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Iron and macronutrients in California coastal upwelling regimes: Implications for diatom blooms

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Abstract

The supply of iron, relative to that of the macronutrients nitrate, phosphate, and silicic acid, plays a critical role in allowing extensive diatom blooms to develop in coastal upwelling regimes. The presence or absence of a broad continental shelf influences the supply of iron. The iron input to central California upwelling waters varies spatially and can be characterized by two end-member regimes. One end member, which includes Monterey Bay and extending north to Pt. Reyes, is an iron-replete regime where upwelling occurs over a relatively broad continental shelf that results in waters with high concentrations of dissolved and particulate iron (>10 nM) entrained together with high concentrations of nitrate and silicic acid. In these iron-replete regions, extensive blooms of large diatoms deplete macronutrient concentrations, which results in correspondingly high chlorophyll *a* concentrations. The other end member, located to the south of Monterey Bay off the Big Sur coast, is an iron-deplete regime where upwelling is focused offshore of a narrow continental shelf. Upwelled waters in the Big Sur region are characterized by low dissolved and particulate iron concentrations (<1 nM), together with high concentrations of nitrate and silicic acid. Extremely low iron concentrations, unused nitrate and silicic acid, and a low abundance of large diatoms characterize surface waters in these iron-deplete regions, and thus represent coastal upwelling, high-nutrient, low-chlorophyll systems limited by the micronutrient iron.

Phytoplankton blooms, defined as the rapid growth and accumulation of algal biomass, occur when nutrient-replete conditions promote rapid algal growth rates temporarily uncoupled from grazing pressure (Smayda 1997). These conditions are common in coastal upwelling regions located along the west coasts of North and South America. Large unicellular or chain-forming diatoms tend to dominate the biomass in phytoplankton blooms that develop in coastal upwelling regimes (Hood et al. 1990; Wilkerson et al. 2000). These coastal upwelling regimes are among the most productive marine systems and are responsible for a disproportionate amount of global new and export production (Eppley and Peterson 1979; Falkowski et al. 1998), and it has been argued that diatom-driven new production ''fuels the food chains leading to fish'' (Smetacek 1998).

A prerequisite for rapid growth rates of diatoms is a large influx of the macronutrients nitrate (NO_3^-), phosphate (HPO_4^{2-}), and silicic acid (H_4SiO_4) to surface waters. Actively growing diatoms require these major nutrients at a C : N : P Redfield Ratio of 106 : 16 : 1, with a Si : N uptake ratio of ~1 : 1 (Brzezinski 1985). Coastal upwelling off central California delivers nitrate, phosphate, and silicic acid close to the ratio at which they are assimilated. Diatom blooms are generally considered to be limited by the exhaustion of these macronutrients, particularly upon depletion of nitrate (Smetacek 1999). Diatoms, however, also appear to be the most susceptible of the marine phytoplankton to iron limitation and the most opportunistic to take advantage of iron additions. Diatoms have consistently outperformed other phytoplankton in iron enrichment experiments carried out in high-nutrient low-chlorophyll (HNLC) waters (e.g., Buma et al. 1991; Martin et al. 1991; Coale et al. 1996; Fitzwater et al. 1996).

Historically, coastal waters have not been considered candidates for biolimitation by any trace metal (including iron), as illustrated by the following comment of the late John Martin: ''Meeting biological iron requirements is relatively easy in neritic waters, where resuspended bottom sediments and associated iron-rich oxides, colloids, etc., occur together with elevated concentrations of iron. Hence, excess nitrate is never observed in coastal upwelling environments such as those off the west coasts of Africa and North and South America'' (Martin 1990). Hutchins and Bruland (1998), however, have recently demonstrated that growth limitation by iron can occur in certain coastal upwelling regions. A series of shipboard grow-out experiments demonstrated that the lack of dissolved Fe can serve to preclude diatom blooms from occurring in otherwise macronutrient-replete, coastal upwelling waters off the Big Sur coast of California and that the addition of dissolved Fe stimulated diatom blooms. On the basis of these grow-out experiments, Hutchins et al. (1998) have proposed a four-level classification scheme for iron limitation in coastal California upwelling regimes, with a mosaic of conditions ranging from severely iron-limited to iron-replete.

Herein we present water column data that support the results of previously published grow-out experiments (Hutchins and Bruland 1998; Hutchins et al. 1998) from the Monterey Bay area shown to represent an iron-replete upwelling regime and from along the Big Sur coast that represents an iron-deplete upwelling regime. Using insight gained from laboratory studies (Sunda and Huntsman 1995), we also predict the iron concentrations necessary for optimal growth rates of coastal diatoms and for optimal development of di-

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atom blooms. These predictions are then compared with field observations to gain additional insight into the role of iron in coastal upwelling regimes. We interpret the distribution of iron in these waters with respect to both the effects of iron on phytoplankton bloom development and, in turn, the effect of phytoplankton blooms on the distribution and chemistry of iron.

Background

Coastal upwelling and the supply of macronutrients—The coastal waters off central California are part of an eastern boundary, coastal upwelling system (Bakun 1990; Bakun and Nelson 1991). During the spring and summer months, periods of strong northwesterly winds induce offshore transport of surface waters, causing the upwelling of cool, nutrient-enriched water from depth. Essential macronutrients such as nitrate, phosphate, and silicic acid are thus brought to the surface layers of the ocean. Typical freshly upwelled waters in this region can have temperatures on the order of 8°C–11°C, nitrate concentrations of 15–35 μM, phosphate concentrations of 1.3–2.6 μM, and silicic acid concentrations of 15–45 μM. This supply of macronutrients can lead to extensive blooms of large diatoms with chlorophyll *a* concentrations of approximately 10–35 μg L^{-1} (Hayward and Venrick 1998).

The most intense coastal upwelling appears to be restricted to a relatively narrow band within 10 km of the coast and is enhanced to the south of prominent points of land such as Point Arena, Point Reyes, Año Nuevo, and Point Sur (Huyer 1983). However, the region influenced by coastal upwelling can be much wider than the band of active upwelling, because the recently upwelled, nutrient-rich water is advected hundreds of kilometers offshore and mixed into the southward-flowing California Current system. The existence of energetic eddies and cross-stream jets are a dominant and persistent component of such eastern boundary current regions (Huyer 1983; Kosro and Huyer 1986; Strub et al. 1991).

Coastal upwelling and the supply of iron—Some iron is upwelled along with the cold nutrient-rich waters as part of the ocean's internal biogeochemical cycles and the nutrient-type distribution of iron (Martin and Gordon 1988; Bruland et al. 1994). Roughly 0.4–1 nM of dissolved Fe can be delivered along with typical concentrations of 15–35 μM nitrate via upwelling of offshore subsurface water. This internal source of dissolved Fe delivered to surface waters in concert with the macronutrients can, however, be augmented by external sources of iron from eolian and fluvial inputs.

In the subtropical gyres of the open ocean, the major input of Fe to surface waters is eolian (Bruland et al. 1994). However, in the coastal upwelling regime off central California during the spring and summer upwelling season, the amount of iron delivered from the atmosphere is not significant in comparison to that delivered by upwelling or remobilization from shelf sediments. Mahowald et al. (1999) and Fung et al. (2000) model the dust deposition and resultant iron supply to the surface ocean and show that the upwelling region off central California has a relatively low atmospheric input due to the prevailing winds from the northwest during the upwelling season.

The major source of iron to surface waters of the central California upwelling regime during June and July is from the continental shelf (Hutchins and Bruland 1998; Martin and Gordon 1988; Johnson et al. 1999). This shelf source of iron originates from fluvial inputs, primarily in the form of iron associated with riverine suspended particles delivered to the shelf by major flood events occurring during the winter months (Griggs and Hein 1980). The fluvial input to the central California coastline is unevenly distributed spatially and temporally (Griggs and Hein 1980). The Big Sur coast is a large stretch of coastline with negligible river input (Fig. 1). In contrast, the coastline between Monterey and San Francisco has a number of rivers discharging considerable amounts of water and sediment (Fig. 1). River flows in this region are dominated by episodic flood events during the period from December to March. For these Central California rivers, often >90% of the water discharge can occur during a 1-wk period in the winter season as a result of heavy rains and intense flooding. The suspended sediment discharge is even more episodic than the water discharge, with the rare, high-energy, and high-discharge events able to carry a tremendous amount of mud. The suspended load of these rivers follows an exponential relationship with the water discharge rate (Griggs and Hein 1980), with 95% of the sediment load discharge from California coastal rivers occurring during a major flood event of less than a few days duration. In marked contrast, during the summer upwelling season, there is no significant discharge from coastal streams and negligible freshwater discharge from the rivers of central California (Huyer 1983).

When a sufficiently broad continental shelf is present, much of the winter fluvial discharge of suspended sediment is rapidly deposited on the adjacent shelf at depths of 50–100 m, centered on the 70 m isobath (Wheatcroft et al. 1997). A relatively broad continental shelf can act as an ''iron trap'' for these fluvial inputs. In the winter months when fluvial input is the greatest during the flood season, upwelling is at a minimum (Pennington and Chavez 2000). In contrast, coastal upwelling is strongest from April through August, when direct river input is negligible in the central California area. The near-shore shelf sediments, however, can act as an iron trap and provide a source of iron to be entrained with upwelled water throughout the year.

