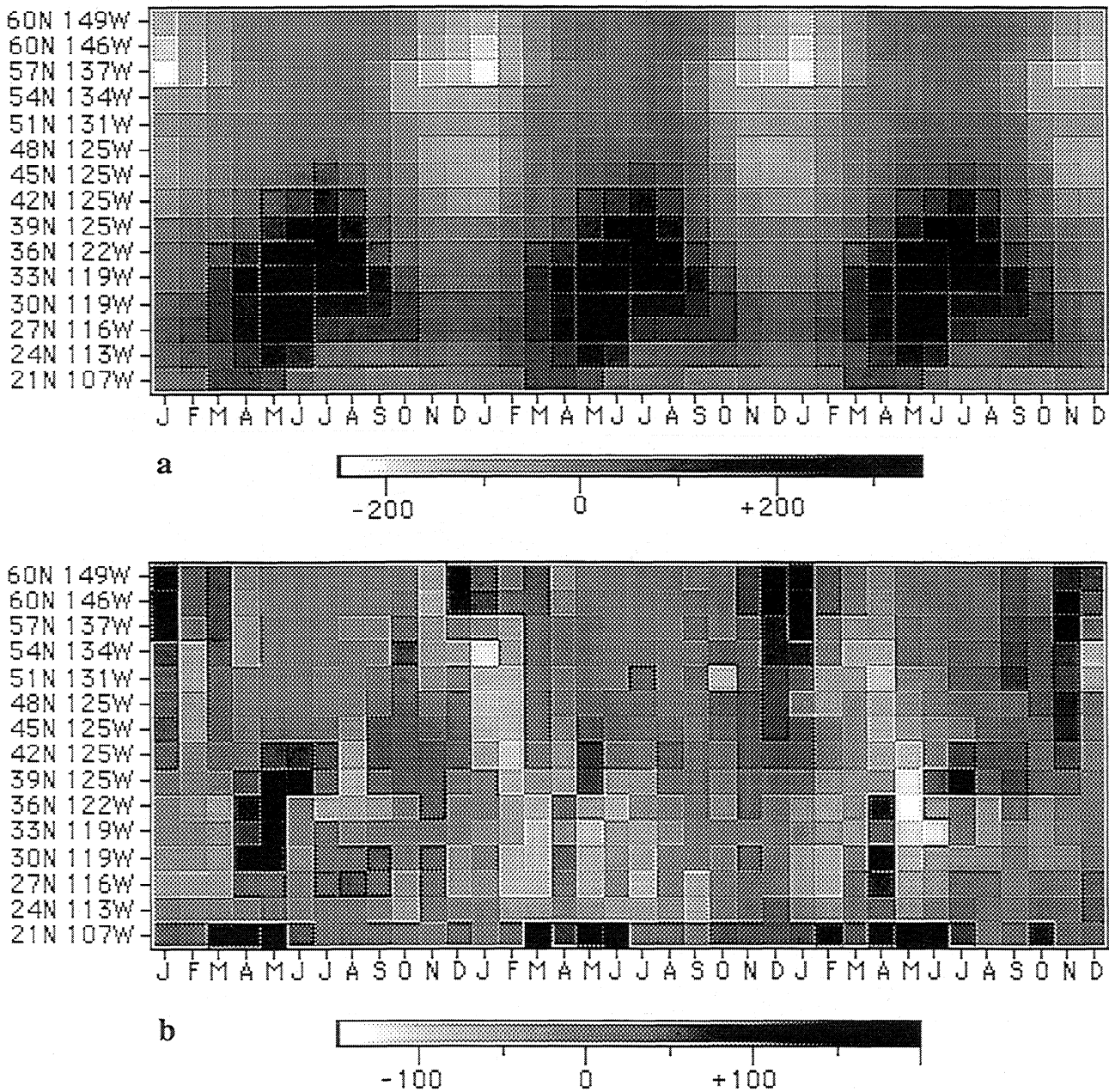


Figure 10. Comparison of 1991-1993 monthly Bakun indices with long-term mean. (a) The 1946-1993 mean of variations in monthly Bakun indices (cubic meter per second per 100 m coastline) as a function of latitude, repeated for 1991-1993. Darker shading corresponds to stronger upwelling. (b) Anomalies in monthly Bakun indices in 1991-1993 (cubic meter per second per 100 m coastline) relative to the long-term mean shown in Figure 10a.

