Bio-optical signatures and biogeochemistry from intense upwelling and relaxation in coastal California

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Abstract

The NSF-sponsored Coastal Ocean Processes Wind Events and Shelf Transport (WEST) experiment investigates the interplay between wind-driven transport and shelf productivity; while eastern boundary shelves are characterized by high productivity due to upward fluxes of nutrients into the euphotic zone, wind forcing also represents negative physical and biological controls via offshore transport and deep (light-limiting) mixing of primary producers. Although this interaction has been well documented for eastern boundary systems generally and for California specifically, one of the primary goals of WEST was to characterize more fully the interplay between positive and negative effects of wind stress, which result in the consistently elevated biological productivity in these shelf regions. During 3 month-long summer cruises (2000–2002) we observed extremes in upwelling/relaxation, using both in situ instrumentation and remotely sensed data. Relationships between optical and physical properties were examined, with emphasis on biogeochemical implications. During 2000, the WEST region was optically dominated by phytoplankton and covarying constituents. During 2001 and 2002, periods of more intense upwelling favorable winds, we observed a transition to optical properties dominated by detrital and inorganic materials. In all years, the continental shelf break provided a natural boundary between optically distinct shelf and open ocean waters. During 2002, we obtained discrete trace-metal measurements of particulate iron and aluminum; we develop a bio-optical proxy for acetic-acid leachable iron from backscatter and fluorescence, and demonstrate that particulate iron is not well correlated to traditional upwelling proxies such as macronutrients, temperature, and salinity. We conclude that the shelf break between ca. 100 and 200 m water depth serves as a natural break point between coastal and oceanic water masses in this region, and that the elevated biomass and productivity associated with this eastern boundary current regime is dominated by these iron rich, shallow shelf waters.

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1. Introduction

As part of the Coastal Ocean Processes (CoOP) program Wind Events and Shelf Transport (WEST), we have been combining satellite remote sensing with in situ observations to provide a mechanism for coupling the high temporal
resolution (mooring) and process-study (shipboard) efforts with a more synoptic view of the coastal ocean. The over-arching objective of this project is to examine critically productivity on wind-driven shelves. The shelf regions off northern California exhibit very strong wind forcing, with strong southward winds during the summer and reversing winds during the winter. During summer, maximum west coast winds are recorded in the vicinity of Bodega Bay (Dorman and Winant, 1995). Intriguingly, the same cross-shelf circulation that explains the high nutrient supply to the euphotic zone also leads to high offshore losses of plankton, while the vertical turbulent entrainment that enhances upward nutrient fluxes serves to mix phytoplankton to depths and reduces the average light level. As summarized in Largier et al. (2006), even though there have been numerous studies of physical oceanography over the northern California shelf (e.g., CODE, Beardsley and Lentz, 1987; Coastal Transition Zone (CTZ), Brink and Cowles, 1991; NCCCS, Largier et al., 1993; SMILE, Dever and Lentz, 1994), few studies have looked at the physical processes that result in enhanced or suppressed biological productivity (but see Wilkerson and Dugdale, 1987; Wing et al., 1995a, b, 1998). We expect that wind-driven shelf systems are most productive under specific conditions for wind strength and temporal variability, but it is not clear what, exactly, constitutes optimal physical conditions for biological productivity.

These spatial and temporal dynamics are further convoluted by the recognition that much of the California Current region, including the WEST site, are potentially iron limited (Hutchins et al., 1998; Bruland et al., 2001). Coastal California has previously been described as a “mosaic” of iron limitation, with constantly shifting boundaries of iron-replete and deplete waters (Hutchins et al., 1998). This mosaic also changes spatially and temporally, driven in large part by the availability of upwelling-favorable winds over a broad, sediment- (and iron-) rich continental shelf (Johnson et al., 1999, 2001; Bruland et al., 2001; Fitzwater et al., 2003). Although iron measurement techniques have improved rapidly, an ongoing issue in oceanography is the lack of robust and simple methods for determining the chemical composition of particles in seawater. This is further exacerbated by the difficulty, especially for coastal waters, of accurate assessment of anything other than chlorophyll and temperature using remote sensing.

The WEST region has been extensively studied in terms of physical hydrography (e.g., Beardsley and Lentz, 1987; Steger et al., 2000). Particular emphasis has been placed on the dynamic nature of these regions and the development of strong offshore flow of upwelled water (“plumes”), using both hydrographic and satellite observations for temperature and pigment fields (e.g., Abbott and Zion, 1987; Huyer and Kosro, 1987; Send et al., 1987; Rosenfeld et al., 1994; Thomas and Strub, 2001) as well as meroplankton (Wing et al., 1995a, b, 1998). Studies that employ bio-optical data or satellite radiometry are most applicable to Case-I waters dominated by the spectral characteristics of water, phytoplankton and the derivative products of phytoplankton (Morel and Prieur, 1977). Although this encompasses more than 80% of the world’s oceans (Morel, 1988), the coastal ocean is estimated to account for a disproportionate amount of production (20% of total oceanic primary production), despite accounting for just 7% of the surface area (Wollast, 1998). In particular, upwelling ecosystems along mid-latitude eastern boundaries of the ocean are well-known for wind forcing and high productivity at lower trophic levels, which account for a disproportionate amount of the annual primary and new production of the coastal margins (Jahnke et al., 1990; Walsh, 1991). A large fraction of this productivity is likely transported across the nearshore/offshore boundary, where it may impact significantly the global carbon budget and offshore biological processes (e.g., Pilskaln et al., 1996).

Biological turnover rates differ in frequency and temporally lag changes in the physical environment. This lag may be a function of one or several species-specific processes including somatic growth, demographics (i.e. reproduction and mortality), or kinematics (i.e. local convergence and divergence). The relative importance of biological and physical processes that influence distribution patterns of bio-optical and remotely sensed variables change across scale. The relationship of these physical processes, wind forcing in particular, and the responses of bio-optical properties such as light absorption, scattering, and attenuation, have been the focus of several recent programs on the east coast of the United States, such as the Coastal Mixing and Optics experiment (Dickey and Williams, 2001), and the Hyperspectral Coastal Ocean Dynamics Experiment (Chang et al., 2002). With the exception of the CTZ program (Brink and Cowles, 1991), and the recently completed Coastal Ocean Advances in Shelf...
there has not been a major emphasis on linking bio-optics with biogeochemical consequences on the west coast. Despite the inherent difficulties of utilizing optics and remote sensing in dynamic coastal waters, recent instrumentation and theoretical advances have allowed oceanographers to link physical processes with biogeochemistry by evaluating how the optical properties of the water column respond. Twardowski et al. (2001) and Boss et al. (2004) have demonstrated that inexpensive optical packages are capable of determining the in situ bulk composition of suspended material. Boss et al. (2001a) also have shown that the same instruments can be used to infer the bulk size class of suspended matter. In combination with semi-analytical remote sensing models (e.g., Maritorena et al., 2001) and algorithms for determination of specific classes of compounds (for example, colored dissolved organic matter, CDOM; Kudela and Chavez, 2004; particulate organic carbon, POC; Stramski et al., 1999) we now possess the necessary tools to link in situ and remotely sensed bio-optical parameters to biogeochemistry.

In this contribution, we characterize the spatial and temporal variability in bio-optical properties for the WEST region, with the goal of identifying bio-optical signatures that may be useful for determining the fate and transport of coastal productivity. Specifically, this paper is divided into three components. First, we describe the spatial and temporal characteristics of the bio-optical properties for the WEST region, emphasizing ocean-color products (absorption, attenuation, scattering, pigments). Second, we develop a new proxy for potentially bio-available iron, using backscatter and fluorescence. Finally, we explore the potential linkages between physical forcing, nutrient availability, and phytoplankton biomass and productivity in response to the variable upwelling encountered during summer 2000, 2001, and 2002.