When coastal upwelling of macronutrient-rich water takes place over these shelf regions, shelf water, with its elevated iron concentrations (both particulate and dissolved), can be entrained resulting in water enriched with both macronutrients and iron (Martin and Gordon 1988; Johnson et al. 1999). However, if the upwelling occurs offshore of a narrow continental shelf, we suggest there will not be a significant external source of iron to complement the macronutrients. In the region between Santa Cruz and Pt. Reyes, the shelf is relatively broad and extends roughly 20 to 50 km offshore (Fig. 1). In contrast, the Big Sur coast has an extremely narrow continental shelf, only a few kilometers in width (Fig. 1).

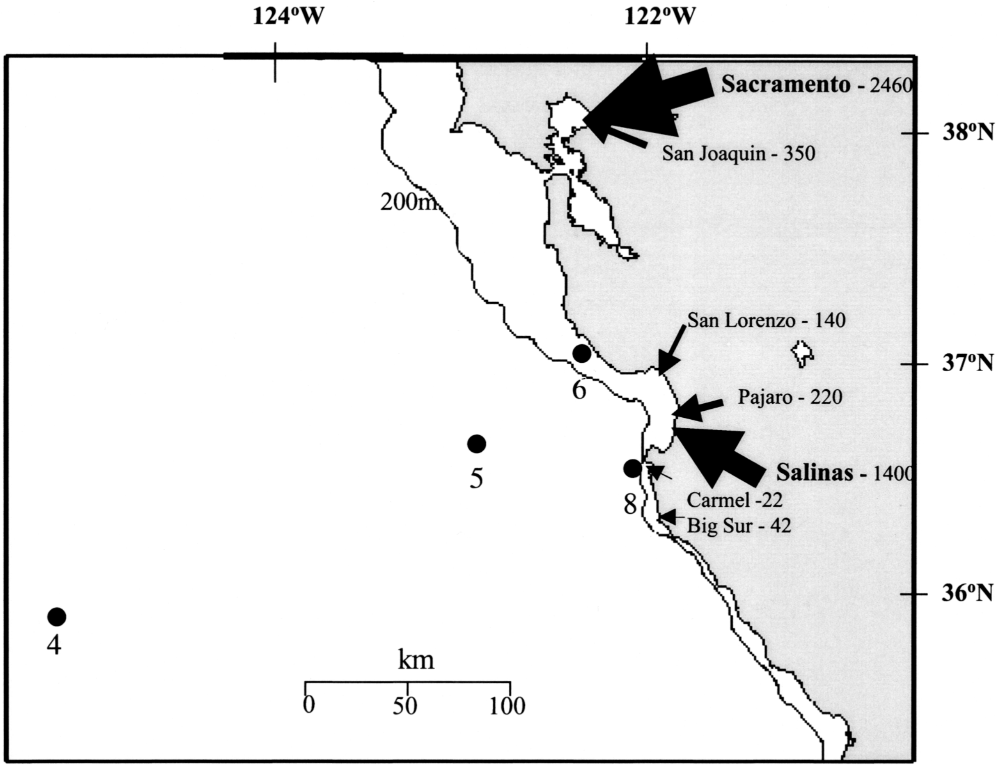


Fig. 1. Map of the central California coast study area, with the 200-m depth contour noted. The size of the arrow depicts the relative amount of annual average suspended sediment discharge by the various rivers as reported by Griggs and Hein (1980). The average yearly value of suspended sediment discharge (in thousand metric tons per year) is reported next to the river name. Also shown are station locations (4, 5, 6, and 8) at which vertical profiles were collected in July 1995.

Requirement of Fe by coastal diatoms—Although the majority of the dissolved iron in surface seawater is chelated with natural organic ligands (Rue and Bruland 1995; van den Berg 1995), the iron is still available to the biological community (Rue and Bruland 1997; Hutchins et al. 1999). For example, diatoms have been shown to utilize a surface reductase system that is effective at reducing the Fe(III) bound to organic ligands (Maldonado and Price 2001) in order to release the iron for subsequent assimilation by the diatoms. In addition, Fe(III) ligand complexes can be assimilated by one type of organism (e.g., Fe(III)-siderophore uptake by bacteria), incorporated into cell machinery and then regenerated back into the water column in other forms via cell lysis or grazing to be reused by other members of the phytoplankton community (Hutchins et al. 1993; Hutchins and Bruland 1994). Thus, we assume here that essentially all of the labile or dissolved Fe we measure in surface seawater is available on timescales of days to the phytoplankton community. This is in contrast to laboratory studies of individual diatom species that have used EDTA-buffered media. In these systems, Fe(III)-EDTA chelates are generally not readily available, and the biologically available forms are the inorganic hydrolysis products, Fe′ [the sum of $\mathrm{Fe(OH)_2^+}$, $\mathrm{Fe(OH)_3^0}$, etc.]. Thus, we argue that laboratory studies of the growth response of diatoms as a function of [Fe′] can be compared with the response of field populations to labile or dissolved Fe.

Coastal diatoms have been shown to have an order-of-magnitude higher iron requirement (on an Fe : C basis) than oceanic diatoms (Sunda and Huntsman 1995). In addition, coastal diatoms tend to be significantly larger than oceanic diatoms. Thus, to achieve maximal growth rates, coastal species need higher iron concentrations than their open ocean counterparts. Sunda and Huntsman (1995) presented data for the coastal diatom *Thalassiosira weissflogii* grown in their laboratory under a range of iron concentrations in EDTA-metal ion buffered seawater media. Their results are replotted here in Fig. 2, which presents the specific growth rate of the coastal diatom as a function of [Fe′]. At $[\mathrm{Fe'}] \leq 0.1$ nM, the cultures are severely iron limited, whereas at $[\mathrm{Fe'}] > 0.5$ nM the coastal diatoms are growing at near optimal rates. In contrast to relatively constant ‘‘Redfield’’ ratios of C : N : P, the cellular Fe : C ratios *vary markedly* (by a factor of 30) as a function of the available [Fe′] (Fig. 2). When iron is severely limiting at low concentrations ($[\mathrm{Fe'}] \sim 0.05$ nM), the coastal diatoms have cellular Fe : C ratios <20 μmol mol^{-1}. At [Fe′] values between 0.5 and 1 nM, the ratios are close to 50 μmol mol^{-1}, whereas with $[\mathrm{Fe'}] \geq 3$ nM, the cellular Fe : C ratio exceeds 100 μmol mol^{-1}. These high cellular Fe : C values (>100 μmol mol^{-1}) appear to be indicative of luxury uptake by diatom cells at high [Fe′] (Sunda and Huntsman 1995).

There are very limited field data for Fe : C ratios in natural phytoplankton assemblages to compare with these laboratory

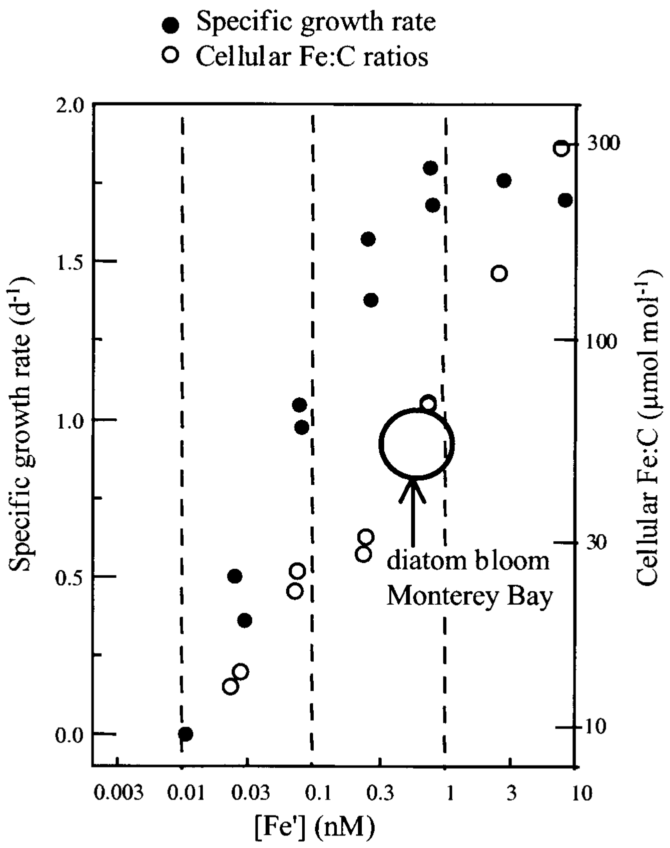


Fig. 2. Data from Sunda and Huntsman (1995) for the coastal diatom *T. weissflogii* grown in the laboratory under a range of iron concentrations set in EDTA–metal ion buffered seawater media. Specific growth rate of the coastal diatom as a function of [Fe′] (the concentration of the sum of all inorganic Fe species) and cellular Fe : C ratios as a function of the available [Fe′] are shown. The large open circle corresponds to field data of cellular Fe : C ratios from a diatom bloom in Monterey Bay (Bruland et al. 1991) and observed concentrations of dissolved Fe in this region.

studies. Bruland et al. (1991) reported cellular Fe : C ratios of 50 μmol mol^{-1} measured in cleanly collected diatom samples under bloom conditions off Monterey Bay. This Fe : C ratio is close to what would be predicted from the laboratory studies of Sunda and Huntsman for [Fe′] of 0.5–1.0 nM (see Fig. 2), which is also consistent with labile Fe values of 0.5–1.0 nM determined in Monterey Bay. Schmidt and Hutchins (1999) carried out a transect in the eastern North Pacific off Vancouver Island and reported Fe : C uptake values of 34–88 μmol mol^{-1} for coastal phytoplankton in the $>$5 μm size fraction.