strength throughout May-June 1992 (Figure 11d). It is worth noting that winds were measured on land at Point Arena (39.0° N) and therefore probably were weaker than offshore. Frictional effects may also explain why winds measured at Point Arena (39.0°N) were weaker than at B42 (36.8°N) over the whole 1991-1993 period (Figure 7b).

Neither Bakun indices nor nearshore winds are good predictors of meridional Cd gradients along the coast. Instead, upwelling tracer maxima along the June 1992 transect correspond more closely to the upwelling pattern obtained from long-term ship observations [Huyer, 1983]. The Bakun index at 36°N does rather closely follow variations in Cd concentrations at Pillar Point (37.5°N) over a 3-year period, however (Figure 7c). This suggests that a simple two-dimensional description of coastal upwelling across the shelf

may not be sufficient to explain the nearshore observations. One possible additional contribution is oceanic upwelling driven by the curl of the wind stress. From a recent recompilation of ship report data, *Bakun and Nelson* [1991] showed that there is a long-term maximum in equatorward winds about 200 km from the coast in the California Current system. The CODE program also demonstrated that offshore Ekman transport and alongshore winds increased with distance from the coast during the upwelling season south of Point Arena (39.0°N) [Lentz, 1987]. For lack of data, the effect of oceanic upwelling is hard to quantify during the period the coastal water samples were taken. A second possibility is that wind-driven oceanic circulation is inherently three-dimensional through interaction of alongshore flows with coastal topography and unstable meandering of equatorward