2. Data and methods

2.1. Study site

The WEST program was located in central California at approximately 38°N, 123°W (Fig. 1). The data presented here were collected aboard the R/V Point Sur during 2000 (June 1–30), 2001 (May 17–June 15), and 2002 (May 30–June 28). Sampling alternated between large-scale surveys typically conducted at the beginning, middle, and end of the field programs which covered the furthest northern, southern, and offshore extent of the study site (Lines A, D, F in Fig. 1), small-scale surveys which focused on stations around Line D, and time-series measurements conducted at the central mooring and in Drake’s Bay (south of Point Reyes) during inclement weather. At each station, vertical profiles (0–200 m or to within 10 m of the bottom) of optical properties were conducted with an instrumented rosette and tethered optical instruments.

2.2. Mooring data

Meteorological time series were acquired from NDBC 46013 directly offshore of the WEST study site. For this contribution we analyzed the surface wind vector data and the thermistor data to provide temporal context to our analyses. Data were low-pass filtered (36 h) to remove the strong tidal signature. Wind vectors were rotated to the major alongshore axis of the coastline (35° from true north).

2.3. Optical measurements

2.3.1. Hydroscat-6 (HS-6, HOBI Labs)

The particulate backscattering coefficient ($b_b(\lambda)$, m$^{-1}$) was estimated using an HS-6, which measures scattering at a single, fixed angle in the backward direction (140°) at six wavelengths: 442, 488, 532, 589, 620, and 671 nm (Maffione and Dana, 1997). The 671 nm channel can be configured to collect fluorescence data, using the 442 nm light source as an excitation wavelength and alternately collecting fluorescence and backscatter data at 671 nm. This provides near-simultaneous estimates of fluorescence and backscatter from the same instrument; this configuration was used for all deployments. Because the 671 nm detector is sensitive to chlorophyll fluorescence (including solar-stimulated fluorescence), the backscatter data from this channel are questionable in high biomass waters. Therefore, we did not use $b_b(671)$ for this study.

Data were processed as follows: HOBI Labs software provides $b_b(\lambda)$ after application of calibration coefficients obtained using a Lambertian reflecting plaque (Maffione and Dana, 1997). Calibrations were conducted annually, typically prior to the field season. HOBI Labs HydroSoft software was then used to correct the calibrated files.
for scattering by water (Morel, 1974) and for loss of photons along the optical pathlength, which can occur in turbid waters (so-called sigma correction). Default values for this correction were used, since we did not routinely have spectral estimates of absorption \((a, \text{ m}^{-1})\) and attenuation \((c, \text{ m}^{-1})\). Boss et al. (2004) used a slightly different correction scheme (more rigorous, since they had access to spectral \(a\) and \(c\) data), but estimated that the overall error due to the corrections and variability between three different backscatter sensors of different design was on the order of \(\pm 10\%\). The HS-6 was mounted in the bottom of an instrumented CTD rosette for deployment, facing downward with a clear-water path.

2.3.2. Beam transmission

Beam attenuation coefficients were measured using a WETLabs 25-cm pathlength transmissometer (660 nm) mounted next to the HS-6 on the rosette. The beam attenuation coefficient is the sum of particle \((c_p)\), colored dissolved material \((c_{CDOM})\), and water \((c_w)\) attenuation. The CDOM signal was negligible at 660 nm for this study site, and can be
removed from the equation. Particle attenuation was therefore calculated as
\[ c_p = c - c_w, \]  
(1)
where \( c_w \) was set to a value of 0.364 m\(^{-1}\).

2.3.3. Fluorescence and chlorophyll

Fluorescence measurements in addition to the HS-6 data were collected using a WETLabs WETStar fluorometer on the CTD rosette, with a second WETStar deployed on a ScanFish towed vehicle. Water samples were processed aboard ship for chlorophyll \( a \) (Chl \( a \)) following EPA Method 445 (non-acidification technique) by collecting the particulate material from 125 ml of seawater on Whatman glass fiber filters (GF/F) filters, extracting in 90% acetone, and measuring on a Turner Designs TD-700 calibrated with purified Chl \( a \) (Sigma Chemical Co.). In situ fluorescence measurements were converted from engineering units (volts) for the CTD casts (Fig. 9) but were not converted from underway mapping data (Fig. 3) because of the substantial scatter in calibration factors compared to the extracted chlorophyll data, attributable to a variety of photochemical and non-photochemical quenching effects from near-surface waters (e.g., Cullen and Lewis, 1995). At select stations, discrete water samples were collected, and variable fluorescence was determined after ca. 30 min dark adaptation at ambient surface water temperatures by measuring raw fluorescence \( (F_o) \), followed by maximal fluorescence \( (F_m) \) in the presence of DCMU. Filtered seawater (0.2 \( \mu \)m) from the same sample, with and without DCMU, was used to blank correct the values. Variable fluorescence \( (F_v/F_m) \) was calculated as
\[ F_v/F_m = (F_m - F_o)/F_m. \]  
(2)

2.4. Absorption spectra

Ancillary bottle measurements were collected using a conductivity-temperature-depth profiler/rosette system (equipped with silicone o-rings and silicone tubing for the internal spring). Absorption coefficients for particulate \( (a_p) \) spectra were determined using a Cary 50 dual-beam spectrophotometer. Water samples (100–1000 ml) were filtered under low vacuum (less than 50 mmHg) onto Whatman GF/F filters, and stored in liquid nitrogen until processing. Total \( (a_p) \) spectra were determined following the filter pad technique (Mitchell and Kiefer, 1988) with a pathlength amplification correction applied as described by Cleveland and Weidemann (1993). Total absorption was partitioned into phytoplankton \( (a_{ph}) \) and detrital \( (a_d) \) components following the methods of Tassan and Ferrari (1995). Dissolved absorption spectra \( (a_g, CDOM) \) also were determined using a Cary 50 dual-beam spectrophotometer as described in Kudela and Chavez (2004). Samples were filtered and kept in the dark (refrigerated) until processing, within ca. 12 h of collection aboard ship. Dissolved spectra were fitted to a single exponential model from 350–600 nm after normalization to 650–700 nm, from which the spectral slope \( (s) \) and absorption at 412 nm \( (a_{412}) \) was determined (Twardowski et al., 2004).

2.5. Trace metals

During the 2002 cruise, particulate iron and aluminum samples were collected at select stations \( (n = 10) \). Stations ranged from nearshore (less than 25 m depth) to past the shelf-break (3000 m depth) as shown in Fig. 1. Water samples were typically collected using Niskin bottle water samples from near-surface (0–5 m) with three samples from depth (25, 100, 125 m). A trace-metal-clean filter apparatus was employed, and reasonable, but not trace-metal-clean, precautions were taken to avoid accidental contamination. Samples were stored frozen and processed in the laboratory for acetic-acid leachable (HAc) iron and aluminum, and total (refractory) iron and aluminum, following the methods as outlined by Bruland et al. (2001) and Landing and Bruland (1987).

Acetic acid leachable particulate iron is similar to the “dissolvable” iron measured by other investigators (e.g., Johnson et al., 1999, 2001; Chase et al., 2002) and accounts for approximately 80% of dissolvable (leachable particulate and dissolved) iron in coastal waters (Bruland et al., 2001). Using the relationship from Bruland et al. (2001; their Fig. 8) for the same region and similar time periods, we can approximately correlate our HAc Fe values to labile dissolved Fe by dividing by a factor of 3.9.

