ASSESSING MULTIPLE INDICATORS OF NUTRIENT LIMITATION IN MARINE

PHYTOPLANKTON ON THE LOUISIANA CONTINENTAL SHELF

by

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ABSTRACT OF THE DISSERTATION

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Dissertation Director: James W. Ammerman

Eutrophication on the Louisiana continental shelf is driven by excess nitrogen (N) and phosphorus (P) delivered by the Mississippi River. While the eutrophication is driven primarily by excess nitrogen, scattered data going back to the early 1990's suggests that the ecosystem on the Louisiana shelf may be seasonally P-limited in the spring and early summer during high runoff periods, primarily in areas of intermediate salinity. These intermediate salinity zones are also the areas where chlorophyll biomass and primary productivity are often maximal. This production likely drives the annual bottom water hypoxia in the region, known in the popular press as the "dead zone." Three very different methods were used to address the question of nutrient limitation on the Louisiana shelf. In July 2002, a Fast Repetition Rate fluorometer (FRRf) was used in conjunction with nutrient addition bioassays and mapping of surface water parameters to examine the response of the phytoplankton community to eutrophication. In incubations, chlorophyll *a* biomass responded to phosphorus additions, but not those of N alone and FRRf parameters indicated a positive response to P additions in the way of higher efficiency in photosystem II. The mapping data was more heterogeneous in nature, but

overall patterns indicated that P limited phytoplankton biomass. Three cruises in March, May and July 2004 were conducted in order to investigate seasonal patterns of dissolved inorganic, dissolved organic, and particulate nutrients on the Louisiana shelf. The combination of low P concentrations, high inorganic and total N:P ratios and high alkaline phosphatase activities indicated P limitation of phytoplankton biomass on the Louisiana shelf during the spring and early summer of 2004. A study of *pstS*, a gene induced under P-stress, revealed that its distribution in oceanic waters is related to location of the sample. The *pstS* gene in *Synechococcus spp.* taken from various sites around the world clustered on a phylogenetic tree closest to other sequences taken nearby. The combination of FRRf, nutrient data, enzyme assays and molecular markers of P-limitation strongly confirm seasonal P-limitation on the Louisiana continental shelf in the spring and early summer, driven by extreme N loads during these seasons.

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Jim Ammerman has been a wonderful advisor, providing me with not only the resources with which to carry out my research, but also invaluable advice concerning my career and life paths. My thinking has undoubtedly been positively shaped by him and I am proud to have been a student of his. My two lab mates, Brian Gaas and Marta Sebastian, provided hours of advice and also conversation when I needed a distraction (often to their detriment).

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1.0 Introduction

Primary production in marine waters is regulated by a number of factors, the most important being nutrient and light supply. Determining controls on primary production is important from both a scientific and practical standpoint. Scientifically, it is necessary to predict the most important factors driving primary production to efficiently model the biogeochemical cycles of carbon and other ecologically relevant elements. Practically, determining how to control eutrophication, or excess phytoplankton growth, is dependent on pinpointing which growth requirements can be controlled to reduce phytoplankton biomass. This is now a significant challenge in many coastal areas due to a combination of anthropogenic effects that have yielded excess phytoplankton growth in coastal areas which can lead to harmful algal blooms, bottom water hypoxia, and unsafe water conditions for recreational purposes. There is a very real economic cost to coastal eutrophication and therefore significant effort is currently being invested in learning what causes eutrophication and how to control it.

Nitrogen (N) and phosphorus (P) are the two major macronutrients required by phytoplankton for balanced growth. Diatoms also have a high demand for silica to produce their frustules, but N and P are the most important macronutrients for all other phytoplankton. Many micronutrients, such as iron and molybdenum, are also necessary in trace amounts, most often as cofactors in enzymes, but are not the focus of this work and will not be discussed in detail here.

N is required for making amino acids, the building blocks of proteins. The N cycle is complex due to the multiple redox transitions N can undergo with the aid of

bacteria. N is supplied to phytoplankton in the photic zone via riverine inputs, upwelling from below and nitrogen fixation *in situ*.

The highest demand for cellular P is the phosphate backbone of nucleic acids and in the phospholipids of the cellular membrane. It does not undergo redox transformations as nitrogen does, but the conversions of P from its inorganic form (predominately HPO_4^{2-} and PO_4^{3-} but hereafter referred to as P_i) to its many organic forms play an important role in marine biogeochemistry (Karl & Bjorkman 2002).

It has been known since the 19th century that plants need nutrients in a specific ratio for maximum growth efficiency. Justus von Liebig first pointed out that whatever nutrient is used up first is present at concentrations limiting further growth of the plant (Liebig 1855). This is called the Law of the Minimum. The next great leap forward was Alfred Redfield's groundbreaking work on elemental stoichiometry in phytoplankton (Redfield 1958), which showed that phytoplankton biomass displayed elemental stoichiometry for C, N and P in the ratio of 106:16:1, now known as the Redfield ratio. The implication of this work is that when supply of N or P (we ignore C here because phytoplankton fix their own carbon and CO_2 is generally saturated in the surface waters of the ocean) are less than the ratio of 16:1, then whatever element is in shorter supply limits primary production.

Two basic forms of nutrient limitation are acknowledged by oceanographers (Cullen et al. 1992). Liebig limitation, also known as biomass limitation, exists when the size of the phytoplankton standing stock is limited by nutrient supply. An addition of the limiting nutrient will incite an increase in biomass concentration. For example, if the N:P ratio is 9, then addition of N should stimulate greater phytoplankton biomass. There is

also limitation upon instantaneous growth rate, when a community of phytoplankton has reached their maximal size, but their growth rate is limited by nutrient supply. This is represented not by a deficiency of one particular nutrient, as with Liebig limitation, but by a low supply of nutrients, as is the case in the open ocean gyres. In this case, the cells are dividing at a slower rate than optimal and addition of the limiting nutrient will cause cells to proceed through the cell cycle at a faster rate. This is known as balanced growth whereas cells growing under Liebig limitation are often referred to as a batch culture (Graziano et al. 1996).

Multiple methods exist to investigate nutrient limitation, including the use of nutrient ratios, enzyme assays, uptake measurements, fluorometric methods and nutrient addition bioassays (Beardall et al. 2001b). Nutrient concentration measurements are rapid and simple to perform, but nutrient data alone is generally considered insufficient to make definitive statements about limitation. When combined with biological data or nutrient ratios, however, these are excellent indicators of the status of an ecosystem. Enzyme activities, especially the use of ectoenzymes located in the periplasm of bacteria or between the cell wall and cell membrane in phytoplankton, are valuable tools for determining nutrient limitation because the measurements are cheap, reliable, simple and rapid, enabling many samples to be taken during a cruise (Ammerman 1993). Like nutrient data, enzyme activities alone are insufficient to make conclusions but are very useful when combined with other data. Uptake measurements generally require the use of radiolabelled substrates to track how fast they are incorporated into the cell. This is a very sensitive method, but, like the others, requires additional data to make solid conclusions and requires special precautions to work with and dispose of radioactive

waste. The fluorometric method Fast Repetition Rate fluorometry (FRRf) is a more recent addition to the field and an extremely valuable tool for determining phytoplankton physiologic status (Kolber et al. 1998). FRRf provides information on the immediate status and photosynthetic potential of the phytoplankton community that cannot be obtained by addition bioassays or nutrient ratios. Nutrient addition bioassays are often considered the ultimate method for determining the limiting factors to primary production but are labor intensive and require at least 24 hours for completion, often more. This makes them difficult to carry out at frequent sampling rates during a cruise. However, one can include all the methods mentioned above on samples in a nutrient addition bioassay, creating a powerful but labor intensive investigation of nutrient limitation.

Successful nutrient management strategies in eutrophic estuaries depend on an accurate understanding of limiting nutrients. For years, the prevailing thought was that P is limiting in freshwater systems while N is limiting in marine systems (Hecky & Kilham 1988). However, in the last two decades researchers have found that marine systems can be limited by P as well as N. This is especially true along estuarine gradients. Freshwater sources to coastal areas, such as rivers, often contain high loads of N as a result of anthropogenic loading. A common source of the extra nitrogen is runoff from farmlands with N-rich soils as a result of fertilizer application (Goolsby et al. 2001). In coastal regions with a significant input of freshwater, it is not uncommon for P to be limiting during the high flow period of the freshwater input, often spring or summer, and N to be limiting the rest of the year (Conley 2000). Examples include Chesapeake Bay (Fisher 1992), Delaware Bay (Pennock & Sharp 1994) and the Black Sea (Cociasu et al. 1999).

Recent work on the Louisiana continental shelf revealed a similar pattern of P limitation in the spring and early summer, when discharge from the Mississippi River is high, and N limitation during the late summer through the winter, when discharge was lower (Sylvan et al. 2006). This study combined data from nutrient addition assays, nutrient uptake rate measurements, inorganic nutrient concentrations and ratios, and AP assays. While compelling, some questions still remained, especially in regards to the role of organic nutrients in relieving P-limitation (Boesch 2004, Dodds 2006) and how reproducible the pattern of spring/early summer P-limitation and fall N limitation would be.

The Mississippi River is the largest river in North America. It drains approximately 40% of the continental United States into the GOM (Turner & Rabalais 1994), creating an open ended estuary in the Mississippi River Plume (MRP). Starting in the 1940's, nitrogen and phosphorus input to the river began to increase as a result of elevated fertilizer use (Rabalais et al. 2002c). While usage of phosphate fertilizer leveled off around 1980, nitrogen fertilizer use continues to rise (Fig. 1.1), resulting in drastic changes in the nutrient ratios within the river (Wiseman et al. 1999). Current nutrient ratios for dissolved inorganic nitrogen (DIN), silicate and phosphate in the river water are approximately 14:14:1, respectively, close to the Redfield ratio. Si:N ratios of 4:1 in the past illustrate how dramatic the change has been (Rabalais et al. 1996).

More than a decade ago it was suggested that nutrient runoff from fertilizer upstream in the Mississippi River might be the cause of the large hypoxic zone in the GOM (Turner & Rabalais 1994). Since then, several studies investigated both bacterial (Pomeroy et al. 1995, Amon & Benner 1998, Pakulski et al. 2000) and phytoplankton

(Smith & Hitchcock 1994, Lohrenz et al. 1999, Sylvan et al. 2006) production in the

MRP. These studies were in agreement that abundance and production are typically
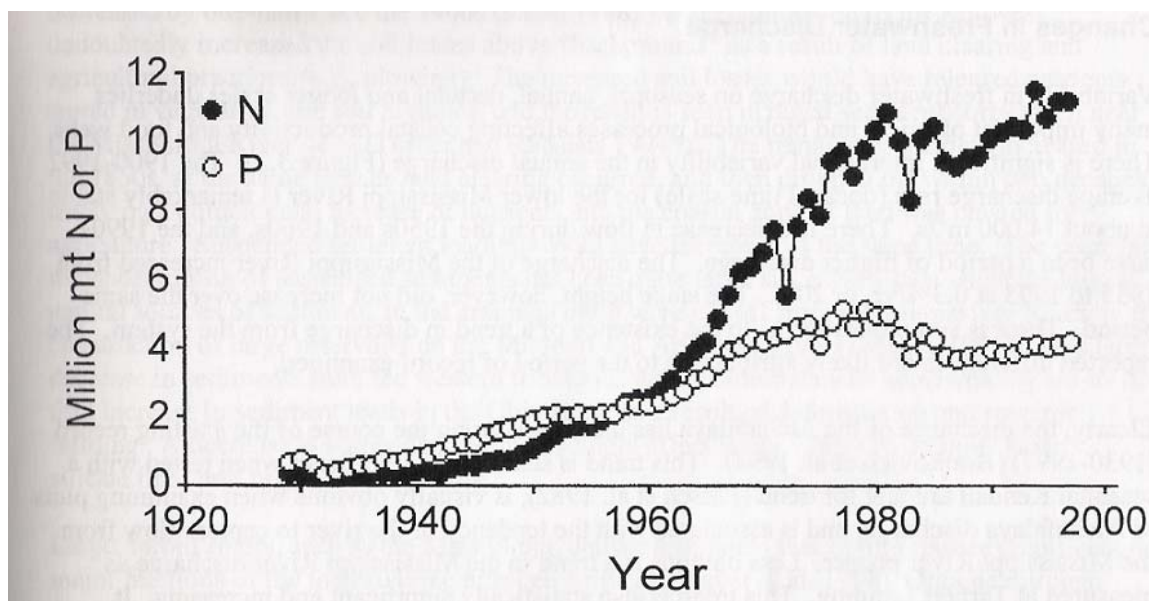
Figure 1.1: Nitrogen (as N) and phosphorus (as phosphate) fertilizer use this century in the
United States up to 1997, according to USDA. From Wiseman et al. 1999.

maximal at intermediate salinities within the plume and, using enrichment experiments

and nutrient ratios, it was shown that there is a potential for phosphorus limitation of both

primary and secondary production in the spring and summer. This period of potential

phosphorus limitation corresponds with the high flow period of the river, which starts in

the early spring and may last through as late as August. Because this high flow period

corresponds with the time that bottom water hypoxia is forming, it is likely that a

reduction of P in addition to reducing the already extremely excessive N load will reduce

biomass on the shelf and, therefore, bottom water hypoxia.

This dissertation covers three methods for assessing nutrient limitation in aquatic

systems applied to the Louisiana continental shelf: FRRf, basic biogeochemical

measurements, including a complete analysis of nutrient pools and their corresponding

ratios, and the use of genetic indicators of P-limitation. These methods are either new to

or much more extensively done than previously in this area and help provide extensive insight into the biogeochemistry of the largest river plume in the country. A brief introduction to each method is now presented followed by an overview of the study area.

