

## The annual cycle of iron and the biological response in central California coastal waters

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**Abstract.** Iron has been measured for 16 months with ~21 day resolution at three stations in the upwelling ecosystem of central California, providing the first detailed assessment of the annual iron cycle in the coastal zone. A large pulse of iron occurs during the first spring upwelling event of the year. Iron concentrations then decay up to 100-fold over several months, although upwelling continues. Excess surface nitrate and low iron are the result during the summer and fall at the two stations furthest offshore (20 and 45 km), while nitrate is depleted and iron high nearshore (5 km). Phytoplankton biomass, primary production and community structure appear to be controlled by iron concentrations in offshore waters during this period.

### Introduction

Recent work has suggested that iron may play an important role in regulating coastal ecosystems [Hutchins and Bruland, 1998; Hutchins *et al.*, 1998]. Nitrate concentrations were generally assumed to be the primary factor regulating the rate of primary production and the accumulation of biomass in coastal areas of the world ocean [Ryther and Dunstan, 1971; Kudela and Dugdale, 2000]. However, surveys of the coastal ocean often show that nitrate concentrations are decoupled from biomass [Chavez *et al.*, 1991a]. This paradox has also been observed in open ocean, High Nitrate, Low Chlorophyll (HNLC) areas such as the Equatorial Pacific and Southern Ocean, where biomass is regulated by iron concentration, rather than nitrate [Martin, 1990; Coale *et al.*, 1996].

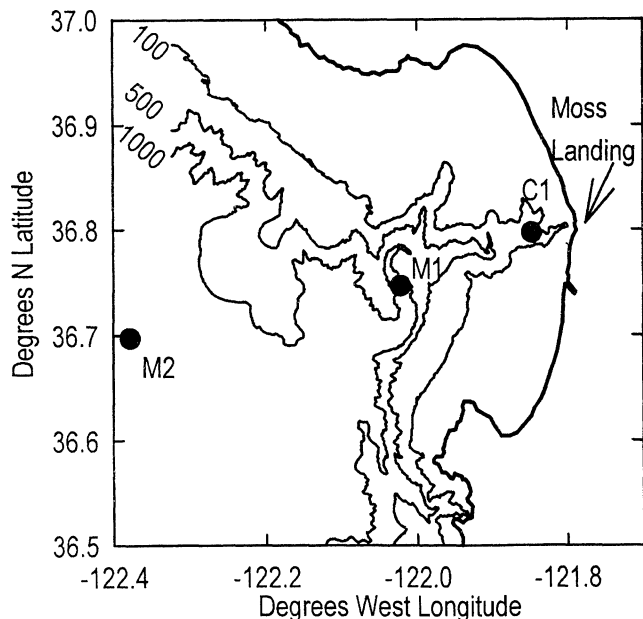
Nitrate is primarily delivered to the surface in coastal ecosystems by upwelling of macro-nutrient (nitrate, phosphate, silicate) rich, offshore waters from depths of 60 to 200 m. These waters are depleted in iron, relative to nitrate [Johnson *et al.*, 1997], resulting in excess nitrate at the surface when open ocean upwelling occurs. Resuspension of sediments as waters flow through the benthic boundary layer on continental shelves, however, can enrich upwelled waters with the iron required to sustain their extraordinary biomass [Johnson *et al.*, 1999]. The decoupling of nitrate and iron sources during upwelling sets up the potential for coastal iron limitation. However, little is known about the temporal variability of iron in coastal systems [Wu and Luther, 1996; Croot and Hunter, 1998] or the interaction of iron with biological processes in coastal ecosystems [Hutchins and Bruland, 1998; Hutchins *et al.*, 1998]. Here we present measurements of iron over a full annual cycle in a coastal

ecosystem. The relationship of iron concentrations to ecosystem parameters is examined.

