Chapter 4

SANTA MONICA BAY OCEAN TIME SERIES

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1. Introduction

Trace metals such as iron (Fe) and manganese (Mn) are essential micronutrients required for enzymatic pathways of respiration, nitrogen and carbon fixation, and electron transfer in photosynthesis in marine biology (Turner and Hunter, 2001). As a result, the ocean depth profiles for Mn (Klinkhammer and Bender, 1980) and iron (Fe) (Martin and Fitzwater, 1988) can be affected by phytoplankton in the ocean

Mn is specifically important for photosynthetic and radical scavenging enzymes (Horsburgh *et al.*, 2002; Kernen *et al.*, 2002). Thermodynamically, Mn within a fully oxygenated ocean at natural pH should be Mn(IV) and precipitate out of the water in the form MnO₂. Dissolved Mn ocean profiles reveal that the surface waters contain high levels of soluble Mn(II). A portion of the soluble Mn is from direct dissolution from atmospheric deposition which contains Mn in the +2 oxidation state (Guieu et al., 1994; Siefert et al., 1998). Slow oxidation to the +3 or +4 state allows Mn to stay dissolved on the order of days; however, Mn still should oxidize over time and precipitate out of the surface ocean (Stumm and Morgan, 1996). This oxidation is prevented by photoreduction of Mn to the soluble +2 state in the presence of organic material (Sunda *et al.*, 1983), resulting in a large concentration of Mn in the surface water available for biological use.

Fe is the fourth most abundant element in the Earth's crust (Wedepohl, 1995). However the thermodynamically stable oxidation state, Fe (III), is relatively insoluble in oxic pH 8 seawater, which limits the inorganic concentration to 0.1 nM (Morel and Hering, 1993). Any inorganic iron above this concentration will either form an Fe oxide solid or quickly adsorb onto nearby surfaces (Rose and Waite, 2002). Despite this limit, oceanic Fe concentrations range from 0.1 - 2 nM (or higher in the coastal ocean). Fe(II) additions to the surface water from wet or dry deposition can elevate the total dissolved Fe concentration (Erel et al., 1993; Johansen et al., 2000); however, these too will quickly oxidize. Therefore, Fe must have a non-inorganic method for maintaining dissolved Fe in the seawater. Organic ligands appear to be responsible for this elevation of Fe concentrations (Barbeau et al., 2001; Buck, 2007; Rue and Bruland, 1995; van den Berg, 1995).

Bottle incubations and mesoscale Fe addition experiments have shown Fe to be important to ocean productivity (Martin and Fitzwater, 1988), and in many locations, the limiting or co-limiting nutrient (Maldonado et al., 1999; Martin et al., 1989; Mills et al., 2004). Furthermore, Fe is hypothesized to have a role in the global carbon budget and glacial cycles (Martin, 1990). The importance of Fe to the ocean has lead to its incorporation into computer models (Aumont *et al.*, 2003; Moore *et al.*, 2006) to more accurately describe overall ocean biogeochemical cycles. However, data comparisons to these models can be difficult due to the lack of complete temporal and spatial coverage of the global ocean. An alternative to the global ocean model is a regional ocean model which can be compared to the global ocean. The coastal ocean is important to the global carbon cycle, (Smith and Hollibaugh, 1993; Tsunogai and Noriki, 1991); we therefore propose that the Southern California Bight may be able to be used as a model environment to study global oceans and the carbon cycle. In general, the Southern California Bight is nitrate (NO₃) limited; however, the region is strongly influenced by the Fe depleted California Current. These interactions are caused by mixing of the California Current through the Channel Islands (Dong and McWilliams, 2007) and may be able to supply the region with Fe depleted water. In addition, Southern California is subject to punctuated wind events, the Santa Ana Winds, which can deposit large masses of particulate Fe onto the ocean surface (200 - 500) μ g Fe • m⁻² • day⁻¹) (Guazzotti et al., 2001; Lu et al., 2003). The changes in Fe concentration caused by these two types of events may cause a change in the biological community or overall production. In both cases, a study of the effects of Fe on the biological production of the coastal ocean is important to the understanding of Fe biogeochemical cycles and the carbon cycle. While the Southern California region has been intensely studied, a continuous high frequency time series (greater than seasonal sampling) of chemically and biologically important species, including trace metals, has not be conducted. This type of time series is needed to capture the events that may lead to changes in the biological production, but more importantly it is required to first understand the basic modes and cycles which characterize the ocean. After these background states have been observed and analyzed, the changes in biological production due to an events can be placed into proper context. We present here the coastal high frequency time series to include Fe and Mn concentrations in conjunction with biological analysis. This time series has been designed to characterize the coastal region. Investigations into biological responses to these events and the eventual effects on the carbon cycle will develop following this analysis.

2. Methods

2.1 Time Series Sample Collection

Time series field work was conducted on the R/V *Seaworld* UCLA at the Santa Monica Bay Observatory Oceanographic Mooring site. The mooring is anchored at 33° 55.9' N, 118° 42.9' W, and drifts about this point depending on the prevailing surface currents, as shown in figure 1. The mooring is located at the mouth of the Santa Monica canyon, a submarine canyon on the continental slope. Seawater was collected using Teflon coated external spring niskin bottles with Teflon coated messengers (General Oceanics Inc. model 1010X-5L) attached to ¹/₄ inch polyester line. Thirteen samples were collected for metal measurements for each profile ranging from the surface (1 m) to the bottom (~400 m). Only twelve samples were taken for all other chemical tracers ranging from the surface to 300 m, no deep water sample was taken. The niskin bottles were rinsed with surface seawater (15 – 40 m) before each day's use and milli-Q (mQ) water after each day of sampling (18.2 MQ•cm, 2 x 500 mL), and then stored wet.

Water was pumped from each niskin bottle through a 0.2 mm cartridge filter (Sartobran cellulose acetate P 150, 0.45 mm prefilter) with a peristaltic pump using C-Flex tubing (acid leached in 10% v/v reagent HCl) into a trace metal clean work space. The filter and tubing were rinsed with at least one liter of seawater before sampling to remove any residual acid and to condition the walls to reduce sample iron adsorption (Buck *et al.*, 2007). Samples were collected in 60 or 125 mL bottles, rinsing each bottle 3 times with the seawater sample before collection. Final samples were stored acidified with hydrochloric acid (12 M, SeaStar[®] HCl) at an acid to seawater ratio of 1:1000, ultimately reaching a pH of 2.0 - 2.3. All sampling and laboratory materials were acid leached using standard trace metal clean techniques.

2.2 Analysis

All samples collected in the Santa Monica Bay time series were analyzed for Fe and Mn concentrations. We used a modified MagIC method (Wu and Boyle, 1998) to concentrate the metals by a factor of twenty in order to analyze them by isotope dilution on the Finnegan Element I Inductively Coupled Plasma (ICP) Mass Spectrometer. Analysis of dissolved inorganic carbon (DIC) was done by Anita Leinweber from the University of California, Los Angeles (UCLA). Nutrient concentration measurements were made at the University of California, San Diego, Scripps Institute of Oceanography (Scripps) nutrient analysis lab. Measurements of chlorophyll, biologic silicate, lithogenic silicate, and cell species counts were done at UCLA in the laboratory of Rebecca Shipe. Temperature and

salinity were measured on the Seabird 19plus Conductivity, Temperature, and Depth Sensor (CTD), which was attached to the bottom of the line during each sample collection.