1.1 Fast Repetition Rate Fluorometry

FRRf is a way to quickly and easily study *in vivo* fluorescence signatures of phytoplankton in a non-invasive manner (Kolber et al. 1998). FRRf has been used extensively in both the laboratory and the field to investigate primary production in nutrient replete phytoplankton as well as their limitation by N and Fe (Kolber et al. 1990, Falkowski & Raven 1997, Behrenfeld & Kolber 1999, Suggett et al. 2001). The FRRf protocol directs a series of subsaturating flashlets at PSII which ultimately induce saturation of the photosystem (Fig. 1.2). These fluorometers provide the user with photosynthetic parameters including the minimal and maximum fluorescence, F_o and F_m, respectively, the quantum yield of photochemistry, F_v/F_m (where $F_v = F_m-F_o$), the functional absorption cross section for photosystem II (PSII), σ_{PSII}, the time constant for photosynthetic electron transport on the acceptor side of PSII, τ_{Qa} and the connectivity factor, *p*, which defines energy transfer between individual photosynthetic units (Gorbunov et al. 2000). The shape and slope of the initial saturation curve yield σ_{PSII} and *p*, while the relaxation curve yields τ_{Qa}. F_o is the minimal or background fluorescence measured after dark adaptation of the cells to avoid photochemical quenching and F_m is the maximum fluorescence measured at saturation of PSII. Collectively, these FRRf parameters can be used to assess the physiological response of a phytoplankton community to a nutrient stress, such as P-limitation. One advantage to FRRF is that it

yields the instantaneous physiology of the cells and responds quickly to environmental perturbations, whereas many other physiological measurements, such as chlorophyll response or protein induction require longer time scales to respond.
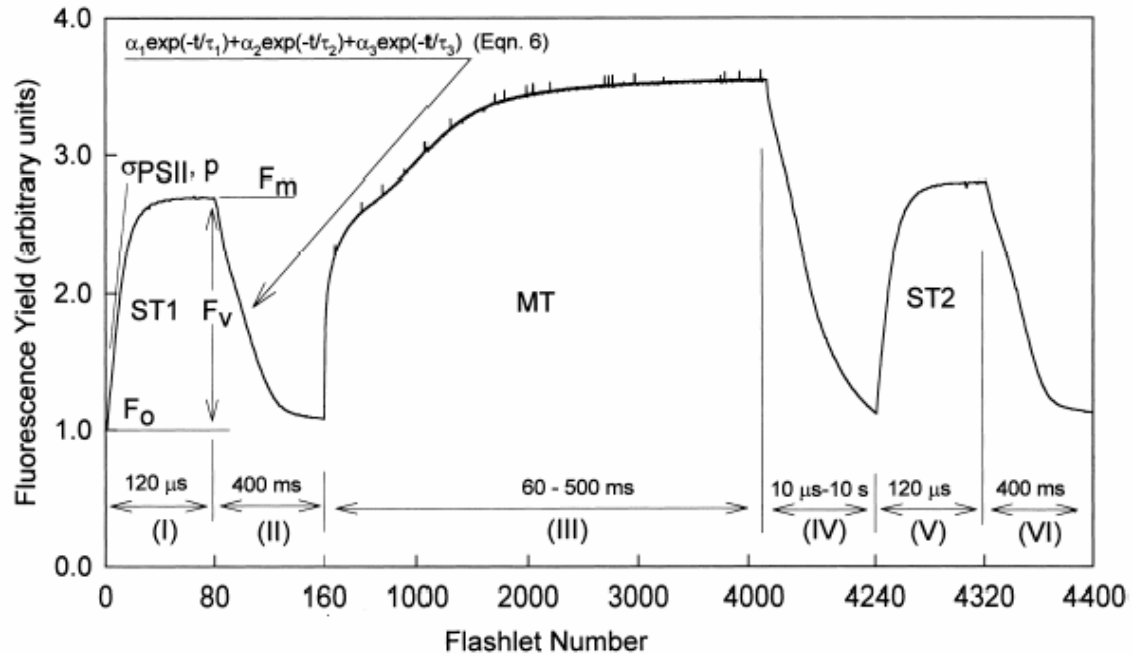
Figure 1.2- Kinetic profile of single (ST) and multiple (MT) turnover flashes as induced and detected by a FRR fluorometer. This study used data from ST flashes only. Note the indication of the parameters F_o, F_m, F_v, σ_{PSII}, p and τ_{Qa} (as indicated by Equation 6). Taken from Kolber et al. (1998).

1.2 Basic Biogeochemical Measurements

With the combination of nutrient concentrations and their ratios, one can predict the potential for limitation. Chlorophyll *a* (Chl *a*) concentrations or enzyme assays in the same samples add further support to these conclusions. While inorganic N and P are often the most bioavailable forms of these nutrients, and this is certainly the case for P, there are often equal or greater concentrations of organic N and P in marine and estuarine waters that may also be bioavailable to phytoplankton. Some phytoplankton and bacteria even prefer organic forms of N to inorganic (Seitzinger et al. 2002).

Most measurements until recently have focused on the inorganic pools of N and P as the drivers of primary production. While it requires extra labor over measuring inorganic nutrients alone, it is important to look at organic nutrient pools as well when assessing nutrient limitation. Many measurements of dissolved organic carbon (DOC) have been made in on the Louisiana shelf, but dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) measurements are much rarer. DON in estuaries tends to range from ~15-30 μM. It is higher in rivers and lower in the open ocean (Bronk 2002). Estuarine DOP concentrations tends to range from ~0.20 μM-0.60 μM (Karl & Bjorkman 2002). It will be valuable to have a more intensive sampling of DON and DOP in the region over a seasonal change to gain insight into dissolved organic matter (DOM) cycling in this area. The DOM data will also allow a comparison to the limited data from older work to look for patterns through time. One argument against P-limitation on the Louisiana shelf is that cells can use organic P and therefore high $DIN:P_i$ ratios are not necessarily indicative of P-limitation (Boesch 2004) and I will be able to assess this criticism with the DOM data.

1.3 Molecular Work

pstS is a gene that codes for the phosphate binding protein, PstS, of the pho regulon of gram negative bacteria and some phytoplankton (Torriani-Gorini 1994). The pho regulon consists of a high affinity P transport system that is not transcribed when environmental P_i is replete and is induced when it is low (Fig. 1.3). This pattern is consistent in field samples of alkaline phosphatase (AP) activity, the enzyme in the pho regulon that liberates PO_4^{3-} from phosphate monoesters (Ammerman & Glover 2000),

making AP an excellent indicator of P-limitation. High AP activity, as measured by a simple fluorescence assay, is an indication of P-limitation while when it is low, P is not considered to be limiting.

While AP (encoded by the gene *phoA*) cleaves PO_4^{3-} from organic phosphate molecules, it is PstS, the phosphate binding protein, that grabs the newly liberated PO_4^{3-} molecule and brings it to the PstA and PstC transmembrane channels. PstS is a periplasmic protein whose gene has been successfully targeted for amplification in the cyanobacterium *Trichodesmium* (Orchard et al. 2003). *phoA* is a desirable target for a genetic study of P uptake in marine phytoplankton, but based on the sequences in currently available genomes, it is not well conserved. This makes it difficult to construct PCR primers targeting more than one species at a time. Additionally, there is some evidence that there may be multiple types of phosphatases responsible for liberating PO_4^{3-} from DOP (Majumdar et al. 2005). *pstS* is a more desirable gene due to its better conservation across multiple groups of phytoplankton and bacteria. Induction of *pstS* is the same as *phoA*, therefore it can also be used as an indicator of P-stress.

The recent genomic revolution has yielded huge amounts of data for use in genetic studies. It is now possible to probe not only genomes, but also look for trends within a gene across geographic boundaries thanks to databases like CAMERA (http://camera.calit2.net), which include environmental data and sample locations with sequences added to the database. I am interested in how phosphate acquisition genes differ across trophic regimes (eutrophic→ oligotrophic) and also whether and how they differ across geographic boundaries. Specifically, I wanted to determine whether P

concentration in an environment has an effect on the presence or absence of P acquisition

genes, and if there was any correlation with AP activity. I chose to investigate these
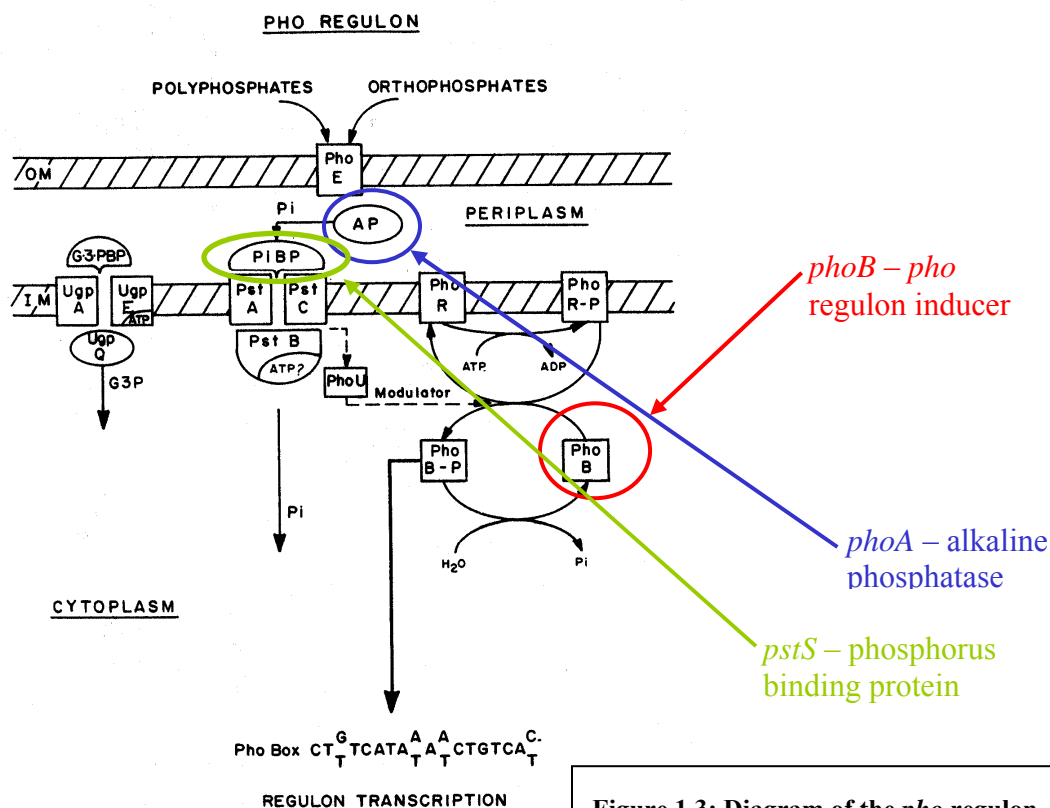
Figure 1.3: Diagram of the *pho* regulon with genes relevant to this project highlighted. From Toriani-Gorini, 1994.

questions using *pstS* in different species of the globally distributed cyanobacteria

Synechococcus. To do so, I isolated *pstS* sequences from two stations in the GOM, one

in the Mississippi River plume and one from out on the continental shelf, and also the

Sargasso Sea. Sequences from the CAMERA database were included to provide data

from locations where I did not have samples.

1.4 Outline of Dissertation

Two cruises to the Louisiana continental shelf and MRP in July 2002 used FRRf

to assess phytoplankton nutrient limitation on the shelf. During the first cruise, we took

surface water samples approximately every 30 minutes to assess for inorganic nutrients, chl *a* concentrations, AP activity and the FRRf parameters F_v/F_m, σ_{PSII}, p, and τ_{Qa}. During the second leg of the cruise, 14 small scale nutrient addition bioassays were performed near the Mississippi River plume. The same measurements as on the first cruise were taken and indicated that addition of P yielded an increase in photosynthetic efficiency.

Three cruises to the Louisiana shelf in March, May and July 2004. These cruises were again mapping surface water biogeochemical parameters. Water sample were collected approximately every 30 minutes, 24 hours a day, for chl *a* biomass, filtration for dissolved inorganic, dissolved organic and particulate nutrients and AP assays. Approximately every hour, the boat was stopped for a CTD cast and I was able to go on deck and use a bucket to sample the surface water to collect cells on a filter for later molecular analysis. The samples ultimately used in my molecular work were taken during the July 2004 cruise and on a May 2006 cruise to the Sargasso Sea.

This project provides a thorough assessment of P-limitation on the Louisiana continental shelf using multiple methods. The molecular work provides the foundation for further genetic studies of P biogeochemistry. It can be combined with future studies of different groups of bacteria or phytoplankton to discern what groups are P-limited and which ones are not, since, it is possible for different groups of bacteria or phytoplankton to be differentially limited (Sundareshwar et al. 2003). This has important implications for the management of eutrophication as different management strategies may be necessary for dealing with phytoplankton and bacteria. As eutrophication is a major problem on the Louisiana continental shelf, this study provides results that hopefully will

guide the decisions of policy makers by providing solid science on which to base those decisions.

2.0 Eutrophication-induced phosphorus limitation in the Mississippi River plume:

Evidence from fast repetition rate fluorometry

Abstract

We assessed nutrient limitation in the Mississippi River plume and Louisiana continental shelf during the summer of 2002 (04-08 July). We measured nutrient concentrations, alkaline phosphatase (AP) activities, chlorophyll a (Chl a) concentrations, and four fast repetition rate fluorescence (FRRF) parameters: the maximum quantum yield of photochemistry in photosystem II (PSII), F_v/F_m, the functional absorption cross section for PSII, σ_{PSII}, the time for photosynthetic electron transport on the acceptor side of PSII, τ_{Qa}, and the connectivity factor, p, in 24 hour long nutrient addition bioassays near the Mississippi River delta. Low phosphorus (P) concentrations, elevated inorganic nitrogen to phosphorus ratios, high AP activities, and Chl a increases in response to P additions in the bioassays all indicated phosphorus limitation that was confirmed by the response of FRRF parameters. This is the first study to use FRRF to confirm results from basic oceanographic methods to demonstrate phosphorus limitation in a marine setting. F_v/F_m and p responded positively to phosphorus addition while σ_{PSII} and τ_{Qa} decreased in the same treatments. When nitrate alone was added, none of the measured parameters differed significantly from the control. We therefore suggest that FRRF can be used to rapidly detect phosphorus limitation in marine ecosystems.

2.1 Introduction

Nutrient limitation of net primary production can be an important control on phytoplankton growth in aquatic environments and understanding it can help to limit eutrophication (Howarth & Marino 2006). Determining the extent of nutrient limitation

has been a fundamentally important question of aquatic scientists for decades. Many methods, both direct and indirect, are available for addressing this problem, including nutrient concentrations and ratios, enzyme assays, fluorescence parameters and nutrient addition bioassays (Beardall et al. 2001b). FRRF allows quick, non-invasive assessment of phytoplankton in vivo fluorescence signatures that provides the user with photosynthetic parameters including F_v/F_m, σ_{PSII}, τ_{Qa}, and p (Kolber et al. 1998). F_v/F_m is an indicator of the photosynthetic efficiency of a cell or community when measured in a dark-acclimated state. Healthy algae can have an F_v/F_m as high as 0.65 (Kolber et al. 1998). The absorption cross section of PSII (σ_{PSII}) changes in response to cellular pigment concentrations and the efficiency of energy transfer from pigments to PSII reaction centers, thus making it subject to both nutrient and light availability (Kolber et al. 1988, Moore et al. 2006). σ_{PSII} is typically lower in nutrient replete cells relative to unhealthy cells (Kolber et al. 1988). The time constant for photosynthetic electron transfer on the acceptor side of PSII (τ_{Qa}) reflects the minimum turnover time for electron transport (Kolber et al. 1988). p is the probability of energy transfer between PSII reaction centers (Kolber et al. 1998). Higher p values indicate higher probabilities of electron transfer and have been implicated in recovery from iron limitation (Vassiliev et al. 1995). Collectively, these FRRF parameters can be used to assess the physiological response of phytoplankton cells and/or communities to nutrient stress, such as P-limitation.

The Mississippi River plume (MRP), herein defined as the area near the Mississippi Delta, especially Southwest Pass, and directly to the west of it (Fig. 1A), is a dynamic system for studying nutrient limitation. The widespread cultivation of maize

and soybeans in the Mississippi River watershed has resulted in high nitrate loads in runoff to the Mississippi River, which in turn have been implicated as a cause of the eutrophication in the river delta. The eutrophication here is thought to be the primary cause of the large hypoxic zone seen each summer off the Louisiana coast (Rabalais et al. 2002b). Production in the MRP is affected by the annual river flow pattern and the water column light regime. While N is thought to control phytoplankton biomass on the Louisiana shelf due to its surplus in the system, a recent study convincingly documented spring and early summer P-limitation in 2001 followed by a switch to N-limitation in the fall (Sylvan et al. 2006). This is important because the P-limitation occurred during the time and in the location of highest phytoplankton primary production that is responsible for much of the formation of summer bottom water hypoxia on the Louisiana shelf (Rabalais et al. 2002b). Other investigations in this area provide corroborating evidence of P-limitation of phytoplankton during the late spring and early summer (Smith & Hitchcock 1994, Lohrenz et al. 1999, Ammerman & Glover 2000).