### Methods

Dissolved and dissolvable iron were determined by flow injection analysis with chemiluminescence detection [Obata *et al.*, 1993] at approximately 21 day intervals from March 1999 through June 2000. Measurements were made on samples from three stations that were 5, 20 and 45 km offshore (Stations C1, M1 and M2, respectively) of Moss Landing, California (Fig. 1). Stations M1 and M2 were collocated with bio-optical moorings [Chavez *et al.*, 1997]. Seawater was collected for iron analysis at a depth of 1 to 2 m with a Teflon<sup>®</sup> pumping system and samples were stored overnight at <5°C. Dissolvable iron samples were acidified to pH 3 with ultrapure acid and analyzed after 1 minute [Johnson *et al.*, 1999]. Dissolved iron samples were filtered (0.45  $\mu$ m) and then acidified to pH 3 for analysis.

Nitrate, phosphate, silicate, chlorophyll, primary productivity and phytoplankton major group biomass were determined at each station [Pennington and Chavez, 2000]. Phytoplankton carbon was estimated from microscopic determinations of major phytoplankton group abundance and

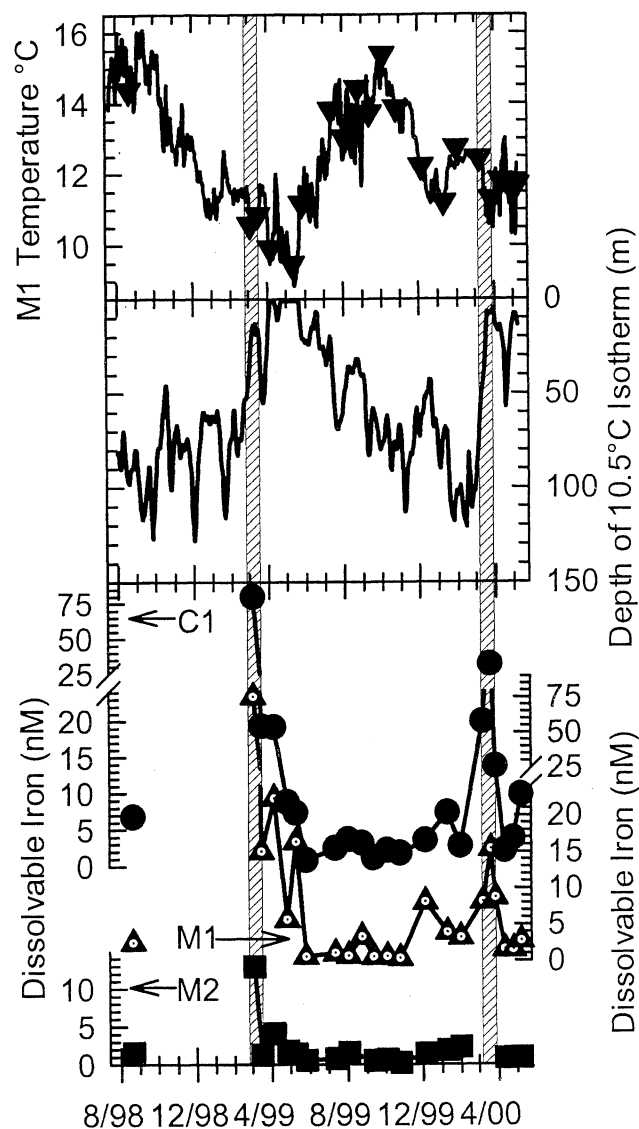


**Figure 1.** Station locations (C1 - 36.797° N, 121.847° W, 230 m depth; M1 - 36.747° N, 122.022° W, 1200 m depth; M2 - 36.697° N, 122.378° W, 1700 m depth). Contour values in meters.

cell volume and application of cell volume to cell carbon algorithms [Chavez *et al.*, 1991b].