2.6. Ancillary measurements

Water collected from the instrument rosette also was sampled for several other parameters at select stations. Nutrients were frozen for later analy-
sis following standard colorimetric methods for nitrate + nitrite, silicate, and phosphate. Total suspended solids were measured using pre-combusted, tared GF/F filters, and partitioned into organic and combustible components by combustion at 450 °C for 4 h. Biogenic and lithogenic silica were estimated following the methods of Brzezinski and Nelson (1995).

Temperature and salinity data were acquired with a SeaBird 911 + CTD using vertical rosette profiles from the ship, and undulating towed vehicle profiles from the ScanFish. Data were binned to 1-m intervals after discarding the up cast, following standard oceanographic methods. For analysis purposes HS-6 data were also binned to 1-m intervals, but the entire profile (down and up) was typically used to increase the vertical resolution of the data.

2.7. Satellite data

Ocean-color Sea-Viewing Wide Field Sensor (SeaWiFS) data were obtained from the Monterey Bay Aquarium Research Institute HRPT station. SeaWiFS data were processed with SeaDAS version 4.5 software (Baith et al., 2001) using the NASA Goddard Distributed Active Archive Center (Goddard-DAAC) standard settings for atmospheric correction, with best available ancillary satellite data (also from the DAAC). Chlorophyll was estimated using the OC4v4 algorithm (O’Reilly et al., 2000).

Sea-surface temperature (SST) was estimated using the multi-channel sea-surface temperature (MC SST) algorithm (McClain et al., 1985), applied to Advanced Very High Resolution Radiometer (AVHRR) data obtained from the NOAA Coastal-Watch West Coast Regional Node. The standard cloud mask was used. Satellite data were spatially projected to maintain maximum spatial resolution (ca. 1.1-km pixel resolution at nadir). For time-averaged composites of satellite data (Fig. 5), images were created by calculating the median (SST) or geometric mean (chlorophyll) value at each pixel from all available daily imagery for each cruise. The use of a median value for SST composites was chosen because it is less influenced by extreme values caused by cloud contamination; similarly, a geometric mean was used for chlorophyll because it is less biased than an arithmetic mean for log-normally distributed data such as chlorophyll (Campbell, 1995).

To determine the relationship between bio-optics and bathymetry, SeaWiFS chlorophyll was used as a proxy for bio-optical variability. Daily imagery for year day 90–200 (April to mid-July) from 2000 to 2003 was used to identify the location of frontal boundaries by analyzing the data along hydrographic lines A, D, and F (Fig. 1) and using the “gradient.m” function in Matlab to identify the first sharp boundary features moving offshore. Briefly, the gradient routine calculates the slope (change in chlorophyll with distance) for the data; we assumed that a sharp (>0.5 mg Chl m⁻³ between adjacent pixels) drop in chlorophyll was indicative of a bio-optical front. The data were visually examined to confirm front locations by discarding frontal locations that occurred due to noisy data (a sharp decrease in chlorophyll at adjacent pixels that was not part of a visually confirmed front). Partially cloudy images also were discarded manually if the front could not be identified visually. The locations of the chlorophyll fronts were then binned to 50-m intervals in bathymetry using National Geophysical Data Center coastal relief bathymetry data with 3-s spatial resolution. Data are presented in Fig. 6.

3. Results

3.1. Interannual wind forcing and physical setting

A detailed analysis of the physical and chemical hydrography is presented elsewhere in this special issue, and is briefly provided here as context for the bio-optical measurements. Largier et al. (1993) described the seasonal forcing of this region as dominated by upwelling (April–July), relaxation (August–November), and storms (December–March). The entire region is embedded in the California Current System, delineated to the west (offshore) by a coastal jet (e.g., Huyer, 1983). Wind vector (Fig. 2) and temperature time series (not shown) demonstrate the strongly wind-forced nature of the system, consistent with the expected dominance of upwelling-favorable winds. During the three summer deployments, winds were predominately out of the northwest and water temperature lagging the onset of alongshore wind forcing by hours to days. The year 2000 exhibited a more “pulsed” system, with alternating upwelling and relaxation events, while 2001 and 2002 demonstrated nearly constant upwelling-favorable winds with fewer relaxations in the alongshore (upwelling favorable) component of the wind. Using the
The criteria of Roughan et al. (2006), i.e. “upwelling” is when 36-h low-pass winds exceed $5 \text{ m s}^{-1}$ equatorward, we calculated that the 2000 field season had seven transitions from upwelling to relaxation or vice versa (wind speeds crossed the $5 \text{ m s}^{-1}$ value), which corresponded to approximately 11 days of upwelling during the cruise period. There were five transitions in 2001, but approximately 21 days were upwelling favorable. Finally, 2002 had four transitions, with about 22 days of upwelling favorable winds. Years 2001 and 2002 also had upwelling events as long as 10 days in both years, versus a few days of upwelling punctuated by relaxation in 2000 (Fig. 2).

The physical environment within the WEST region exhibited similar variability to the interannual wind forcing. During 2000, there was intrusion of warm, lower-salinity waters from offshore, reducing the average surface salinity (measured from the underway shipboard mapping system) when compared to 2001 and 2002 (33.4 versus 33.8, Table 1) and increasing the scatter in observed values (Fig. 3). There was a corresponding increase in average surface temperature (Fig. 4). Surface temperature and salinity within the WEST region (shipboard transects) ranged from ca. 7.7 to 17.0°C and 32 to 34.6, respectively.

Surface mixed-layer depth (MLD; calculated as the depth where there was $0.1^\circ \text{Cm}^{-1}$ change in vertical temperature) along the D-line was shallow nearshore (ca. 5 m) during 2000, and tended to deepen offshore to ca. 25 m at a distance of 45–50 km; MLD was variable but similar in depth throughout the cruise period. During 2001, the MLD was initially shallow across the entire D-line (<5 m), and deepened fairly uniformly with time to about 20 m. The year 2002 demonstrated the most variability. At the beginning of the cruise period MLD was <5 m nearshore deepening to 25 m offshore, with excursions to >50 m ca. 35 km offshore, coincident with a sharp density front (Fig. 4) and the formation of an offshore-propagating filament observed from satellite imagery. As the cruise progressed, the MLD deepened considerably from 30 km offshore and shoreward to 40–50 m, with similar deepening offshore (>60 km). By the end of the cruise period, MLD had shoaled across the entire transect to ca. 5 m, with some excursions
to 25 m approximately 15–25 km offshore, again associated with frontal features.

3.2. Satellite-derived chlorophyll and SST

During all 3 years, chlorophyll and fluorescence was largely constrained to the MLD, although subsurface features associated with filaments from further north (Fig. 4I) were occasionally apparent in the data. Biomass was always highest from the shelf break shoreward, consistent with the patterns from a much longer time series reported by Thomas and Strub (2001). Spatially, the variability induced by the formation of offshore propagating filaments associated with coastal morphology and bathymetry is evident. Steger et al. (2000) described the Gulf of the Farallones, immediately south of the WEST region, as an area of reduced alongshore wind stress, enhanced mixing, and longer residence times relative to the region immediately north of Point Reyes. Satellite observations from 2000, 2001, and 2002 are consistent with this pattern, showing this region to be consistently warmer and enriched in biomass (Fig. 5; see also Vander Woude et al., 2006). There is also a persistent offshore chlorophyll feature southwest of Point Reyes.