Hudson and Morel (1993) evaluated the Fe′ concentration at which the growth rate of oceanic phytoplankton become limited as a function of cell size. For cells $>$10 μm diameter, diffusion limitation at the low [Fe′] observed in the open ocean surface waters was a critical factor limiting their growth rate. The areas in the central California upwelling regime with high Chl *a* (i.e. bloom conditions) tend to be dominated by large unicellular or chain diatoms (Hood et al. 1990). In bloom situations examined by Hood et al. (1990), the bulk of the biomass was composed of diatoms with equivalent spherical diameters between 20 and 80 μm. The peak in the biomass occurred in the 40–50 μm equivalent spherical diameter size fraction. Hutchins et al. (1998) observed that species of the large chain-forming centric diatom *Chaetoceros* commonly dominated the phytoplankton community off central California under bloom conditions. Exceptionally large unicellular centric diatoms (on the order of 80–100 μm) of the family *Coscinodiscaceae* were important in terms of biomass. Olivieri and Chavez (2000) reported mean spherical diameters ranging from 15 to 30 μm for phytoplankton from Monterey Bay during the spring and summer upwelling period. They observed an increase in mean spherical diameter of the diatoms to values close to 30 μm associated with bloom conditions.

We took the approach of Hudson and Morel (1993) and calculated the cell diameter at which [Fe′] would become diffusion limiting for coastal diatoms. For cellular Fe : C ratios of 50 μmol mol^{-1} (the value observed in diatom samples collected in Monterey Bay under bloom conditions), cells of 30 μm diameter require at least 0.3 nM Fe′ (or labile dissolved Fe) to not have their growth rate be $>$60% diffusion limited for $\mu = 1$ d^{-1}. Because maximum growth rates for coastal diatoms in this region can be on the order of 1.5–2 d^{-1}, a growth rate of only 0.6 d^{-1} would be severely diffusion limited (see Fig. 2). We predict that diffusion limitation will severely limit growth rates of coastal diatoms at dissolved Fe concentrations below 0.1 nM and preclude blooms from occurring, even in the presence of high concentrations of macronutrients. In contrast, concentrations of dissolved Fe on the order of $\geq$0.5 nM appear adequate to keep iron from being rate limiting and would allow a high growth rate of even the largest diatoms.

Liebig limitation, the limitation of a bloom by a substance that is least available relative to its requirement for biomass synthesis, is a critical factor determining the extent of any phytoplankton bloom development (de Baar 1994). The maximum potential biomass realized in a bloom has historically been thought to be dependent primarily on the original fixed nitrogen (primarily nitrate) concentration (Smetacek 1999; Kudela and Dugdale 2000). Nitrate concentrations in upwelled waters thus provide a useful parameter on which to assess the relative requirements of other essential macronutrients and micronutrient metals.

Nitrate in freshly upwelled water generally ranges from 15–35 μM. A representative concentration of nitrate in coastal upwelled water has been argued to be 20 μM (Chavez and Toggweiller 1995). The uptake of 20 μM nitrate would produce a bloom with roughly 20 μg L^{-1} of Chl *a* (Kudela and Dugdale 2000; Wilkerson et al. 2000). Diatoms growing at near optimal rates would also require 20–25 μM silicic acid and 1.3 μM phosphate to complement the assimilation of 20 μM nitrate. Relative to the requirement of the phytoplankton, there is generally a slight excess of silicic acid and phosphate over nitrate in these coastal upwelling regions (Brzezinski et al. 1997; Hutchings et al. 1995). This is the case if the system has adequate iron available, with a resulting Si : N assimilation ratio close to 1 : 1 (Hutchins and Bruland 1998). If, however, the system is partially iron limited, then a preferential drawdown of silicic acid relative to nitrate can take place and silicic acid could also become a

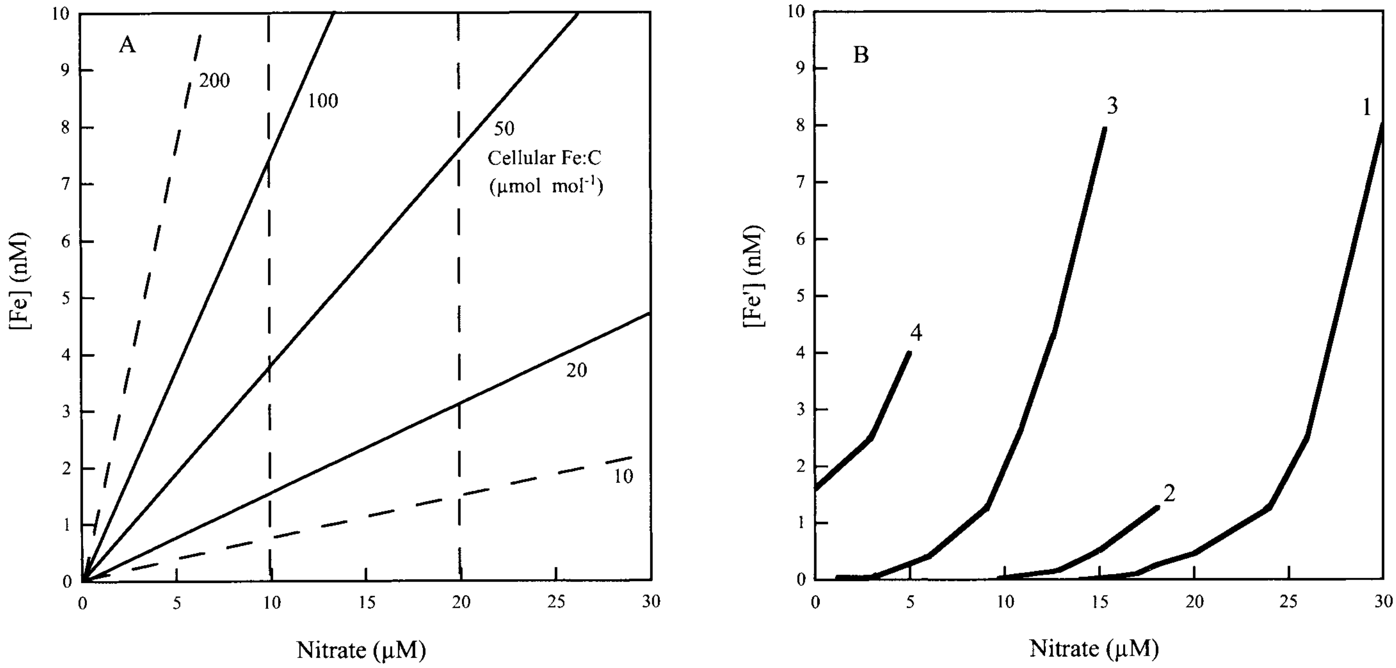


Fig. 3. (A) The amount of available Fe required to complement nitrate for a bloom of coastal diatoms to develop at a range of different constant cellular Fe : C ratios. (B) dissolved nitrate and Fe draw-down curves for a bloom of coastal diatoms under four differing starting conditions of available Fe and NO_3^- where the Fe : C ratio is dependent on the concentration of available Fe (Fig. 2). The different cases represent (1) high initial nitrate and high iron, (2) average nitrate with low initial iron, (3) medium nitrate with high iron, or (4) relatively low initial nitrate with medium iron. Cases 1, 2, and 3 end up as iron-limited systems.

limiting nutrient in low-iron waters (Hutchins and Bruland 1998).

The amount of Fe required to complement nitrate for a bloom of coastal diatoms to develop at a range of different constant cellular Fe : C ratios is presented in Fig. 3A. Coastal diatoms growing at near optimal rates assimilate iron at cellular Fe : C ratios between 20 and 100 μmol mol^{-1} (see Fig. 2). Diatoms growing with a cellular Fe : C ratio of 50 μmol mol^{-1} (e.g., the value observed in the diatom sample collected off Monterey Bay under bloom conditions), would require ~7 nM of available Fe to complement the drawdown or assimilation of 20 μM nitrate. At a cellular Fe : C ratio of 20 μmol mol^{-1}, 3 nM Fe would be required, whereas at a cellular Fe : C ratio of 100 μmol mol^{-1}, 14 nM of Fe would be required along with the 20 μM nitrate. Thus, the concentrations of Fe required to allow an extensive bloom of coastal diatoms to develop without becoming Liebig limited by Fe is significantly greater than that needed to keep the diatoms from becoming growth rate limited at any particular moment. As discussed earlier, however, the cellular Fe : C ratio for diatoms is not a constant but instead *varies markedly* as a function of [Fe′]. Thus, the cellular Fe requirements need to be examined as a function of a variable [Fe′].