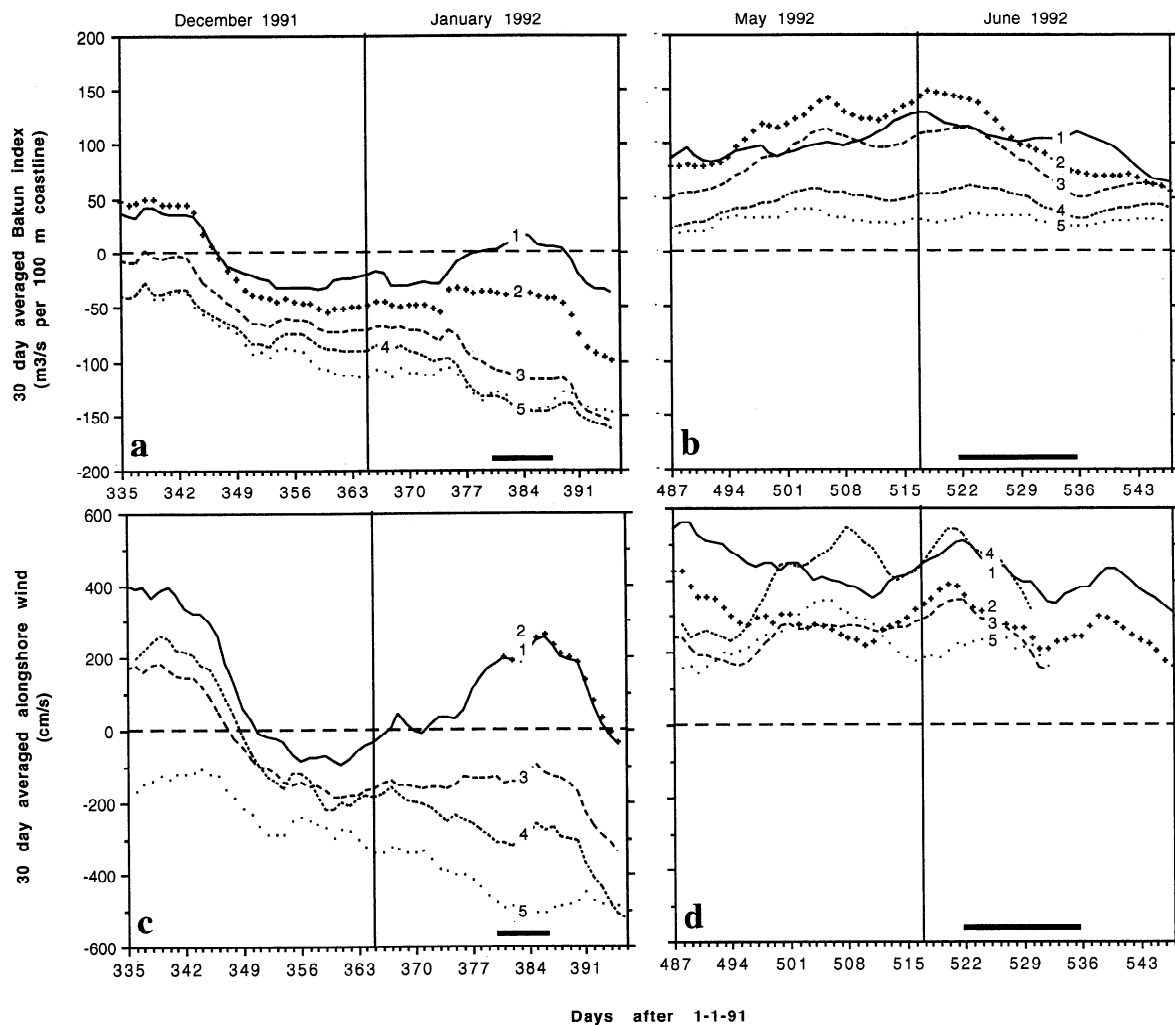


Figure 11. Measures of wind forcing during weeks preceding 1992 alongshore transects. Daily Bakun indices for (a) December and January 1992 and (b) May and June 1992, averaged with a 30-day running mean. Number labels correspond to (1) 36°N, (2) 39°N, (3) 42°N, (4) 45°N, (5) 48°N. Horizontal bars indicate period transect samples were collected. Measured alongshore winds for (c) December and January 1992 and (d) May and June 1992, averaged with a 30-day running mean. Number labels correspond to: (1) B42 at 36.8°N, (2) B12 at 37.4°N, (3) Point Arena lighthouse at 39.0°N, (4) B22 at 40.7°N, (5) B41 at 47.4°N. Horizontal bars indicate the period transect samples were collected.

jets separated from the coast. The Coastal Transition Zone (CTZ) program has shown that offshore transport of cold nutrient-rich water is typically concentrated in filaments extending from prominent capes along the coast [Chavez *et al.*, 1991]. Data from repeated transects, both alongshore and across the shelf, will be needed to evaluate this effect on nearshore water composition.

Long-Term Changes in Upwelling

Even though variations in the Bakun index with latitude are inconsistent with the distribution of Cd along the coast, the data collected between 1991 and 1993 can still be brought into perspective by looking at the distribution of monthly Bakun index anomalies. These anomalies calculated relative to the mean for 1948-1967 are shown in Figure 10b. The discussion focuses on the April-August upwelling season in the region between 27° and 42°N. Bakun index anomalies were positive throughout this region in April and May 1991. This suggests that coastal Cd concentrations probably were particularly elevated at the time over the whole length of the Oregon and California coast. In June and July 1991, anomalies remained

positive at 39° and 42°N but turned negative at the 36°N reference site for the Cd time series. Conditions at 36°N were still upwelling-favorable but less so than the long-term mean for this time of the year. In August 1991, anomalies turned negative over the whole region covered by the Bakun index north of 33°N. This broad pattern may be linked to the onset of the warm phase of the El Niño-Southern Oscillation at lower latitudes [Halpert *et al.*, 1994]. Throughout the 1992 upwelling season, Bakun indices were less upwelling favorable than the long-term average between 27° and 36°N. At 39° and 42°N, anomalies remained negative through June and July 1992. The pattern of anomalies suggests that Cd concentrations probably were lower than the long-term mean for this time of the year over the whole length of the transect in June 1992 (Figure 1c). In May and August 1992, however, anomalies at 39° and 42°N turned positive. As in 1991, Bakun index anomalies were of opposite sign during part of the upwelling season north and south of the region between 36° and 39°N in 1992. Comparison of the Cd time series with different measures of wind forcing suggested that variations in coastal water composition at Pillar Point (37.5°N) within this