Across all three seasons, there is elevated chlorophyll and SST immediately north of Point Reyes, within roughly the 100 m isobath. Relaxation events can result in significant poleward transport nearshore (e.g., Send et al., 1987), while the Gulf circulation has a distinct, aseasonal northward component (Steger et al., 2000), likely resulting in the observed patterns of enhanced chlorophyll and SST in these regions. Moving offshore, there was a distinct thermal and biomass boundary between coastal upwelled waters on the shelf and the California Current; this frontal system was most intense in 2000, coincident with the weaker upwelling winds and more frequent relaxations, with cold (<11 °C) waters extending further offshore in 2001 and 2002. Latitudinally, colder waters associated with upwelling are apparent south of Pt Arena, with a broadening of the upwelling plume southward in the monthly median images.

Differences in chlorophyll patterns across years were less evident than for SST, with the distinctive fronts between coastal upwelled water and offshore California Current water seen in the SST less apparent in chlorophyll fields. Although there was substantial variability, the primary coastal front was generally well correlated with bathymetry (Fig. 6). The boundary between high-chlorophyll waters over the shelf and offshore waters was nearly always on the shelf (less than 200 m water depth), although there was a tendency for a secondary peak in offshore fronts (deeper than 350 m water depth) especially at the northern boundary of the WEST study site, which appeared to be associated with upwelling filaments formed off the headlands to the north. Consistent with the broadening of upwelling plumes to the south in the SST imagery, the chlorophyll front frequency generally peaked at shallower depths in the southern region of the WEST study area where the shelf widened, and were further offshore at the central and northern hydrographic lines (Fig. 6).

Underway fluorescence data plotted in T–S space (Fig. 3) were distinctly different between years. During 2000, maximum fluorescence was associated with cool, saline waters, indicative of aging upwelled coastal water. During 2001, maximum

| Table 1 |
| Select physical, chemical, and optical properties observed during 2000, 2001, and 2002 |
|          | 2000       | 2001       | 2002       |
| Temperature, °C | 11.30 (1.85), 192 | 10.15 (0.85), 155 | 9.61 (1.19), 64 |
| Salinity      | 33.62 (0.33), 192 | 33.87 (0.12), 155 | 33.89 (0.23), 64 |
| NO3 + NO2, µM | 11.69 (10.39), 183 | 18.43 (9.20), 109 | 22.18 (11.32). 69 |
| SiO4, µM      | 16.31 (13.21), 183 | 22.48 (15.64), 109 | 33.07 (15.90), 69 |
| a(412), m−1   | 0.495 (0.512), 212 | 0.115 (0.088), 73 | 0.089 (0.056), 125 |
| aQ(412), m−1  | 0.380 (0.492), 212 | 0.066 (0.065), 73 | 0.059 (0.229), 125 |
| aQ(412), m−1  | 0.114 (0.116), 212 | 0.049 (0.027), 73 | 0.030 (0.017), 125 |
| aQ(412), m−1  | 0.003 (0.003), 125 | 0.079 (0.035), 63 | 0.304 (0.262), 25 |

Values indicated are means, standard deviation in parentheses, and number of samples. Physical and chemical properties (first four rows) represent all available surface samples collected from the CTD casts. Chl a values are from matching absorption spectra samples. Absorption values represent the mean value from all depths (<100 m) and stations.
fluorescence was constrained to waters of about 12°C and 33.8, suggesting bloom formation as upwelled water warmed but did not mix with lower-salinity source water. In 2002, there is a pronounced maximum in the coldest upwelled source water, with a high fluorescence feature extending into warmer, less saline T–S space. When mapped spatially (not shown), this ‘V’ pattern is found to be associated with a cross-shelf gradient in temperature and salinity source water. In 2002, there is a pronounced maximum in the coldest upwelled source water, with a high fluorescence feature extending into warmer, less saline T–S space. When mapped spatially (not shown), this ‘V’ pattern is found to be associated with a cross-shelf gradient in temperature and salinity, suggesting that these high fluorescence waters were advecting and mixing offshore.

3.3. Optical properties

Water-column bio-optical properties were also strongly influenced by upwelling conditions, but were dominated by particles, with a relatively minor contribution from colored dissolved organic material in 2000 (Fig. 7). In contrast, CDOM became progressively more important as particulate absorption declined in 2001 and 2002, associated with increasing wind stress from 2000 to 2002. CDOM values were consistent with previously reported values for the west coast, with a spectral slope of 0.0155 (±0.006, n = 213) versus 0.0173 for surface values from the same region during winter (Kudela and Chavez, 2004), and 0.0185 for the CalCOFI dataset (Kahru and Mitchell, 2001). Although the spectral slope is lower than that previously reported, this can be dependent on how the slope is estimated, and the range (0.009–0.027 m⁻¹) is well within the range for other regions worldwide (Twardowski et al., 2004).

CDOM can often exhibit strong relationships to salinity if the regional source is riverine (Boss et al., 2001b), and significant relationships were found between runoff and CDOM for this region (Kudela and Chavez, 2004). During this period, when terrestrial input is expected to be at a minimum, we found very little variation the spectral slope between the three cruise periods (ANOVA, p = 0.46). The spectral slope and \( a_g \) values were weakly related to chlorophyll, with a tendency towards lower \( a_g \) values and higher spectral slopes as chlorophyll decreased. Similarly, there was a weak but statistically insignificant relationship between decreasing salinity and increasing \( a_g \) values (\( r^2 = 0.12 \)); this is not unexpected, however, given that the salinity range observed during this study was from 32.5 to 34.2.

We did not routinely conduct vertical profiles for CDOM, and we have insufficient vertical resolution.
to assess whether the benthos is a significant source of CDOM for the region, as has been reported for upwelled and/or coastal waters (Boss et al., 2001b; Twardowski and Donaghay, 2001; Twardowski et al., 2004). Where vertical profiles were taken, however, CDOM concentrations generally increased with depth, while spectral slopes decreased with depth, although not more than the range of surface variability observed from spatially close (few km) sampling within the same water mass as determined by temperature and salinity. Values for this study ranged from 0.002 to 0.971 m$^{-1}$ (a$\alpha_412$), with lowest values in 2000 (median = 0.026, 2000; 0.068, 2001; 0.214 m$^{-1}$, 2002). As expected (Kahru and Mitchell, 2001), values were consistently highest at the nearshore (< 25 m depth) stations both within a season and between years, and decreased offshore of the shelf break (Fig. 7).

In contrast to dissolved spectra, the particulate fraction showed pronounced variability both within and between cruises (Fig. 7). Absorption spectra were ca. five times higher on average during 2000 as compared to 2001 and 2002, consistent with the higher average chlorophyll concentration during 2000 of 5.29 (6.07) mg Chl m$^{-3}$ versus 1.98 (1.99) and 1.42 (1.44) for 2001 and 2002 (mean ± SD). Detrital absorption was a much larger fraction of $a_p$ during 2001 and 2002 when compared to 2000 as well. To determine within-cruise variability, the particulate absorption spectra were further divided into shallow (0–10 m), deep (greater than 10 m), inshore (less than 10 km from shore, over the shelf), and offshore (greater than 30 km from shore, past the shelf break) spectra. Within each cruise, there was a general pattern of highest particulate absorption nearshore, with deep and offshore waters similar in spectral shape and absolute values. The exception to this pattern was the offshore 2002 absorption spectra, which exhibited very little detrital absorption relative to $a_{ph}$, higher $a_{ph}$ values than any other grouping from 2002, and pronounced accessory pigment peaks between 450 and 500 nm. However, this grouping should be interpreted with caution, since only nine spectra were used due to the difficulty of getting offshore during that year.