Until now, FRRF has not been employed to address the issue of nutrient limitation on the Louisiana shelf. During a cruise from 04-08 July 2002, we used FRRF to confirm results from Chl *a* response to added nutrients in nutrient addition bioassays conducted in the MRP to examine nutrient limitation in the region. Dissolved inorganic nitrogen (DIN= NO_3^- + NO_2^- + NH_4^+) and dissolved inorganic phosphate (P_i) concentrations, DIN:P_i ratios, and AP activities were also measured in the initial samples from those bioassays. Our findings support the hypothesis that P was the limiting nutrient during early July in this ecosystem.

2.2 Materials and methods

2.2.1 Sample collection – Seawater samples were collected aboard the R/V *Pelican* at the surface (1 m) in 5 L Niskin bottles and subsampled for nutrient addition incubation experiments, AP assays, nutrient and Chl *a* concentrations, and FRRF analysis during 04 - 08 July 2002. Fourteen samples in total were collected within the MRP (Fig. 2.1A).
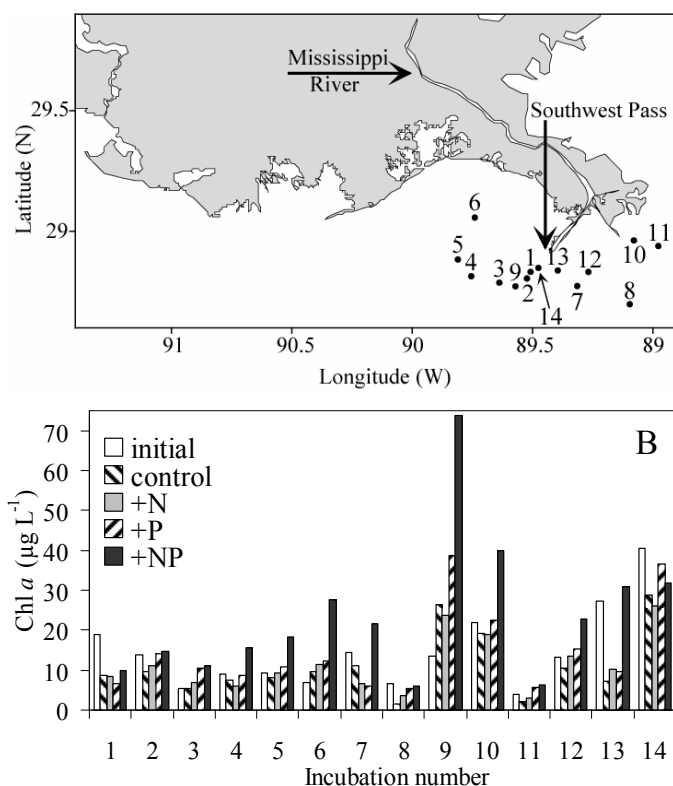
Figure 2.1. (A) Location of stations used for nutrient addition bioassays during the 04 – 08 July 2002 cruise. Large arrows point to the locations of the Mississippi River and Southwest Pass. Small arrow indicates the location of station 14. (B) Chl *a* biomass (µg L^{-1}) for each treatment and all incubations. Initial Chl *a* was taken at *t*=0 h and control, +N, +P, and +NP were taken at *t*=24 h.

2.2.2 Chl a *and nutrient concentrations* – Seawater was filtered onto GF/F filters and frozen immediately in liquid nitrogen. After returning to the lab (≤6 days later), filters were thawed on ice and placed in DMSO/90% acetone (40:60) in the dark at room temperature for 2-6 hours. Chl *a* fluorescence was measured using a calibrated Turner 10AU fluorometer. Concentrations of Chl *a* (corrected for phaeopigments) were determined according to (Lohrenz et al. 1990).

Nutrient samples were filtered through pre-rinsed 0.45 μm cellulose ester filters (Millipore) to remove particulates. Filtrate was placed in acid washed (10% HCl) 250 mL polyethylene Nalgene bottles rinsed twice with filtrate from the sample, and then frozen until analysis on a Lachat QuikChem AE autoanalyzer for P_i and DIN.

2.2.3 Alkaline phosphatase (AP) assays – AP is an enzyme that cleaves inorganic phosphate from organic phosphate esters when environmental inorganic phosphate is low, but is very low or absent when phosphate concentrations are replete, >0.30 μmol L^{-1} P_i (Hoppe 2003). It is therefore used as an indicator of microbial community P stress. AP activity was measured according to Ammerman and Glover (2000) using a Tecan Genios fluorescent microplate reader, the substrate 6,8-difluoro-4-methylumbelliferyl phosphate (DifMUP) and its respective standard, 6,8-difluoro-7-hydroxy-4-methylcoumarin (DifMU), both from Molecular Probes. Substrate was added directly to seawater in quadruplicate microplate wells at a saturating substrate concentration of 10 μmol L^{-1}, based on prior kinetics data (Ammerman & Glover 2000). Fresh blanks and standard curves were included with each run. Killed controls were run periodically and indicated no significant autohydrolysis of the substrate.

2.2.4 FRRF data acquisition – A Chelsea Instruments first generation commercial FAST[tracka] FRR fluorometer was used in bench top mode with only the dark chamber active. The instrument was configured to generate single turnover flashes. The single turnover consisted of a sequence of 100 excitation flashlets, each 1 μs duration, separated by a 1 μs interval, and a series of 20 relaxation flashlets. This protocol allowed for 3-4 quanta to be absorbed per reaction center in PSII (Kolber et al. 1998) and has been used successfully before in field experiments (Suggett et al. 2001). The same excitation protocol was maintained throughout the cruise. Samples taken during the day and after dusk were low light acclimated in opaque polyethylene bottles and kept in a cooler with surface water for 30 min prior to assessment with the FRRF. This may not be enough time to allow for complete repair of photodamaged PSII, but it is assumed to be sufficient to eliminate photoinhibition by allowing for all PSII reaction centers to relax, making it possible to measure the maximum potential quantum yield. We assume no photodamage because there is no correlation between photosynthetically active radiation (PAR) and mapped underway F_v/F_m in surface water samples during this cruise when plotted versus each other (data not shown). On the same plot are high values of F_v/F_m at high PAR levels, but one would expect to see depressed F_v/F_m correlate with elevated PAR levels if photodamage had occurred. Depressed quantum yields were therefore correlated to nutrient limitation rather than to photoinhibition (Kolber et al. 1998). Further details can be found in Kolber et al. 1998 and Suggett et al. 2001.

2.2.5 FRRF data processing – Data was acquired and processed with a program coded in TurboPascal as described by Kolber et al. (1998) to determine the parameters F_v/F_m, σ_{PSII}, τ_{Qa}, and *p*. This program is not related to the FRS.EXE program distributed with the Chelsea FAST^{tracka} unit. We present only data derived from single turnover analysis and τ_{Qa} was calculated with a monophasic function. A baseline correction for all gain levels was applied for scattering correction based on measurements using ultrapure deionized water. Comparisons with filtered seawater and ultrapure deionized water yielded similar results, as found in other studies (Behrenfeld et al. 2006), indicating no significant background fluorescence from our blanks.

2.2.6 Nutrient addition bioassays – Seawater collected from Niskin bottles was analyzed before the addition of any nutrients at $t = 0$ hours for Chl *a*, nutrient concentrations, AP activity, and FRRF parameters. This sample is hereafter referred to as the 'initial' sample. Aliquots were subsequently placed into acid washed 250 mL Nalgene polyethylene bottles and received one of four additions: control (no additions), +N (30 μmol L^{-1} NO$_3^-$), +P (2 μmol L^{-1} PO$_4^{3-}$) or +NP (30 μmol L^{-1} NO$_3^-$ + 2 μmol L^{-1} PO$_4^{3-}$). While an addition of 2 μmol L^{-1} PO$_4^{3-}$ reagent could introduce trace amounts of Fe or Zn, Fe limitation is unlikely in the MRP due to dissolved Fe concentrations of 7-30 nmol L^{-1} in the river plume, even during the spring of 2000 when the high river flow was only half of normal (Powell & Wilson-Finelli 2003). Bottles were incubated in a clear incubator on deck with continuous surface water flowing through for 24 hours before they were sampled again for Chl *a* and FRRF. Samples taken at 24 hours will be referred to as control, +N, +P, and +NP, respectively. The average photoperiod during the cruise was

13:11 h light:dark with a mean photosynthetically active radiation (PAR) of 824 μmol quanta m^{-2} s^{-1}, measured by an on deck PAR meter. Samples in the incubator received approximately 55±12% (354-552 μmol quanta m^{-2} s^{-1}) of ambient light. One-way analysis of variance (ANOVA) was used to assess statistical relationships between the different treatments. Post hoc comparisons were performed using the Tukey test. Statistical analyses were performed using JMP 5.1 (SAS Institute, Inc.).

2.3 Results

Fourteen nutrient addition incubations were performed in the MRP area near Southwest Pass over a 5 day period. This area is known to be P limited in July based on elevated DIN:P_i ratios and high AP activities found in previous studies (Ammerman & Glover 2000, Sylvan et al. 2006). Station locations are shown in Fig. 2.1A and seawater characteristics from each station are given in Table 2.1. The area in July 2002 was characterized by low P_i (mean = 0.18 μmol L^{-1}), high DIN:P_i ratios (mean = 53) and very high AP activities (mean = 347 nmol L^{-1} h^{-1}).

The +P incubations yielded higher Chl *a* concentrations than the +N incubations in 11 of the 14 nutrient addition experiments (Fig. 2.1B). The +NP incubations had higher Chl *a* biomass after 24 h than the +N incubation for all 14 nutrient addition experiments and higher biomass than the +P incubation for 13 of 14 experiments. To summarize all 14 incubations, we calculated mean parameters for each treatment using the values from all the incubations (Fig. 2.2). The average Chl *a* concentration in the initial samples was 14.6 μg L^{-1}. This was greater than the mean concentration of Chl *a* in both the control (11.1 μg L^{-1}) and +N (11.3 μg L^{-1}) treatments after 24 h. The mean Chl *a* concentration in the +P treatment was 14.5 μg L^{-1} at 24 h, similar to that in the initial sample. Only the

Table 2.1. Station data for incubation experiments. All water was collected at 1 m with a CTD. DIN and P_i are units of μmol L^{-1}, DIN:P_i, F_v/F_m and p are unitless, Chl a is in μg L^{-1}, AP activity is in nmol L^{-1} h^{-1}, σ_{PSII} is in Å^2 quanta^{-1} and τ_{Qa} is in μs. N.D. = no data

Station	Date and time (July 2002)	Latitude (°N)	Longitude (°W)	Sal.	Temp. (°C)	DIN	P_i	DIN: P_i	Chl a	AP Act.	Initial F_v/F_m	Initial σ_{PSII}	Initial p	Initial τ_{Qa}
1	04, 22:53	28.804	89.523	12.9	31.3	14.30	0.21	68	19.0	240	0.426	245	0.287	460
2	05, 10:58	28.832	89.508	14.7	30.5	5.12	0.21	24	13.9	315	0.351	255	0.281	558
3	05, 12:27	28.787	89.639	16.5	30.9	8.33	0.21	40	5.3	81	0.437	258	0.274	425
4	05, 14:12	28.814	89.755	17.5	31.1	N.D.	N.D.	N.D.	8.9	151	0.407	254	0.299	486
5	05, 15:43	28.883	89.811	16.9	31.1	7.48	0.20	37	9.2	143	0.518	178	0.438	403
6	05, 18:11	29.057	89.740	15.7	30.7	7.75	0.14	55	7.0	218	0.355	270	0.327	430
7	06, 11:37	28.773	89.315	24.4	28.8	10.88	0.21	52	14.3	65	0.372	238	0.271	407
8	06, 14:53	28.698	89.096	29.3	30.2	3.27	0.06	55	6.6	2190	0.404	244	0.356	446
9	07, 22:57	28.772	89.571	16.2	30.2	23.71	0.21	113	13.4	193	0.413	256	0.315	404
10	07, 14:00	28.961	89.079	21.2	30.9	9.56	0.23	42	22.0	418	0.507	207	0.407	386
11	07, 15:34	28.939	88.974	30.5	30.1	3.79	0.10	38	3.9	74	0.398	252	0.223	501
12	07, 19:49	28.831	89.268	27.8	29.9	6.38	0.15	43	13.1	140	0.311	270	0.386	311
13	07, 20:39	28.838	89.396	22.3	30.2	10.48	0.18	58	27.2	340	0.457	238	0.332	364
14	07, 21:42	28.848	89.476	19.1	30.3	14.87	0.22	68	40.4	291	0.504	219	0.303	374
Mean				**20.4**	**30.4**	**9.7**	**0.18**	**53**	**14.6**	**347**	**0.42**	**242**	**0.32**	**425**
Median				*18.3*	*30.4*	*8.33*	*0.21*	*52*	*13.3*	*206*	*0.41*	*249*	*0.31*	*416*

+NP treatment yielded an increase of Chl *a* over the initial sample (62%; 23.6 µg L^{-1}) after 24 h. The control and +N treatments were significantly lower than all the others (*p*=0.033, one-way ANOVA).

FRRF parameters give a snapshot of the overall status of the phytoplankton community, enhancing our understanding of the effects of the added nutrients. For this reason, the F_v/F_m ratio is commonly used to rapidly assess the status of phytoplankton cultures (Kolber et al. 1998) and field populations (Suggett et al. 2001). The mean F_v/F_m value in the initial samples was 0.42 ± 0.004 (standard error, Fig. 2.2). In both the control and +N treatment, mean F_v/F_m decreased after 24 hours to 0.32 ± 0.004 and 0.32 ± 0.006, respectively. F_v/F_m in the +P treatment was 0.41 ± 0.004 after 24 hours and was 0.41 ± 0.003 in the +NP treatment. Both were higher than the corresponding control and close to the initial ratio. The control and +N treatments were again significantly lower from all the others (Fig. 2.2, *p*<0.001).

The mean σ_{PSII} in all the initial samples was 238 ± 3.19 Å^2 quanta^{-1}. The control treatment yielded a mean σ_{PSII} of 228 ± 7 Å^2 quanta^{-1} after 24 hours and the +N treatment had a mean σ_{PSII} of 237 ± 6 Å^2 quanta^{-1} (Fig. 2.2). Mean σ_{PSII} was significantly lower in the +P and +NP treatments after 24 hours, 207 ± 3 and 194 ± 3 Å^2 quanta^{-1} respectively, than the initial and +N treatments (*p*<0.001). The control treatment was significantly higher than the +NP treatment, but was not significantly different from either the initial and +N nor the +P.

Mean τ_{Qa} was 421 ± 17 µs in the initial samples and increased dramatically for both the control (535 ± 43 µs) and +N (519 ± 42 µs) incubations after 24 hours (Fig. 2.2), while the +P treatment showed a very slight increase over the initial sample to 425 ± 15

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Fig. 2.2. Mean responses in incubations of Chl *a*, F_v/F_m, σ_{PSII}, τ_{QA}, and *p* after 24 h (± standard error) for all incubations. Sampling and notation are the same as in Fig. 2.1. For FRRF parameters, data from the +P addition of incubation 3 and all of incubation 13 were lost and so were not included.

μs, the +NP treatment decreased from the initial sample to 412 ± 12 μs. None of the treatments were statistically significant from each other ($p > 0.05$).

Mean initial p was 0.32 ± 0.02 (unitless) and decreased to 0.24 ± 0.02 and 0.22 ± 0.01 in the control and +N treatments, respectively, after 24 hours (Fig. 2.2). However, p remained the same in the +P treatment (0.32 ± 0.01) after 24 hours and increased in the +NP treatment to 0.36 ± 0.01. The initial sample and +P and +NP treatments were found to be significantly higher than the control and +N treatments ($p < 0.001$).