3. Results

3.1 Manganese

The pattern of Mn concentration in the Santa Monica Bay was similar to open ocean Mn depth profiles (Klinkhammer and Bender, 1980), (Fig. 2a). In the Santa Monica Bay, Mn concentration was 2-15 nM in the surface waters (1-20 m) and fell with depth. Surface water concentrations did not have a seasonal signal and were highest from February to October 2005. Sub-surface Mn concentrations were as low as 0.5 nM. Mid-depth Mn peaks did occur below the surface and were correlated to Fe and lithogenic silicate (L-SiO₄) peaks. There was a slight increase in Mn concentration in the bottom water; however, this increase was small, typically increasing 0.5 - 1.0 nM above mid-depth values and never exceeding 3 nM.

3.2 Iron

Fe concentrations in the Santa Monica Bay were highly variable. Concentrations ranged from below 0.1 nM at the surface in late summer to over 25 nM in the deep water (Fig. 3). Overall, the average Fe depth profile was similar to a nutrient profile (Fig. 2b). Average mixed layer concentrations were about 2 nM and grew to over 5 nM at a persistent 75 m depth peak. Below 75 m, the Fe concentration decreased and remained constant between 4 - 5 nM until the bottom. Bottom water concentrations increased rapidly with depth below 300 m, growing to over 8 nM between 350 – 450 m.

The high Fe peak at in the region of 75 m depth was a consistent feature in most of the Fe depth profiles; however, there was variability in the absolute value of the Fe concentration,

the number of peaks, and the depth at which the peaks appeared. A few of the Fe peaks were small, rising above the background Fe concentrations 0.5 nM and spanning as little as 10 m in depth (Fig. 4a); however, most peaks were relatively large. These peaks were several nM higher than the background deep water concentration and span 50 m or more in depth (Fig. 4b). In addition, there were many profiles with two high Fe peaks. Typically the high Fe peaks correlate with lithogenic silicate, although the location of the peaks maxima were not always at the same depth, with the lithogenic silicate usually peaking one sample lower in depth than the Fe peak. (Fig. 4c).

The profile from 10/11/05 (Fig. 4d) shows a good example of three of the four types of high Fe peaks. The top peak was thin and relatively small (1-3 nM) and was seen in the top 50 m. The second peak was composed of a large broad layer of water that had the most dramatic high Fe peak. This peak had an Fe concentration of 5-10 nM and was as much as 50 m thick. The third type of peak was not present in this profile, as it was the most transient peak in the time series. As seen in the profile from 8/16/05 (Fig. 4e), this peak was a broad layer of water ranging from 100 – 150 m in depth with a salinity of about 33.8 - 34.0 PSU. The final peak of Fe seen in the 10/11/05 profile was the deep peak. The deep water occupying 175 - 300 m in depth, was the most salty, and had high Fe concentrations between 5.0 - 8.0 nM.

Bottom water is a thin layer of water just above the sediments, typically enriched in Fe compared to deep water. Due to the layer's location above the sediment and its thickness, true bottom water was not sampled in every profile. For example, the profile collected on 10/11/05 contains a sample from 400 m; the Fe concentration in this deepest sample was 4 nM smaller than the deep layer above (5.4 - 5.6 nM at 200 - 300 m). The next profile, taken on 10/25/05 (Fig. 4f), also contained a sample from 400 m. Unlike the previous profile, this bottom sample had a Fe concentration of 11.5 nM and was likely collected from the bottom water. The inconsistency in sampling from this bottom water layer was partly due to our sampling location (see Section 2.1 Time Series Sampling Sample

Collection). Sample collection was conducted by positioning the boat above the mooring location. During collection of clean samples, the boat's engines were shut off, leaving the boat to drift with the wind and surface currents. With our location near the continental slope, the boat may have drifted into water of a different depth. Thus, the bottom sample may have been 1 - 5 m from the ocean bottom, resulting in our sampling of the bottom water; or the bottom sample may have been 10 - 20 m from the ocean bottom, resulting in our sampling our missing the bottom water layer. In addition, we were limited in measuring our sampling depth by "line out," measured by counting 5 m marks on the line. Comparison between our CTD depth at sampling depths and "line out" depths was good for a majority of samples (<1 m error). However, errors in "line out" accumulated with depth and line angle will affect the deepest sample the most, resulting in shallower depths readings.

4. Discussion

4. 1 Manganese

The typical Mn depth profile for the Santa Monica Bay (Fig. 2a) had a high concentration at the surface with reduced values at depth. This profile was similar in shape to the open ocean Mn depth profile (Klinkhammer and Bender, 1980), although, due to the proximity to land, the Mn concentrations in the Santa Monica Bay were much larger. The shape of the Mn profile results from continual production of reduced Mn in the surface ocean (Sunda *et al.*, 1983). The large input of Mn from aerosol deposition and river water adds soluble Mn(II) and insoluble Mn(III) & Mn(IV) to the ocean. At ocean pH and oxygen concentration, all Mn should slowly oxidize to Mn(IV) and precipitate out in the form MnO₂. However, due to the large amount of humic material in the surface ocean, these oxidized Mn species are continually photo-reduced to soluble Mn(II). Mn(II) is oxidized to the stable Mn(IV) form, but this is a slow process (Stumm and Morgan, 1996) which may take days to complete in surface ocean conditions. Together, the photo-reduction of oxidized Mn species and the slow re-oxidation generated the large Mn concentration we found in the surface ocean.

4.1.1 Manganese Input

In the remote open ocean, the two largest sources of Mn are dry deposition of terrestrial aerosols smaller than 20 mm and terrestrial Mn dissolved in rain water (Guieu et al., 1994). The coastal waters have other sources of Mn, including river input, deposition of coarser particles, and both wet and dry deposition of anthropogenic aerosols (Duce and Tindale, 1991; Siefert *et al.*, 1998), leading to larger Mn concentrations. The sources of Mn to the ocean are not continual processes, but rather punctuated events. Therefore, Mn concentrations in our time series grew and dissipated along with the onset and withdraw of these events (Fig. 5). A significant feature in the Mn time series was the large surface concentration beginning in February 2005 and extending into April 2005. This feature represented an elevation in Mn concentrations over 12 nM to depths of 50 m for over 8 weeks. From January 10th to March 28th, 2005 over 25 cm of rain fell on the Santa Monica Bay area (The Weather Underground, 2008). This rain resulted in low surface salinities in each of the profiles measured over this time extending to March 22nd. We therefore conclude that Mn was washed into the Santa Monica Bay by the large influx of rainwater, most of which was transported via Southern California storm drains. The large quantities of organic material found in this water would serve as the reductant needed to keep Mn in solution. Furthermore, while the initial portion of this event was dominated by the salinity and Mn features, beginning on March 1st, we see an increase in lithogenic silicates at, and just below, the surface (Fig. 6). While the influx of lithogenic silicates supports our conclusion that runoff was the ultimate source of this Mn feature, it is unclear why it only appeared at the end of the event. One explanation may be that storm water runoff supplied the initial Mn pulse. Because this water is largely composed of urban runoff, without erosion, this water contained anthropogenic material such as Mn without an equally large lithogenic silicates component. As the event developed, more standard river channels filled with water and began to carry eroded silicates and Mn to the ocean.

