Fe(II) Kinetic Variability in Different Water Masses Across the Equatorial Pacific

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10/30/2023

Abstract

Iron(II) is a species of iron that is highly soluble in water, making it the most bioavailable form of iron to organisms living in the ocean. Iron is a vital micronutrient for various plankton species and can be the limiting nutrient in much of the open ocean. Fe(II) kinetics in the world's oceans have been revisited in numerous studies but little has been done to quantify the oxidation rates of Fe(II) in natural waters. Understanding the rate at which Fe(II) is oxidized is essential for determining iron's bioavailability. Oxygen concentration, temperature, and pH are just some of the variables that contribute to changes in oxidation rates of Fe(II) and they are all related to one another, further making it difficult to attribute a change in oxidation rate to a specific environmental condition. The oxidation rates at each station in the equatorial Pacific were within 0.1 μM/s of one another. The difference in oxidation rates and physical properties between the water masses sampled in this research was small. Although there was a slight difference in oxidation rate at each station, we are unable to conclude that pH or oxygen concentration is responsible for the change.

Plain Language Summary

Iron is a vital but scarce nutrient across the world's oceans. The rate at which iron changes from a state that is usable by organisms to non-usable is an important process for understanding biological activity. This rate of transformation is dependent on factors like acidity, the concentration of oxygen, and temperature. Because pH and oxygen concentration change throughout the world's oceans, the rate at which this iron is transformed or used also changes. The goal of this research was to measure and compare the rates at which iron is used or transformed at different locations around the equator. The oxidation rates of Fe(II) were only slightly different in different water masses in the equatorial Pacific. The physical properties of the locations sampled were also very similar which could have been the reason for similar oxidation rates at each location.

Intro

Fe(II) is thought to be the limiting nutrient for phytoplankton growth in the majority of high-latitude seas (Martin et al., 1990a,b). There are two significant oxidation states of iron in the ocean, Fe(II) and Fe(III). Fe(III) is a form of iron that precipitates and hydrolyses in seawater at a high rate (Pham, N.A. and Waite, D.T. (2008)). When this happens Fe(III) becomes unusable for biological activity. Fe(II) is the form of iron that is essential for biological activity and is the limiting nutrient over one-third of the world's oceans (Maritn 1990, Boyd 2007). Fe(II) is a less stable version of Iron that stays dissolved in natural waters for longer periods before being oxidized, making it usable for biological processes.

The physical properties of seawater have a large impact on the rate at which Fe(II) is oxidized. In more alkaline waters, the most abundant species of Iron are FeCO3(OH) - and Fe(OH)2, which are not as soluble in seawater (Pham, N.A and Waite, DT (2008)). In water masses that are less alkaline, the most abundant species of iron are Fe(II), the species of iron that is available for biological use (Pham, N.A and Waite, DT (2008)). The pH level of seawater sits between 7 and 8.4, meaning there are regions of the ocean where Fe(II) oxidation rates are drastically different from one another (Morgan, B. a and Lahav, O. b (2007)). The Oxidation rate of Fe(II) is highly dependent on the pH of the water (Gonzalez). Rate of change experiments were conducted to quantify this relationship between pH and Oxidation rate. However, pH is not the only property of water that can change the rate of iron oxidation. Fe(II) oxidation rates are also affected by salinity. Saltier water is more conductive and increases the concentration of ions in water, this accelerates Fe(II) oxidation (Millero, F.J., Sotolongo, S. and Izaguirre, M. (2003)). Another important property of seawater that affects oxidation rates of Fe(II) is oxygen concentration. Water masses that have high concentrations of oxygen have high rates of Fe(II) oxidation. Understanding the rates of Fe(II) oxidation is essential for understanding how organisms interact with it.

Methods

The research was conducted onboard the R/V Thompson. On December 29th, 2023, the vessel departed Pago Pago, American Samoa, and conducted a transect from 5 degrees south to five degrees

north. Water samples were collected at 7 locations along the transect (Figure 1). Using a CTD rosette equipped with twenty, ten-liter Niskin bottles, samples were collected at a depth of 140 meters. Oxygen concentration, temperature, and pH values were obtained using an SBE CTD 911 attached to the bottom of the rosette.

On deck, 3.5-liter bags were filled all the way and sealed to avoid oxygen and various other gases from mixing with the sample. (Bundy lab, 2024) The methods in this experiment were inspired by a previous protocol but the experimental setup is unique to this experiment. In the lab, the 3.5-liter bags were weighed using a hand scale hanging from the ceiling of the vessel.