2.4 Discussion

In this work, multiple lines of evidence demonstrated P limitation of the phytoplankton community in the MRP along the Louisiana continental slope during early summer 2002. In combination, the FRRF parameters F_v/F_m, σ_{PSII}, τ_{Qa}, and p supported findings based on Chl a, AP activities and nutrient concentrations and ratios, thereby providing a mechanistic understanding of how the community responded to changes in nutrient availability. This study confirms and extends temporally the seasonal pattern of P-limitation on the Louisiana shelf, recently shown by Sylvan et al. (2006).

On the Louisiana continental shelf, DIN concentrations and primary productivity rates are typically highest in the late spring and early summer, shortly after the annual peak discharge of the Mississippi River (Lohrenz et al. 1997, Lohrenz et al. 1999). The high levels of DIN carried in the river stimulate phytoplankton growth and result in high DIN:P_i ratios and high AP activities. Chl a concentrations >30 μg L^{-1} were observed in separate cruises during July-August 1990 (Lohrenz et al. 1999). In July 2001, mean Chl a concentration for the entire Louisiana shelf was >17.0 μg L^{-1}, with concentrations >24 μg L^{-1} closer to the MRP (Sylvan et al. 2006). Although we focused on a smaller area in

the current study, mean Chl *a* concentration was still high, 14.6 µg L^{-1} (Table 2.1). AP activities during this study were very high (Table 1) and in combination with those seen in this area in the past (Ammerman & Glover 2000, Sylvan et al. 2006) are among the highest reported for marine and estuarine ecosystems (Hoppe 2003).

Nutrient addition experiments were conducted in the high Chl *a*, mid-salinity area adjacent to the Mississippi river mouth (Table 2.1) where phytoplankton production is typically highest (Lohrenz et al. 1997). Chl *a* biomass in the control bottles decreased, on average, after 24 h of incubation. While the mean biomass in the control and +N additions decreased by 22 and 24%, that of the +P addition maintained the original biomass (Fig. 2.2). Biomass in the +NP addition increased by 62%. This type of result for nutrient addition bioassays is not uncommon, especially in short incubations (<48 h) and appears to reflect the physiological lag between nutrient uptake and conversion to biomass (Downing et al. 1999). Grazers were not examined during this study, so it is possible that they were responsible for the decrease in Chl *a* in the control and +N incubations. However given the short duration of the incubations, this was unlikely. The decrease in Chl *a* biomass was likely a result of isolation of an already P-depleted water mass with no new sources of P available, making new growth difficult. The higher Chl *a* biomass in the +NP treatment than the +P treatment likely resulted from additional growth fueled by the added N above what could be achieved with the added P alone. Cells in the +P addition could only use the excess P in combination with the N already present in the initial sample, resulting in N limitation following draw down of the initial N, while additional growth was possible in the +NP treatment. Additionally, it may take more than 24 h to see an increase in Chl *a* concentrations above the initial in the +P

treatments. However, the response in the +NP treatments indicates that the phytoplankton were indeed nutrient limited because if their nutrient uptake systems were saturated, Chl *a* in the +NP treatment would not have increased above the initial. Therefore, the higher Chl *a* biomass in the P additions (compared with the control) is important evidence for P-limitation in the region.

Further supporting evidence was revealed by careful examination of the physiological parameters measured using FRRF. Mean F_v/F_m values for the +P and +NP treatments were nearly equal to the initial, untreated sample while the treatments lacking added P suffered a decline in F_v/F_m. These results indicated that the P additions either maintained the phytoplankton at their pre-treatment physiological status, or that the added P enhanced photosynthetic efficiency of cells after an initial decline, thereby allowing them to maintain a relatively higher F_v/F_m. The lack of increase of F_v/F_m over the initial in the +P and +NP treatments indicates that perhaps there was some additional stressor in the incubations preventing these treatments from approaching the theoretical maximum F_v/F_m. Perhaps, as seems to be the case with the Chl *a* concentration in the +P treatments, 24 h was not enough time for slowly resilient assemblages to attain their maximum F_v/F_m. Alternatively, a lack of additional P may have caused the already P-limited cells to crash in the control and +N treatments while the additional P in the +P and +NP treatments allowed the cells in these treatments to maintain their F_v/F_m. It may have required more P to see a further increase in F_v/F_m over the initial. While photodamage was not evident in the initial samples, it is possible that cells experienced a low level of photodamage in our incubators during the experiment. However, in combination with the increase in Chl *a*, especially that of +NP over the initial, our results

indicate that P-limitation was the ultimate cause for the changes in Chl a biomass and F_v/F_m. Cells in the +P and +NP treatments experienced a higher growth rate due to the added P, resulting in higher overall Chl a and elevated F_v/F_m values compared to the control and +N treatments.

σ_{PSII} decreased below the control in the +P and +NP treatments and was lowest in the +NP treatment. Both the +P and +NP treatments were significantly lower than the initial. Previous work has shown an increase in σ_{PSII} under N-limitation (Kolber et al. 1988), but this is the first evidence of a decrease under release from nutrient limitation, illustrating that σ_{PSII} is responsive to nutrient conditions. The decrease in σ_{PSII} in the +P and +NP additions was correlated with an increase in F_v/F_m in those treatments.

The time for the reoxidation of Q_a is given by τ_{Qa}. Q_a reoxidation occurred slightly faster in treatments with P added than those without, supporting the improvement in the physiological status of the cells, consistent with an increased F_v/F_m in the +P treatments (Fig. 2.2). Due to high background noise inherent to the measurement of τ_{Qa} (Gorbunov, M., pers comm), it was not possible to obtain statistically significant results, but mean τ_{Qa} was shorter in treatments with added P than those without.

Lastly, an increase in p indicates a higher probability that energy will be passed between the reaction centers in PSII. Decreased p is associated with N-limitation in laboratory grown cultures (Kolber et al. 1988), but has not been examined in the field. Mean p was greatest in the +NP treatment and greater in the +P treatment (which was equal to the initial sample) than in the control and +N treatment (Fig. 2.2). Overall, the FRRF results for these bioassays confirmed the nutrient data and enzyme assays from the initial samples and the Chl a responses to added nutrients in our bioassays, indicating that

phytoplankton were P-stressed near the MRP in July 2002. The increase in F_v/F_m and p and coincident decrease in σ_{PSII} and τ_{Qa} provide a signature for release from P-limitation by the phytoplankton in this area, supporting the value of the FRRF and combined used of derived parameters to assess nutrient limitation.

Previously, F_v/F_m has been measured in N- and Fe-stressed or limited laboratory and field phytoplankton, but the only field study to measure F_v/F_m in conjunction with observations of P-limitation used pulse amplitude modulated (PAM) fluorometry in an estuary in the Netherlands (Kromkamp & Peene 1999), where decreased F_v/F_m correlated with low DIN and P_i. There are no published field studies of P-limitation using FRRF. However, a few laboratory studies of P-limitation using fluorometrically derived parameters also exist. Cultured *Microcystis aeruginosa* displayed an increase in F_v/F_m when PO_4^{3-} was added to P-limited cells (Wood & Oliver 1995). *Dunaliella tertiolecta* grown in a chemostat exhibited lower F_v/F_m when grown under P-starved conditions than when P-replete (Graziano et al. 1996), and lab grown *Sphaerocystis*, *Scenedesmus*, *Nitzchia*, and *Phormidium* exhibited an increase in F_v/F_m within 24 hours of P addition to P-limited cells (Beardall et al. 2001a). P-limitation caused a decrease in F_v/F_m and $\Delta F'/F_m'$ compared to P-replete cells, and spiking the P-limited cells with P caused a recovery of $\Delta F'/F_m'$ to the same level as P–replete cells in *Alexandrium minimum* (Lippemeier et al. 2003). While these studies used either a spectrofluorometer (Wood and Oliver 1995) or a PAM fluorometer (Graziano et al. 1996, Beardall et al. 2001a, Lippemeier et al. 2003) with laboratory grown phytoplankton, their results supported our finding that F_v/F_m increases with the relief of P-limitation and that F_v/F_m is decreased in nutrient stressed phytoplankton.

One potential drawback to the FRRF is that it cannot be effectively used to study species whose effective absorption bands of the light harvesting pigments in PSII do not overlap with those of the FRR fluorometer, such as the filamentous cyanobacteria *Nodularia spumigena* and *Aphanizomenon sp.* (Raateoja et al. 2004), which contain phycoerythrocyanin instead of phycoerythrin. While we did not perform species level identifications of the phytoplankton taxa in this study, past work in this area indicates that filamentous cyanobacteria are not present at high concentrations. In April and October of 2000, the single celled *Synechococcus* dominated coastal waters while *Prochlorococcus* was abundant at high salinity stations (Liu et al. 2004) along the Louisiana coast. These same distributions were seen in May 2000 (Jochem 2003).

Some lab studies suggest that F_v/F_m may not be an accurate method for assessing nutrient limitation in the field. (Parkhill et al. 2001, Kruskopf & Flynn 2006). (Yentsch et al. 2004). These authors also found F_v/F_m to vary directly with nutrient input at multiple field sites and indicated that the ratio can be used to measure potential nutrient stress, as it has in many other studies. It is likely that a limited response of F_v/F_m to nutrient changes in lab cultures is a result of the variable stress tolerances of different species to ranges of nutrient conditions. Future FRRF and other fluorometric studies should continue to assess and then validate the usefulness of this method for evaluating nutrient limitation.

This work used a combination of traditional measurements and FRRF to demonstrate P-limitation in coastal Louisiana, influenced by the Mississippi River runoff. The high concentrations of DIN and high DIN:P_i ratios measured during this study indicate that the P-limitation was driven by surplus DIN in addition to low P. Our

findings are consistent with past studies that also measured P-limitation of phytoplankton on the Louisiana continental shelf using direct (Smith & Hitchcock 1994, Sylvan et al. 2006) and indirect methods (Lohrenz et al. 1999). Here we have provided the first field measurements using FRRF to study P-limitation in marine phytoplankton. In a set of nutrient addition bioassays near the MRP, low P_i concentrations and high $DIN:P_i$ ratios and AP activities in the initial samples coupled with Chl *a* response over a 24 hour period in nutrient addition bioassays were indicative of P-limitation. FRRF parameters measured in these bioassays showed statistically significant responses that corresponded to the traditional data and outlined a fluorescence signature for release from P-limitation consisting of increased F_v/F_m and *p* coupled with decreased σ_{PSII} and τ_{Qa}. This study suggests that the use of FRRF coupled with short-term incubations can provide more rapid results than traditional bioassays of nutrient limitation requiring multiple days, and more detailed information about the physiological state of the community in the region being assessed, all without a significant increase in effort.

3.0 Fast repetition rate fluorometry as a method for mapping phytoplankton community status and phosphorus limitation on the Louisiana continental shelf

Abstract

Surface (0.5-1 m) mapping was used to assess nutrient limitation on the Louisiana continental shelf and Mississippi River plume (MRP) during 29 June – 08 July, 2002 in an effort to better understand phytoplankton productivity in this region as well as better inform effective nutrient management strategies. Surface nutrient concentrations (PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+), alkaline phosphatase (AP) activity, chlorophyll *a* biomass, and four Fast Repetition Rate fluorescence (FRRF) parameters: the maximum quantum yield of photochemistry (F_v/F_m), the functional absorption cross section for PSII (σ_{PSII}), the time for photosynthetic electron transport on the acceptor side of PSII (τ_{Qa}), and the connectivity factor (*p*), were measured during continuous underway mapping. Results from traditional methods to assess phytoplankton nutrient stress indicated widespread phosphorus limitation from the Mississippi River plume to the Atchafalaya River, manifested as high inorganic N:P ratios and AP activities. The FRRF data were more nuanced and revealed complex patterns of phytoplankton adaptation to rapidly changing conditions in local surface water as a function of the greater spatial resolution achievable with this technique. Differing response times between traditional measurements and FRRF parameters were also cited as possible causes for the less obvious results from the FRRF mapping. Still, our results indicate that FRRF can be used to address questions of phosphorus limitation in marine ecosystems, even a complex system like the MRP.

3.1 Introduction

Fast repetition rate fluorometry (FRRF) allows quick, non-invasive assessment of phytoplankton *in vivo* fluorescence signatures (Kolber et al. 1998). It has been used extensively in laboratory and field studies to investigate the immediate state of photosynthetic competency in phytoplankton populations in nutrient replete phytoplankton as well as those whose productivity was limited by Fe, N, and P (Behrenfeld & Kolber 1999, Suggett et al. 2001, Sylvan et al. 2007). FRRF can provide the user with the photosynthetic parameters outlined in Table 1, including F_v/F_m, σ_{PSII}, τ_{Qa} and the connectivity factor, *p* (Kromkamp & Forster 2003). F_v/F_m is an indicator of the photosynthetic efficiency of a cell or population when measured in a dark-adapted state. It can be as high as 0.65 in healthy cells (Kolber et al. 1998). σ_{PSII} changes in response to cellular pigment concentrations and the efficiency of energy transfer from pigments to PSII reaction centers, thus making it subject to both nutrient and light availability. σ_{PSII} is typically lower in nutrient replete cells relative to nutrient deprived cells (Kolber et al. 1988). τ_{Qa} reflects the efficiency of the photosynthetic apparatus and is the minimum turnover time for electron transport (Kolber et al. 1988). The probability of energy transfer between PSII reaction centers is a function of the connectivity (*p*) between reaction centers. Higher *p* values indicate higher probabilities of electron transfer and therefore are indicative of nutrient replete conditions and a more efficient photosynthetic apparatus (Kolber et al. 1998). Collectively, these FRRF parameters can be used to assess the physiological response of phytoplankton cells and/or communities to nutrient stress, such as P-limitation. Sylvan et al. (2007) recently presented the first study to use FRRF to demonstrate P-limitation in a marine field setting.

Table 3.1. Notation used throughout text. Adapted from (Gorbunov et al. 2000).

Symbol	Parameter	Typical Units
FRRF	Fast Repetition Rate Fluorescence (or Fluorometry)	---
PSII	Photosystem II	---
ST	Single Turnover	---
F_o	Minimum yield of chl a fluorescence measured after dark adaptation	Relative fluorescence units
$F_{m(ST)}$	Maximum yield of chl a fluorescence measured after dark adaptation using ST flash	Relative fluorescence units
F_v	Variable fluorescence ($=F_m - F_o$)	---
$F_v/F_{m(ST)}$	Maximum quantum yield of photochemistry in PSII measured after dark adaptation using ST flash	Dimensionless
σ_{PSII}	Functional cross section of PSII	$\text{Å}^2 \text{ quanta}^{-1}$
p	Connectivity factor, the exciton energy transfer between individual photosynthetic units	Dimensionless
τ_{Qa}	Time constant for photosynthetic electron transport on the acceptor side of PSII (Q_a reoxidation)	μsec

The ability of some FRRF instruments to operate in continuous mapping mode is an additional advantage. It allows an area to be extensively sampled on fine spatial scales so one can assess the differing degrees of nutrient stress that are present, and to a lesser extent, the type of nutrient stress. Operation of FRRF in mapping mode in conjunction with continuous mapping of nutrients provides an additional tool for diagnosing the health of the phytoplankton community and allows far greater spatial coverage than nutrient addition bioassays alone. Because nutrient addition bioassays can only be done on discrete samples, they are not conducive to the intensive sampling needed to map nutrient limitation over large areas. The time and effort required for their execution does not permit many nutrient addition bioassays per cruise.