Fig. 3B presents scenarios of what would happen to both the dissolved nitrate and dissolved Fe during a bloom of coastal diatoms under differing starting conditions of available iron and nitrate. For example, if the freshly upwelled water contained 8 nM of readily accessible dissolved Fe along with 30 μM nitrate, then the initial cellular Fe : C ratio would be on the order of 200 umol mol^{-1} (see Fig. 2). Such a high Fe : C ratio would rapidly deplete the dissolved Fe relative to nitrate. Because the dissolved Fe was depleted to lower [Fe′], the cellular Fe : C ratio of the diatoms would respond and drop to ~100 (at [Fe′] ~ 3 nM), then to ~50 (at [Fe′] = 0.5 to 1 nM), and finally to low values of ~20 μmol mol^{-1} as [Fe′] dropped to a few tenths of a nM. This preferential removal of iron would lead to dissolved Fe becoming diffusion limiting for larger coastal diatoms as [Fe′] dropped below a few tenths of a nM. The lack of iron would severely limit the growth of diatoms at a point where there was still 10–15 μM nitrate remaining (Fig. 3B). Thus, iron would become the Liebig limiting nutrient for the development of this diatom bloom and leave surface waters high in macronutrients with diatoms being severely diffusion limited by the lack of dissolved Fe. This value of a few tenths of a nM dissolved Fe is also the point at which nitrate assimilation decreases relative to silicic acid assimilation and where the Si : N utilization shifts to higher values (Hutchins and Bruland 1998; Hutchins et al. 1998).

Other scenarios with various initial dissolved Fe and nitrate concentrations are also presented in Fig. 3B. In most scenarios, the system becomes iron limited while leaving excess major macronutrients. Thus, in these upwelled waters with a high delivery rate of macronutrients, we predict dissolved Fe to often become a critical Liebig limiting nutrient in controlling the extent of blooms of large diatoms. The ever-changing ratio of cellular Fe : C, which varies as a function of available iron in a non-Redfield manner, will result in many systems being driven to the point where growth rates of larger diatoms become diffusion limited by lack of dissolved Fe. At this point, the use of any excess cellular Fe previously assimilated as luxury uptake (Sunda and Huntsman 1995) and/or regenerated Fe (Hutchins et al. 1993; Hutchins and Bruland 1994) can play an important role in helping reduce Liebig limitation.

Methods

Sampling—Samples for iron determinations were collected by two different methods. Subsurface samples were collected by use of 30 L Teflon-coated GO-Flo bottles (General Oceanics) hung on Kevlar hydroline (Bruland et al. 1979). Surface samples were collected with a clean surface pump system by use of an all PTFE Teflon diaphragm pump (Osmonics Bruiser) and PFA Teflon tubing with a PVC "fish" deployed off the forward side of the ship (outside of the wake) at speeds from 1 to 7 knots. Samples were filtered through acid cleaned 0.4 μm absolute pore size polycarbonate track-etched (PCTE) membrane filters (Nuclepore) or 0.45-μm nominal pore size polypropylene capsule filters (Calyx, MSI). No significant differences in the "dissolved" metal concentrations were observed between the two filtering methods.

Analysis—Dissolved iron was measured by two different methods. Labile dissolved Fe was determined at sea using adsorptive cathodic stripping voltammetry (ACSV) on ultraviolet (UV)–irradiated samples (Rue and Bruland 1997). This UV irradiation pretreatment coupled with ACSV has been shown to provide an accurate measurement of total dissolved Fe on open ocean samples (Rue and Bruland 1997) in the presence of strong Fe-binding organic ligands that bound the Fe under ambient conditions. The UV-oxidation treatment was adequate to destroy the Fe-binding character of these ligands and liberate the bound Fe in oceanic samples for the subsequent ACSV determination. Total dissolved Fe was measured by PDC/DDC (dithiocarbamate) organic solvent extractions of samples that had been stored strongly acidified to a pH of 1.7–1.8 (4 mL of 6 N quartz sub-boiled hydrochloric acid per liter of seawater), followed by graphite furnace atomic absorption spectrometry (GFAAS) (Bruland et al. 1979). This method has been well documented to provide an accurate measurement of total dissolved Fe (Martin and Gordon 1988; Bruland and Rue 2001). Particulate samples were pressure filtered at ~0.5 atm overpressure through 142-mm, 0.4 μm PCTE Nuclepore filters. Particulate samples were analyzed for the trace metal content in both the 25% acetic acid (HAc) leachate and the residual refractory "bomb" digested fraction. Details of particulate Fe analyses are presented in Landing and Bruland (1987).

Nitrate and silicic acid concentrations were measured on either a Technicon AutoAnalyzer II or a Lachat Quick Chem 8000 Flow Injection Analysis system with use of standard methods (Parsons et al. 1984). Chl *a* measurements were performed at sea by use of fluorometry following the methods outlined in Parsons et al. (1984). Size fractionation studies were carried out by gentle filtration by use of 25-mm diameter 8 μm Poretics PCTE filters and GF/F filters.

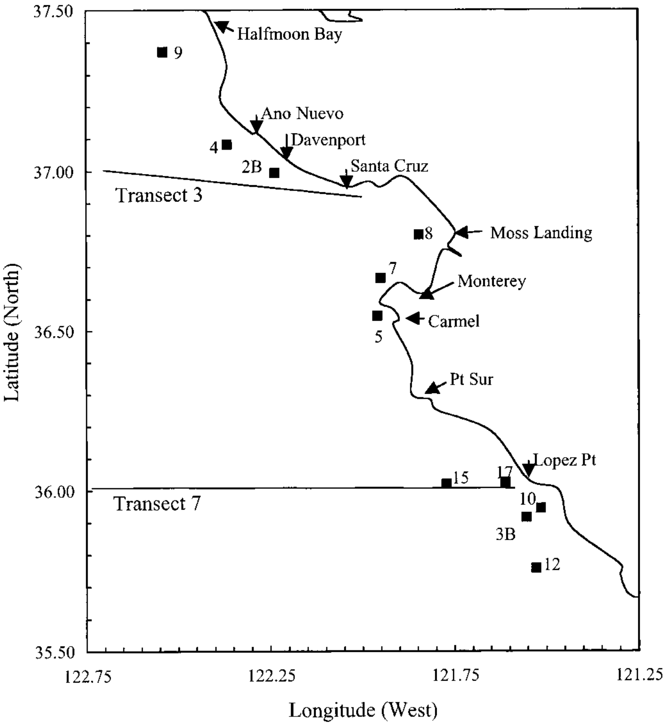


Fig. 4. Station locations for the June/July 1996 study where subsurface samples from a depth of 45 m within the center of active upwelling were taken. Also presented are the locations of surface transects 3 and 7.

Results and Discussion

Herein we present data from two initial field studies that investigated coastal upwelling regimes along the central California coast. Locations of vertical profiles representative of different water masses from offshore in the middle of the California Current to onshore in active coastal upwelling areas are shown in Fig. 1. Station locations where subsurface samples were collected from 45 m depth and two horizontal surface transects from onshore to offshore are shown in Fig. 4.

Vertical profiles—Vertical profiles of temperature, salinity, nitrate, silicic acid, labile Fe, and total dissolved Fe in the upper 300 m of the water column at a series of stations during July 1995 (*see Fig. 1*) are presented in Fig. 5. The southward flowing California Current (Sta. 4) is characterized by surface waters of relatively low salinity (32.8), warm temperature (16°C), depleted nitrate (<0.1 μM), and silicic acid (<0.5 μM), and low dissolved Fe (<0.05 nM). Sta. 5 was located offshore in the transition region between the California Current and the upwelled waters off Monterey Bay. Surface waters at Sta. 5 were warm (16.7°C), relatively low in salinity (33.07), low in nitrate (<0.1 μM) and silicic acid (~4 μM), and had intermediate dissolved Fe concentrations (0.4 nM). Coastal upwelled surface waters (Sta. 6 and 8, with Sta. 8 representing freshly upwelled waters) were characterized by high salinity (>33.8), low temperature (10°C), high nitrate (24 μM) and silicic acid (28 μM), and higher dissolved Fe concentrations (2–3 nM).