Particulate backscatter values exhibited a reasonably wide dynamic range, ranging from 0.0015 m$^{-1}$ ($b_h$620) to 0.35 m$^{-1}$ ($b_h$442). This range is similar to values reported for a coastal upwelling site off the Mid-Atlantic Bight, where Boss et al. (2004) reported an estimated accuracy from similar instrumentation as 0.003 m$^{-1}$, with uncertainties on the order of 10%. Our lowest readings (ca. 0.0015 m$^{-1}$) are also similar to the value of 0.0016 m$^{-1}$ reported by Petzold (1972) for clear ocean waters. It is unlikely that our offshore coastal stations were that clear, but if we assume a 10%
Fig. 5. Median sea-surface temperature (°C; top row) and standard deviation (second row), geometric mean chlorophyll (mg Chl m⁻³; third row) and standard deviation (fourth row) for each cruise period from 2000, 2001, and 2002 are presented (the time period used is indicated by the gray shading in Fig. 2). Means and medians were created by compositing daily imagery for the length of each cruise period, ca. 30 days; SST data are from the NOAA CoastWatch program; chlorophyll data are from the NASA Goddard Distributed Active Archive Center (DAAC). Bathymetric contour lines for 100, 200, and 1000 m are overlayed for reference.
error, the observed range is reasonable. Given the large dynamic range observed relative to the expected accuracy of the instrumentation, we are reasonably confident in the spatial and temporal patterns observed for our study site. Generally, as with CDOM and absorption spectra, there was a trend of decreasing spectral backscatter values moving from onshore to offshore (not shown).

Of more interest than the onshore–offshore gradient in backscatter were the smaller scale vertical and temporal dynamics. In shallow waters (less than ca. 25 m depth) during strong upwelling favorable wind events, backscatter was essentially uniform throughout the water column (Fig. 8), with values typically near the upper end of the observed dynamic range. During these periods, fluorescence was low. Inorganic sediment has a much higher index of refraction than organic (phytoplankton) material, resulting in much higher backscatter values than for phytoplankton (Stramski et al., 2004; Twardowski et al., 2004). These uniform backscatter profiles are indicative of periods when the surface mixed layer and bottom mixed layer merged, resulting in an essentially homogeneous water column in terms of optical properties. Further offshore in deeper waters and during periods of less intense wind forcing, vertical profiles exhibited a typically three-layer system, with the surface dominated by elevated fluorescence and moderately high backscatter values (phytoplankton), a layer below the MLD with a minimum in fluorescence and backscatter, and a deep bottom mixed layer with increased backscatter due to resuspended sediment. These patterns are similar to what has been observed in other regions using beam transmission (Gardner et al., 2001) and backscatter (Boss et al., 2004), although it is important to note that backscatter often identifies layers not seen in beam transmission values, due to the differing sensitivities of backscatter and beam attenuation (Boss et al., 2004).

To isolate the effects of inorganic versus organic material on the backscatter patterns, backscatter values were normalized to fluorescence obtained from the HS-6 as described in the methods. A representative time-series collected from an inshore station (ca. 100 m bottom depth) of this ratio is provided in Fig. 8, obtained during a period ranging from upwelling-favorable to relaxation-favorable wind forcing. As has been reported for other sites (Wu et al., 1994; Chang and Dickey, 2001), we found that particulate backscatter (or attenuation using the beam transmissometer) versus fluorescence provided an excellent indicator of upwelling intensity, with a characteristic boomerang-shaped pattern (Fig. 9). During strong upwelling, backscatter is elevated and fluorescence is low, indicative of inorganic particle dominance of the optical signature. As upwelling favorable winds relax and a phytoplankton bloom initiates, $b_{488}/fl_{671}$ reaches a minimum inflection point, followed by a steady increase, as the ratio of inorganic to organic particles changes.

Using all available CTD casts, similar ‘boomerang’ patterns were obtained for property–property plots of beam transmission versus chlorophyll derived from fluorescence (Fig. 9). The relationship was essentially linear for 2000, when the bio-optical properties of the water column were largely dominated by pigmented particles (see Fig. 7), with a small fraction of the data exhibiting a low fluorescence, high attenuation relationship indicative of inorganic or detrital material (Chang and Dickey, 2001; Gardner et al., 2001). During 2001 and 2002, there was a more pronounced contribution of detrital/inorganic material, with a pronounced boomerang pattern similar to that observed temporally in the $b_{488}/fl_{671}$ relationship during 2002.

![Fig. 6. Daily SeaWiFS imagery was used to identify the primary bio-optical front at hydrographic lines A, D, and F for year days 90–200, 2000–2003, as described in the text. The location of the fronts was then binned to the corresponding bathymetric depth using data from FGDC and plotted, showing front frequency versus binned water depth.](image-url)
Fig. 7. Particulate absorption spectra partitioned into total ($a_p$), phytoplankton ($a_{ph}$), and detrital ($a_d$) components, and colored dissolved organic matter spectra ($a_g$, dashed line). All data are in inverse meters. Mean values for each cruise period during 2000 (panel A), 2001 (B), and 2002 (C) are further partitioned into 0–10 m depth (D–F), greater than 10 m depth (G–I), nearshore (J–L), and offshore (M–O) components. Note that the ordinate axis for 2000 is greater than for 2001 or 2002, and that $a_g$ in 2002 could not be partitioned by depth (all samples were from 5 m). For panels C, L, and O, $a_g$ is plotted on a separate $y$-axis (right) due to the disparate absorption values for particulate and dissolved matter in that year.
Fig. 8. Representative plots of particulate backscatter ($b_b (\lambda)$, m$^{-1}$) are plotted from Spring 2000. At top, temperature from mooring D-090 (located at the “TS” station in Fig. 1) is provided for reference. The triangles (left ordinate) indicate thermistor depths; the solid near-surface and near-bottom lines indicate the thermocline and bottom boundary layer boundaries. The solid vertical lines indicating the sampling periods utilized in Panels C and D. Panel A: vertical profile from Station D2 (the “TS” station) during a relaxation period showing a three-layer system, with the surface dominated by phytoplankton, an optically clear middle layer, and a deep layer dominated by resuspended sediment. Note the “crossover” of $b_b(671)$ in the surface layer, caused by stray light contamination from phytoplankton fluorescence. Panel B: vertical profile from Station D1 (inshore of D2) during intense upwelling; Panels C, D: time-series of near-surface (0–5 m) backscatter versus fluorescence showing the characteristic boomerang pattern using profiles from D2 collected from hydrographic casts; superimposed on panel D are indications of the oceanographic conditions associated with the development of the boomerang pattern. Upwelling exhibits low fluorescence but high backscatter, while a relaxation event results in initially low backscatter (loss of inorganic particles) followed by increasing fluorescence and scatter as the phytoplankton assemblage blooms. Similar patterns were observed over the shelf (< 100 m depth) during other time periods and cruises. For panels A–B, the colors indicate the wavelength from the HS-6 meter (442, 488, 532, 589, 620, and 671 nm correspond to dark blue, blue, green, yellow, orange, red, black). For panels C–D, the different symbols denote the discrete hydrographic casts.
3.4. Trace metals