The Mississippi River plume (MRP), here defined as the area near Southwest Pass and directly to the west of it, and the Louisiana continental shelf (Fig. 1) together

comprise an excellent system for studying nutrient limitation. Factors limiting phytoplankton growth are dynamic and affected by the annual river flow pattern. While N is typically the limiting nutrient during late summer through early spring, there is a potential for P-limitation throughout late spring into early summer following the annual peak in river discharge (Lohrenz et al. 1999). The amount of N in the Mississippi River transported to the coastal ecosystem has increased with increasing fertilizer application since the 1950's (Rabalais et al. 2002c). This nitrogen is a cause of the eutrophication at the river delta that is the primary cause of the large hypoxic zone seen each summer off the Louisiana coast (Turner & Rabalais 1994). Past investigations in this area have shown a potential for P-limitation of phytoplankton during the late spring and early summer through both indirect methods, including nutrient ratios and enzyme assays (Lohrenz et al. 1999, Ammerman & Glover 2000, Pakulski et al. 2000) and direct methods such as nutrient addition bioassays (Smith & Hitchcock 1994, Sylvan et al. 2006).

We used FRRF in mapping mode to address the issue of nutrient limitation on the Louisiana shelf and assess the feasibility of mapping nutrient limitation in an estuarine setting. During a cruise from 29 June – 08 July, 2002, we mapped nutrient concentrations and ratios (DIN:P$_i$), chl *a* biomass, AP activity and FRRF parameters in surface water samples on the Louisiana continental shelf and MRP to examine nutrient limitation in the region. Our findings support the hypothesis that P was the limiting nutrient during early July in this ecosystem.

3.2 Materials and methods

3.2.1 Sample collection – Seawater samples were collected from the Louisiana continental shelf between the Atchafalaya River and the MRP between 28.585- 29.530º N latitude and 88.655- 92.535º W longitude aboard the R/V *Pelican*. The two cruise legs were 29 June- 03 July and 05-08 July, 2002. Surface water (0.5-1 m) was continuously pumped into the ship's wet lab via a hose attached to an arm off the side of the boat. Sensors on the arm and inline with the hose measured multiple hydrographic parameters including salinity, temperature and depth, allowing for real time data analysis and continuous sampling. During the first leg, discrete samples were collected every 30 minutes from the outlet in the wet lab into polyethylene bottles that had first been rinsed three times with sample water. These samples were used immediately for the determination of nutrient and chlorophyll (chl) *a* concentrations and AP assays. During the second leg, the intake was used to supply sample water to the FRRF, only. Data was plotted on contour maps using the kriging method of Surfer 7 (Golden Software). Kendall's tau was used to assess statistical relationships between measured parameters. Statistical analyses were performed using JMP 5.1 (SAS Institute, Inc.).

3.2.2 Chl a *and nutrient concentrations* – Seawater was filtered onto GF/F filters and frozen immediately in liquid nitrogen. After returning to the lab (≤10 days later), filters were thawed on ice and placed in DMSO/90% acetone (40:60) in the dark at room temperature. Chl *a* fluorescence was measured using a Turner 10AU fluorometer (Lohrenz et al. 1990). Reported chl *a* values are corrected for phaeopigments (chl *a* only).

For the determination of nutrient concentrations, seawater was filtered through 0.2 μm polycarbonate filters or 0.45 μm cellulose ester filters (Millipore) to remove particulates. The larger pore size filters were used after using all of the smaller. The filtrate was placed in acid washed 250 mL polyethylene Nalgene bottles rinsed twice with filtrate from the sample, and then frozen until analysis on a Lachat QuikChem AE autoanalyzer for inorganic phosphate (P_i) and DIN (DIN= NO_3^-, NO_2^-, NH_4^+).

3.2.3 AP assays – AP activity was measured according to Sylvan et al (2007) using a Tecan Genios fluorescent microplate reader, the substrate 6,8-difluoro-4-methylumbelliferyl phosphate (DifMUP), and its respective standard, 6,8-difluoro-7-hydroxy-4-methylcoumarin (DifMU), both from Molecular Probes. DifMUP was used instead of the more traditional substrate, 4-methumbelliferyl phosphate (MUF-P) because it requires no pH adjustment to maximize fluorescence and therefore facilitates continuous assays (Gee et al. 1999).

3.2.4 FRRF data acquisition – A Chelsea Instruments first generation commercial FAST[tracka] FRRF was used in bench top mode with only the dark chamber active as in Sylvan et al (2007). The same excitation protocol was maintained throughout the cruise rather than varying it for optimization with different samples because the frequent sampling schedule (every 30 mins) did not allow enough time to optimize every sample. Additionally, environmental conditions ranging from near freshwater to full salinity water could be sampled within a few hours during our cruise, making it even harder to optimize samples with different protocols. During the day, and 1 hr before dawn and

after dusk, samples were low light acclimated in opaque polyethylene bottles and kept in a cooler with surface water for 30 mins prior to their assessment with the FRRF. This time allowed for all PSII reaction centers to relax and measure the maximum potential quantum yield. Depressed quantum yields were therefore correlated to nutrient limitation rather than to photo-inhibition. After sundown, the FRRF was operated in continuous mode because cells were in the dark and did not require low light acclimation prior to sampling. All data from leg two was collected at night, and therefore was used in continuous mode.

Data was acquired and processed with a program coded in TurboPascal, as described in Kolber et al. (1998). Note that this program is not related to the FRS.EXE program distributed with the FAST[tracka] machine. We present only data determined from single turnover analysis. τ_{Qa} was calculated from a monophasic function. Comparisons with filtered seawater and ultra pure deionized water yielded similar results, indicating no significant background fluorescence from our blanks.

3.3 Results

Salinity was lower near the Louisiana coast and increased further offshore in deeper water (Fig. 3.1a). DIN was generally >10 μmol l^{-1} near the coast east of and including Terrebonne Bay, with peak concentrations found at Southwest Pass and <5 μmol l^{-1} offshore (Fig. 3.1a). West of Terrebonne Bay, DIN was >5 μmol L^{-1} at stations near shore, but <5 μmol L^{-1} for most of that transect. P$_i$ was more variable but remained <0.5 μmol l^{-1} at nearly all the stations, with the exception of those near Southwest Pass and some west of Atchafalaya Bay (Fig. 3.1b), likely a result of westward currents
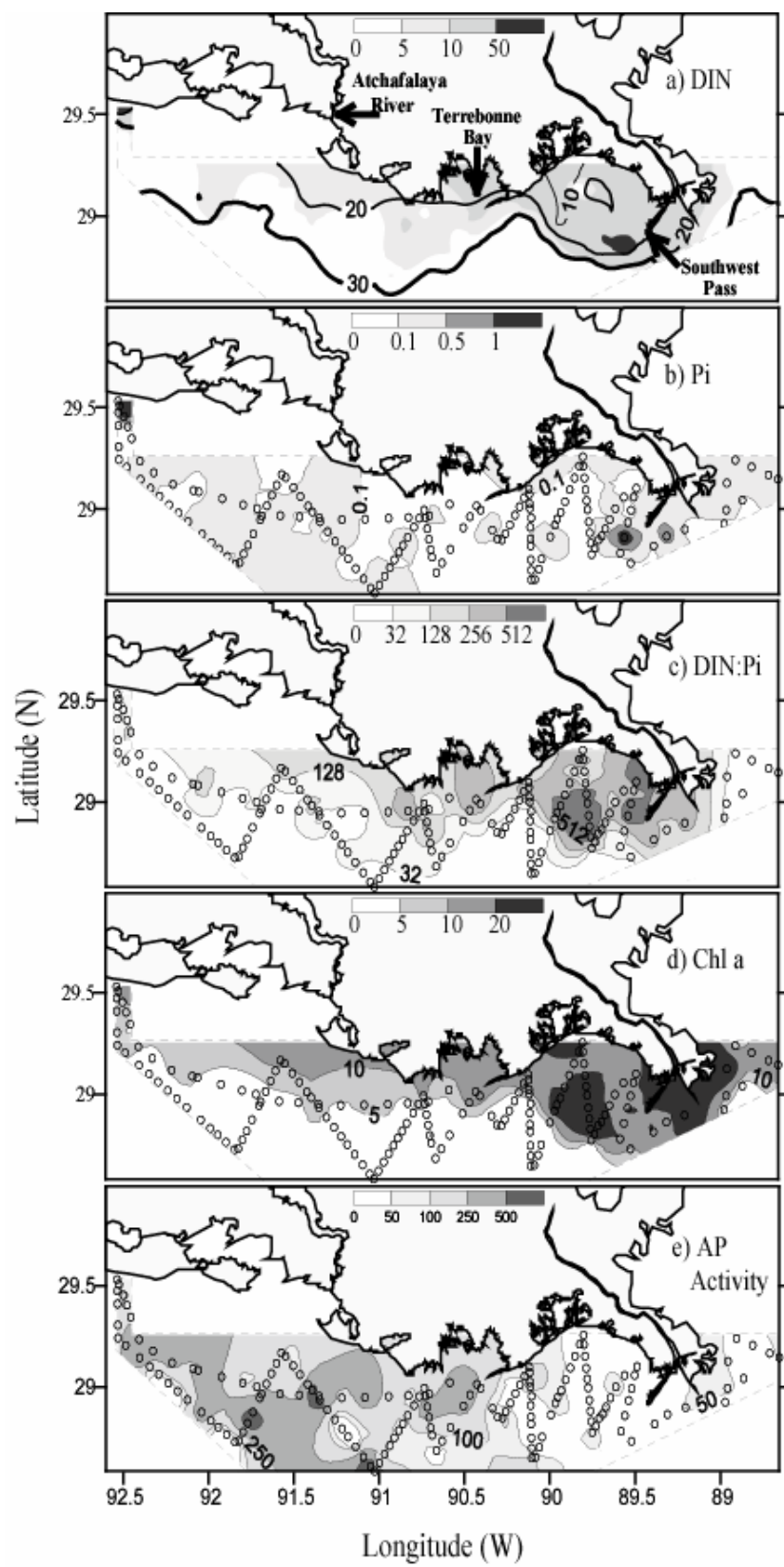
Figure 3.1. 29 June – 3 July, 2002 mapping data. (a) DIN in μmol l^{-1}, (b) P_i in μmol l^{-1}, (c) $DIN:P_i$, (d) chl *a* in μg l^{-1}, and (e) AP activity in nmol l^{-1} h^{-1}. Dots represent sampling stations and dotted lines indicate the boundary of the contoured area. Note that contours near the Atchafalaya River are interpolated. Samples could not be collected in there because the water was too shallow for the *R/V Pelican*. The unit for the x-axis is degrees of longitude (W) and that for the y-axis is degrees of latitude (N). Contours of salinity overlie DIN in (a). Salinity contour intervals are 0, 10, 20 and 30. Contour lines are thicker with increasing salinity. DIN contours are colors only, no lines.

carrying water from the Atchafalaya River offshore. The stations south of the Atchafalaya River had P_i generally >0.10 µmol l^{-1} while P_i was <0.10 µmol l^{-1} at many stations between Atchafalaya Bay and Southwest Pass. The combination of high DIN and low P_i resulted in the highest DIN:P_i ratios near and to the west of Southwest Pass, where many stations had ratios >256, 16 times the Redfield ratio (Fig. 3.1c). DIN:P_i was >128 along the Louisiana coastline. This ratio declined offshore. Chl a distributions closely mirrored that of DIN (Fig. 3.1d). The highest levels of Chl a (>20 µg l^{-1} at some stations) were seen near Southwest Pass and to the northwest of it. Further to the west and offshore, Chl a was frequently <5 µg l^{-1}. AP activity was highest south and southwest of the Atchafalaya River (Fig. 3.1e). Peak activities were >500 nmol l^{-1} h^{-1} and most stations west of 90.5º W exhibited activities >100 nmol l^{-1} h^{-1}.

To explore the feasibility of making predictions about phytoplankton community health over large, dynamic areas, we mapped the FRRF parameters F_v/F_m, σ_{PSII}, τ_{Qa} and p in the same locations as the physio-chemical parameters (Fig 3.2). The data was broken into two regions for presentation due to a gap of data between these two areas. This avoided artifacts due to contouring over regions with no data points. Mapping of F_v/F_m showed higher values (>0.40) just west the Mississippi River delta and much lower values (about 0.20-0.40) south of the Atchafalaya River (Fig. 3.2a). High values of F_v/F_m, up to 0.65 for nutrient-replete phytoplankton, (Falkowski & Kolber 1995) indicate that the photosynthetic apparatus is operating at its highest efficiency while lower values indicate physiological stress on the cell, e.g. nutrient limitation. Mapped F_v/F_m closely matched that of mapped chl a, DIN and P_i. The higher F_v/F_m values near the river mouth coincided with the highest DIN and P_i concentrations seen during mapping as well as the
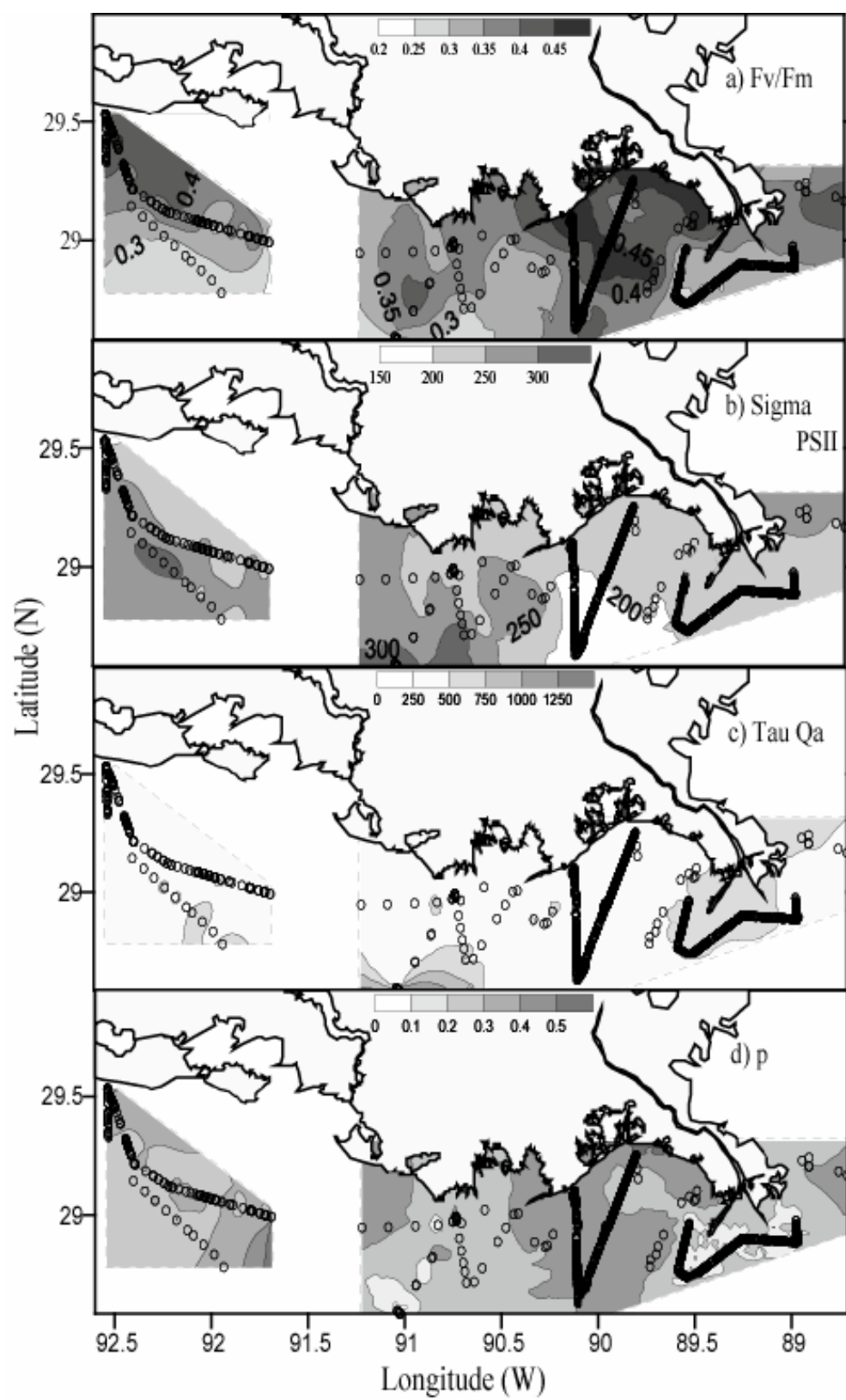
Figure 3.2. 29 June – 3 July, 2002 FRR Fluorometry mapping data. (a) F_v/F_m (no units), (b) σ_{PSII} in $Å^2$, (c) τ_{Qa} in μsec, and (d) p (no units). The unit for the x-axis is degrees of longitude (W) and that for the y-axis is degrees of latitude (N). Dotted lines outline areas with data gaps. Two separate contour boxes were made and combined into one map to avoid inaccurate interpolation of data where few stations are present.

highest chl *a* biomass. The lower F_v/F_m values, found in higher salinity waters further offshore, corresponded with elevated AP activity, low chl *a* biomass and low DIN and P_i.