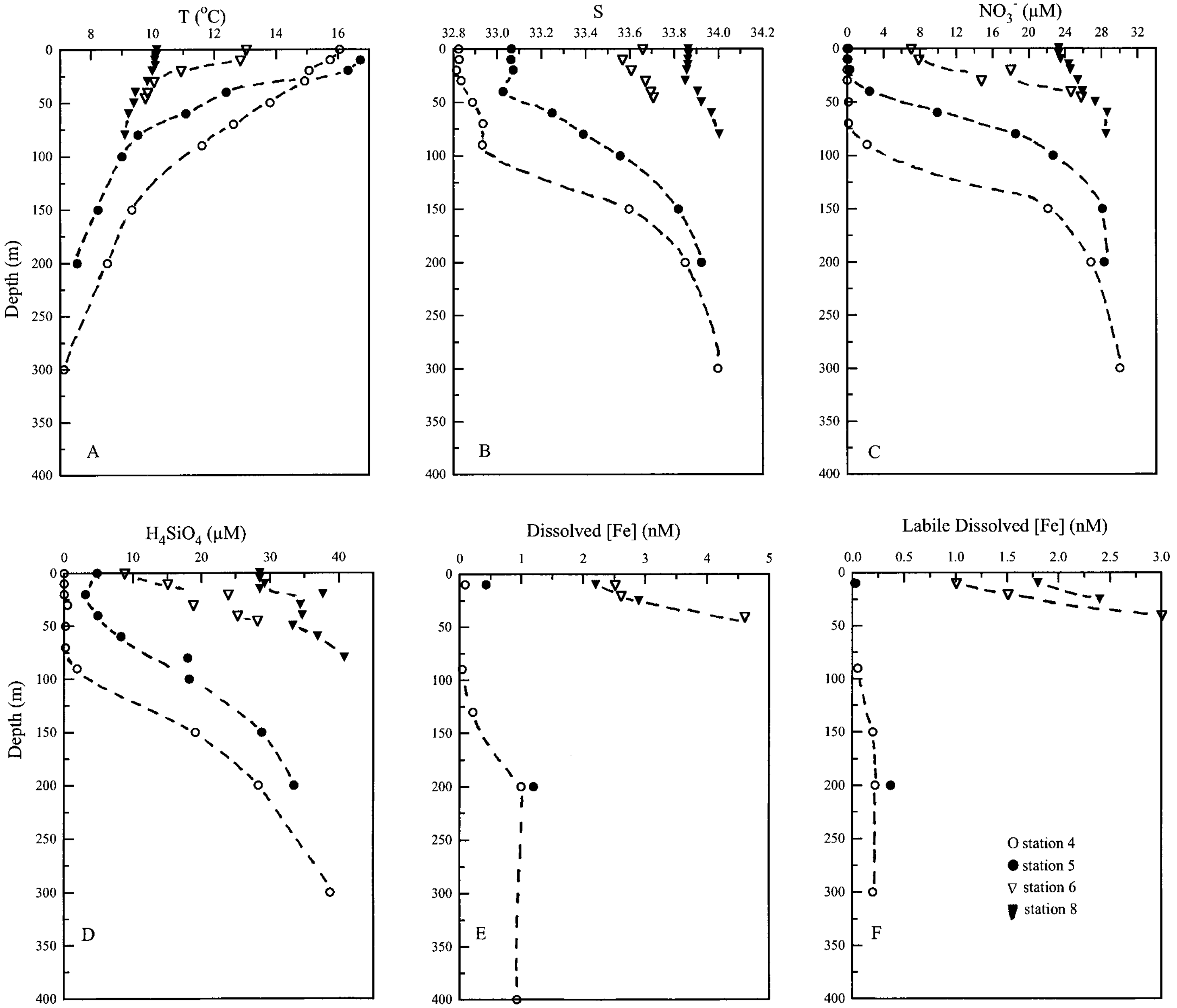


Fig. 5. Vertical profiles of (A) temperature, (B) salinity, (C) nitrate, (D) silicic acid, (E) total dissolved Fe, and (F) labile dissolved Fe in the upper 300 m of the water column at a series of stations beginning offshore in the middle of the California Current (Sta. 4), in transition waters (Sta. 5) and continuing onshore into active coastal upwelling areas (Sta. 6 and 8).

It is apparent from the salinity, temperature, and nitrate and silicic acid distributions that freshly upwelled surface waters (Sta. 8) have characteristics similar to waters found offshore in the California Current at depths of 150–200 m. In contrast, dissolved Fe observed at these coastal upwelling stations requires a major additional external source. The dissolved Fe concentrations offshore at depths of 150–200 m are only a small fraction of those observed in the surface waters at Sta. 8. Sta. 8 is representative of fresh upwelled water with low Chl *a* concentrations ($\sim$1 μg L^{-1}) that had not had a chance to bloom. Sta. 6 represents upwelled water in the Monterey Bay region that had begun to age, warm, and bloom, yielding higher Chl *a* concentrations ($\sim$5 μg L^{-1}).

Surface water dissolved Fe—Results of both labile dissolved Fe and total dissolved Fe for the coastal upwelled waters off central California during July 1995 are presented in Fig. 6. In these near-shore coastal waters the labile dissolved Fe is generally 0.3–2 nM lower than the total dissolved Fe. It appears that in these coastal waters the UV-oxidation treatment was not adequate to release all the dissolved Fe. In subsequent studies, we have found it necessary to include an acidification step in the sample pretreatment in order to release all the dissolved Fe from these coastal samples (Rue et al. unpubl. data). Acidification to pH 1.7 (with either storage or microwave treatment to speed the Fe release) coupled with subsequent analysis by ACSV, flow injection analysis, or our dithiocarbamate extraction fol-

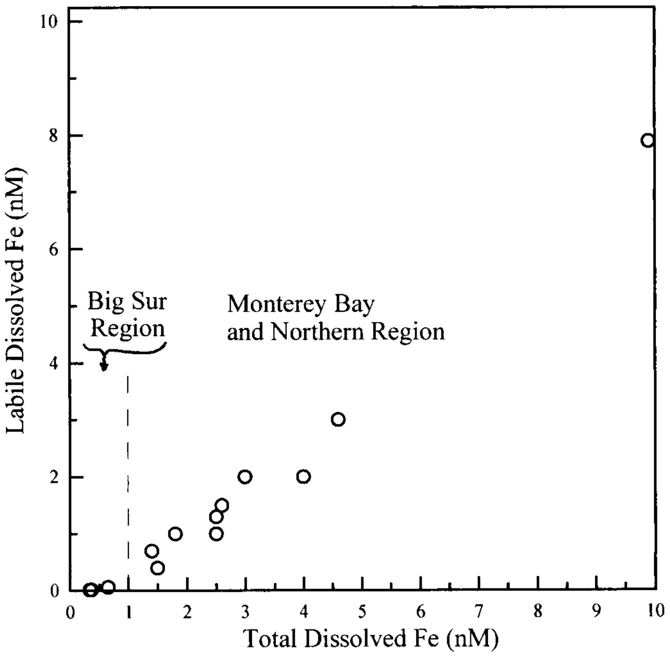


Fig. 6. Dissolved Fe (determined on acidified samples with the solvent extraction/graphite furnace atomic absorption method) and dissolved labile Fe (determined on UV-oxidized samples with the adsorptive cathodic stripping voltammetric method) for the coastal upwelling surface waters off central California during July 1995.

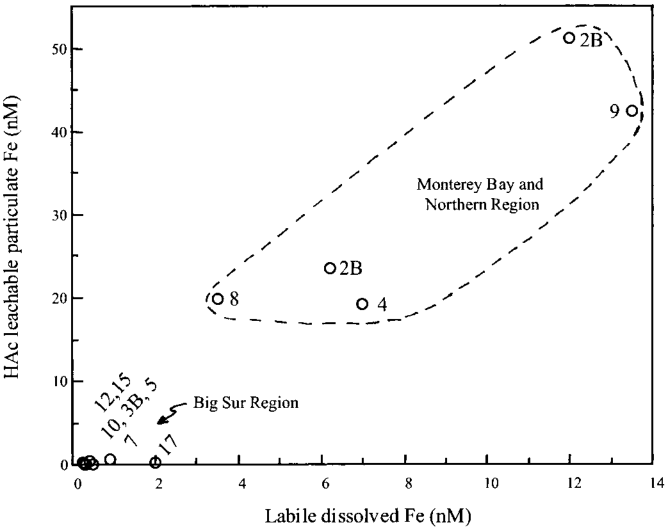


Fig. 7. Labile dissolved Fe versus the HAc leachable particulate Fe for the 45-m subsurface samples of "upwelled" water (see Fig. 4 for station locations).

lowed by GFAAS method provides an accurate estimate of total dissolved Fe in these coastal waters. On the basis of these results, it appears that there is a fraction of the dissolved Fe not detected by ACSV in these coastal waters that exists in a more refractory (perhaps colloidal) phase that is not released by UV irradiation without the additional step of acidification.

The origin of much of the upwelled water observed in the Monterey Bay area is to the north along the coast off Año Nuevo and Davenport (Rosenfield et al. 1994). This upwelling occurs over a region with a wide shallow shelf. The origin of much of the upwelled water off the Big Sur coast was just south of Pt. Sur. The coast in this region has an extremely narrow continental shelf, with most of the upwelling focused seaward of the shelf. In Monterey Bay and coastal upwelling regions further to the north, the labile dissolved Fe values ranged from 0.3 to 7.9 nM, whereas the total dissolved Fe ranged from 1 to 10 nM (Fig. 6). In contrast, in upwelled surface waters off the Big Sur coast the dissolved labile Fe was only 0.02–0.05 nM, whereas the total dissolved Fe was on the order of 0.3–0.6 nM.