## Results and Discussion

Oceanographic conditions at the M1 site over the past decade have recently been described in detail [Pennington



**Figure 2.** Annual cycle of surface temperature, depth of the 10.5°C isotherm, and dissolvable Fe. (A) Daily average values of surface (1 m) temperature measured on the M1 mooring are shown (solid line) from March 1999 through June 2000. Triangles show the temperature measured at 1 m with a CTD on sampling cruises. Temperature was not determined on 2 of the 23 cruises. (B) Depth of the 10.5°C isotherm (m) interpolated from daily average of temperature measurements each 10 minutes from 1 to 300 m with 10 to 20 m vertical resolution in the upper 100 m on the M1 mooring. Data has been smoothed with a 5 point running mean. (C) Dissolvable iron concentrations measured at C1 (●), M1 (▲) and M2 (■) in samples collected at 1 to 2 m depth. The hatched boxes pass through the iron maxima and show the linkage to shoaling of the 10.5°C isotherm. No samples were collected at M2 during March 2000.

and Chavez, 2000]. Strong upwelling and lowest water temperatures occur during March through June. Upwelling continues into October, albeit as a series of short term events (1 to 2 weeks). Temperatures are significantly higher during the July to October period (Fig. 2). Nitrate concentrations generally remain above levels thought to limit phytoplankton rate processes [Dugdale and Wilkerson, 1989].

The annual cycle of iron concentration that we observed at each station is dominated by a large pulse of iron into surface waters during the first event of spring upwelling in 1999 and 2000 (Fig. 2). In 1999, the highest iron concentrations were measured 3 days after the beginning of the first strong upwelling event of the year (Fig. 2). We do not have measurements of iron immediately prior to that event. However, measurements in August of 1998 and winter of 1999/2000 strongly imply that iron concentrations were low prior to that event (Fig. 2). Dissolved iron accounted for only about 20% of the dissolvable iron that we measured during the 16 month period, although the relationship was not linear. Dissolved Fe ( $Fe_D$ ) was related to dissolvable Fe ( $Fe_P$ ) by the equation:

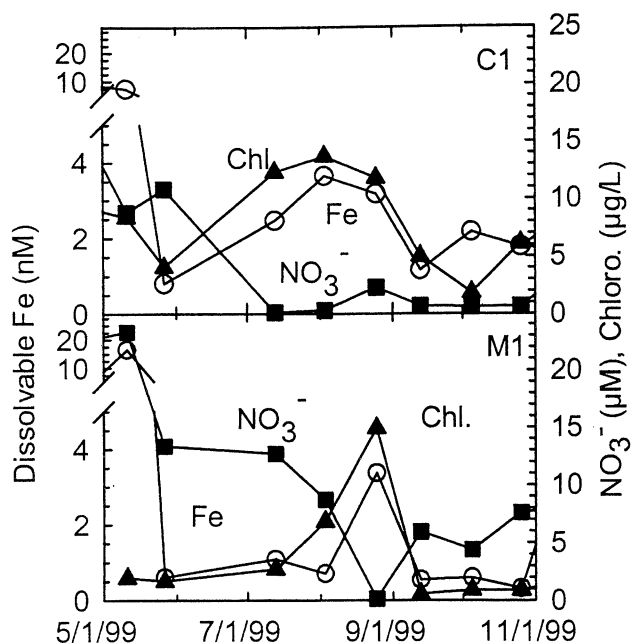
$$Fe_D = \frac{3.5 \times Fe_P}{4.9 + Fe_P}, R^2 = 0.60 \quad (1)$$

The dissolved and dissolvable Fe concentrations were not significantly different at concentrations <0.7 nM. The elevated concentrations of dissolvable iron were dominated by particulate sources.

The rapid increase in iron concentration during each spring was coincident with the initial shoaling of the 10.5°C isotherm (Fig. 2). The depth of the 10.5°C isotherm is near 75 m during winter. We believe that this water entrains iron rich particles from the benthic boundary layer when it is on the continental shelf [Johnson *et al.*, 1999]. The iron sorbed on particles may be derived from diagenetic remobilization of iron oxides buried in sediments, remineralization of sinking plankton or terrestrial material transported by rivers. These particles are carried to the surface with the first upwelling event of the year, which raises dissolvable iron concentrations. However, upwelling continues for several months while iron concentrations begin to drop shortly after the first upwelling event. Isopycnal surfaces tilt after upwelling commences so that the water reaching the surface may encounter the boundary layer for a shorter period of time in the inner shelf. This may result in little resuspended iron reaching the surface, rather than a change in composition of the resuspended particles.