Mapped σ_{PSII} showed inverse patterns to F_v/F_m (Fig. 3.2b). Near Southwest Pass, values were 200-250 $\mathring{A}^2$ quanta^{-1} while the values in higher salinity waters were >350 $\mathring{A}^2$ quanta^{-1}. West of the Atchafalaya River, σ_{PSII} was lowest near shore and increased in deeper waters.

τ_{Qa} was minimal between Southwest Pass and the Atchafalaya River (Fig. 3.2c). This is the same region where σ_{PSII} was highest. Values closest to Southwest Pass were between 500 and 750 µsec while slightly to the west of the Mississippi River plume, τ_{Qa} was most frequently between 250 and 500 µsec. τ_{Qa} values in the mapped area to the west of the Atchafalya River ranged from 250-500 µsec.

p showed a similar distribution to F_v/F_m. To the west of Southwest Pass, values were higher (0.4-0.5) than directly around Southwest Pass (Fig. 3.2d). West of the Atchafalaya River, with the exception of one sample at the end of that transect, *p* was higher closer to shore and decreased with increasing salinity.

During Leg 2 of this cruise, we mapped FRRF parameters in continuous mode at night near the MRP to assess differences in FRRF mapping of large, heterogeneous systems (the entire shelf, Leg 1) versus a smaller area (the MRP plume). Visually, contour patterns of F_v/F_m were more similar to *p* than during Leg 1 (Fig. 3.3). Both were high surrounding the river delta and to the northwest of the delta, where local currents carry water issuing from Southwest Pass this time of year. This same pattern of higher F_v/F_m and *p* to the northwest of SW Pass was seen during Leg 1 as well. F_v/F_m values
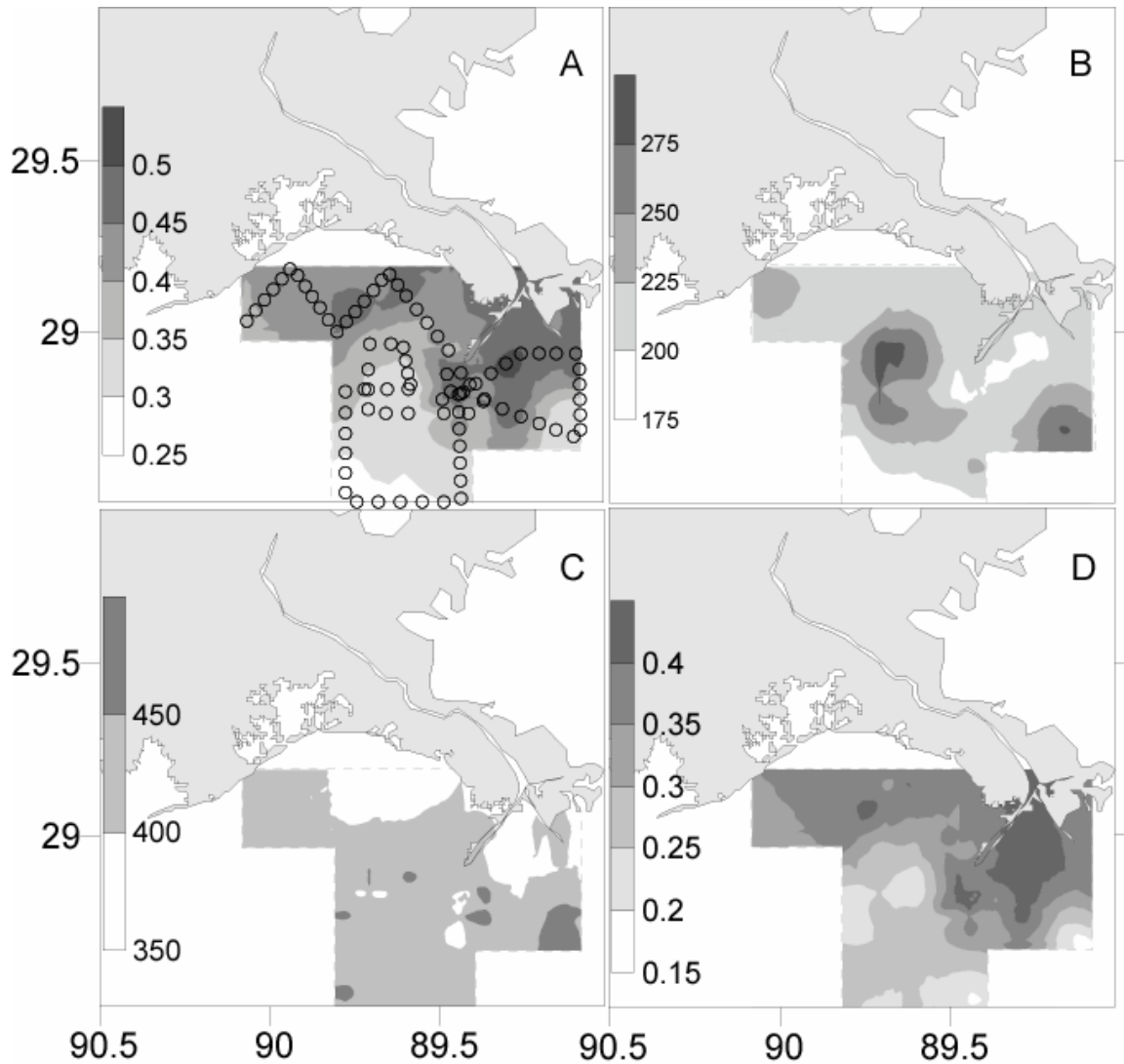
Fig. 3.3. 05 − 08 July, 2002 FRR Fluorometry mapping data. (a) F_v/F_m (no units), (b) σ_{PSII} in $\mathring{A}^2$, (c) τ_{Qa} in µsec, and (d) p (no units). The unit for the x-axis is degrees of longitude (W) and that for the y-axis is degrees of latitude (N). Dotted lines outline contoured areas. Circles in (a) indicate cruise track and sampling stations. Every 50th station was included on the plot. Cruise track was the same for all four parameters.

were slightly higher during Leg 2 while *p* was higher at SW Pass during Leg 2 but similar to the northwest on both legs.

The contour patterns F_v/F_m and *p* were more obviously inverse those of σ_{PSII} during Leg 2 than Leg 1. σ_{PSII} showed little variation in the MRP during Leg 1 but was more clearly lower at SW Pass and higher to the east and west of that during Leg 2.

Like $\sigma_{PSII,}$ contours of τ_{Qa} were inverse those of F_v/F_m and *p*. τ_{Qa} was 350-400 μsec in the area to the northeast of SW Pass, where F_v/F_m and *p* were highest. It was highest in the southeast corner of the mapped region, >500 μsec, where F_v/F_m and *p* were lowest.

Kendall's Coefficient of Rank Correlation (τ) was determined for all pairs of parameters measured (Table 3.2). As expected in an estuarine environment, DIN was negatively correlated to salinity. The correlation between DIN and $DIN:P_i$ was higher than between P_i and $DIN:P_i$, indicating that DIN concentrations were the primary driver of the high $DIN:P_i$ ratios seen in Fig. 3.1d. Chl *a* biomass was most closely correlated with salinity (-0.6290) and DIN (0.6018). Despite the similarities in spatial distribution between FRRF and other parameters (nutrients, chlorophyll *a* biomass), only five correlations between FRRF and these other parameters were statistically significant (Table 3.2). F_v/F_m was weakly correlated to salinity (-0.2362), DIN (0.2358) and chl *a* (0.2673). τ_{Qa} and P_i showed a correlation of 0.1927. The best correlation to an FRRF parameter was AP activity with σ_{PSII} (0.4310).

Kandall's tau was separately calculated for the FRRF parameters alone because there are many stations where only FRRF parameters were measured, such as when the instrument was used in continuous mode at night (Table 3.3). Both legs were included in

Table 3.2. Kendall's Tau, all parameters. N=60 stations where all parameters were

measured, ns = not significant.

Variable	By Variable	Kendall Tau b	P-value
DIN	Salinity	-0.6836	<0.0001
P_i	Salinity	-0.2602	0.0070
P_i	DIN	0.2347	0.0151
DIN:P_i	Salinity	-0.4154	<0.0001
DIN:P_i	DIN	0.5684	<0.0001
DIN:P_i	P_i	-0.2819	0.0035
Chl a	Salinity	-0.6290	<0.0001
Chl a	DIN	0.6018	<0.0001
Chl a	P_i	ns	---
Chl a	DIN:P_i	0.5144	<0.0001
AP Activity	Salinity	ns	---
AP Activity	DIN	ns	---
AP Activity	P_i	ns	---
AP Activity	DIN:P_i	ns	---
AP Activity	Chl a	ns	---
F_v/F_m	Salinity	-0.2362	0.0077
F_v/F_m	DIN	0.2358	0.0078
F_v/F_m	P_i	ns	---
F_v/F_m	DIN:P_i	ns	---
F_v/F_m	Chl a	0.2673	<0.0011
F_v/F_m	AP Activity	ns	---
σ_{PSII}	Salinity	ns	---
σ_{PSII}	DIN	ns	---
σ_{PSII}	P_i	ns	---
σ_{PSII}	DIN:P_i	ns	---
σ_{PSII}	Chl a	ns	---
σ_{PSII}	AP Activity	0.4310	<0.0001
p	Salinity	ns	---
p	DIN	ns	---
p	P_i	ns	---
p	DIN:P_i	ns	---
p	Chl a	ns	---
p	AP Activity	ns	---
τ_{Qa}	Salinity	ns	---
τ_{Qa}	DIN	ns	---
τ_{Qa}	P_i	0.1927	0.0461
τ_{Qa}	DIN:P_i	ns	---
τ_{Qa}	Chl a	ns	---
τ_{Qa}	AP Activity	ns	---

the analysis. During Leg 1, σ_{PSII} showed no significant correlation with F_v/F_m or F_o. F_m and F_v and showed very low correlation, although significant, to τ_{Qa} (-0.0638) and p (-0.0634). All the other parameters showed at least weak but significant correlations to each other. The strongest correlations were between F_v/F_m and F_o, F_m and F_v.   During Leg 2, correlations between all FRRF parameters were statistically significant (p<0.001). The relationship between F_v/F_m and both σ_{PSII} and p was stronger while that between F_v/F_m and τ_{Qa} was weaker in this smaller area. All correlations with σ_{PSII} were higher during Leg 2. Those with τ_{Qa} (but not σ_{PSII}) were lower.

3.4 Discussion

In this work, multiple lines of evidence confirmed P limitation of the phytoplankton community on the Louisiana continental slope during early summer. In combination, the FRRF parameters F_v/F_m, σ_{PSII}, τ_{Qa} and p supported findings based on chl *a*, AP activities and nutrient concentrations and ratios, thereby providing a mechanistic understanding of how the phytoplankton community responds to changes in nutrient availability. The study strongly indicates that future mapping work with FRRF in this and other areas will be valuable to assessing the condition of the phytoplankton community (F_v/F_m as an indicator of physiological status, with σ_{PSII}, τ_{Qa} and p) over large spatial scales, and with nutrient analyses, mapping the nutrient limiting primary production in a designated area.

Our mapping data for surface nutrient concentrations and ratios mirrored past findings in the area from July 2001 of high DIN concentrations and elevated DIN:P_i ratios (Sylvan et al. 2006). A combination of results from nutrient concentrations and

Table 3.3. Kendall's Tau, variable fluoresence parameters only. N=895 samples for

entire cruise. ns = not significant.

Variable	By Variable	Kendall Tau, Leg 1	P-value	Kendall Tau, Leg 2	P-value
F_v/F_m	σ_{PSII}	ns	---	-0.3122	<0.0001
F_v/F_m	p	0.4501	<0.0001	0.5104	<0.0001
F_v/F_m	τ_{Qa}	-0.3618	<0.0001	-0.2835	<0.0001
F_v/F_m	F_o	0.6461	<0.0001	0.5542	<0.0001
F_v/F_m	F_m	0.6990	<0.0001	0.6055	<0.0001
F_v/F_m	F_v	0.7637	<0.0001	0.6678	<0.0001
σ_{PSII}	τ_{Qa}	-0.0638	0.0044	0.2264	<0.0001
σ_{PSII}	p	-0.0634	0.0046	-0.2543	<0.0001
σ_{PSII}	F_o	ns	---	-0.1130	<0.0001
σ_{PSII}	F_m	ns	---	-0.1464	<0.0001
σ_{PSII}	F_v	ns	---	-0.1818	<0.0001
τ_{Qa}	p	-0.2184	<0.0001	-0.1308	<0.0001
τ_{Qa}	F_o	-0.3382	<0.0001	-0.2335	<0.0001
τ_{Qa}	F_m	-0.3571	<0.0001	-0.2472	<0.0001
τ_{Qa}	F_v	-0.3688	<0.0001	-0.2627	<0.0001
p	F_o	0.4429	<0.0001	0.4304	<0.0001
p	F_m	0.4353	<0.0001	0.4600	<0.0001
p	F_v	0.4331	<0.0001	0.4905	<0.0001
F_o	F_m	0.9471	<0.0001	0.9487	<0.0001
F_o	F_v	0.8825	<0.0001	0.8863	<0.0001
F_m	F_v	0.9354	<0.0001	0.9376	<0.0001

ratios, enzyme assays, nutrient addition assays, and nutrient uptake assays during four cruises spanning March through September 2001 demonstrated that P is limiting between the MRP and the Atchafalaya River during the spring and early summer. During March – July, elevated DIN:P_i ratios and high AP activities were observed, P_i turnover times were <30 minutes in May and July and <3.5 hours in March, and added PO_4^{3-} yielded the greatest chl *a* response in bioassays. DIN concentrations on the Louisiana shelf are highest in the late spring and early summer, shortly after the annual peak discharge of the Mississippi River (Lohrenz et al. 1999). The high levels of DIN carried in the river stimulate phytoplankton growth and result in high spring DIN:P_i ratios as P_i concentrations remain relatively stable while DIN concentrations fluctuate on a seasonal basis. These trends are reversed in autumn. In September 2001, DIN:P_i ratios were all <5, AP activities were significantly lower, added NO_3^- yielded the greatest chl *a* response, not P_i, and P_i turnover times were >12 hours (Sylvan et al. 2006).