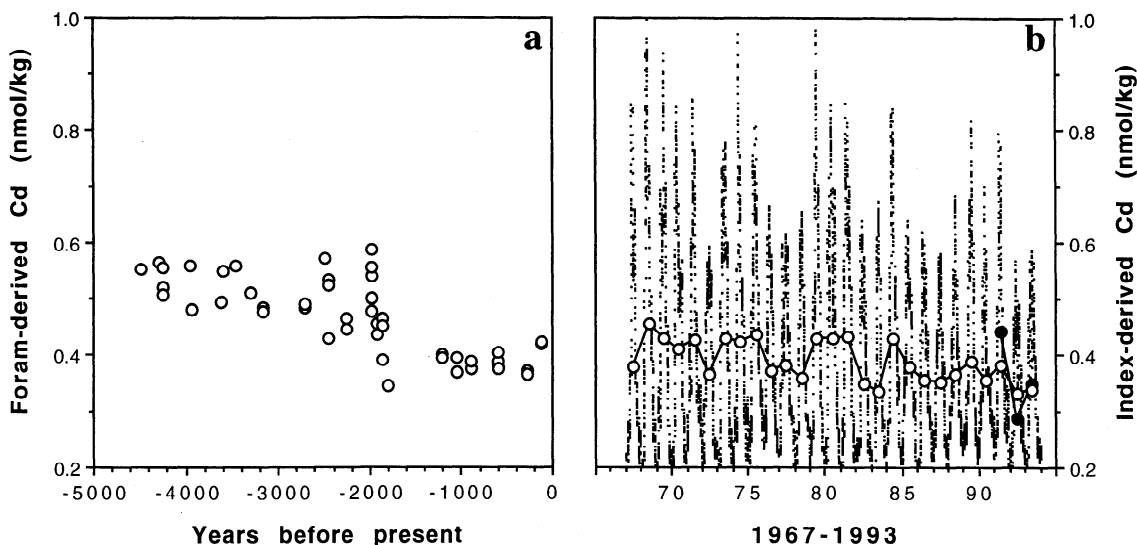


Figure 12. Long-term variations in upwelling inferred from coastal Cd. (a) Coastal Cd over the past 4500 years inferred from Cd/Ca ratios in foraminifera from San Francisco Bay. Cd/Ca data are from van Geen *et al.* [1992] and A. van Geen and S. N. Luoma (manuscript in preparation, 1995). Individual Cd/Ca determinations integrate coastal Cd variations over several decades. Better reproducibility over the 0- to 1000-year interval is due to a modification in the analytical procedure. (b) Daily coastal Cd concentrations (small dots) inferred from 1967-1993 record of daily Bakun index at 36°N filtered with 30-day running mean and polynomial relation in Figure 9a. Open circles show annual means in inferred coastal Cd concentrations. Solid circles show annual means of coastal Cd measured during 1991-1993.

transition zone were more closely related to atmospheric forcing from the south. The pattern of Bakun index was more complex in 1993. Upwelling was stronger than average in April 1993 south of 36°N and weaker than average at 39° and 42°N. Negative anomalies became more pronounced and expanded to the 27°-42°N range in May 1993 (Figure 10b). This period corresponds to a sharp drop in coastal Cd concentrations confirmed on two occasions at Pillar Point (37.5° N, Figure 2c) and to strongly downwelling-favorable winds measured at B42 (36.8° N). On this occasion the coastal response may have been in phase over most of the region covered by the Bakun index. Later in the upwelling season, generally positive anomalies at 39° and 42°N again contrasted with weaker than average upwelling to the south (Figure 10b). The 1991-1993 pattern of Bakun indices suggests that San Francisco Bay may mark a transition between upwelling regimes that are seasonally in phase but with anomalies relative to the long-term mean often in opposite phase.