It is unlikely that iron is limiting during the early spring upwelling period due to the high dissolvable iron concentrations that are transported with the initial upwelling events. However, iron concentrations drop as much as 100-fold, while nitrate, phosphate and silicate concentrations generally remain within a factor of four of the maximum during most of the summer and early fall. The exception occurred at the station nearest shore (C1), where iron concentrations were substantially higher than at M1 or M2 during the warm period (Fig. 3). Nitrate became depleted at C1 (Fig. 3) with a mean concentration of 1.2  $\mu$ M. The silicate mean was 6.4  $\mu$ M, and less likely to limit primary production.

These observations suggest that iron may become limiting during the warm period. The relationships between iron concentration and biological parameters during the July through October warm period are shown in Figure 4. Rates of



**Figure 3.** Chlorophyll (▲), nitrate (■) and dissolvable iron (○) from May through October 1999 at C1 and M1. All samples were collected at 1 to 2 m depth.

primary productivity, chlorophyll to carbon ratios, and phytoplankton biomass are all positively correlated with dissolved iron. The fraction of pico-phytoplankton carbon (cell diameter  $<2 \mu\text{m}$ ) is negatively correlated with iron. Diatoms and, in one case, dinoflagellates comprise the majority of the phytoplankton not contained within the picoplankton.

All of the correlations shown in Figure 4 are significant at the 0.05 level. We have used dissolved iron measurements in Figure 4, rather than dissolvable iron, to avoid the possibility that any relationships are driven by iron released from phytoplankton during analysis of unfiltered samples. However, the very labile particulate fraction of the dissolvable iron pool may be bioavailable [Johnson *et al.*, 1999]. The significance level increases for all correlations if dissolvable iron is used, rather than dissolved iron. The relationship between dissolved and dissolvable iron (Equation 1) may be driven by a rapid exchange equilibrium between dissolved iron and iron sorbed to particle surfaces.

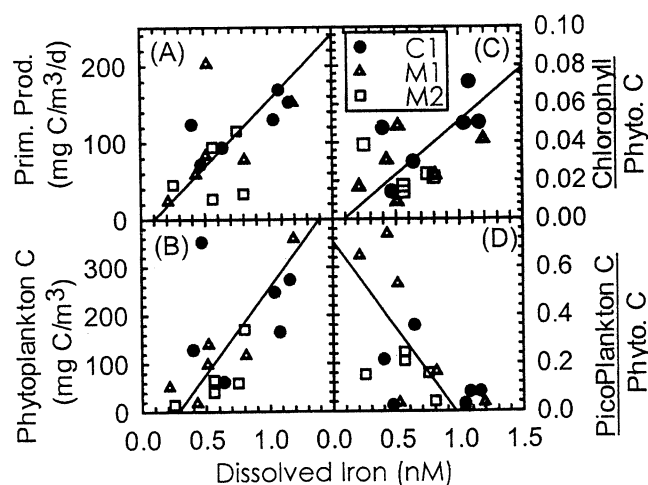
Reductions in the chlorophyll to carbon ratio (chlorosis), similar to that shown in Figure 4c, are a regular response of phytoplankton grown in culture to iron stress [Geider and LaRoche, 1994; Sunda and Huntsman, 1997]. Low chlorophyll to carbon ratios can also be demonstrated in nitrogen deficient cultures [Riemann *et al.*, 1993]. There is not a significant correlation of chlorophyll to carbon ratio with nitrate in our data set ( $R^2=0.05$ ), suggesting that iron limitation is the mechanism driving variations in the ratio in coastal California waters.