After this rain event, surface Mn concentrations fell to 2-6 nM, but increased below the thermocline. This sub-surface Mn concentration increase extended from 50 - 400 m, and in general Mn concentration were 2-3 nM below 100 m (Fig. 5). We believe the source of this deep Mn was the rain event the previous two months. Slow oxidation resulted in a delay in the transport of Mn from the surface ocean to depth.

The next large Mn surface feature in May 2005 was correlated to a smaller rain event. Between April and May 2005, the Southern California area received 2.5 cm of rain spread over three separate days (April 26th, April 28th, and May 9th) (The Weather Underground, 2008). The salinity signature of these rain events were the fresh water peaks between 5 - 15 m (Fig. 7), and were the result of storm water and river flux into the Santa Monica Bay. From February 2006 to May 2006, Mn concentrations at the surface rose and fell with rain events. During this period of time, Southern California received about half as much rain as it did in the previous year (The Weather Underground, 2008). As a result, the intensity of the Mn peaks was substantially lower than in 2005. In addition, this was the other period in our time series during which there was a large pulse of lithogenic silicates into the surface ocean. We therefore feel confident that these smaller Mn peaks were caused by the smaller rain events in 2006.

The last Mn surface feature in September 2005 is not linked to a rain event. While the region did received light rain (0.5 cm) on September 20th (The Weather Underground, 2008), this occurred at the end of the Mn feature. The high Mn surface concentrations were first measured on August 30th and continued for five weeks. Chlorophyll was high during this period of time, lagging Mn by 2 weeks (Fig. 8). Additionally, this chlorophyll bloom was the largest dinoflagellate bloom seen during the time series and was composed of the red tide forming *Lingulodinium polyedra* (R. Shipe pers. comm.). During this period there were no weather events except one day of light rain. In fact, from August 2005 to September 2005, the wind speed, wind direction, daily temperatures, and cloud cover never deviated from an average Southern California summer diurnal pattern (The Weather Underground, 2008).

Ash deposition from nearby fires did not coincide with this event. There were two fires in the greater Los Angeles area during this time. The Blaisdell Fire burned 5,493 acres in North Palm Springs from August 26 to September 29 (California Department of Forestry and Fire Protection, 2008). Satellite images from this period of time did not show smoke over the Santa Monica Bay (MODIS, 2008), and the Palm Springs watershed does not empty into the Santa Monica Bay. The Topanga Fire, near the Santa Monica Bay, was centered in Simi Valley, CA. This fire burned over 24,000 acres (California Department of Forestry and Fire Protection, 2008), although the wind was directed west, leading smoke away from our sampling area. Furthermore, this fire started on September 28, well after the Mn peak developed, and cannot be the cause of the high Mn concentrations. Thus, we do not have a reasonable explanation for the high surface Mn concentrations in September 2005.

4.1.2 Sub-Surface Manganese Peak

The last Mn feature from the Santa Monica Bay is the persistent large deep peak between 50 - 75 m. This peak first developed in mid-February 2005, after the first of the large rain events, and extended to October 11, 2005. After October 2005, there was no similar Mn peak in our time series. This peak correlates to a shallow Fe peak in the time series (discussed in the Fe section); however, the Mn peak only appears at this particular time, while the shallow Fe peak appears at this depth the following year. While the Mn peak only exists during this one period of time, it is possible that the peak represents a particular water mass, which was influenced by the large 2005 rain event. A shallow water mass which moved close to shore could interact with the surface water, incorporating trace material from the surface. As this water mass moved away from shore and sank to 75 m, it would carry the additional surface material. As described above, this rain event deposited a large quantity of Mn in the Santa Monica Bay. Because 2004 and 2006 did not have these large events, it is possible that the same water mass only incorporated a high Mn concentration after the 2005 rain event.

4.2 Iron

Variations in the individual Fe profiles which differ from the typical nutrient profile shape can be divided into three sections. We define these sections as the surface waters (0 - 15 m), the sub-surface and deep waters (15 - 300 m), and the bottom waters (> 400 m). We will discuss each section separately and present hypotheses for their Fe variability.

4.2.1 Surface Ocean Iron

Fe concentrations in the surface waters were highly variable due to direct influence by the atmosphere and weather. The surface was affected by climate events, upwelling events, and biological blooms. During periods of rain, surface Fe was high and correlated to Mn concentrations (Fig. 9b), resembling a scavenging type profile. During warm periods, Fe concentrations dropped below 0.1 nM. In each of the three years we sampled, the lowest Fe concentrations were reached after the mixed layer was at least 10 - 12 m deep for a month, with moderate surface temperatures (Figs. 3 & 10). Fe concentrations dropped to below 0.1 nM in August and early September 2004; to 0.2 - 0.3 nM in late July and early August 2005; and to 0.4 - 0.5 nM in late May early June 2006. In each of these cases, the mixed layer was below 10 m for several weeks before and during the low Fe event, with temperatures about $17 - 19^{\circ}$ C (Fig. 3). As summer temperatures rose, the surface ocean further stratified, forming a shallow mixed layer (4 - 6 m). Fe and Mn concentrations increased following these events.

We hypothesize that the Fe concentrations in the Santa Monica Bay and the greater Southern California Bight region can be driven low enough to cause Fe limitation. Given the proper combination of surface water stratification, temperature, and biological blooms, Fe concentrations can drop to between 50 - 200 pM, which have been found to cause Fe limitation (Martin and Gordon, 1988). We believe the mechanism for Fe depletion in this region is the rapid uptake of Fe and other nutrients in combination with a moderately large mixed layer. In the month preceding the low Fe periods we observed an upwelling event (Fig. 10) and correspondingly higher NO₃ concentration (Fig. 11). With an increase of NO₃, there can be an increase in biological production and removal of other nutrients such as Fe from the water (Wong *et al.*, 2002). With the moderate depth mixed layer, any input of Fe from atmospheric deposition or river flux was more effectively diluted. As the NO₃ concentrations dropped (Fig. 11), biological uptake of Fe slowed. This was followed by rising temperatures and a reduction in mixed layer depth, thus reducing the dilution from the deeper mixed layer. In each of these events, Fe concentrations rose following the increased stratification of the surface ocean, eliminating the brief possibility of Fe limitation (Fig. 3). Our attempts at observing Fe limitation in the Santa Monica Bay in 2006 were not successful (data not shown). These experiments were conducted in July to September 2006, a time frame when low Fe concentrations were observed in 2004 and 2005. However, in 2006, the lowest Fe concentrations were between May and June, and were not at a concentration (0.4 - 0.5 nM) that Fe limitation has been observed. Fe concentrations during our experiments were between 1 - 3 nM, and their profiles were consistent with recent atmospheric input. We therefore observed only NO₃ limitation, as would be expected in those situations.

Other surface processes involving Fe, biological blooms, and carbon uptake are currently being examined by several research groups, including ourselves. These studies will not be discussed here. However, we will continue to work on these processes and present the work elsewhere.