Although only 10 samples were obtained during the 2002 cruise, the range of HAc and refractory Fe and Al spanned a large fraction of previously observed dynamic range for these metals in coastal waters, with values from 0.2–121.6, 0.4 to 146.0, 4.2 to 688.6, and 38.2 to 2744.5 nM for HAc Fe and Al, and refractory Fe and Al, respectively (Fig. 10). In comparison, Bruland et al. (2001) reported values from 0.05 tp 0.64 nM HAc Fe for the iron-deplete Big Sur region of California, and 20–50 nM for Fe-replete Monterey Bay. Off the Oregon coast, Chase et al. (2002) reported values for total dissolvable Fe from <0.3 to 300 nM, while Johnson et al. (2001) reported values from ca. 0 to 75 nM for an annual cycle in Monterey Bay, similar to our reported results. Ratios of refractory Al:Fe and HAc Al:Fe were relatively uniform (3.2 ± 0.5 and 1.6 ± 0.3, respectively) except for one offshore station (ratios of 9.4 and 1.8), where the lowest HAc Fe was determined (0.2 nM). The elevated ratio at the one offshore station suggests that the HAc Fe offshore may have been lower than our lowest recorded value, assuming the difference in Al:Fe ratios was due to contamination. Our lowest values (0.2 nM HAc Fe and 38.2 nM total Fe) and the Al:Fe ratios suggest, however, that we did not uniformly contaminate our samples, despite the lack of true trace-metal sampling protocols, and that there was a common particulate source, presumably resuspended sediment, during this time period. Using the ratio of HAc to refractory metals as an indicator of available iron, we determined the mean percent
available iron to be 21.2 ± 12.8%, ranging from 5.7% to 42.6% \((n = 10)\). This is similar, but substantially higher, than the 2–7% reported for Monterey Bay (Bruland et al., 2001).

Given the apparent relationship between upwelling intensity and the relative proportion of particulate inorganic/detrital versus organic matter, we expected a similar relationship between HAeFe and other indicators of upwelling, such as macronutrient concentrations, temperature, and salinity. Property–property plots of both HAeFe and refractory Fe showed no significant relationships (using linear regression analysis) to any of these variables. Similarly, there was no significant relationship between HAeFe or refractory Fe and total suspended sediment (both the organic and inorganic fraction), or biogenic silica. HAeFe was also compared to variable fluorescence \((F_v/F_m)\) and total extracted chlorophyll. There was again no obvious linear relationship. The ratio of \(F_v/F_m\) typically plateaus at a value of 0.65–0.70 in unicellular algae under optimal growth conditions, with decreases in this ratio often attributed to nutrient stress, in particular, iron (Greene et al., 1994; Behrenfeld and Kolber, 1999). Values corresponding to the HAeFe measurements ranged from 0.30 to 0.70, averaging 0.56; these values would typically be interpreted as ranging from moderate nutrient stress (0.30) to optimal growth (0.70). However, the lowest \(F_v/F_m\) values reported here occurred at the site of most recent upwelling \((8.2^\circ C, 121.6\ nM\ HAeFe)\). When HAeFe is plotted versus \(F_v/F_m\) and chlorophyll (Fig. 11), there is a pattern suggestive of very high iron in upwelling centers (cold, high macronutrients), with HAeFe declining with time/distance from shore as chlorophyll gradually increases and \(F_v/F_m\) peaks. As chlorophyll reaches a maximum (blooms), \(F_v/F_m\) begins to decline, accompanied by the lowest HAeFe concentrations. Because of the limited number of observations, it is difficult to determine whether the general pattern of high iron from upwelling with subsequent depletion accompanying aging of the water mass and bloom development is accurate; however, given the poor relationship between HAeFe, macronutrients, temperature and salinity, it is clear that particulate iron concentrations are not simply associated with upwelled waters.

We utilized the ratio of backscattered light and fluorescence \((b_{442}/f_{671})\) from the HS-6, and compared this to HAeFe from the same locations and depths (Fig. 12). A high ratio of scatter to fluorescence indicates freshly upwelled, particle-rich waters, which develop into high-fluorescence, high-backscatter waters as phytoplankton (primarily diatoms for this region) bloom. We found a much stronger relationship between these two variables than from any of the other properties tested, with an \(r^2\) value of 0.98 \((n = 10, p < 0.01)\). Although a
similar relationship existed when using beam transmissometer data and fluorescence, there was considerably more scatter and a significantly lower correlation ($r^2 = 0.71$; not shown). Similarly, using HS-6 channels other than 442 nm produced very good, but less robust ($r^2 = 0.96−0.97$) correlation, with variable slopes. In contrast to the very good relationship between HAc and the HS-6 data, the relationship to refractory Fe was not as strong ($r^2 = 0.77$) with considerable scatter. Iron in bomb-digestible particles is dominated by the refractory Fe in the alumino-silicate mineral matrix and is thought not to be biologically available.

4. Discussion

4.1. Interannual variability

Dorman et al. (2006; Fig. 6) show that monthly average wind stress curl was substantially higher during the field season in 2001 versus 2002. Botsford et al. (2006) show that calculated shelf transit time, which is directly related to wind stress, decreases from 2000 to 2001, and 2001 to 2002, demonstrating that on average, upwelling-favorable wind stress increased each year. Roughan et al. (2006) quantitatively identified 2000 as the weakest upwelling field season, and 2002 as the strongest, consistent with Botsford et al. (2006). Using the criteria of Roughan et al. (2006), we calculated that there were progressively fewer upwelling/relaxation transitions for each successive year, accompanied by an increasing number of days of upwelling-favorable winds (> 5 m s$^{-1}$ equatorward). These variable conditions resulted in markedly different mean SST patterns. Cold upwelled waters were bounded by a sharp thermal front in 2000 offshore of the shelf break, while 2001 and 2002 exhibited uniformly colder waters across the domain, with coldest nearshore waters in 2001, but a greater spatial extent of cool waters in 2002 (Fig. 5). We cannot compare directly wind stress to bio-optical variability, as we do not have a corresponding time series of in situ data (e.g., absorption spectra) at a single location. However, the clear pattern of increasing wind stress and increased upwelling from 2000 to 2002 is accompanied by a corresponding increase in the CDOM and particulate absorption spectra (Fig. 7), and in the detrital signature of the beam attenuation versus fluorescence relationship (Fig. 9), consistent with this increase in upwelling duration and intensity causing a shift from biogenic to detrital dominance of the optical signatures for the water column.

Despite these dramatic differences in physical forcing, the mean chlorophyll fields from SeaWiFS were essentially similar, showing enhancement of chlorophyll onshore and south of Point Reyes. There is a discrepancy between the mean SeaWiFS chlorophyll fields (Fig. 5) and the mean extracted chlorophyll measurements from shipboard surveys (Table 1); from the shipboard data, 2000 was substantially more chlorophyll-rich than 2001 and 2002. In contrast, the satellite imagery suggests that 2000 and 2002 were similar, with 2001 (when the coldest nearshore waters were observed) exhibiting lower biomass. Some of this discrepancy could be explained by the inherent biases of the SeaWiFS chlorophyll algorithm when applied to coastal, Case 2 waters (Kudela and Chavez, 2002, 2004; Otero and Siegel, 2004).