Iron speciation studies (which use competitive equilibration/adsorptive cathodic stripping voltammetry; Rue and Bruland 1997) on these central California coastal surface water samples indicated the presence of a relatively small excess of strong Fe-binding organic ligands at each of the surface stations. It appears that phytoplankton, diatoms in particular, are somehow accessing dissolved Fe, even though it is chelated by strong Fe-binding organic ligands (Rue and Bruland 1997; Hutchins et al. 1999). For example, diatoms have been shown to use a surface reductase system that is effective at reducing the Fe(III) bound to organic ligands (Maldonado and Price 2001) in order to release the Fe for subsequent assimilation.

Subsurface upwelling waters characterized for dissolved and particulate Fe—A series of subsurface samples were collected from a depth of 45 m within the center of different active upwelling regions during the June/July 1996 study (*see Fig. 4* for sample locations). This was an attempt to collect freshly upwelled water just prior to its appearance at the surface, before biological or surface water processes could substantially alter its chemistry. Fig. 7 presents the labile dissolved Fe and the HAc leachable particulate Fe from these subsurface samples. In the northern upwelling areas off Davenport, Año Nuevo, and Half Moon Bay, the labile dissolved Fe concentration in the 45-m depth waters was high and ranged from 6 to 14 nM, whereas the HAc leachable particulate Fe concentrations were very high and ranged from 20 to 50 nM. In marked contrast, the 45-m samples from upwelling regions along the Big Sur coast had low labile dissolved Fe values ranging from 0.2 to 1 nM (2 nM at one near shore station), with very low HAc leachable particulate Fe concentrations ranging from 0.05 to 0.64 nM. The samples from the Northern Region were taken at active upwelling sites located over a broad shelf region, whereas the active upwelling regions to the south, along the Big Sur coast, were centered off the shelf break over the continental slope. The labile dissolved Fe concentrations were 6–70 times lower in the subsurface 45-m depth off the Big Sur coast, whereas the HAc leachable particulate concentrations were 30–1,000 times lower off the Big Sur coast than in the Monterey Bay and the region to the North.

The high concentrations of HAc leachable particulate Fe on these 45-m samples in the northern region averaged 7% of the total particulate Fe. In the surface waters, the percentage of the particulate Fe that was leachable with 25% acetic acid averaged only 2%. Thus, the high concentrations of HAc leachable particulate Fe observed in these subsurface samples in the northern areas could serve as a substantial additional source of dissolved Fe to the phytoplankton community. The concentrations of dissolved Fe observed in these waters is considerably higher than estimates of the solubility of Fe on the basis of inorganic chemistry (Millero et al. 1995; Wells et al. 1995). We suggest that the excess of strong Fe-binding ligands observed in these surface waters plays an important role in solubilizing this reservoir of particulate Fe, allowing the high concentrations of dissolved Fe to exist in these coastal waters. The chelation of Fe by the slight excess of strong Fe-binding ligands provides a mechanism for a significant portion of the particulate Fe to become solubilized and available to the phytoplankton community. This appears particularly important in the coastal upwelling systems to the north of Monterey Bay where high concentrations of HAc leachable particulate Fe are entrained in the upwelled waters. Phagocytosis of particulate Fe may also be a mechanism for making this fraction of iron available to the phytoplankton community (Raven 1997; Maranger et al. 1998), either directly or subsequently as regenerated Fe.

Fe-replete and Fe-deplete coastal upwelling regimes—During both the 1995 and 1996 studies, we observed two markedly different types of coastal upwelling regimes along the Central California coast with respect to the concentrations of iron. The first type occurs over a relatively broad continental shelf typified by the coastal region between Monterey Bay and Pt. Reyes. This shelf is resupplied each year with a fresh source of fine-grained sediment from winter floods via riverine input (Fig. 1). In this regime, coastal upwelling occurs over a broad shallow shelf. Near-shore shelf water, with its enhanced concentration of particulate and dissolved Fe, is entrained along with the macronutrient enriched upwelled water. The second type of upwelling system is exemplified by the Big Sur coast, a region with an extremely narrow continental shelf and without any significant river inputs to provide a fresh source of Fe. In this system, there is little entrainment of particulate or dissolved Fe along with the upwelled water, because upwelling is focused off the shelf over the deeper continental slope. As a result, the freshly upwelled water lacks an adequate external supply of the micronutrient Fe to complement the high input of macronutrients and support the formation of extensive blooms of large coastal diatoms.

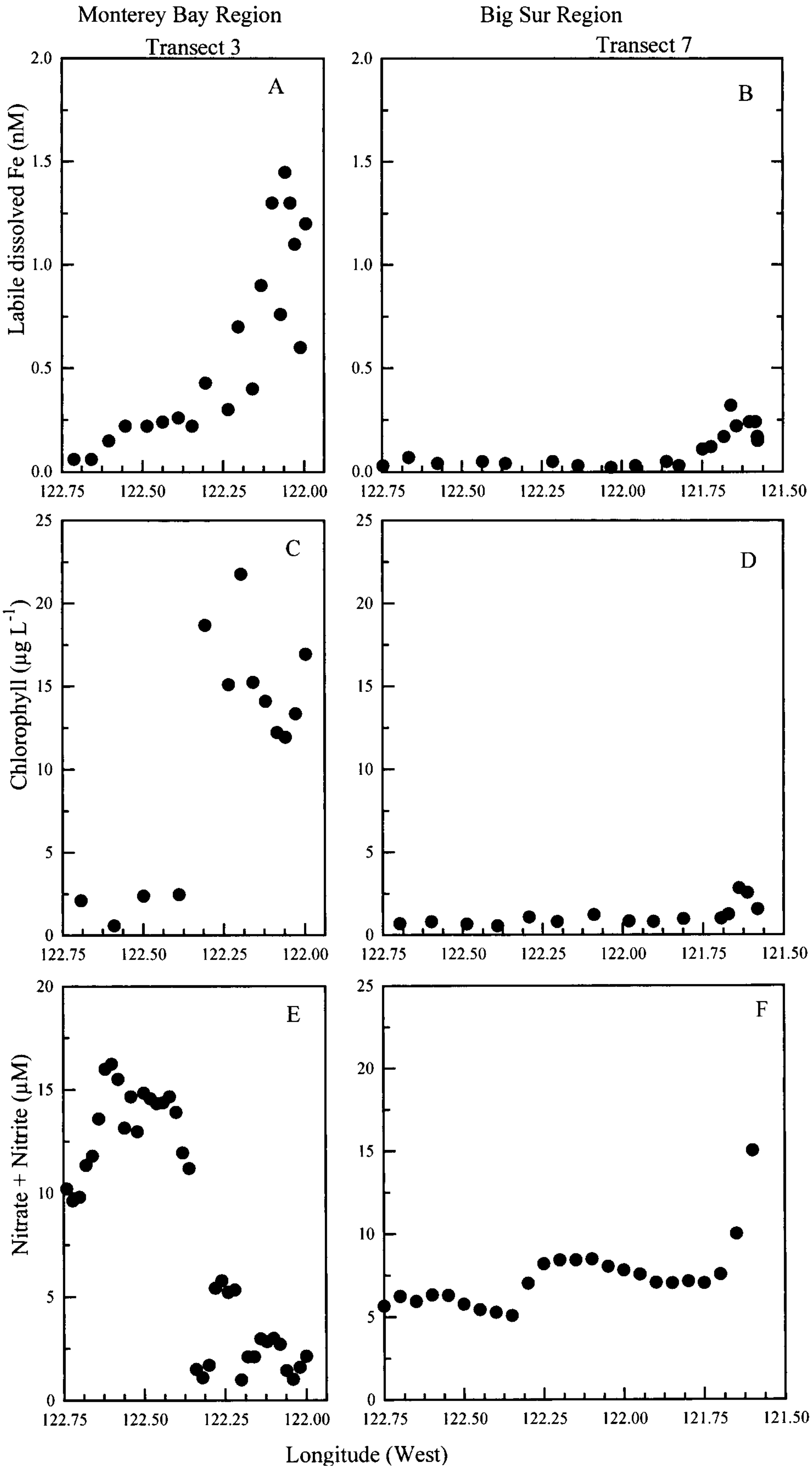
Two surface water transects in which labile dissolved Fe and Chl *a* were measured during the June/July 1996 study are presented in Fig. 8. In Transect 3, located off Santa Cruz, the labile dissolved Fe in surface waters over the shelf region was on the order of 1–1.5 nM and decreased to 0.2 nM offshore (Fig. 8A). The Chl *a* concentrations were high and varied from 12 to 22 μg L^{-1} over the shelf region where extensive blooms of large diatoms were observed (Fig. 8C). The nitrate had been drawn down in these high chlorophyll shelf waters to values between 1 and 6 μM (Fig. 8E). The Chl *a* concentration decreased offshore to 1–3 μg L^{-1} and the nitrate increased to concentrations of 10–17 μM. When labile dissolved Fe concentrations were $>$0.3 nM, high chlorophyll concentrations were observed. This threshold Fe concentration of $\sim$0.3 nM is consistent with that predicted to be required for high growth rates of coastal diatoms in Fig. 2. This region provides a good example of a high-Fe, high-nutrient, high-chlorophyll, coastal upwelling regime dominated by extensive blooms of large diatoms.