4.2.2 Temperature and Salinity Structure of the Santa Monica Bay

Analysis of Fe concentrations within the sub-surface and deep water requires a discussion of the temperature and salinity (TS) structure of the Santa Monica Bay. Within the time series, the TS structure was composed of seven water bodies, including the surface water (section 4.2.1) and bottom water (section 4.2.4). Figure 12 shows these water bodies and their mixing patterns. Within the sub-surface and deep water, we define the water bodies as:

- 1. Deep Water: Salinity 34.1 34.3 PSU, Temperature 8.5 9.8 °C,
- 2. Shallow Fresh Water: Salinity 33.2 33.5 PSU, Temperature 10.2 12.9 °C,
- 3. Shallow Salty Water: Salinity 33.4 33.9 PSU, Temperature 9.8 11.7 °C,
- 4. Mixed Layer Fresh Water: Salinity 32.0 33.3 PSU, Temperature 11.8 16.4 °C,
- 5. Mixed Layer Salty Water: Salinity 32.4 33.5 PSU, Temperature 11.4 20.0 °C.

Figure 13 shows four distinct water mass end members which mixed together within the Santa Monica Bay. These were the bottom water, the deep water, the shallow water, and surface water masses. The mixed layer water mass was formed from mixing between the surface water and the shallow water and spans the thermocline. The TS characteristics of the surface water mass and its mixing were largely controlled by seasonal atmospheric temperatures as discussed in section 4.2.1.

In general, each water mass changed depths over the year. During the winters of 2004-2005 and 2005-2006, the Santa Monica Bay had a deep mixed layer, 40 - 50 m (Fig. 10). Within this mixed layer, temperatures were cool, ranging from 14.5 - 16 °C, and due to sporadic rain fall the salinity was low and variable (<32 - 33.3 PSU) (Figs. 7 & 10). The fresh mixed layer water mass occupied the region above and to the base of the thermocline, while the fresh shallow water mass occupied the base region below the thermocline. The temperature change across the thermocline was about 4 °C, while the change in depth was as much as 80 m. Upon the onset of spring (in both 2005 and 2006), the prevailing winds changed, from a weak on-shore/off-shore diurnal pattern to a strongly off shore pattern (The Weather Underground, 2008), which corresponded to a brief upwelling event each year characterized by a shallow cold salty water. Atmospheric temperatures rose, causing a stratification of the water column, isolating the cold water, and forming a shallow mixed layer. Just as in the deep winter mixed layer, the salty mixed layer water mass was within the mixed layer extending to the base of the thermocline, while the salty shallow water mass was below the new thermocline. However, the salty water masses (mixed layer and shallow) were more salty and occupied shallower depths, 5 - 15 m for the mixed layer

water and 25 – 60 m for the shallow water. The mixed layer water still defined the thermocline. Due to the rising summer temperatures and increased stratification, the temperature change over the thermocline was as much as 10 °C (Fig. 13), but now the change in depth was at most 30 m (Fig. 10). The shallow mixed layer persisted until September or October, when atmospheric temperatures fell, lowering the temperature of the surface ocean and deepening the mixed layer back to 50 m in December or January. The bimodal nature of both the mixed layer and shallow water masses did not perfectly correspond to mixed layer depth. The mixed layer depth was controlled by the region's three seasons, with the spring upwelling separating the shallow mixed layer in the summer and the deep mixed layer in the winter. This divided the year into March through October and October through March (Fig. 10). The two modes divided the year in March through August and August through March (Fig. 13). While the mixed layer depth remained shallow in August, the mixed layer water and shallow water masses returned to their fresh mode.

The deep water mass rose and fell with the change in the mixed layer; however, its TS properties were consistent throughout the year (Fig. 13). During the late summer and winter, the deep water mass was between 250 - 300 m and rose to between 150 - 200 m during the spring (Figs. 7 & 10).

4.2.3 Sub-Surface Iron

The Fe concentration profiles (Fig. 2b) showed large peaks within the sub-surface and deep water. We identified these peaks (as described in section 3.2) and overlaid their TS properties onto figure 12 (Fig. 13). We also overlaid the depths of these peaks onto the time series contour plots of temperature and salinity to identify a temporal pattern in peak depth (Figs. 14). Figure 13 shows that the different peaks corresponded to the different water masses, and as these water masses changed, both their TS properties and depth, they remained associated with the high Fe peaks. The top peak (as defined in section 3.2) was within the mixed layer during the winter and extended to the base of the thermocline in the

spring and summer (Fig. 14a). The second large peak occupied the shallow water mass and was located below the thermocline. As the thermocline depth shallowed in the summer, so did the depth of this shallow water Fe peak (Fig. 14a). Both the top and shallow Fe peaks followed the change in depth associated with temperature, rather than salinity (Fig. 15). The third small transient peak lay along the mixing line between shallow and deep water (Fig. 13) and also changed depth with the temperature depth change (Fig. 15). The fourth broad peak is found within the deep water mass and occupied a large depth range from 175-300 m (Fig. 13).

The consistency of each type of Fe peak to occupying a specific water mass indicates that the Fe source for each type of peak was specific to that water mass, rather than random additions of Fe into the system. Therefore, further understanding of the water mass movements may lead to an understanding of the source of the Fe peaks. We also found that lithogenic silicate concentration peaks were consistently within specific water masses and correlated well with Fe peaks (Fig. 4). The correlation between Fe and lithogenic silicate potentially gives us a history of the water mass movements and possible source of Fe.

To investigate this correlation between Fe and lithogenic silicate, we normalized the lithogenic silicate and Fe concentrations with equation 1

$$T_{norm} = \frac{T_i - T_{Tot}}{\sigma_{T_{Tot}}} , \qquad \text{Eq. 1}$$

where *T* is the tracer, *i* represents individual samples, \overline{T}_{Tot} represents the mean of the tracer in the whole data set, and σ represents standard deviation of the tracer in the whole data set. We plot the histograms of normalized Fe and lithogenic silicate in figure 16. Both populations were skewed from a Guassian, with an extended tail into high values. In addition, Fe appeared to have two large populations centered at -1 and 0. Lithogenic silicate may have two large populations, but the double peak feature may also be due to under-sampling.

From inspection of the time series, we hypothesized that the large tails in both histograms correspond to the large peaks which are seen in both lithogenic silicate and Fe profiles (Figs. 3 & 6). However, the histograms do not link the lithogenic silicate and the Fe together; the histograms only show that there are similar populations. Therefore, we cannot determine if the peaks within the histograms corresponded to each other. We then plotted the cross histogram of the Fe and lithogenic silicate histograms. This was done by selecting a bin within the Fe histogram (starting with normalized Fe values between -1.5 and -1.3). We identified the lithogenic silicate data points which corresponded to the Fe data points within that bin. A histogram was constructed from these lithogenic silicate data, and the process was repeated for all the Fe histogram bins (-1.5 – 4.2). We plot the normalized Fe and normalized lithogenic silicate cross histogram in figure 17.

Figure 17 demonstrates that while there was correlation between lithogenic silicates and Fe, there were also several modes in both tracers which do not correlate. We identified four regions of this cross plot with possible oceanographic significance.