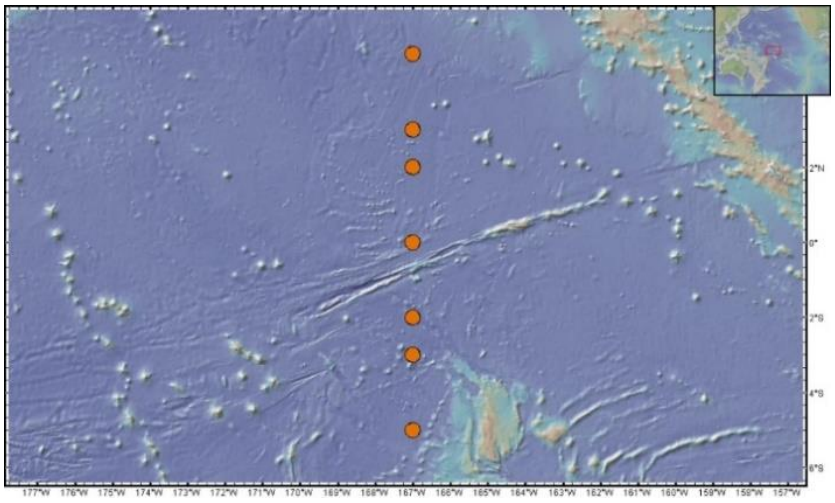

Figure 1. A map of 7 stations in the equatorial Pacific where water samples were taken at 140 meters.

The seawater sample bags were drained until they weighed 2.0 kg or 2.0 liters. The 1.5 liters of seawater removed were used to create 9 standard Fe(II) concentration solutions. The standards were spiked with different concentrations of 500 micromolar Ferreous Ammonium Sulfate, Fe(II), creating standards.

The remaining 2 kg or 2 liters of seawater was used to conduct a rate of change experiment, measuring the change in Fe(II) concentration over time. 20 mL of seawater was removed from the bag and 1.25 milliliters of 4mM ferreous ammonium sulfate, Fe(II), was injected into the sample. The 20 mL removed was then injected back into the sample to flush any Fe(II) remaining in the QWORK 3-way stopcocks attached to the sample bag.

Once the bags had been spiked and mixed with the Fe(II), sub-samples of 20 milliliters were removed and acidified using 20 microliters of hydrochloric acid. The acid acts as a stabilizing agent in the solution, preventing the concentration of Fe(II) from changing. The first sub-sample taken represents the starting concentration of Fe(II) in the rate of change experiment. The process was repeated for the next 30-40 minutes with varying time intervals in between sub-samples. Fourteen samples were taken from the Fe(II) spiked bags of seawater. One mL each of ammonium acetate and ferrozine was added to the 9 standard solutions and the 14 samples were taken from the Fe(II) spiked seawater sample. Ferrozine is the reagent used to change the color of the sample. The color change of the sample was an indication of the concentration of Fe(II) at the time the sample was taken. Samples were placed into a 10 cm long cuvette and were measured in a Genesys 10 spectrophotometer at a wavelength of 562 nm.

The Fe(II) concentration standard curve created by the standard concentrations of Fe(II) and the measured values from the Genesys 10 spectrophotometer were then used to calculate the concentration of Fe(II) in the 14 samples. This process was repeated at 7 locations along the transect and a new standard curve was created at each site.

All stock solutions were created using Mili-Q water and refrigerated in the dark when not in use. 4 mM ferreous ammonium sulfate was created by dissolving 0.157g of Ferreous ammonium sulfate in 100 mL of Mili-Q water. It was wrapped in foil, refrigerated, and stored in the dark to avoid degradation. 500 micromolar Ferreous Ammonium Sulfate used in creating standards was made by pipetting 6.25 mL of the 4 mM ferreous Ammonium Sulfate into 43.75 mL of Mili-Q water. 0.257 g of ferrozine was dissolved in 50 mL of Mili-Q water to create a 0.01 Ferrozine stock solution. 23 g of Ammonium Acetate was dissolved in 50 mL of Mili-Q water to create a 6 M Ammonium Acetate stock solution.