This final section uses the relation between the Bakun index and coastal Cd to reinterpret a long-term change in upwelling intensity recorded by Cd/Ca ratios in 4500 year-old foraminifera [van Geen *et al.*, 1992]. The relation between coastal Cd concentrations and the filtered daily Bakun index at 36°N (Figure 9a) is first applied to the continuous record of Bakun indices since 1967 to estimate interannual variability over the past several decades. Results of this calculation in Figure 12b show the expected seasonal cycle in nearshore water composition repeated over 26 years. Extrapolation of the Cd-Bakun index relation back in time suggests that maximum Cd concentrations reached in 1991 (0.8 nmol/kg) were representative of about 9 other years since 1967. The data also suggest that Cd concentrations may have been even higher in 1968, 1969, 1974, and 1979 than in 1991. Conditions were comparable to 1992 and 1993 during 11 of the years covered by the record. El Niño conditions generally prevailed during these years of weaker upwelling, as indicated

by the El Niño-Southern Oscillation index [Ropelewski and Halpert, 1987]. To provide a perspective for coastal Cd variations over longer time scales, annually averaged Cd concentrations over the past 26 years were calculated from the daily values obtained from the Bakun index. Interannual variability derived in this manner ranges from 0.33 to 0.46 nmol/kg (Figure 12b). Annual means calculated from the Bakun index for 1991, 1992, and 1993 are 0.38, 0.33, and 0.34 nmol/kg, respectively. Actual annual means calculated by linear interpolation between measured Cd concentrations followed by averaging over each year vary over a considerably wider range, 0.44, 0.29, and 0.35. This suggests that annual means in coastal Cd since 1967 probably also varied over a wider range than shown in Figure 12b. Despite this limitation, the record of inferred Cd variations over the past 26 years provides a useful reference for long-term changes in coastal upwelling determined from the Cd content of calcitic foraminiferal shells from San Francisco Bay.

From the Cd content of *E. hannai* shells in a shallow core from Richardson Bay, an embayment near the mouth of San Francisco Bay, van Geen *et al.* [1992] concluded that prior to industrialization, dissolved Cd concentrations in the bay were comparable to levels in nearby coastal waters. Before interpreting the record of long-term change, the assumption that the Cd content of estuarine foraminifera reflects the composition of coastal water is examined more closely. In a new shallow core from Richardson Bay, Cd/Ca ratios in *E. hannai* were found to average 272 ± 13 nmol/mol ($n=14$) between 80 and 150 cm depth (A. van Geen and S. N. Luoma, manuscript in preparation, 1995). Each Cd/Ca determination requires 10-15 shells and is believed to integrate Cd concentrations over several decades due to sediment mixing in the estuary. The shells record estuarine water conditions between roughly 900 and 1800 AD based on the age of mollusc shell fragments from the same core radiocarbon dated by accelerator mass spectrometry. Radiocarbon ages were

corrected for the 680 year apparent age of nearshore water [Robinson, 1981] and secular variations in radiocarbon production [Stuiver *et al.*, 1986]. For comparison, Cd/Ca ratios in foraminifera collected from intertidal rocky pools at Pillar Point average 228 ± 13 nmol/mol ($n=25$) [van Geen *et al.*, 1992]. Several factors could explain slightly higher Cd/Ca values measured in preindustrial shells from Richardson Bay, assuming that mean upwelling conditions before industrialization were comparable to today. One possibility is that mean Cd concentrations in San Francisco Bay have always been higher than at Pillar Point (37.5°N) because coastal water contributing to the estuary originates from a region closer to the Cd maximum farther north (Figure 1c). While the persistence of this feature is not documented, the available data could accommodate a 20% reduction in mean coastal Cd between the mouth of San Francisco Bay (38.0°N) and Pillar Point (37.5°N). If this is the case, then past coastal Cd concentrations at Pillar Point inferred from Cd/Ca ratios in Richardson Bay should be reduced proportionately to correct for the difference in latitude relative to San Francisco Bay. Two other explanations for the offset between Pillar Point and San Francisco Bay would require a similar adjustment. One is that the lower salinity of the estuary perhaps increases the concentration of free Cd sufficiently to increase its incorporation into the shell. Alternatively, there may be a constant, relatively weak natural source of Cd to the water column within the estuary. The basic interpretation of the 4500-year record does not depend on a resolution of these issues.