- 1. "High LSi": identified by lithogenic silicate > 0.9 and Fe < 0.7,
- 2. "High Fe": identified by Fe > 0.7 and lithogenic silicate < 0.5,
- 3. "Fe mode 2": identified as the intersection between the higher of the two Fe modes and the large lithogenic silicate peak,
- 4. "Correlation section": these data points lie within a region of the cross plot outlined by the two dashed lines of slope 1 (Fig. 11). This section encompasses the lower large Fe mode, "Fe mode 1," and extends out to higher normalized concentrations of both lithogenic silicate and Fe.

It is significant that the region of the cross plot with both high lithogenic silicate and high Fe is empty. This signifies that the two tails of the individual histograms are not correlated, and that the correlation we observe in the individual profiles is predominately within the lower concentration modes. In an attempt to map these population distributions onto the ocean and gain some knowledge about their spatial structure, we divided the Fe and lithogenic silicate histograms into depth regions (Fig. 18 & 19). This allowed us to view the spatial distribution of the normalized concentration populations. From figures 18 and 19, we see that most of the large lithogenic silicate peaks are clustered within the top 10 m of the ocean without a corresponding high Fe population, while about half of the high Fe peaks are found within the bottom water. This spatial disconnect between the two histograms' tails means that there are separate oceanographic processes working each species.

We hypothesize that the "High LSi" region is occupied by points which result from atmospheric deposition. Either wet or dry deposition can add lithogenic silicate to the surface ocean in high concentrations (section 4.1.1), but due to solubility limitations, the Fe concentration may not be significantly increased (Chapters 2 and 3). We can see an example of this lithogenic silicate addition without an addition of Fe in figure 9c. An example of a large lithogenic silicate addition with only a moderate Fe addition is shown in figure 9a. Furthermore, we hypothesize that half of the high Fe population within the tail is the result of the flux of Fe into the bottom water from the sediment (discussed in section 4.2.4). Unfortunately, the bottom water samples do not have lithogenic silicate measurements (see Methods), and we cannot rule out Fe sources such as sediment entrainment, which would increase colloidal Fe and also carry a high lithogenic silicate signature. In addition, these bottom points are not represented in the cross plot because there is no corresponding lithogenic silicate (Fig. 17). Therefore, the "High Fe" region of the cross plot is not explained by the bottom water Fe flux.

To explain the oceanographic relevance of the "High Fe" region, the peaks within the "High LSi" not explained by atmosphere-ocean interactions, and the observed correlation between lithogenic silicate and Fe, we divided the normalized lithogenic silicate and Fe cross plot into depth regions (Figs. 20 & 21). The depths chosen are identical to those in the depth-specific histograms, and roughly correlate to the depths in which we see the different types of high Fe peaks. Scanning through these depth cross plots we see that there is little correlation between lithogenic silicate and Fe in the top 30 m. There are three points within the correlation region that correspond to high Fe points (Fig. 20c), but most of the high peaks in Fe do not directly correlate to the high lithogenic silicate peaks. From 30 - 50 m (Fig. 20c-e), the data is spread through the three regions with only 10 points within the correlated region, also indicating that there is little correlation between lithogenic silicate and Fe. However, looking at figure 14 we see that 39 of the 40 mixed layer high Fe peaks are within the top 50 m, whereas only 14 of the 41 shallow water high Fe peaks (1 mid-depth water) are within the top 50 m. Identifying the location of each of the shallow peaks within the top 50 m reveals that there are 2 high Fe peaks between 20 - 30 m, 5 high Fe peaks between 30 - 40 m, and 8 high Fe peaks between 40 - 50 m (Fig. 14), roughly the same number of points in the correlated region of the depth cross plots (Fig. 20c-e). There is correlation between lithogenic silicate and Fe in the 50 - 75 m and 75 - 100 m depth regions, as seen in the high density of points within the correlated area. Inconsistencies in the correlation at these depths may be due to the differences in depth between the tracer's peak maxima (as described in section 3.2). In the 100 - 175 m depth range, Fe mode 2 begins to develop, but correlation between the two tracer peaks is still present. Between 175 - 300 m, Fe mode 2 dominates the depth region and high lithogenic silicate peaks vanish. This depth-dependent tracer correlation can lead us to a greater understanding of the mechanism behind Fe addition to these water masses.

We conclude that only one type of high Fe peak is correlated to lithogenic silicate. The mixed layer high Fe peaks are not correlated with lithogenic silicate. High lithogenic silicate

in this region is mostly due to atmospheric deposition, and high Fe peaks are from an, as of yet, unknown source. The shallow water high Fe peaks are correlated to high lithogenic silicate. Both high Fe and high lithogenic silicate peaks follow the depth changes of the water mass; therefore, they must be added to this water mass before it enters our observation station, rather than added at a constant depth and moving towards our location. The deep water high Fe peaks showed little correlation with lithogenic silicate, and the middepth high Fe peaks which correlated to lithogenic silicate were most likely due to the mixing of high Fe and lithogenic silicate in the shallow water with the deep water mass. The correlation between Fe and lithogenic silicate in the shallow water was preserved in the new mixture. The irregularity of these high Fe peaks within the mid-depth water mass in time, depth, and concentration may be explained by changes in the mixing pattern of these two water masses.

Fe and lithogenic silicate may be added to the shallow water mass through sediment interaction as the shallow water mass approaches the shore. One possible mechanism for both Fe and lithogenic silicates to be added to a sub-surface layer in 400 m ocean water is for the water mass to have moved close to shore at one point in its history and interacted with the continental slope. Because breaking internal waves can generate turbulence at the sediment-water boundary (Taylor, 1993), the shallow water mass only needs to flow past the continental slope when internal waves break. In addition, our proximity to the continental slope increases the likelihood of wave breaking due to vertical movement of water upslope as wave fronts propagate towards the shore (Lorke *et al.*, 2005). This upslope movement can disturb the stratification within the water column, causing convective mixing at the slope's sediment-water interface. Mixing of the sediments and pore fluid into the water layer will add both Fe and lithogenic silicates. Within the sediments there is Fe(II) production, which can supply the pore fluid enough Fe to generate the observed peaks (see section 4.2.4). In addition, lithogenic silicates will be prevalent in

the coastal sediments due to the proximity to land. Therefore, any suspension of these sediments will incorporate both lithogenic silicate and Fe into a nearby water mass.

Despite the likelihood of sediments to become entrained in a water mass interacting with the continental slope, our data cannot specifically determine if this is the cause of the high Fe and lithogenic silicate peaks. However, Changming Dong from University the of California Los Angeles (UCLA) was able to run a physical oceanography model of the Santa Monica Bay and surrounding region to answer that question. Based on wind data from May and June 2002, he ran the ocean model and tracked the water masses which reached the observation site. He then compiled that data and produced a movie which followed the top 80 m of the water column from our station back through time (Mov. 1). The movie shows that one day before entering our location, the water mass at 30 - 70 m flows past the Palos Verdes peninsula. Because the mixed layer is shallow in late May and June, the shallow high Fe peaks will occupy the 30 - 70 m depth range. Although this brief movie does not show direct contact with the sediment, it is encouraging that the shallow water mass stays near the shore and towards the Palos Verdes peninsula rather that away from the shore and the sediment. Thus, the mechanism of sediment entrainment from the continental slope remains a possibility.