Results

The change in concentration of Fe(II) over time at each station was plotted (Figure 2). In each sample, there was a decrease in the concentration of Fe(II) over time. This is an expected outcome of the rate of change experiment. A linear trendline was fitted to the first 250 seconds of the experiment for each station (Figure 3). At the beginning of the experiment, the decrease appears to have a linear relationship. The

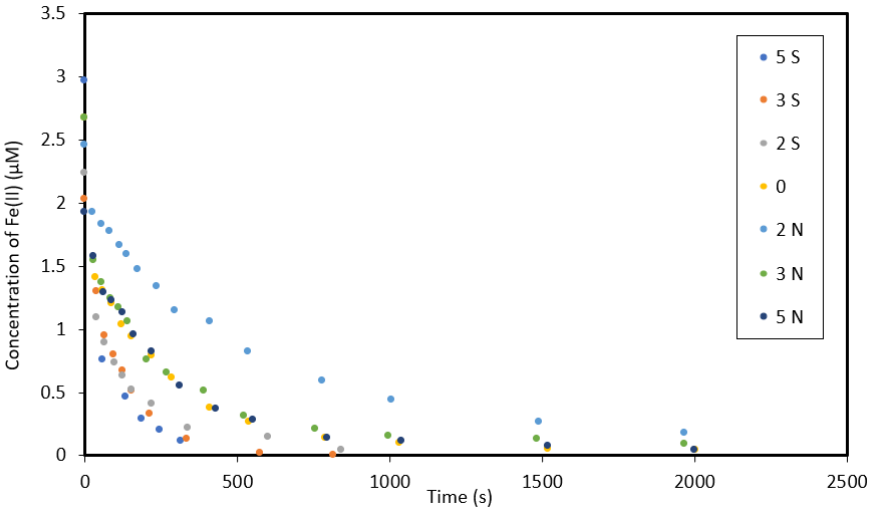

figure 2. Measured concentration of Fe(II) over time in sea water samples

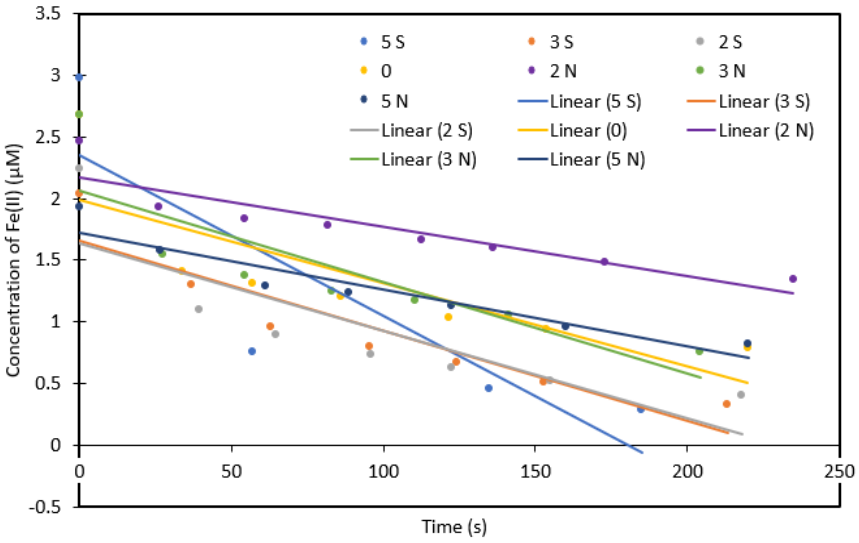

Figure 3. Linear rates for the first 250 seconds at each sample location.

rates for the first 250 seconds were then plotted as a function of pH level and oxygen concentration (Figure 4). At 5 degrees south, the recorded pH was 8.00, the highest pH value of the different sample

locations. 5 degrees south also had the highest oxidation rate of Fe(II) at 0.0131 micromolar per second. At 2 degrees north, the water had a pH value of 7.88, the lowest of the 7 stations. 2 degrees north also had the lowest oxidation rate at 0.004 micromolar per second (Figure 4).