Transect 7, located off the Big Sur coast, had labile dissolved Fe concentrations of 0.1–0.3 nM close to shore and values on the order of 0.05 nM offshore (Fig. 8B). Low phytoplankton biomass was observed, with Chl *a* concentrations of 2–3 μg L^{-1} near shore and on the order of 1 μg L^{-1} offshore (Fig. 8D). Nitrate (plus nitrite) concentrations ranged from 5–15 μM in this region (Fig. 8F). The Big Sur region provides a good example of a low-Fe, HNLC coastal upwelling regime where the growth rate of diatoms is limited by the lack of iron.

Data collected from a variety of surface stations in July 1995 provided another opportunity to examine the effect of iron on phytoplankton bloom development. The labile dissolved Fe concentrations are plotted against the Chl *a* concentration for surface water samples in the Monterey Bay region and the Big Sur region during the 1995 study (Fig. 9A). The offshore waters of the Big Sur region, with labile dissolved Fe between 0.02 and 0.05 nM, had nitrate concentrations between 11 and 15 μM, yet had low Chl *a* concentrations between 0.6 and 2 μg L^{-1}. One nearshore station with slightly elevated labile Fe had Chl *a* values on the order of 5 μg L^{-1}. In marked contrast, surface waters throughout the Monterey Bay region had labile Fe concentrations varying from 0.3 to 2.0 nM, with Chl *a* concentrations ranging from 5 to 23 μg L^{-1}. In the Monterey Bay region, where extensive blooms of large diatoms are observed, the concentrations of labile dissolved Fe appear to be high enough to allow large diatoms to grow at near maximal rates and bloom. High Chl *a* concentrations do not necessarily correspond directly with high dissolved Fe, because much of the original Fe will have been assimilated by the high biomass and exists intracellularly. In fact, at an Fe : C ratio of 50 μmol mol^{-1} in the coastal diatoms, a Chl *a* value of 20 μg L^{-1} would be associated with $\sim$8 nM cellular Fe. Thus, the greatest reservoir of Fe in the waters with a well-developed diatom bloom will usually be cellular Fe.

Size fractionation of chlorophyll in the contrasting regimes—Figure 9B presents total Chl *a* concentrations versus the percentage of Chl *a* $>$8 μm in size from stations in the 1995 study. In the high-Fe, high-nutrient, high-chlorophyll regions of the Monterey Bay, the percentage of Chl *a* $>$8 μm ranged from 80% to 98% (Fig. 9B), with large diatoms dominating the phytoplankton community (Hutchins et al. 1998). In contrast, in the low-Fe, HNLC regions such as off the Big Sur coast, the percentage of the chlorophyll in the $>$8 μm fraction was much lower (between 5% and 40%). This observation is consistent with our predictions based on diffusion limitation of iron being more critical for larger diatoms.

''Aging'' of upwelled waters—As an upwelled parcel of water ages, temperature will increase because of either insulation or mixing with warmer water. Nitrate can become depleted as a result of phytoplankton assimilation and biomass increase, or it can decrease as a result of mixing with


Monterey Bay Region
Transect 3
Big Sur Region
Transect 7
A
B
C
D
E
F
Labile dissolved Fe (nM)
2.0
1.5
1.0
0.5
0.0
Chlorophyll (μg L-1)
25
20
15
10
5
0
Nitrate + Nitrite (μM)
20
15
10
5
0
122.75
122.50
122.25
122.00
121.75
121.50
Longitude (West)

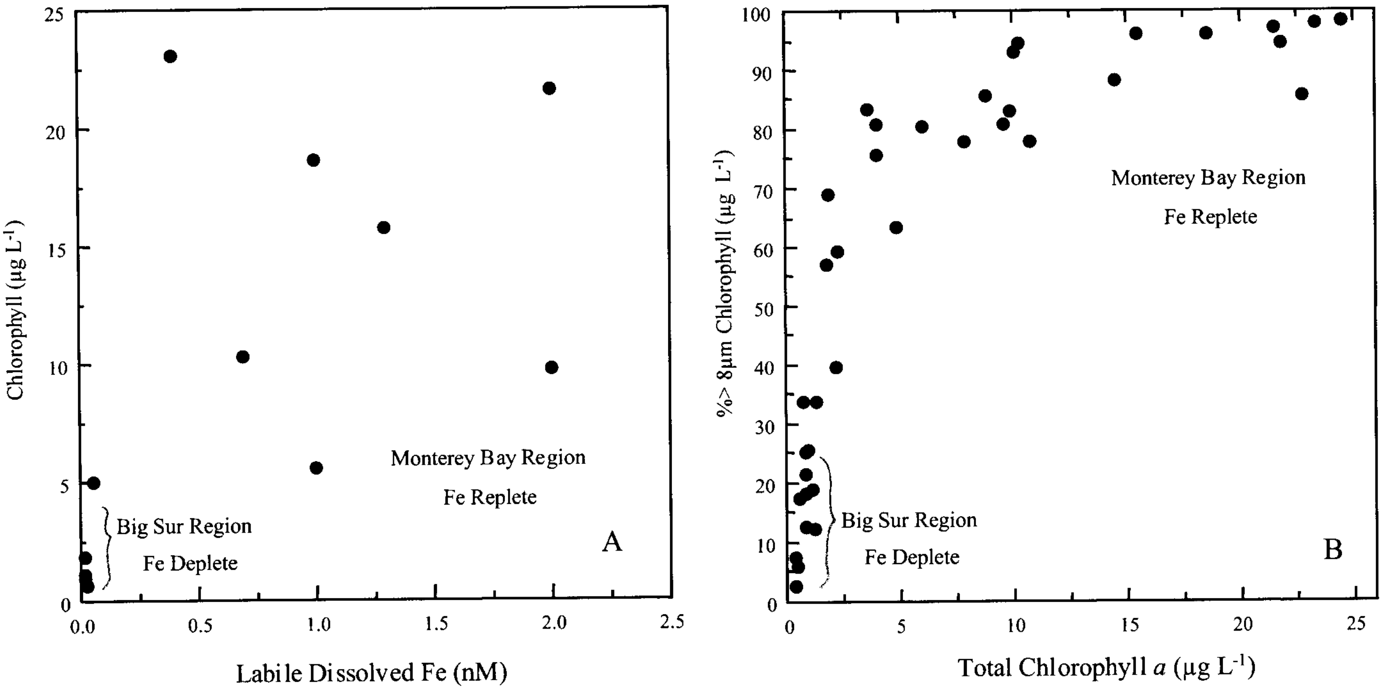


Fig. 9. (A) Labile dissolved Fe versus Chl *a* concentrations for surface water samples in the Monterey Bay region and the Big Sur region during the July 1995 study. (B) Total Chl *a* concentrations versus the percentage of Chl *a* in the >8 μm size fraction from stations in the July 1995 study.

low nitrate offshore water. Salinity is a conservative tracer and will not change unless there is mixing of water masses. Thus, salinity can help differentiate between warming and aging of initially cold, higher salinity, upwelled waters versus mixing with warm, low salinity, nutrient deplete offshore waters. In July 1995, surface water at the upwelling center located just south of Año Nuevo was characterized by an initial temperature of 10.2°C, a salinity of 33.6, a nitrate concentration of 22 μM, and a silicic acid concentration of 24 μM. Total dissolved Fe in this water was 4.6 nM, with labile dissolved Fe of 3 nM. This upwelled water advected southwards into Monterey Bay during a time of lessening wind that allowed this water mass to warm and stratify and time for the phytoplankton community to bloom. The salinity remained almost constant as the temperature rose from 10.2°C to between 12.5°C and 13°C. During this time, the nitrate was drawn down to values of only 1–4 μM, silicic acid was drawn down to 4 μM, and the Chl *a* increased markedly to concentrations between 20 and 23 μg L^{-1}. This large chlorophyll increase was due to an extensive bloom of large diatoms with ~95% of the Chl *a* present in the >8 μm size fraction.

Complementary shipboard grow-out experiments of freshly upwelled water from this region carried out during the same time interval also exhibited similar nutrient drawdown and chlorophyll increases (Hutchins and Bruland 1998). Nitrate and silicic acid were completely drawn down during a period of 4 d with or without additions of iron. Initial nitrate values in freshly upwelled waters were 23–24 μM (silicic acid was 27 μM), and Chl *a* values were <1 μg L^{-1}. Maximum Chl *a* values of 20–23 μg L^{-1} were observed after 4 d in the shipboard grow-out experiments just as the nitrate was depleted (Hutchins and Bruland 1998).