We have considered other mechanisms for Fe addition. Sub-surface ground water discharge into the ocean has been characterized in the Mediterranean (Swarzenski *et al.*, 2006) and can carry dissolved metals. However, it is also characterized by decreases in salinity, as large as 20 PSU, depending on the flow of ground water and the depth of the coastal ocean (Swarzenski *et al.*, 2006). We did not see a consistent association of the high Fe peaks with decreases in salinity; however, we did observe a seasonal salinity decrease which corresponded to the period of time when the mixed layer high Fe peaks were predominately above the thermocline (Fig. 14a). Due to their seasonality, the peaks occurring between October 2004 and April 2005 may more likely be explained by river plumes rather than ground water (Buck *et al.*, 2007).

To truly identify the sources of the Fe peaks, and the nature the Fe cycles in the coastal water, we must have a better understanding of the water masses themselves. We have begun to identify the TS structure of these water masses, as well as the seasonal changes in depth and salinity. However, we do not have a good understanding of the flow patterns and sources of these water masses outside the California Bight. Despite this lack of knowledge, we have been able to determine that there is structure in the subsurface Fe data despite the many processes occurring.

4.2.4 Bottom Water Iron

There was a large increase in Fe concentration with the bottom water depth (Fig. 2b). This increase in concentration can be explained by the interaction between the sediment pore fluids and the bottom water. Within the sediments, organic carbon oxidation depletes oxygen concentrations several cm below the sediment water interface. Under the suboxic region, organic carbon is oxidized by a series of other species, including Fe, each with decreasing oxidative power (Froelich et al., 1979). Fe(II), resulting from Fe oxidation of organic carbon, enriches the pore fluids which diffuse into the bottom water (Hammond et al., 1990). Fe(II) fluxes from the Central California coast (Monterey Bay) are 1.3 - 11 umol·m⁻²·day⁻¹ (Berelson et al., 2003). Although the measurements of oxygen concentration we have for the entire time series are in sensor voltage from November 2005 – September 2006 (Fig. 22), they show reduced values at depth, and we know from others that the bottom of the Santa Monica Bay is suboxic $(5 - 35 \mu mol/Kg)$ (Berelson, 1991). In addition, we have O2 concentration measurements for the San Pedro Basin on 11/07/04 and the Santa Monica Bay from November 2005 (Fig. 23). The San Pedro Basin is a suboxic basin adjacent directly up-current of our observation station, with bottom water O₂ concentration of 5.5 µmol / Kg (Fig. 24). We believe that the source of bottom water in the Santa Monica Bay can be identified in the San Pedro Basin water column.

We compared the TS structures of the San Pedro Basin on 11/07/04 and the Santa Monica Bay on 11/02/04 and 11/16/04. The San Pedro Basin TS structure mapped well onto both

Santa Monica Bay profiles (Fig. 25). The deep water, as defined in section 4.2.2, was particularly similar between the San Pedro Basin and the later Santa Monica Bay profile, although there is fresh deep water intrusion in the Santa Monica Bay profile from 11/02/04. The deep water mass in both locations was found at the same depth (210 - 250 m), and the mixing line between it and bottom water followed the same pattern in all three profiles. Bottom water from these two days in the Santa Monica Bay had a temperature of 7.3 - 7.6°C and salinity of 34.25 – 34.26 PSU. Water with this TS characteristic in the San Pedro Basin corresponded to a depth range of 385 - 430 m, the same depth of our bottom water. We conclude that the bottom water found at our observation station in the Santa Monica Bay was a mixture of the region's deep water mass and the bottom water mass found in the San Pedro Basin. Therefore, the oxygen concentration found in the San Pedro Basin at 400 m, 28 µmol/Kg, should be found in the bottom water of the Santa Monica Bay. This is at the high end of suboxic conditions (Johnson et al., 1996), and the Fe(II) half life in this water is 4 times smaller than in San Pedro Basin bottom water (30 minutes. compared to 2 hours) (Murray and Gill, 1978; Rose and Waite, 2002; Sung and Morgan, 1980). This is slow enough to maintain approximately 2.5 % of the average bottom water Fe concentration as Fe(II) (Rose and Waite, 2002). This is within range of (Ussher et al., 2007), who found suboxic bottom waters from the English Channel and North Sea to contain 8% Fe(II). The remaining total iron concentration was composed of ligand complexed Fe(III) >50% and colloidal Fe(III) in the form FeOOH.

The Fe concentration in the bottom water had several seasonal components. We plot the difference in Fe concentration between the bottom two samples (400 - 300 m) against the bottom temperature (Fig. 26). There are two distinct water masses which arise from this plot. The first water mass had a mixing pattern with a slope of -0.14 °C/ nM and extended from the cloud of data centered at a temperature of 7.7 °C to the coldest temperatures. The other water mass had a mixing pattern with a shallower slope and extended to the largest Δ [Fe]. We labeled each point with the corresponding date in figure 26 to show the seasonal

pattern of these two water masses. The colder water mass (mixing along a line with slope - 0.14 °C/ nM) occurs in the spring, from March to early May in both 2005 and 2006. The high Fe water mass (mixing along a line with slope -0.02 °C/ nM) is composed of profiles from both the winter and summer and does not appear to have any further seasonal pattern. This seasonal appearance of the cold water mass was seen in the Fe time series (Fig. 3), as the low Fe masses which occurred during the spring. In addition, there is a decrease in bottom water temperatures (Fig. 10) corresponding to the upwelling events in both 2005 and 2005 and 2006. Thus, upwelling in the Santa Monica Bay affected the entire water column, and pulled cold Fe poor water in from another source.

Isolation of this spring event from the other Fe profiles allowed us to discern another seasonal pattern. We divided the remaining profiles into winter and summer profiles. The winter was defined as the period of time after mixed layer deepening until the spring event, while the summer was defined as the onset of mixed layer warming following the spring event until the deepening of the mixed layer. Typically, the summer was from mid-May to late November or early December, while the winter was from late November or early December to March or April. Averaging the Fe profiles for the summer and winter seasons showed the second seasonal pattern (Fig. 27). Both the summer and winter bottom water masses had Fe concentrations of 8 - 9 nM. However, while the winter bottom water mass appeared to have a linear and conservative mixing with the deep water mass at 300 m, the summer bottom water mass appeared to lose Fe at a greater rate than was explained by deep water mixing. There are two possible explanations for this non-conservative mixing. The first is that oxygen concentrations in the deep water mass were lower in the winter, allowing Fe(II) to mix into the deep water without additional oxidation and subsequent precipitation from solution. We do not believe that this is a likely scenario. The oxygen concentrations (in voltage, Fig. 22) from November 2005 to February 2006 in the bottom and deep water were equivalent or slightly higher than in the summer of 2006; therefore, the opposite Fe mixing pattern would be expected to result. In addition, Fe (II) is a small

component (< 10%) of the total Fe concentration; thus, a change in O₂ concentration would only effect a small percentage of the total Fe. The second hypothesis is that Fe(III) is scavenged from the water column at a greater rate during the summer as compared to the winter due to a greater particle flux to the sediment. Berelson et al., (2003) observed a seasonal cycle of organic carbon oxidation correlated to primary production in the Monterey Bay. They concluded that because primary production varied over the year, peaking in early summer following the seasonal upwelling events, the rain of organic carbon out of the surface ocean to the sediments varied, supplying the sediment with a seasonal flux of fresh organic material to be oxidized. Seasonal fluxes of particles have also been observed in the Southern California Bight (Rathburn et al., 2001; Shipe and Brzezinski, 2001). In each case, biogenic silicates were observed in the bottom water particle fluxes following diatom blooms in the late spring and summer. Our data show that there was a seasonal increase in biogenic silicates corresponding to the spring blooms (Fig. 28) and that this increase was not limited to the surface waters but extended into the deep water (Fig. 28 53). Furthermore, deep ocean biogenic silicates were more concentrated in the summer than the winter (Fig. 29). Because Fe is a particle reactive element (Stumm and Morgan, 1996), both ligand bound Fe (defined in Chapter 2) and colloidal Fe can readily adsorb onto particles. An increase in particles in the deep ocean would lead to increased Fe adsorption and removal from the dissolved phase. We conclude that the seasonal removal of Fe from deep water was caused by the seasonal flux of particles, with biogenic silicates being a likely source of these particles.