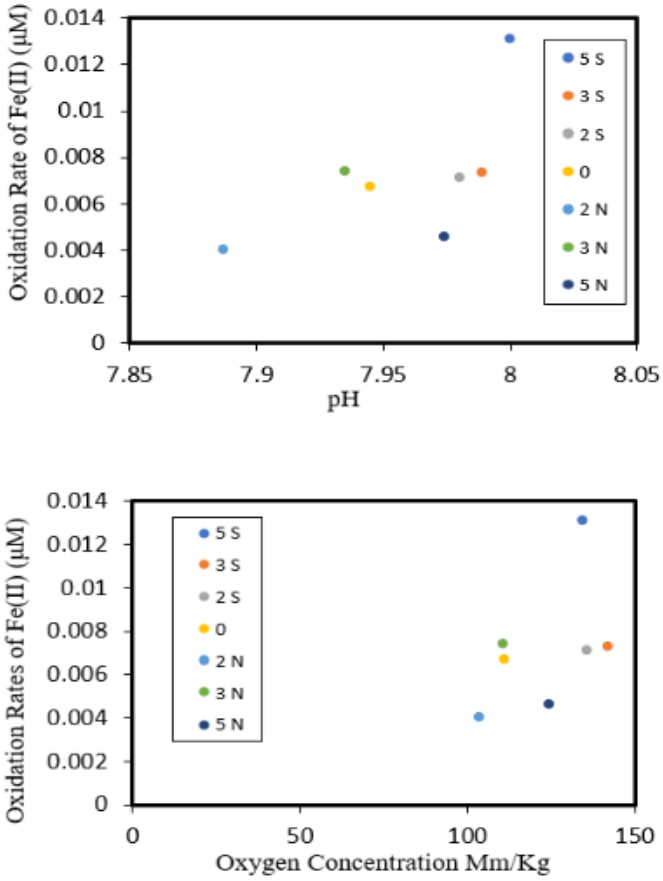

Figure 4. Fe(II) oxidation rates as a function of pH and oxygen concentration at each of the seven sample locations

The rates of change in Fe(II) concentration were plotted as a function of oxygen concentration (Figure 4). The water sampled from 2 degrees north had the lowest concentration of oxygen at 103.80 Mm/kg and the lowest rate of change in concentration of Fe(II), 0.004. At 3 degrees north, the location with the highest concentration of oxygen did not have the highest oxidation rate.

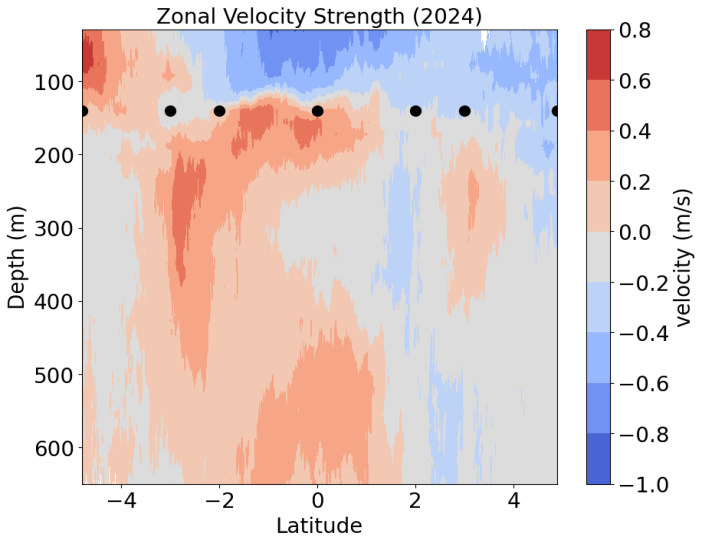

Figure 5. Zonal velocities at each of the 7 stations where water was sampled.

The zonal velocity at each sampling location was plotted (Figure 6). At five and two degrees south as well as the equator, the water had an eastward velocity between 0.2 and 0.4 meters per second. All other locations had a westward velocity between 0 and -0.4 meters per second and relatively high rates of change in Fe(II) concentration.

Lat	O_2 (Mm/Kg)	pH	Correlation coefficient	Oxidation Rate
5° S	134.62	8.00	0.7332	0.0131
3° S	142.17	7.98	0.8510	0.0073
2° S	135.68	7.98	0.7063	0.0071
0°	111.27	7.94	0.6524	0.0067
2° N	103.80	7.88	0.8344	0.004
3° N	110.70	7.93	0.7127	0.0074
5° N	124.71	7.97	0.8959	0.0046

Table 1. Oxygen concentration, pH, oxidation rate, and correlation coefficient at each station.

Discussion

The rapid decrease in concentration of Fe(II) over time is a great indication that Fe(II) is quickly converted into Fe(III) in these waters. This rapid conversion is a great example of why iron is a limiting nutrient in much of the world's oceans. In our experiments, the concentration of Fe(II) decreased to near zero concentrations in less than 40 minutes. In previous studies in controlled environments, the decrease in nanomolar concentrations of Fe(II) has been observed to take anywhere between 15 minutes at a pH of 8.00 and 100 minutes at a pH of 6.0 (Pham, N.A. and Waite, D.T. (2008)). It is suggested that the oxidation rate of Fe(II) is strongly pH dependent between the values of 6 and 8, and that on either side of these values, pH has little to no effect on oxidation rates (Barak, M., & Lahav, O. (2007, March 21)). Conducting these rate-of-change experiments in controlled environments is essential for understanding the relationship between pH and oxidation rate. Using the relationships established in controlled environments allows us to interpret the change in Fe(II) oxidation rates observed in the field. Unfortunately, the oxidation rates of Fe(II) are very similar at all locations sampled in this experiment. This similarity in oxidation rates could be due to the similarity in physical water properties at each station, such as pH values, which ranged from 7.88 to 8.00. Although these changes are small our findings proved to be relatively consistent with previous studies.