The CDOM signal was low and not strongly correlated to other physical measurements. In contrast to CDOM, the particulate detrital signal ($a_g$) decreased from 2000 to 2002. However, the relative proportion of $a_g$, which provides an indication of how much the detrital particulate signal contributes to the bulk optical properties, was lowest in 2000 (23%), peaked in 2001 (42%), and decreased again in 2002 (34%). This is consistent with the property–property plots of beam-c to chlorophyll and the variability in backscatter, which suggested that the particulate signal was dominated by phytoplankton in 2000, with relatively more inorganic/detrital material in 2001 and 2002. Across years, there was a statistically significant relationship between $a_g$ and chlorophyll ($r^2 = 0.89$, $p < 0.001$) in 2000, a weaker relationship ($r^2 = 0.56$, $p < 0.001$) in 2001, and no relationship ($r^2 = 0.33$, $p = 0.72$) in 2002. Taken together, this suggests, as is evident from the mean chlorophyll concentrations, that frequent upwelling-relaxation events promote bloom formation (2000) while more intense and steady upwelling conditions result in decreased phytoplankton and increased detrital and resuspended material (2001–2002). The low but increasing $a_g$ values and decreasing relationship between $a_g$ and chlorophyll provide evidence for increasingly accurate SeaWiFS retrievals across years, as this upwelling system went from Case 1, phytoplankton-dominated waters to Case 2, detritally influenced and non-chlorophyll covarying waters.
4.2. The importance of detrital/inorganic material

In addition to the interannual variability, there was considerable spatial and temporal variability in optical properties within each year. In 2000, when phytoplankton dominated the optical properties of the water column, CDOM absorption was a small fraction of the total absorption. On average, $a_g 412$ was 2.5% of $a_d 412$, which in turn was only 23% of $a_p 412$. Particulate absorption spectra were similar to $a_{ph}$ across all regions (onshore versus offshore, deep versus shallow), consistent with this dominance, although there were differences in magnitude. Previous authors have identified these patterns as characteristic of coastal waters (Roesler et al., 1989; Cleveland, 1995; Sosik et al., 2001). During 2001 and 2002, however, the relative importance of $a_g$ increased substantially, while $a_g 412$ increased from a few percent of $a_g 412$ (2000) to ca. a factor of 2 and 11 for 2001 and 2002, respectively. In other words, except for 2000, the dissolved and detrital absorption spectra became increasingly dominant.

Kahru and Mitchell (2001) reported that, for the entire west coast over multiple years, the $a_g$ signature was significant, but did not bias satellite chlorophyll retrievals from ocean color remote sensing. Globally, however, Siegel et al. (2002) showed that approximately 50% of blue light absorption is due to CDOM, while several authors (Nelson and Guarda, 1995; Boss et al., 2001b) have shown that during storm events, CDOM and detritus can be a dominant signal in the water column. Photo-oxidation is thought to be the predominant loss term for CDOM in surface waters (Boss et al., 2001b; Twardowski and Donaghay, 2002). Since there was only a weak relationship between CDOM absorption and salinity, indicative of coastal runoff (Twardowski and Donaghay, 2001), we assume that the $a_g 412$ signal derived predominantly from food-web processes and injection from deeper waters. Based on our results within and across seasons, we suggest that in eastern boundary current regimes, intense coastal upwelling provides similar physical forcing, resulting in enhanced sediment resuspension and CDOM mobilization into the euphotic zone. While the west coast may on average be negligibly impacted by these processes (Kahru and Mitchell, 2001), localized events lasting on the order of weeks, but not related to storm events or river discharge, can significantly bias water column optical properties, and hence remote sensing retrievals which rely on band-ratio type algorithms (O’Reilly et al., 2000).

4.3. Relationship between backscatter and metals

Because the optical properties of the water masses in the WEST study region are heavily influenced by particulate signals, it is reasonable to assume that there might be an optical signal associated with the injection of bio-available particulate iron. We found a very robust relationship between HAc Fe and $b_v 442/467$. While these results must be interpreted with a great deal of caution, given the small data set and the fact that this represents one time period from 1 year, this relationship is intriguing, and suggests that a purely bio-optical proxy for particulate iron might be developed. The light scattering properties of particles depends on the size, composition, shape, and index of refraction of the particle (van de Hulst, 1981). Inorganic and organic (e.g., phytoplankton) particles exhibit substantially different indices of refraction, ranging from ca. 1.02 to 1.07 for plankton, 1.08 for biogenic silica (opal), and 1.14–1.26 for common marine minerals relative to the index of refraction for seawater in vacuum, 1.34 (Twardowski et al., 2001 and references therein). By utilizing the ratio of spectral backscatter to total scatter, several studies have demonstrated that it is possible to identify the bulk refractive index of suspended marine particular matter, thereby identifying the dominant particle type (organic versus inorganic, and potentially inorganic mineral classes) in coastal waters (Twardowski et al., 2001; Boss et al., 2004).

Unfortunately, we did not have an estimate of spectral scatter (such as can be obtained from a WET Labs ac-9). We can, however, estimate the approximate backscatter ratio by assuming that at 660 nm (the wavelength of the beam transmissometer), attenuation is predominantly due to scattering, with little influence from particulate or dissolved absorption. This is justified based on the mean $c_p 660$ value from the depth bins where trace-metal samples were collected ($c_p 660 = 0.49 \pm 0.29 \text{ m}^{-1}$) and the mean $a_p 660$ value (0.02 m$^{-1}$). With that assumption, we can estimate the backscatter ratio using $b_v 620/c_p 660$. Doing so provides a range of values from 0.0055 to 0.0146, or a range of indices of refraction from ca. 1.08 to 1.12, using Eq. (14) from Twardowski et al. (2001). Griggs and Hein (1980) classified the offshore clay-mineral sediments in the WEST region as composed of...
approximately equal components smectite, iolite, and kaolinite/chlorite. Assuming equal proportions of these minerals, the index of refraction would be 1.14. Stramski (1999) reported a range of ca. 1.04–1.06 for the index of refraction at 660 nm for the diatom Thalassiosira pseudonana; given the dominance of diatoms in our study region during upwelling and bloom conditions (Wilkerson et al., 2000; Lassiter et al., 2006), the observed range of values from our limited data set is consistent with a bulk particle assemblage composed of a mixture of living phytoplankton, biogenic silica, and mineral particles. The index of refraction trended downward with decreasing metal concentrations (HAc Fe or Al, refractory Fe or Al), consistent with a shift from inorganic particles to phytoplankton as the particulate metals were removed from the water column. Given the small sample size, these relationships were not statistically significant ($r^2 \approx 0.45$, $p \approx 0.1$ for each relationship).

While the $b_{442}/f_{671}$ relationship to HAc Fe is an empirically derived function, the robustness of the covariance ($r^2 = 0.98$) was significantly higher than for any other property–property plot between metals and in situ values. The $b_{442}/f_{671}$ relationship was also strongly correlated to the source water, and provides an excellent indicator of freshly upwelled waters dominated by inorganic optical constituents and aged water dominated by phytoplankton (Fig. 8). The $b_{442}/f_{671}$ relationship to HAc Fe is not simply an indicator of freshly upwelled or particle-rich waters, since there was poor correlation between HAc Fe and temperature or salinity, and a less robust relationship between refractory Fe or Al and our bio-optical measurements. One potentially confounding factor in the application of this relationship results from the characteristic boomerang shape exhibited for the optical data (e.g., Figs. 7 and 8), which implies that for some conditions, there may be a large change in backscatter or attenuation with very little change in fluorescence. This could potentially result in a predicted change in HAc Fe which is driven solely by the particle load in the water column. If these particles were detrital organic material (e.g., during relaxation) rather than inorganic material rich in adsorbed metals, our empirical relationship would incorrectly predict high bio-available iron. However, this seems unlikely to be a serious issue for these data because biogenic detritus is unlikely to have a backscatter intensity as strong as inorganic materials, which generally have a higher index of refraction. However, we suggest that this relationship could be improved in future applications by simultaneously collecting spectral attenuation data so that the index of refraction (a good indicator of bulk particle composition) could be determined concurrently; although temperature and salinity were not good predictors of HAc Fe in this study, we would not rule out the use of these variables to further differentiate upwelled versus aged waters, which could also presumably be used to indicate bio-available iron in some cases. While it must clearly be validated for other regions and time periods, our results suggest that bio-optical estimates of the water column derived from in situ instrumentation, or potentially remote sensing, could be used to produce maps of HAc Fe; at a minimum, backscatter/fluorescence ratios would provide a useful alternative to other bulk property measurements, such as beam attenuation or remote sensing reflectance, for identifying phytoplankton versus inorganic/detrital dominated waters. As discussed by Stramski et al. (2004), the potential application of backscatter measurements as a proxy for biogeochemical properties has not been fully explored, despite the promising relationships developed for POC (Stramski et al., 1999) and bulk particle composition (Twardowski et al., 2001; Boss et al., 2004). Because backscatter can be derived directly from ocean color remote sensing (Maritorena et al., 2001; Moline et al., 2004) these relationships could potentially be applied relatively easily to large spatial and temporal geographic regions.