In July 1995, there was an extensive area in the Monterey Bay region with high salinity surface waters indicative of upwelled waters extending to 50 km offshore. This area exhibited relatively high dissolved Fe concentrations for offshore waters of 0.2–2 nM, variable nitrate concentrations of 1–10 μM, and high and variable chlorophyll concentrations of 10–25 μg L^{-1} (with >90% being in the >8 μm size fraction; Fig. 9B). The sum of the Chl *a* (μg L^{-1}) and nitrate (μM) was generally between 20 and 25, which is consistent with Chl *a* increasing as nitrate is assimilated at an ~1 : 1 ratio (μg L$^{-1:}\mu$M).

A series of plots depicting changes in temperature, nitrate, and Chl *a* content in the water masses from the Año Nuevo/Monterey Bay area are presented in Fig. 10A–C. The dashed lines at relatively constant salinity imply that the water masses were roughly the same and that as they "aged," they warmed, and the phytoplankton community bloomed and

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Fig. 8. Comparison of two surface transects during June/July 1996 in the Monterey Bay region (Transect 3) and the Big Sur Region (Transect 7). (A and B) Surface water labile dissolved Fe concentrations. (C and D) Surface Chl *a* concentrations. (E and F) Surface nitrate (plus nitrite) concentrations.

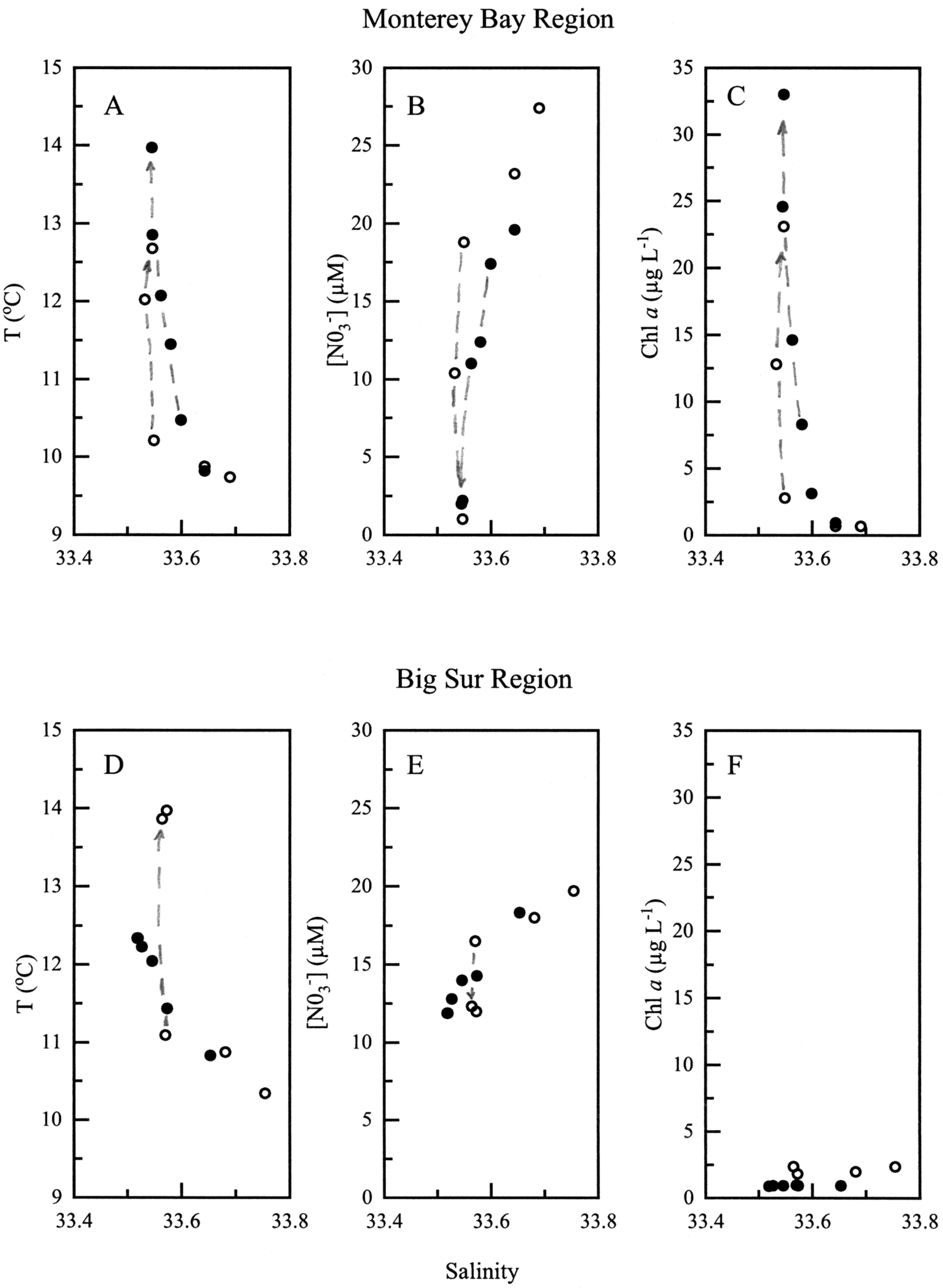

Fig. 10. (A) Temperature, (B) nitrate, and (C) Chl *a* concentrations versus salinity during two studies where water parcels were followed as they advected offshore, aged, and warmed in the Monterey Bay region. (D) Temperature, (E) nitrate, and (F) Chl *a* concentrations versus salinity where two different water parcels were followed as they aged and warmed in the Big Sur region. The dashed lines at relatively constant salinity infer that the water mass was roughly the same and that as it "aged," the water warmed.

drew down the nitrate. As the nitrate (μM) was drawn down, there was a corresponding increase in Chl *a* (μg L^{-1}). This is an example of a typical bloom with minimal grazing occurring in these high-Fe, high-nutrient, and high-chlorophyll waters.

During this same period (July 1995), the Big Sur area had upwelled waters characterized by an initial temperature of 11°C and a salinity of 33.6. Initial nitrate concentrations were 16–18 μM, and silicic acid concentrations were 18–20 μM. We observed and sampled this water during a relaxation period of low winds as it warmed to 12.5°C to 14°C, while maintaining roughly the same salinity (Fig. 10D). The nitrate and silicic acid values decreased only a small amount to concentrations of 10–15 μM, whereas the Chl *a* increased

Table 1. Characteristics of upwelled surface water 3–50 km offshore along the central California coast during June/July 1995 and June 1996.

Parameter	Fe-replete region, Monterey Bay and north	Fe-deplete region Big Sur Coast
Nitrate	1–15 μM (originally $\sim$25 μM)	10–15 μM (originally $\sim$25 μM)
Silicic acid	Depleted along with nitrate (originally $\sim$25 to 30 μM)	Depleted relative to nitrate (originally $\sim$20–30 μM)
Labile dissolved Fe	0.2–8 nM (originally 6–14 nM)	0.02–0.1 nM (originally 0.2 to 1 nM)
Total dissolved Fe	0.3–10 nM	0.1–0.6 nM
HAc particulate Fe	(Originally 20–50 nM)	(originally 0.05–0.64 nM)
Chlorophyll *a*	5–25 μg L^{-1} 80% $>$ 8 μm	0.4–3 μg L^{-1} 80% $<$ 8 μm (only $\sim$20% $>$8 μm)
Diatom blooms?	Yes: high chlorophyll extensive blooms of large diatoms	No: low chlorophyll, low abundance of large diatoms

only to 1–2 μg L^{-1} (Fig. 10E,F). In this case, there was a large area from 5 to 60 km offshore where the labile dissolved Fe averaged only 0.02 nM (with total dissolved Fe $\sim$0.3 nM). In these surface waters, $>$75% of the Chl *a* occurred in the $<$8 μm size fraction and typified a coastal upwelling HNLC region. In shipboard incubations, Hutchins and Bruland (1998) and Hutchins et al. (1998) have demonstrated that surface waters in this region off the Big Sur coast were Fe limited and responded with a marked increase in Chl *a* and draw-down of nitrate after the addition of 2–10 nM iron.

Thus, the low dissolved Fe concentrations in the Big Sur area provide an excellent example of Liebig limitation. Specifically, the lack of Fe, relative to the supply of nitrate, phosphate, and silicic acid, severely limits the drawdown of nitrate and the development of extensive blooms of large coastal diatoms in this area. The upwelled surface waters off the Big Sur coast had only 0.02–0.10 nM of labile dissolved Fe and 0.2–0.6 nM of total dissolved Fe, concentrations that are inadequate relative to the potential uptake of 16–18 μM nitrate by coastal diatoms.

Table 1 summarizes the differences between the Fe-deplete Big Sur region and the Fe-replete Monterey Bay region. Freshly upwelled water in both regions are low in Chl *a* and high in macronutrients. In the Monterey Bay and regions north to Pt. Reyes, there appears to be adequate Fe to allow the full utilization of the available macronutrients and the development of extensive blooms of large diatoms downstream of the upwelling centers. In marked contrast, the Big Sur region lacks a significant source of iron to be entrained with the upwelled waters; the phytoplankton community in the region becomes Liebig limited by the lack of adequate iron, and larger bloom-forming diatoms are rate limited by the resultant low concentrations of dissolved Fe.

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