

The effect of pH on phytoplankton growth and iron solubility

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Summary

The oceanic uptake of antropogenically produced CO₂ is predicted to continue to lower ocean pH in the future; this has the potential to shift phytoplankton species assemblages and affect iron solubility. A series of shipboard incubation experiments will be conducted at 3 different pH levels: ambient (approximately 8.1), 7.0 and 6.0 with water samples collected from a region of low iron/low productivity and a region of high iron/high productivity. For samples collected from the low iron region, additional iron will be added to half the samples; for samples collected from the high iron region, an iron-binding siderophore will be added to half the samples. This will create a batch of relatively high iron concentrations as compared to the other half of the samples.

Picophytoplankton are expected to initially dominate in the samples collected in the low-iron region and diatoms are expected to initially dominate samples collected from the high-iron region. This experiment will determine how these different starting assemblages of phytoplankton respond to pH decrease and changes in iron solubility. Samples will be incubated onboard for three days then samples will be size fractionated and chlorophyll *a* biomass will be calculated.

Introduction

The burning of fossil fuels has resulted in elevated levels of carbon dioxide in the atmosphere. The oceans absorb half of the annual output of CO₂ and this has helped mitigate the rate of climate change. But the hydrolysis of CO₂ leads to an increase in pH; already ocean pH has dropped by 0.1 units since pre-industrial times to its current value of 8.1. Modeling experiments suggest that ocean pH may be reduced by a further 0.7

units over the next 300 years (Caldeira and Wickett, 2003). The acidification of the oceans as a result of the uptake of CO₂ is predicted to have deleterious effects on calcifying organisms such as the corals and some phytoplankton species (Orr, et al., 2005). Very few studies, however, have examined the effect of pH on marine phytoplankton. Hinga (2002) found only 21 such studies, which he reviewed in his paper; all of these studies focused on coastal marine phytoplankton. Phytoplankton were found to grow over a wide range of pH with some species being more tolerant of pH shifts while others were sensitive to changes of just 0.1 units (Hinga, 2002).

Numerous studies have been conducted in the equatorial Pacific examining the effects of iron on phytoplankton growth and primary productivity. Iron enrichment experiments have supported the hypothesis that iron limitation in high-nutrient, low-chlorophyll regions inhibit phytoplankton growth (Gordon et al., 1998; Lindley and Barber, 1998; Martin, et al., 1994). The availability of iron for primary production is limited by the solubility of Fe(III) in seawater; at decreasing pH levels, the solubility of Fe(III) increases (Millero, 1998; Xuwu and Millero, 2002). Future acidification of the oceans could potentially make iron more available to phytoplankton.

The Galapagos Islands lie in the pathway of the Equatorial undercurrent (EUC) and it is the upwelling of the EUC that creates the iron rich environment that supports phytoplankton growth near the islands (Gordon et al., 1997). Though the extreme low pH levels predicted as a result from anthropogenic CO₂ additions are centuries away, ocean pH is already changing. This experiment will provide insight into how phytoplankton communities may shift in response to this change. This could have serious implications where phytoplankton form the base of the trophic pyramid in the productive

regions around the islands. Shifts in phytoplankton growth rates have the potential to impact not only marine life in the waters near the islands but terrestrial life on the islands as well.

Proposed research

Incubation experiments will be conducted to determine how lowering pH affects phytoplankton growth and iron solubility. The pH of seawater samples will be lowered using HCl to approximately 7.0 and 6.0. A pH of 6.0 is much lower than the oceans are predicted to drop to in the near future, but this will provide insight into open ocean phytoplankton dynamics at a low pH. (Note I may just limit it to 8.1, 7.5 and 7.0 if not enough HCl is onboard, I was concerned that I may not see noticeable change over that range)

It will not be possible to collect samples in such a way to avoid iron contamination, nor will it be possible to determine starting levels of iron in the samples. Rather, this experiment will seek to compare relative iron levels between the samples collected from each region. To achieve this, additional iron will be added to the half of samples collected from the low iron region. To achieve low-iron samples from the high-iron region, the iron-binding siderophore, deferoxamine mesylate salt (DFOM), will be added to half of the samples (Hutchins et al., 1999; Wells, 1999). All samples will be incubated onboard for 3 days. Additionally, one bottle for each pH will be incubated in the dark to estimate zooplankton grazing. This will not provide a robust measurement of grazing rates but will at least provide a rough calculation of the zooplankton grazing rate relative to pH. Three samples will be collected from the CTD to be size fractionated and

analyzed immediately to determine the species composition and starting Chl *a* biomass prior to the incubations.