4.4. Biological implications

Eastern boundary currents are highly productive regimes in terms of both primary and new production because of the confluence of vigorous upwelling from both local and large-scale physical forcing (Carr and Kearns, 2003) injecting macronutrients into the euphotic zone, and the presence of a continental shelf which provides biologically available iron (Johnson et al., 1999, 2001; Bruland et al., 2001). Although these regions are highly variable both spatially and temporally (Fig. 5), with a significant fraction of cross-shelf transport resulting from frequent, but transient, coastal filaments (Fig. 4; Barth et al., 2002), the general pattern in these regions is for maximal biomass and productivity nearshore, with a strong onshore-offshore gradient (Fig. 5; Thomas and Strub, 2001; Carr, 2002; Chavez et al., 2002; Carr and Kearns, 2003).
Recent measurements of coastal water iron concentrations in eastern boundary current systems have emphasized the critical importance of bio-available iron to promote the large diatom blooms associated with these high productivity regimes. In contrast to the more permanently Fe-limited high-nutrient, low-chlorophyll (HNLC) regions of the open ocean, coastal upwelling systems can transition from iron-replete to iron-limited, as well as exhibiting a range of iron limitation, over relatively small spatial scales and temporally on scales from days–weeks (e.g., storm events) to seasonal and interannual patterns (Hutchins et al., 1998; Johnson et al., 1999, 2001; Bruland et al., 2001; Chase et al., 2002; Firme et al., 2003).

Although sedimentary iron sources associated with coastal runoff in winter, with subsequent mobilization during the onset of vigorous upwelling in spring, have been implicated as the primary source of iron in coastal California waters (Bruland et al., 2001; Johnson et al., 2001), Chase et al. (2002) argued that the lack of strong correlation between total dissolvable iron and macronutrients off the Oregon coast was inconsistent with injection of sedimentary iron from upwelling alone. Instead, they hypothesized a combination of wind mixing (upwelling), outcropping of the bottom boundary layer, and thickening of the bottom mixed layer. Under this scenario, iron and macronutrients would be injected into the mixed layer during upwelling, while iron-rich sediments in the bottom mixed layer would be remobilized primarily during wind reversals.

From our albeit limited data, we suggest that the multiple input scenario proposed by Chase et al. (2002) is consistent with our observations. As in the coastal Oregon study, we found a poor correlation between HAc Fe and other upwelling signatures such as temperature, salinity, and macronutrients. Although we do not have trace metal measurements from other years, there were pronounced differences between years, which we attribute to the differential local forcing (frequent upwelling-relaxation events versus more prolonged upwelling) resulting in enhanced productivity during 2000 relative to 2001–2002.

The only unambiguous way to identify macro- or micronutrient limitation requires nutrient addition experiments (Hutchins et al., 1998; Firme et al., 2003; Franck et al., 2003); however, variable fluorescence has been suggested as a quick and sensitive estimate of nutrient limitation, and in particular iron stress (e.g., Greene et al., 1994; Behrenfeld and Kolber, 1999; Chase et al., 2002). Our results suggest that these data must be interpreted with caution in freshly upwelled waters. In this study, the lowest $F_v/F_m$ values (0.3) were associated with freshly upwelled waters characterized by moderate chlorophyll concentrations ($0.9 \text{ mg m}^{-3}$), elevated macronutrients, and very high concentrations of HAc Fe. Although our iron measurements are not necessarily immediately biologically available since the iron is still associated with the particulate fraction, Bruland et al. (2001) showed a strong correlation between HAc Fe and labile Fe. Using their relationship, we can estimate that in this freshly upwelled water contained approximately 30 nM iron, or about 100 times more than the threshold for Fe-limitation identified for this region (Bruland et al., 2001).

The observed pattern of low variable fluorescence in freshly upwelled waters is commonly observed in central California coastal waters (Kudela and Chavez, 1999). From our results (Fig. 11), there was ample iron, macronutrients, and biomass (ca. $1 \text{ mg m}^{-3}$ Chl) at this site. Two possibilities suggest themselves as an explanation for the low photochemical competency observed. First, freshly upwelled waters frequently exhibit a biological lag similar to phytoplankton cultured in the laboratory (Kudela et al., 1997; Kudela and Dugdale, 2000). The low photochemical competency therefore would be indicative of a “lag” phase in freshly upwelled phytoplankton populations. Second, upwelling water is typically very poor in organic substrates, and enriched in trace metals. It has long been hypothesized that these metal-rich, upwelled waters may need to be organically “conditioned” to chelate excess bio-active metals such as copper (Barber et al., 1971; Jackson and Morgan, 1978). Regardless of the mechanism, we suggest that variable fluorescence data should be interpreted with caution in upwelling regions.

5. Conclusions

Bio-optical characteristics of the CoOP WEST region are dominated by the interaction of physical forcing (upwelling intensity and duration) and water depth. Across cruises, considerable variability appears to be associated with the frequency of upwelling-relaxation events. CDOM absorption is low but variable, and can be a significant source of
variability in the optical signature of the water column. We suggest that intense upwelling behaves similarly to storm events on the east coast of the continental US, and results in enhanced CDOM absorption independent of chlorophyll. The same conclusion was reached by Kahru and Mitchell (2001) based on remote sensing analyses for the California Current. Those authors reported a good correlation between CDOM and chlorophyll offshore, but a weak relationship nearshore where other sources of CDOM (besides phytoplankton) exist. This variability likely causes the WEST region to alternate between Case-1 and Case-2 conditions as a function of upwelling intensity and duration, which could reduce the accuracy of ocean-color remote sensing.

There was a variable but persistent boundary between onshore (<200 m depth) and offshore (>200 m) waters in terms of bio-optical properties, biomass, and trace-metals, although there was substantial variability in the location of this boundary on any given day (Fig. 6). Bruland et al. (2001) demonstrated that, because of non-Redfield assimilation of iron relative to macronutrients, coastal regions can be forced into HNLC conditions even when high initial concentrations of iron and macronutrients are present. From our data, we suggest that the WEST region shallower than 200 m is iron sufficient, fed by a large reservoir of leachable iron associated with resuspended sediments. The shelf break appears to act as a natural boundary in this system, separating the high productivity, diatom-dominated coastal waters from more oceanic offshore waters. As previous authors have found, the Farallones are distinctly different from the open coastal region north of Point Reyes. The persistently higher biomass immediately north of Point Reyes is consistent with the Farallones acting as a biological reservoir for northward transport during periods of relaxation (Vander Woude et al., 2006).

Based on a very limited data set, we have found a promising relationship between the $b_{442}/fl671$ ratio and HAc Fe, and more generally between waters dominated by inorganic/detrital material and phytoplankton. Future work should examine the utility of these measurements from both in situ and remote sensing platforms for other regions and times. If these relationships are robust spatially and seasonally, this could provide an easily estimated proxy for extending direct estimates of in situ iron concentrations from shipboard platforms.

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