Five degrees South had the highest measured pH value of 8.00, and the highest oxidation rate of Fe(II) at 0.0131 micromolar per second. At two degrees north, the pH level was 7.88, and the oxidation rate of Fe(II) was the lowest at 0.004. This is consistent with findings from previous studies that show a positive correlation between the rate of Fe(II) oxidation and pH (Pham, N.A. and Waite, D.T. (2008)). The decrease in pH observed between 5 degrees south and 2 degrees north could contribute to the observed

decrease in oxidation rate, however, we are unable to rule out that this change wasn't due to other factors. Water sampled from two degrees north also had the lowest concentration of oxygen at 103.8 Mm/kg. This finding is consistent with previous studies that there is a direct relationship between the concentration of Oxygen and the oxidation rate of Fe(II) (Barak, M., & Lahav, O. (2007, March 21)).

Using pH level, oxygen concentration, and the coordinates from this experiment, we were able to perform multiple linear regression analyses to define the relationship between the physical properties of the water and the measured oxidation rates. From this multiple linear regression analysis, the model created was able to determine that pH, oxygen concentration, and latitude account for 78% of the variability in the measured oxidation rates. This value indicates that there is a strong positive correlation between the oxidation rate and the physical properties measured. It is important to note that in this model roughly 21% of the variability in oxidation rate measurements cannot be accounted for by the data collected. There are plenty of other variables that can affect the oxidation rate of Fe(II). In future studies, it is important to collect as much physical data as possible to generate a model that can more accurately devise the relationship between these variables and the oxidation rate of Fe(II).

Numerous variables are affecting the oxidation rates of Fe(II) at these locations. Water masses originating in different locations will have various unique water properties. The research conducted identified the various water masses across the equatorial Pacific using ADCP data and the data is essential for providing context as to why the water properties at these locations are different.

Using ADCP data we were able to plot the water velocity at 140 m at each location along the transect (figure 6). Plotting the ADCP data allowed for the identification of different water masses. Water sampled from 5 degrees south had an eastward or positive zonal velocity of 0.2 to 0.4 m/s. The identification of these water masses is important to provide a broader context of where the water is coming from and whether seawater sampled at different stations is coming from the same source or different sources.

Fe(II) kinetics is interesting in the equatorial Pacific region because of the Equatorial undercurrent, a counter current that supplies nutrients to the region. The vertical displacement of the EUC in the water column influences the supply of iron and various other nutrients to the surface water (Ryan, J. P., Ueki, I., Chao, Y., Zhang, H., Polito, P., & Chavez, F. (2006, June 7). This experiment had the potential to detect small concentrations of Fe(II) in seawater but the detection method was not sensitive enough to provide in situ concentration measurements. If the EUC is supplying Fe(II) to the equatorial Pacific waters sampled in this experiment, the oxidation rates observed provide insight as to how long that supply of iron will be available to organisms if in the form of Fe(II).

Conclusion

There was a difference in Fe(II) oxidation rates at all 7 stations across the equatorial Pacific. At each station, there was a difference in pH and oxygen concentrations. The station with the highest pH level also had the highest oxidation rate. The station with the lowest pH level had a low oxidation rate. These findings are consistent with prior research that establishes a positive correlation between pH and oxidation rate. The station with the lowest oxygen concentration also had the lowest oxidation rate of Fe(II). It is unclear what the cause of these changes in oxidation rate is but using the data collected it is possible to do multiple linear regression analysis that would provide insight as to what variable could have the largest effect on Fe(II) oxidation rate. More data and further research is needed to say with any sort of confidence that one, pH or oxygen concentration is the leading variable that affects oxidation rates of Fe(II).

Acknowledgments

I would like to acknowledge the crew of the R/V Thompson for making this cruise possible and for teaching students and faculty alike what it means to work on a research vessel. I would like to acknowledge Jaqui Neibauer and Rick Keil for turning my vision into a feasible research project and the entire University of Washington Oceanography department for allowing students to participate in such a unique experience.

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