5. Conclusions

We have observed the Santa Monica Bay Observatory Oceanographic Mooring site for two and a half years. Over that time we have determined that the coastal ocean has three distinct seasons, a long summer, a winter, and a brief spring associated with a yearly upwelling event. Mn concentrations are elevated to as much as 25 nM in the surface ocean. Rain events appear to increase the surface concentration of Mn as well as lithogenic silicate. Furthermore, the large influx of Mn to the Santa Monica Bay during the winter of 2004-2005 caused an increase in Mn concentrations below the thermocline.

We have observed the several seasonal changes within the water column, from the surface to the bottom water. Summer mixed layer depths are between 5 - 15 m, while winter mixed layer depths are 20 - 50 m. The water masses associated with the surface mixed layer and the shallow water mass below the thermocline have a change in both their salinity and temperature in response to the season change. The sub-surface iron peaks are associated with these specific water masses, and remain with those masses throughout the seasons. In addition, we concluded that lithogenic silicate and Fe in these high tracer peaks have a specific terrigenous source, which we hypothesize is the entrainment of sediment and pore fluids following sub-surface wave breaking against the continental slope. We also observed a season change in bottom water Fe concentrations and the mixing patterns with the deep water mass. Seasonal changes in biological productivity changed the flux of particles to the deep, changing the reactive surface concentration in the water. During the summer these particles are in high concentration and scavenge Fe from the water column. During the less productive winter, the particle concentration is lower, and thus bottom water Fe concentrations mix with the deep water without scavenging.

FIGURE CAPTIONS

Figure 1: The Santa Monica Bay Observatory Oceanographic Mooring site is anchored at 33° 55.9' N, 118°42.9' W. Due to surface and sub-surface currents the mooring rotates on its chain about this point. Time series samples were collected as close to this mooring site as possible.

Figure 2: Depth profile of dissolved Mn (A) and Dissolved Fe (B). Both profiles are an average of all profiles in the time series. Mn concentrations were high (7 - 10 nM) in the surface ocean, and rapidly decrease in concentrations. Fe concentrations were lowest in the surface ocean (2 nM), and increased to over 12 nM in the deep. The peak in Fe concentration at about 75 m was a persistent feature throughout the time series.

Figure 3: Contour plot of dissolved Fe concentration over time within the Santa Monica Bay. Our time series ran from July 20, 2004 to September 19, 2006. Individual samples are plotted as black dots. Fe concentrations are contoured every 1 nM from 0 - 12 nM, and are lowest in the period following the spring upwelling events when mixed layer depths are 10 - 15 m (Fig. 10). Overlaid in the shallow water panel is the mixed layer depth (black line). Moderately deep summer mixed layer depths (15 m) were observed in July –August 2004 and 2005, and May – June 2006. In each of the timeframes Fe concentrations were at their lowest for the year. After each of these periods, the mixed layer depth shallowed and Fe concentrations increased.

Figure 4: Profiles of Fe (blue), Mn (green), and lithogenic silicate (red) from the Santa Monica Bay from February 15, 2005 (A), May 9, 2005 (B), November 16, 2004 (C), October 11, 2005 (D), August 16, 2005 (E), and October 25, 2005 (F). The high Fe peaks seen in these profiles can be divided into four categories based on their depth and shape: a mixed layer peaks seen in D, and shallow water peaks seen in B and C, a mid-depth peak seen in A and F, and a deep water peak seen in E. The shallow water peaks have a strong correlation to lithogenic silicate.

Figure 5: Contour plot of dissolved Mn concentration over time within the Santa Monica Bay. Individual samples are plotted as black dots. Mn concentrations are contoured every 1 nM from 0 - 12 nM. High Mn concentrations at the surface are driven by reduction by organics and large rain fall events. Overlaid in the shallow water panel is the mixed layer depth (black line).

Figure 6: Contour plot of dissolved lithogenic silicate concentration over time within the Santa Monica Bay. Individual samples are plotted as black dots. Samples were only collected from the surface to 300 m. Lithogenic silicate was measured in the Rebecca Shipe's lab at UCLA, and are contoured every 0.1 μ M from 0 – 1.0 μ M. High lithogenic silicate concentrations at the surface are caused by wet and dry atmospheric deposition as well as storm water runoff. Sub-surface lithogenic silicate peaks were correlated with dissolved Fe peaks.

Figure 7: Contour plot of salinity over time within the Santa Monica Bay. Data was taken from the CTD sensors, which had a 1 m depth resolution. The location of the samples taken along with the CTD cast are plotted as black dots. Overlaid in the shallow water panel is the mixed layer depth (black line). Salinity is contoured every 0.1 PSU from 32.5 – 34.3 PSU. Fresh water additions during the rain events of 2005 were observed between January and April

2005. The relative high surface water salinity in the winter of 2005-2006 was the result of reduced rain fall.

Figure 8: Contour plot of chlorophyll-a over time within the Santa Monica Bay. Individual samples are plotted as black dots. Samples were only collected from the surface to 300 m. Chlorophyll-a measurements were made in the Rebecca Shipe's lab at UCLA, and are contoured every $0.3 \ \mu g/L$ from $0 - 3.0 \ \mu g/L$. Chlorophyll-a was higher in concentration during the two spring upwelling events, the result of diatom blooms. In addition, the period of time between September 2005 and October 2005 had the largest recorded chlorophyll-a concentrations within the time series, and resulted from the red-tide causing dinoflagellate - *Lingulodinium polyedra*.

Figure 9: Profiles of Fe (blue), Mn (green), and lithogenic silicate (red) on September 21, 2004 (A), May 1, 2005 (B), and September 27, 2005 (C). In A, The surface water increases in Fe, Mn, and lithogenic silicate correlate to the shallowing of the mixed layer and atmospheric deposition. In B, the surface water increases in Fe, Mn, and lithogenic silicate correlate to heavy rains during the winter of 2005. In C, the surface water increases in Mn and lithogenic silicate are due to atmospheric deposition.