The samples that are left at ambient pH will provide a control for phytoplankton response to lower pH. At each of the pH levels, the low iron sample will provide insight into phytoplankton response to pH while the high iron samples will allow for an estimation of phytoplankton response to increased iron solubility (I still need to think that one through).

Picoplankton and nanoplankton (the ultraplankton) are known to dominate HNLC areas and diatoms (the microplankton) are known to dominate blooms where there is ample iron (need to find good reference). After the incubation is complete the samples will be size fractionated to determine the Chl *a* biomass of the ultraplankton versus the microplankton (Wells, 1999).

Methods

Sample collection

Samples will be collected from the *R/V Thomas G. Thompson* during the January 12th – 20th, 2005 cruise. Water samples will be collected from two sites: a region of low productivity south of Isabella Island and a region of high iron and high productivity in Elizabeth Bay. Figure 1 shows the two proposed sample sites. (Note these locations are approximate as the coordinates have not been finalized).

Samples will be collected using a CTD rosette from the chlorophyll maximum as determined by the CTD profiler, salinity will also be measured with the CTD. To minimize the presence of zooplankton grazers, samples will be collected during daylight

hours. To further reduce the presence of zooplankton, water will be discharged from the CTD Niskin bottles through a 200-micron Nitex mesh filter. Samples will be collected from the CTD into four 10-liter carboys and twelve 2-liter bottles (nine of these will be incubated, three will be analyzed immediately). All collection carboys and incubation bottles will be acid washed and rinsed with seawater prior to use.

Sample preparation

The water in the four carboys will be acidified using 2 Normal HCl. The pH in two of the carboys will be lowered to approximately 7.0 using XX mL of HCl and to approximately 6.0 using XX mL of HCl in the remaining two carboys. The carboys will be agitated and allowed to equilibrate then pH will be measured with a Brand X pH meter. The pH will be measured for the unacidified samples in the 2-liter bottles at this time. Adjustments with additional HCl will be made to bring the pH in each of the two sets of carboys as close to each other as possible. (Note: I've spoken with Kathy Kroglund in marine chemistry and next week I am going to go into the lab and try acidifying 1L and 10L samples to determine how much HCl I will need. That will appear in my final proposal). After acidification, water from the carboys will be decanted into nine 2-liter bottles for each of the two pH levels.

For each pH, ambient, 7.0 and 6.0, there will be two conditions: relatively high iron and relatively low iron. For the samples collected in the region of low iron, three bottles will have additional iron added; for the samples collected in the region of high iron, three bottles will have DFOM added. (need to talk to Kathy about quantities) For each pH level, one bottle will be wrapped in aluminum foil to block light, in order to

allow for an estimate of zooplankton grazing. Sample bottles will then be incubated in a flow-through shipboard incubator for three days.

Sample analysis

The three extra 2-liter bottles collected from the CTD will be analyzed as soon as possible by methods described below to determine the starting Chl *a* biomass. The remaining bottles will be analyzed after the 3-day incubation period.

Size fractionated chlorophyll *a* measurements will be made by filtering the samples through a XXnm and a XXnm Brand filter. Chl *a* will be extracted with acetone, sonicated and measured with a fluorometer.

(As per Llyd, I will be able to more accurately describe how the samples will be processed after we practice with Kathy next week).