July is typically a period of high phytoplankton biomass in the MRP. Chl *a* concentrations in excess of 30 µg l^{-1} were observed in separate cruises during July-August 1990 (Lohrenz et al. 1999). In July 1993, which was a high flood year for the Mississippi River, chl *a* biomass was >16 µg l^{-1} 10-60 kilometers northwest of Southwest Pass, while chl *a* was <16 µg l^{-1} directly at Southwest Pass and to the east and south of that point (Kim 1996). In July 2001, mean chl *a* biomass for the entire Louisiana shelf was >17.0 µg l^{-1} (Sylvan et al. 2006) while the median biomass was >18.0 µg l^{-1} and values were in excess of 24 µg l^{-1} closer to the MRP and the maximum value was 46.9 µg l^{-1} near Terrebonne Bay (Sylvan et al. 2006). Our results revealed similar patterns; chl *a*

was >10 µg l^{-1} at stations near the MRP and at intermediate salinities and was much lower at salinities >25.

AP activity is absent when phosphate concentrations are replete, is inducible, and follows Michaelis-Menten kinetics (Hoppe 2003). It cleaves inorganic phosphate from organic phosphate esters when environmental inorganic phosphate is low. Due to these traits, AP activity is often used to assess phosphorus stress by aquatic scientists. Mean AP activity during July 2002 was 151±15 nmol l^{-1} h^{-1}. In a review of AP activity in several marine ecosystems, the only systems that exhibited a higher mean AP activity were a river plume and a hypereutrophic fjord, both in the Baltic Sea (Hoppe 2003). Another review suggested that an AP activity:chl a ratio >5 nmol µg^{-1} h^{-1} is indicative of "extreme deficiency" (Guildford & Hecky 2000). Mean AP activity:chl a biomass during this cruise was 112 nmol µg^{-1} h^{-1}.

That our AP values showed similar spatial trends to nutrient ratios and FRRF parameters (Figs. 3.1 and 3.2) further supports the utility of this enzyme assay for detecting P-limitation. It should be noted that past work in the area has shown AP activities to be higher near Southwest Pass than they were during this cruise. 18 of 28 AP assays near Southwest Pass that displayed activities <50 nmol l^{-1} h^{-1} were probably underestimates because an error resulted in 100-fold lower substrate concentrations in these assays. This error could not be fixed by using kinetic corrections. The pattern of high AP activity where DIN:P$_i$ ratios were high is a more typical pattern, seen in this area in July of 1990 (Ammerman 1992) and 1993 (Ammerman & Glover 2000), and March, May and July 2001 (Sylvan et al. 2006). When combined, nutrient data and enzyme assays provide powerful but indirect data about nutrient limitation of phytoplankton.

There was a significant positive correlation between AP activity and σ_{PSII} during leg 1 of 0.4310 (p<0.0001). High AP activities and high σ_{PSII} are both indicative of P-stress (Sylvan et al. 2007), and the positive correlation between these two parameters provides strong support for P-limitation. One might expect to see a negative correlation between AP activity and F_v/F_m and p given the positive correlation between AP activity and σ_{PSII}, and the opposite patterns of F_v/F_m and p to σ_{PSII} in Figure 3.2, but these correlations were not observed. This is likely because the relationship between AP activity and P_i is not linear. When AP activity is plotted versus P_i, there is an extreme increase in AP activity at P_i <0.25 µM and very low activities at higher P_i concentrations (Hoppe 2003). Therefore, AP activity does not show a linear correlation with most parameters that are linear.

The mapping data collected during this study revealed higher chl a biomass, higher F_v/F_m (>0.4) and lower AP activities near the Mississippi delta (Figs. 3.1 & 3.2). At the opposite end of our sampling grid, in the western portion of the mapped area south of the Atchafalaya River, we measured low chl a concentrations and low values of F_v/F_m (0.2-0.4) where AP activity was highest (Fig. 3.1). As low F_v/F_m suggest nutrient depleted cells and high AP activities suggest P-deficiency, these two indicators together point to more severe P-deficiency south of the Atchafalaya River compared to the MRP. DIN:P_i ratios were >32 in the same region (Fig. 3.1c), consistent with P-limitation.

F_v/F_m has been found to vary directly with nutrient input at multiple field sites and indicating the ratio can be used to measure potential nutrient stress (Yentsch et al. 2004). We also found that F_v/F_m worked for this application. F_v/F_m weakly correlated to salinity (negatively), DIN and chl a. Since F_v/F_m is a measure of phytoplankton health, the

positive correlation with biomass and nutrients and negative correlation with salinity makes qualitative sense, but a higher correlation might have been expected. One possible reason for the lack of a stronger correlation is the time scale of response for these parameters. Salinity, DIN and chl a all respond on slower time scales than F_v/F_m and therefore F_v/F_m (and the other FRRF parameters as well) indicate instantaneous physiology while the chl a concentrations measured may reflect either increasing or decreasing biomass concentrations in response to nutrients or other conditions and therefore could be lagging behind the trend of the phytoplankton community. This may be especially true in a system with rapidly evolving trophic gradients such as the MRP. τ_{Qa} showed a very weak but significant correlation to P_i, which is interesting given the lack of correlation between τ_{Qa} and any other parameters. Further studies would be necessary to discern whether this correlation is consistent and what it means.

Contours of σ_{PSII} were generally opposite to those of F_v/F_m and to a lesser extent, p, with higher F_v/F_m and p onshore and decreasing offshore while σ_{PSII} was lower nearshore and higher in deeper waters (Fig. 3.2). This relationship was clearer during Leg 2, when the survey was focused on a smaller area. τ_{Qa} did not show similar patterns to the other parameters during Leg 1, but was opposite F_v/F_m and p and similar to σ_{PSII} during Leg 2. While the contour maps provide a visual representation of the data that is useful for understanding gradients of individual parameters, it is not a most rigorous method to compare different parameters with each other, especially when differences in contour patterns are not visually obvious. The statistical comparisons between different variables provide insight here and show that while weak, τ_{Qa} was indeed statistically opposite (in sign) to F_v/F_m and p (Table 3.3) during Leg 1. This relationship was slightly

less robust during Leg 2 in the smaller surveyed area. On the other hand, during Leg 1, σ_{PSII} did not correlate significantly to F_v/F_m and the correlations with τ_{Qa} and p, while significant, were nearly absent. During Leg 2, these same correlations were significant and much higher. F_v/F_m had a stronger correlation to p as well during Leg 2.

A reason for the difference in interpretation between the visual contours and Kendall's tau measurements may be the scope of the mapping. During Leg 1, we traversed regions from estuarine to full ocean salinity and coastal to blue water, which results in a very diverse set of measurements for each parameter, all of which are considered together in the statistical analysis. FRRF correlations from Leg 2 were stronger, likely because there were taken in a more concentrated area. When the same four FRRF parameters were measured in 14 nutrient addition incubations near Southwest Pass during Leg 2, the results were also simpler to interpret (Sylvan et al. 2007). F_v/F_m, σ_{PSII} and p showed statistically significant differences between treatments with added P and those without, indicating P-limitation in the region. τ_{Qa} did not vary significantly in the different treatments, but was lower in those additions with P and higher in those without. The two sets of data from Leg 2 indicate that FRRF results were clearer when sampled in a consistent environment. Although the discharge from the Mississippi River varies dramatically over the course of the year, conditions were fairly consistent during our sampling during the five days of Leg 2. This smaller area exhibited less steep gradients in salinity than the rest of the shelf since the river discharge keeps this area in a state much like an open ended estuary. Salinities were all estuarine, ranging from 13-30 (mean = 20) in the 14 incubation experiments (Sylvan et al. 2007), whereas those across the entire shelf displayed a greater range.

It may be that FRRF is better suited for studies where less heterogeneity is present. In studies where F_v/F_m was mapped across fertilized regions of the open ocean, higher F_v/F_m was measured inside the fertilized patch than outside (Behrenfeld & Kolber 1999, Boyd & Abraham 2001). In these studies, transects crossed from large, uniform areas outside the patch, through large patches with significantly different phytoplankton dynamics inside the patch, back into waters on the far side of the patch similar to the initial conditions. Similar success was found mapping F_v/F_m through a mesoscale eddy, where elevated F_v/F_m was measured inside a cold-core eddy off of Hawaii (Benitez-Nelson et al. 2007). This is an analogous situation to mapping from oligotrophic waters through a fertilized ocean patch and yielded clear results. Recent work in the North Sea illuminated the uses and challenges of mapping F_v/F_m and σ_{PSII} in heterogeneous waters (Moore et al. 2003, Moore et al. 2005). These authors found that FRRF parameters correlated well in stratified waters, but less so in other parts of the water column (Moore et al. 2003). Also, σ_{PSII} varied with phytoplankton species (Moore et al. 2005). High F_v/F_m and low σ_{PSII} were correlated in diatoms, but coccolithophores displayed a direct relationship between the two parameters. Our past results in this area indicate diatom dominance, as one would expect in the MRP, based on these relationships between F_v/F_m and σ_{PSII} (Sylvan et al. 2007). These authors work correspond with our findings of better correlations near the MRP, where the water is strongly stratified.

Our findings are consistent with past studies that also measured P-limitation of phytoplankton on the Louisiana continental shelf using direct (Smith & Hitchcock 1994) and indirect methods (Lohrenz et al. 1999). The high concentrations of DIN and high DIN:P_i ratios seen during this work indicate that the P-limitation was not driven by a

dearth of P as much as a surplus of DIN in addition to low P. DIN drives the eutrophication in the area, which is thought to cause the annual hypoxic zone each summer (Rabalais et al. 2002c), and also results in the P-limitation seen during this study. Recent studies have suggested dual control of N and P to reduce eutrophication in coastal marine systems because P can often be limiting in these systems when the N load is high (Howarth & Marino 2006). Our work confirms this view.

This work used FRRF to confirm P-limitation in coastal Louisiana, influenced by Mississippi River runoff. FRRF has been used before in such widespread applications as assessing phytoplankton nutrient limitation in HNLC areas (Behrenfeld & Kolber 1999), examining community status of benthic fauna including coral and seagrass (Gorbunov et al. 2000), and identifying the presence of phototrophic bacteria in surface ocean waters (Kolber et al. 2000). Here we mapped basic biogeochemical and FRRF data in surface waters along the Louisiana continental shelf between the Mississippi and Atchafalaya Rivers. There were some correlations between biogeochemical measurements and FRRF parameters, but many comparisons provided no significant relationships. This may be due to the complex and diverse nature of the area studied and it would be interesting to see if these relationships were different in other heterogeneous areas. Relationships between FRRF parameters were more robust in the more stratified waters near the MRP versus shelf-wide comparisons. Despite the variability, the mapped FRRF parameters were indicative of nutrient limitation on the Louisiana shelf, and confirmed the data attained from nutrient concentrations and ratios, Chl a concentrations and AP assays illustrating P limitation. Mapping of F_v/F_m over large areas has been done before, but underway mapping of all four FRRF parameters as done here is less common. It

provided a visual picture of phytoplankton community health and a method for assessing phytoplankton physiology over large areas that will hopefully become more common in the future.

4.0 Seasonal Distributions of Inorganic and Organic Nutrients on the Louisiana Continental Shelf and Implications for Nutrient Limitation and Hypoxia Formation

Abstract

It is of paramount importance to understand the factors controlling phytoplankton biomass when designing management programs to mitigate eutrophication. Nutrients delivered by the Mississippi and Atchafalaya Rivers to the Louisiana continental shelf cause local eutrophication and feed phytoplankton growth, resulting in an annual summertime bottom water hypoxia zone that can be as large as Massachusetts. Data on organic and particulate nutrient distributions on the Louisiana shelf are limited to a few studies and a small number of samples. We measured dissolved inorganic, dissolved organic, and particulate carbon, nitrogen and phosphorus as well as chlorophyll *a* concentrations and alkaline phosphatase activities in surface water along the Louisiana continental shelf between the Mississippi and Atchafalaya Rivers during three cruises in March, May and July 2004. Altogether, 400-500 samples of each parameter were measured, providing an excellent picture of riverine impact on nutrient distributions. Mean inorganic nitrogen to phosphorus ratios were highest in May (60) but were still high (>32) in March and July. Total nitrogen to total phosphorus ratios were even higher, averaging ~100 in March and May and ~50 in July. Dissolved organic nitrogen was higher than dissolved inorganic nitrogen in higher salinity waters, but was lower near the two rivers. Dissolved organic phosphorus was lower than inorganic phosphorus at most stations and does not appear to alleviate inorganic P stress. Alkaline phosphatase activities were high (mean $\cong 200$ nmol L^{-1} h^{-1}), indicating inorganic P stress. The

combination of low P concentrations, high inorganic and total N:P ratios and high alkaline phosphatase activities indicated P limitation of phytoplankton biomass on the Louisiana shelf during the spring and early summer of 2004. This P limitation occurs during the period of hypoxia formation as a result of excess N loads delivered by the rivers, indicating that controls of both N and P are necessary to reduce the size of the hypoxia. P reduction methods are easier to implement, but reductions of P without concurrent N reductions result in displacement of eutrophication, and therefore bottom water hypoxia as well, downstream. Because of this, N reductions, although more difficult to achieve, must be realistically and aggressively pursued.

4.1 Introduction

The Mississippi River is the largest river in North America. It drains approximately 40% of the continental United States into the Gulf of Mexico (GOM). Starting in the 1940's, nitrogen and phosphorus input to the river began to increase as a result of elevated fertilizer use (Rabalais et al. 1996). While application of phosphate fertilizer leveled off around 1980, nitrogen fertilizer use continues to rise (Wiseman et al. 1999). This resulted in drastic changes in the nutrient ratios within the river. Current nutrient ratios for inorganic phosphate (P_i), silicate (Si) and dissolved inorganic nitrate (DIN) in the river water are approximately 1:14:14, respectively, up from SI:DIN ratios of 4:1 in the past (Wiseman *et al.*, 1999). Ratios are now close to the Redfield ratio, 1P:16Si:16N, needed by phytoplankton to perform photosynthesis efficiently (Redfield 1958).

Recent work on the Louisiana continental shelf revealed a pattern of P limitation in the spring and early summer, when discharge from the Mississippi River is high, and N limitation during the late summer through the winter when discharge was lower (Sylvan et al. 2006). This study combined data from nutrient addition bioassays, nutrient uptake rate measurements, inorganic nutrient concentrations and ratios, and AP assays. The seasonal transition in the northern Gulf of Mexico (GOM) of nutrient limitation from P in the spring to N in the fall has been hinted at in the past using inorganic nutrient data (Lohrenz et al. 1999), but no extensive surveys of seasonal distributions of organic nutrients on the Louisiana shelf exist. This information would be valuable for gaining further insight into the driving factors of phytoplankton growth on the shelf as well as helping guide eutrophication management strategies.