Figure 10: Contour plot of temperature over time within the Santa Monica Bay. Data was taken from the CTD sensors, which had a 1 m depth resolution. The location of the samples taken along with the CTD cast are plotted as black dots. Upwelling events were observed in April 2005 and March 2006. These are characterized by cold waters (< 11 °C) rising to the surface and bottom water temperatures falling to 6 - 7 °C. Overlaid in the shallow water panel is the mixed layer depth (black line) which changed depth over the seasons, deep in the winter (40 – 50 m) and shallow in the summer (5 - 20 m). This change in mixed layer depth divided the year into three seasons: summer, winter, and spring when the season upwelling event occurs.

Figure 11: Contour plot of NO₃ concentrations within the Santa Monica Bay. Individual samples are plotted as black dots. Samples were only collected from the surface to 300 m. Surface values of NO₃ were typical low (< 0.01 μ mol/Kg), however the spring upwelling events brought NO3 concentrations of ~ 5 μ mol/Kg to the surface.

Figure 12: Temperature (T) versus salinity (S) plot. The block dots represent the TS properties of the individual samples. There are 6 distinct water masses, which are characterized as the vertices of the curved regions of the TS plot.

Figure 13: TS plot with labeled water masses, and overlaid with of the high Fe peaks as defined in section 3.2. The block dots represent the TS properties of all the individual samples, the high Fe peaks are labeled with red circles (mixed layer peaks), blue squares (shallow water peaks), green diamonds (mid-depth water peaks), purple triangles (deep water peaks), and orange crosses (bottom water peaks). There are 6 distinct water masses, circled and labeled as bottom water, deep water, shallow water (fresh and salty), and surface water (fresh and salty).

Figure 14: Contour plot of shallow water temperature (A) and salinity (B) within the Santa Monica Bay. Data was taken from the CTD sensors, which had a 1 m depth resolution. The location and type of high Fe peaks are indicated by the symbols, mixed layer peaks (circles), shallow water peaks (squares), mid-depth peaks (diamonds). Overlaid is the mixed layer depth

(black line). Each type of peak stays within a range of temperatures and moved up and down in the water column with the depth of the mixed layer and temperature contours.

Figure 15: Contour plot of temperature within the Santa Monica Bay. Data was taken from the CTD sensors, which had a 1 m depth resolution. The location and type of high Fe peaks are indicated by the symbols, mixed layer peaks (circles), shallow water peaks (squares), middepth peaks (diamonds), and deep water (triangle). Each type of peak stays within a range of temperatures and moved up and down in the water column with seasons.

Figure 16: Histogram of normalized Fe concentrations (A), and normalized lithogenic silicate concentrations (B). The population of each concentration was multi-modal and skewed towards larger concentrations. The conversion line between the normalized number and the concentration are seen in the inset.

Figure 17: The cross plot of the normalized Fe and lithogenic silicate histograms. The separation of the normalized histograms in the cross plot allows for analysis of correlation between lithogenic silicate and Fe. There are four regions of interest: High LSi (Fe < 0.7, lith. $SiO_4 > 0.9$), High Fe (Fe > 0.7, Lith. $SiO_4 < 0.5$), Fe mode 2 (Fe \approx 0.3), and the region of correlation between lithogenic silicate and Fe (occupied the region between the dashed gray lines).

Figure 18: Depth specific normalized Fe histogram. The normalized Fe histogram (Fig. 27) is divided in depth regions associated with high Fe peaks. Low concentration modes are seen in the upper 40 m, where the higher concentration mode develops. The tail associated with the Fe histogram is split between the bottom water and depth range of 50 - 75 m.

Figure 19: Depth specific normalized lithogenic silicate histogram. The normalized lithogenic silicate histogram (Fig. 28) is divided in depth regions associated with high Fe peaks. There is no data below 350 m for lithogenic silicate. High lithogenic silicate is seen in the 0 - 20 m depth range.

Figure 20 – 21: Depth stack of the cross plot of the normalized Fe and lithogenic silicate histogram. Depth regions are equivalent to those used in the depth specific histograms. From 0 - 30 m there is little correlation between Fe and lithogenic silicate. There is correlation between the shallow water high Fe peaks and lithogenic silicates. Bottom water high Fe peaks are not seen in these cross plots because there is not corresponding lithogenic silicate points.

Figure 22: Contour plot of oxygen (reported in sensor voltage) within the Santa Monica Bay. Data was taken from the CTD sensors, which had a 1 m depth resolution. The conversion to chemically relevant units could not be done on all profiles due to sensor failures, therefore contour data profiles are reported in voltage.

Figure 23: Oxygen profile from November 11, 2005. Sensor conversions were working properly for this profile, and units are in μ mol O₂/Kg. Bottom water O₂ concentrations were 25 μ mol O₂/Kg.

Figure 24: CTD profile of the San Pedro Basin on November 11, 2004. The San Pedro Basin is a 880 m deep suboxic basin to the south of the Santa Monica Bay. Oxygen concentrations fall to 5.5μ mol O₂/Kg at 880 m, and 28 μ mol O₂/Kg at 400 m.

Figure 25: TS plot of two profiles from the Santa Monica Bay, 11/2/04 (blue line) and 11/16/04 (red line), and the profile from November 11, 2004 in the San Pedro Basin (black line). TS characteristics of all three water masses are similar. Water located between 385 - 430 m in both the San Pedro Basin and the Santa Monica Bay have the identical TS properties. High Fe peaks are shown with circles, filled blue from the Santa Monica Bay and open for the San Pedro Basin.

Figure 26: Temperature versus Δ Fe for the bottom water. Δ Fe was calculated by subtracting the bottom sample (~400 m) from the deep sample (~300 m). The data fit fall along two trends. The first is the Cold Water Mass which extends below 6 °C and has a slope of -0.14 °C/nM, and the High Fe Water Mass which extends to Δ Fe values above 6 nM and has a slope of -0.02 °C/nM. Each data point is labeled with the date it was collected. The Cold Water Mass trend is composed of points which correspond to March, April, and early May 2005 and 2006 (blue text), while the High Fe Water Mass has no correlation to time of year (red text). There is a period of four profiles (6 – 8 weeks) in which the deep water mass warmed; these profiles are represented by the four data point in black forming a vertical line at Δ Fe = 8 nM. The remaining data is labeled in green text.

Figure 27: The three season average Fe profiles over the entire time series. We divided the Santa Monica Bay into three seasons, defined as: summer (red), the period after upwelling to the mixed layer deepening (> 20 m); winter (blue), the period from the mixed layer deepening to the upwelling event; spring (green), the time of the upwelling event.

Figure 28: Contour plot of biogenic silicate over time within the Santa Monica Bay. Individual samples are plotted as black dots. Measurements of biogenic silicate were made in the Rebecca Shipe's lab at UCLA and are contours every 0.3 μ M from 0 – 3 μ M. Surface biogenic silicate is composed of diatoms and is highest following the spring upwelling events into the summer. Winter concentrations are lower than spring and summer concentration.

Figure 29: Integrated deep biogenic silicate (75 - 315 m). Integration of each profile is drawn in black, while the seasonal average is draw as red bars. The two spring upwelling events have the largest deep biogenic silicate concentration. The summer integrated biogenic silicate concentration.



















Fe, Mn (nM)







Temperature



Temperature





Histograms of Iron and Lithogenic Silicate Distributions









Normalized Lithogenic Silicate



Normalized Lithogenic Silicate



Density of Samples

















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