Phytoplankton community structure changes from a system dominated by diatoms at high iron concentrations to a picoplankton dominated population at low iron [Morel *et al.*, 1994; Coale *et al.*, 1996; Landry *et al.*, 1997]. However, community growth rates (primary production divided by phytoplankton carbon; not shown) did not decrease significantly with iron concentration during the warm period,

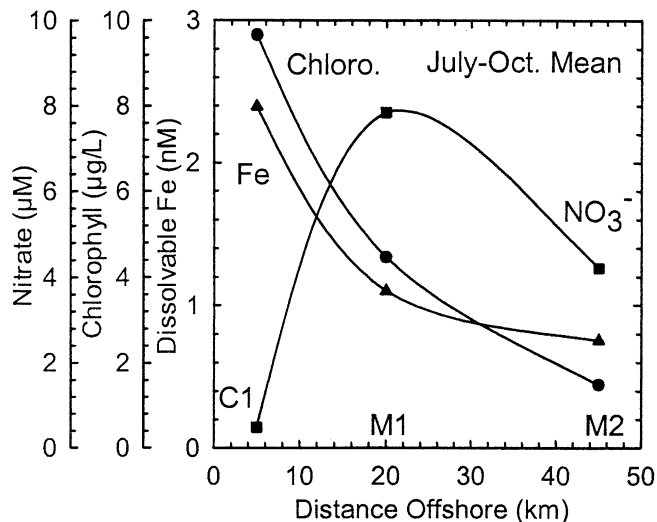
as the best fit lines to primary production and phytoplankton carbon (Figs. 4a and 4b) are parallel. The absolute abundance of picoplankton (not shown) is also independent of iron and primary production in the  $<5\mu\text{m}$  size fraction remains constant at  $20\pm 20 \text{ mg C m}^{-3} \text{ d}^{-1}$  with no significant trend versus iron. These observations demonstrate that low concentrations of iron shift population structure in the coastal zone by limiting growth of large phytoplankton, which require high iron. Smaller phytoplankton, capable of high intrinsic growth rates at low iron concentrations, are less affected by iron concentration. Grazing is believed to prevent pico-phytoplankton biomass from accumulating [Morel *et al.*, 1991].

The observations are consistent with iron regulation of phytoplankton biomass (Fig. 4b), phytoplankton rate processes (Fig. 4a), phytoplankton physiology (Fig. 4c) and ecosystem structure (Fig. 4d) during the warm period in the central California coastal region. High iron concentrations at C1 allow larger phytoplankton to accumulate (Fig. 4d) and nitrate to be depleted (Fig. 3). Low nitrate at C1 may, therefore, be the proximate limit on growth at that station during summer and fall. The limiting nutrient appears to switch to iron within the large iron gradient found at distances of 5 to 20 km from shore (Fig. 5). Episodic upwelling events that introduce iron then have a pronounced impact in offshore waters. A moderate increase in dissolvable iron occurred at M1 (Fig. 2) from 0.7 nM on 8/3/99 to 3.3 nM on 8/28/99 (dissolved Fe: 0.5 to 1.2 nM). This pulse of iron appears to have caused the largest bloom observed within this system during the warm period (Fig. 3). This bloom drew nitrate concentrations to near zero values at M1.

Threshold changes in marine ecosystem behavior have been described by effects such as the "shift-up" hypothesis, which suggests that phytoplankton undergo a distinct physiological change at a nitrate concentration near  $10 \mu\text{M}$  [Dugdale and Wilkerson, 1989]. Our results from central California would imply that variations in the relative abundance of nitrate and iron may play an important role in



**Figure 4.** Primary production (A), total phytoplankton carbon (B), chlorophyll/phytoplankton carbon ratio on a weight basis (C) and picoplankton carbon to all phytoplankton carbon ratio (D) at 1 m. Measurements are from the period July through October, 1999 at C1 (●), M1 (△) and M2 (□). Picoplankton include *Synechococcus* and Red Fluorescing Picoplankton [Chavez *et al.*, 1991b].



**Figure 5.** Mean nitrate (■), chlorophyll (●) and dissolvable iron (▲) at 1 m for the period July through October 1999 versus distance of the station from Moss Landing.

creating such thresholds. The relative abundance of iron and nitrate may also exert an influence over ecosystems at geological time scales as the morphology of continental margins changes due to accumulation of ice on land and a corresponding drop in sea level. At low stands of sea level, narrow continental shelves were a global feature. This would act to limit the magnitude of the spring pulse of iron, but it would not affect the supply of nitrate. Such a process may account for the low rates of primary production that occurred during the last glacial maximum along the west coast of the America's [Dean *et al.*, 1997; Ganeshram *et al.*, 1998].

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