Project Budget

Item	Unit Cost	No. of Units	Total Cost	Effective Cost
<i>R/V Thompson</i>	\$18,000/day	8	\$144,000	\$ 0
CTD (seacat)	\$45.00/day	2	\$90.00	\$0
2 L Sample btl	\$3.00/day	6	\$18.00	\$0
pH meter	\$0	6	\$0	\$0
Deck Incubator	\$3.00/day	6	\$18.00	\$18.00
Filter rack & Pump	\$6.00/day	2	\$12.00	\$12.00
Centrifuge	\$6.00/day	2	\$12.00	\$12.00
Sonicator	\$0	2	\$0	\$0

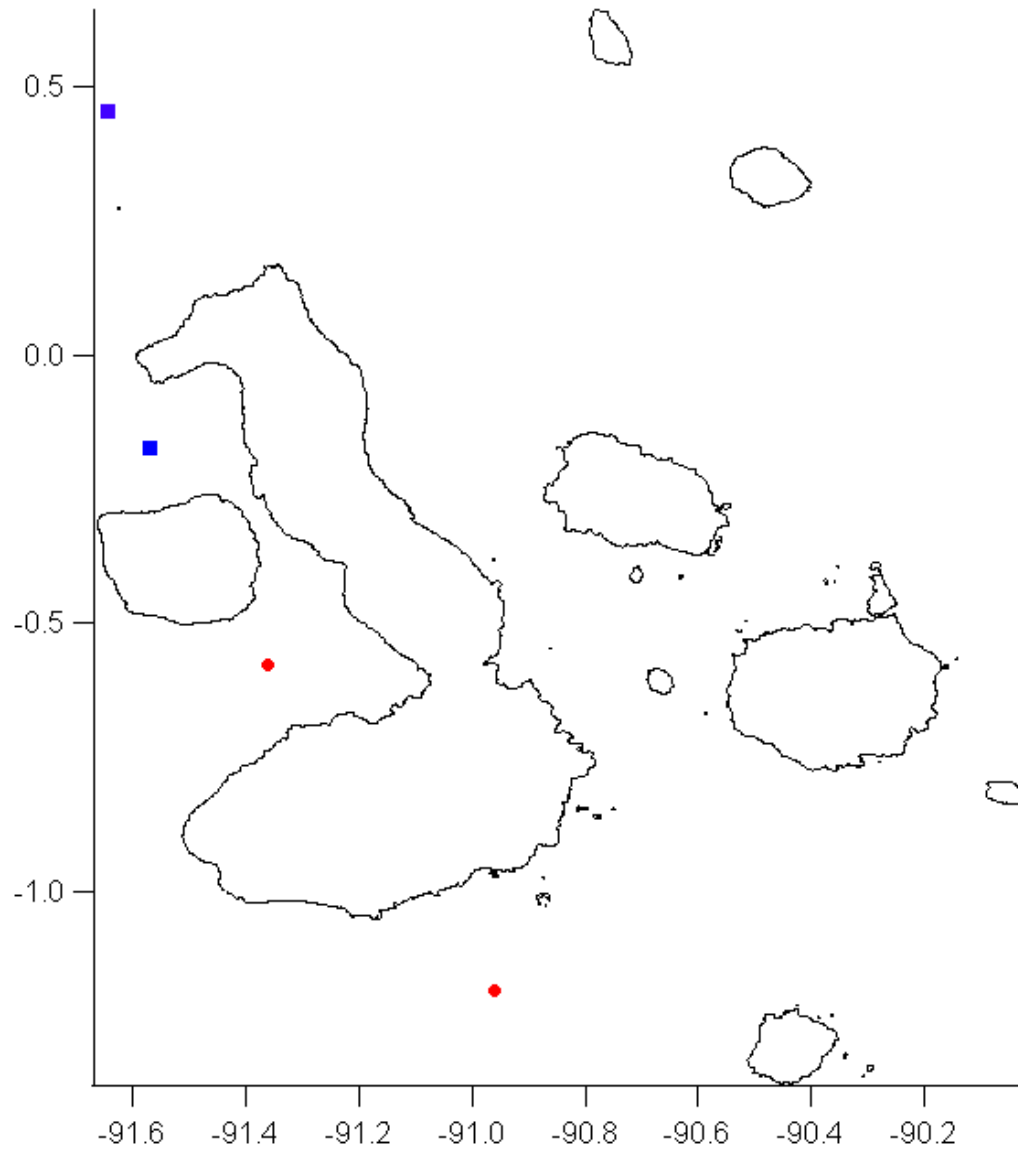


Figure 1. Locations of collection locations.

(Note: The ship track has not been finalized so these are approximates. If we go south, the red circles will be the sample sites; if we go north, the blue squares will be the locations. I will have exact coordinates for the final proposal).

References

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