Coastal Cd concentrations were calculated from foraminiferal Cd/Ca and corrected for the apparent offset between the coastal and the estuarine location (Figure 12a). The age model for the long core is based on radiocarbon-dated mollusc shells listed by van Geen *et al.*, [1992]. Better reproducibility of Cd/Ca determinations between 100-1000 years before present (B.P.) relative to the 2000- to 4500-year B.P. interval reflects recent improvements in the analytical procedure. Despite scatter in the older section it appears that mean nearshore Cd concentrations west of San Francisco Bay were significantly higher than today. The records suggest that average upwelling 2000-4500 years B.P. was comparable to the few years of strongest upwelling recorded over the past 26 years (Figure 12b). Stronger upwelling than today off California is consistent with colder water temperatures around the Channel Islands, 400 km southeast of San Francisco, determined from the oxygen isotopic composition of 5900-4500 year old mollusc shells [Glassow *et al.*, 1995]. One mechanism that could explain the apparent decline in upwelling over the past several thousand years is the orbitally-determined reduction in summer insolation relative to a maximum 9000 years B.P. [COHMAP Members, 1988]. According to this explanation, the data would suggest that a 3% reduction in summer insolation over the past 4500 years was sufficient to cause a significant reduction in the intensity of upwelling-favorable winds. The high sensitivity of atmospheric circulation to insolation is not the only possible explanation for the apparent reduction in upwelling. The response of coastal Cd concentrations over the past 26 years to the El Niño-Southern Oscillation inferred from the Bakun index record suggests an alternative mechanism. If El Niño years are excluded, the mean of coastal Cd concentrations between 1976 and 1993 increases significantly and approaches the level indicated by 2000- to 4500-year-old

foraminifera (Figure 12). This suggests that weaker upwelling off California today relative to 4500 B.P. could instead reflect an increase in the frequency of El Niño like conditions. The available pre-historic evidence of variations in the frequency and magnitude of the El Niño-Southern Oscillation is presently too ambiguous to distinguish between these two possible explanations for the decline in coastal upwelling off California [McGlone *et al.*, 1992].

Conclusions

Nearshore Cd, P, and Si concentrations between 36° and 41°N latitude unequivocally indicate the subsurface origin of nearshore waters of the California Current system during periods of intense upwelling. All three tracers indicate that coastal water sampled from the beach during the upwelling season originates from up to 300 m depth relative to a profile taken 200 km offshore. Cd appears to be a more consistent tracer of upwelling than Si and P, particularly during periods of weaker upwelling or downwelling. Transect samples collected in 1992 indicate a strong upwelling center near 39°N . The time series data show that maximum nearshore Cd concentrations reached during the upwelling season can vary within a twofold range from one year to the other. The available data suggest there is little variation in the composition of source waters at depth. The remarkable correlation between Cd at Pillar Point (37.5°N) and the Bakun index at 36°N over a 3-year sampling period suggests variations in the composition of nearshore water are driven by large-scale changes in wind forcing. The more ambiguous relations between north-south gradients in Cd, the Bakun index, and nearshore winds suggest other contributing factors such as oceanic upwelling and coastal topography. The Cd-Bakun index relation was used to infer annually averaged coastal Cd concentrations near Pillar Point (37.5°N) since 1967. The decrease in mean coastal Cd concentrations over the past 4500 years inferred from San Francisco Bay foraminifera underlines the sensitivity of the California Current system to climate change.

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