Freshwater sources to coastal areas, such as rivers, often contain high loads of N as a result of anthropogenic loading. A common source of the extra nitrogen is runoff from farmlands with N-rich soils as a result of fertilizer application (Goolsby et al. 2001). In coastal regions with a significant input of freshwater, it is not uncommon for P to be limiting during the high flow period of the year, often spring or summer, and N to be limiting the rest of the year (Conley 2000). Examples include Chesapeake Bay (Fisher 1992), Delaware Bay (Pennock & Sharp 1994) and the Black Sea (Cociasu et al. 1999).

The prevailing thought that P limits freshwater systems while nitrogen (N) is limiting in marine systems (Hecky & Kilham 1988) has traditionally resulted in fewer studies of P biogeochemistry than of N, but recent interest has yielded great advances in the field. While P does not undergo redox transformations like N does, the conversions of P from P_i to its many organic forms play an important role in marine biogeochemistry

(Karl & Bjorkman 2002). Multiple methods exist to investigate P limitation, including nutrient addition bioassays, uptake measurements, fluorometric methods, nutrient ratios and enzyme activities (Beardall et al. 2001b). Nutrient concentration measurements are rapid and simple to measure, but nutrient data alone can be insufficient to make definitive statements about nutrient limitation. Nutrient concentrations combined with biological data or nutrient ratios can provide excellent indicators of the status of an ecosystem. Enzyme activities, especially the use of ectoenzymes located in the periplasm of bacteria or between the cell wall and cell membrane in phytoplankton, are valuable tools for determining nutrient limitation because the measurements are cheap, reliable, simple, and rapid, enabling many samples to be taken during a cruise (Ammerman 1993). Like nutrient data, enzyme activities alone are insufficient to make conclusions about P-limitation but very useful when combined with other data.

Dissolved organic carbon (DOC), dissolved organic nitrogen (DON), and dissolved organic phosphorus (DOP) can all be utilized by phytoplankton and bacteria when inorganic nutrients are limiting. Because of this, it is important to look at organic nutrient pools as well as the inorganic pools when assessing nutrient limitation. DON in estuaries (because the Mississippi River is so large, the Louisiana shelf displays the characteristics of an open ended estuary) tends to range from ~15-30 μM, and is higher in rivers and lower in the open ocean (Bronk 2002). It is typically the majority of the dissolved nitrogen pool. DOP in estuaries and coastal regions tends to range from ~0.20 μM-0.60 μM (Karl & Bjorkman 2002). Many DOC measurements have been made on the Louisiana shelf, but DON and DOP measurements are less common.

We measured concentrations of dissolved inorganic, dissolved organic, and particulate carbon, nitrogen and phosphorus on the Louisiana shelf during March, May and July 2004 in an effort to fully understand their role in eutrophication in the region. Chlorophyll *a* (Chl *a*) concentrations and AP activities were measured as well. A seasonal pattern of P limitation during the spring and early summer was evident. Indices of P limitation such as inorganic and total nutrient ratios and AP activities were higher following periods of higher discharge.

4.2 Methods

4.2.1 Cruises and sampling – Three cruises to the Louisiana shelf aboard the R/V *Pelican* occurred from 10-14 March, 15-19 May and 16-20 July 2004. The *Pelican* is equipped with a sampling arm that projects over the side of the boat with a hose. The hose samples surface water (>1m) about 10 m away from the boat and continuously sends it to the lab inside the boat. Basic water parameters like temperature, salinity, chl fluorescence, depth, transmittance, etc are measured by sensors on board the ship and displayed on a computer screen in the labs. Samples that do not need to be trace metal clean or sterile (Chl *a* biomass, nutrient concentrations and enzyme assays) are taken from this system, named Multiple Instrument Data Acquisition System (MIDAS). MIDAS took readings of all its parameters and recorded them to a computer every ten seconds during the cruises.

During these cruises, the R/V *Pelican* started in the Mississippi River, at Head of Passes, and then cruised continuously on transects from Southwest Pass to Atchafalaya Bay (Fig. 4.1). While heading west across the Louisiana shelf, these transects were made

from brackish water near the coast out to open ocean salinity and then back again towards the coast. Water samples were collected approximately every 30 minutes, 24 hours a day, for chl *a* biomass, nutrient filtration and AP and aminopeptidase assays.
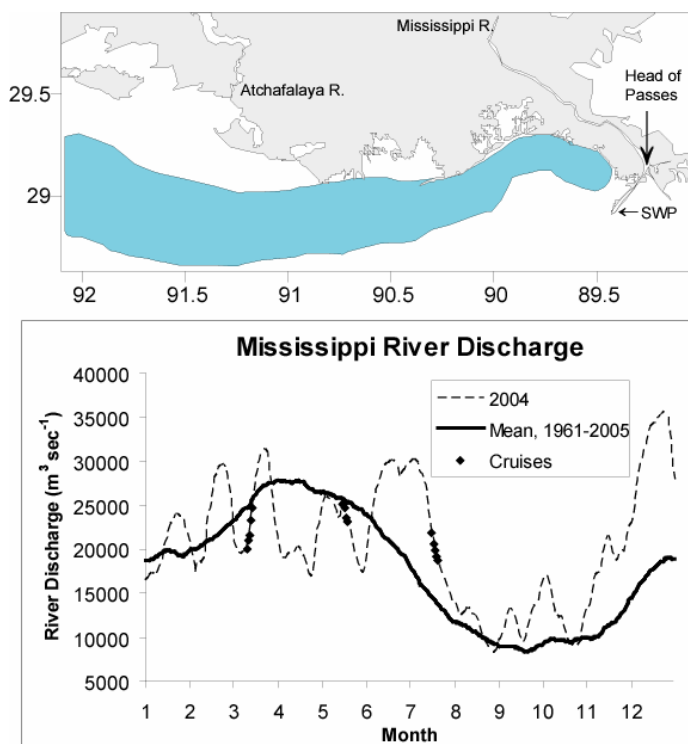
Figure 4.1. (Top) Map of Louisiana continental shelf. The hypoxic zone, measured in July 2001, is the blue shaded area. Adapted from Sylvan *et al.* (2006). (Bottom) Annual pattern of Mississippi River discharge. Discharge from 2004 is dotted line, mean discharge from 1961-2005 is heavy line, and cruise dates are indicated by diamonds.

4.2.2 Nutrient measurements – Nutrient samples were filtered through 0.45 μm polycarbonate filters into acid washed polyethylene bottles for dissolved nutrient determination and then frozen for later analysis. Dissolved inorganic nutrients were analyzed on a Lachat nutrient autoanalyzer for $NO_2^- + NO_3^-$, NH_3^+, P_i and SiO_3^- using the standard colorimetric methods (Strickland & Parsons 1972). This data was used to obtain $DIN:P_i$ ratios.

Dissolved inorganic carbon (DOC) and dissolved organic nitrogen (DON) were measured using high temperature combustion (Walsh 1989) on a Shimadzu TOC-5000A (DOC) and Antek 7000 (DON) set up in series to run the same sample. The sample is first run by the Shimadzu and then transferred to the Antek for analysis. For sample prep, 8 μL concentrated HCl are added to 3.5 mL of thawed sample in a glass tube and the samples are placed in the autosampler on the Shimadzu machine. CHN analyses were carried out on a Carlo Erba NA-1500 Series 2 analyzer (Verardo et al. 1990).

Because AP cleaves P_i from organic P molecules, it is essential to look at organic P as well as P_i to obtain a complete picture analysis of P limitation in a system. DOP was measured using acid persulfate digestion to convert organic phosphorus to P_i (Ridal & Moore 1990). Total dissolved phosphorus (TDP) was measured using the same method used for P_i (above). TDP minus P_i yields DOP. In summary, 0.020 ml of 5.6 N HCl was added to 10 ml of sample in acid washed and baked glass vials with plastic caps. 0.20 ml of 0.18 M potassium persulfate was then added to each sample, the tubes were capped tightly and autoclaved at 120˚C for four hours. Samples were then run for standard PO_4^{3-} on a LACHAT autoanalyzer.

4.2.3 AP assays – Enzyme assays were performed aboard the ship within 4 hours or less of sample collection. The substrate 6,8-difluoro-4-methylumbelliferyl phosphate (DifMUP, Molecular Probes, Eugene, Oregon) was used to assay for AP activity according to Ammerman (1993). Basically, substrate was added directly to the sample in a microplate well and the assay was run at *in situ* temperature in a fluorescence microplate reader (Tecan Genios), which took 11 readings over the specified time course (typically 30 minutes to two hours), yielding the slope of enzyme activity. A standard curve (6-8-difluoro-4-methylcoumarin, or DifMU, also from Molecular Probes) was run on each plate and used to determine the AP activity for that plate. A final substrate concentration of 10 μM was used and samples were run in quadruplicate and averaged to give the AP activity for each station. Aminopeptidase activity was measured the same way using the substrate L-leucine-7-amido-4-methylcoumarin hydrochloride and its reference standard, 7-amino-4-methylcoumarin. The final substrate concentration was 20 μM for aminopeptidase activities. For both enzyme assays, enzyme activity in nmol l^{-1} h^{-1} was determined by dividing the slope of the assay (fluorescence units per hour) by the slope of the standard curve (fluorescence units nM^{-1}).

4.2.4 Data analysis – Contour plots of cruise data were made using Golden Software's Surfer 7.

Analysis of variance (ANOVA) was run to determine statistical differences between parameters and cruises. Statistical analyses were computed using the JMP Software by SAS.

4.3 Results

Discharge during the March and May cruises was lower than the 45 year average (Fig. 4.1). March and May are typically the highest discharge periods of the year, but there were a series of lesser peaks in discharge during 2004 rather than one large on in the spring. Because many of the distributions of measured parameters were similar in March and May, they are discussed together here, using contour plots from May for illustrative purposes. Due to the lower than average discharge during the two cruises, higher salinity water encroached close to the shore and the river plume is barely evident in the salinity contours (Fig. 4.2). DIN was highest near the two rivers during both months (Fig 4.2). In May, DIN was 10-25 μmol L^{-1} west of Southwest Pass (SWP). DIN was generally 5-10 μmol L^{-1} along the coast west of there. At salinities >30, DIN was almost always <5 μmol L^{-1}. March DIN contours were similar but concentrations were lower concentrations were found closer to shore. Overlaying the salinity contours on the DIN contours shows indicates that DIN distributions are largely influenced by discharge. DOC and DON displayed similar distributions. DOC was >400 μM coming out of Atchafalaya Bay, but only 2-300 μM near SWP. Concentrations were 2-300 μM across the western shelf where salinities were <30 and 1-200 for most of the area east of 90.5˚. These results were similar to March, but March DOC concentrations were a little lower and there was enrichment in DOC exported by the Atchafalaya River versus the Mississippi River. May DON was >10 μmol L^{-1} near the Mississippi but was higher near the Atchafalaya where values were >20 μmol L^{-1} (Fig. 4.2). Concentrations were <10 μmol L^{-1} at salinities >30. This was similar in March, but DON was not higher near the Atchafalaya. In both March and May, TN topped 50 μmol L^{-1} at both river mouths. It
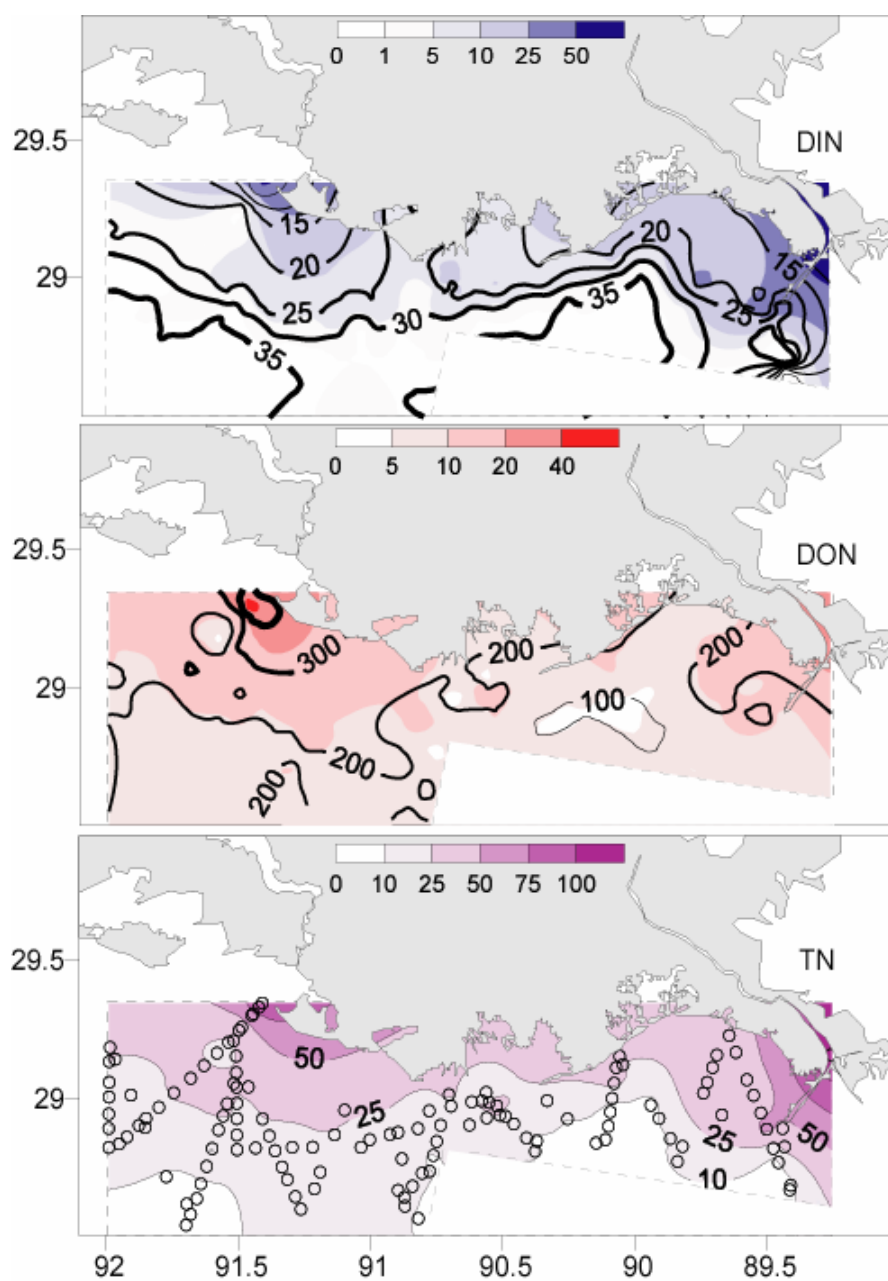
Figure 4.2. May 2004 DIN (NO$_3^-$ + NO$_2^-$ + NH$_3^+$), DON and TN contours, all concentrations in μM. Contours of salinity (lines only) overlay DIN contours (colors only, no lines) and contours of DOC (μM, lines only) overlay DON contours (colors only, no lines).

was >25 µmol L^{-1} along the entire coast and >10 µmol L^{-1} at most stations in full salinity waters.

P$_i$ displayed similar contour patterns to DIN (Fig. 4.3). It topped 1 µmol L^{-1} at some stations closest to the rivers, but was <0.1 µmol L^{-1} at most stations, even some near shore. In March, concentrations were >2 µmol L^{-1} near Southwest Pass and slightly higher than in May right near Atchafalaya Bay. P$_i$ was generally 0.1-0.5 µmol L^{-1} along the coastline and more stations offshore were 0.1-0.5 µM than in May. Conversely, DOP was lower offshore in March than in May. DOP was highest (>0.5 µmol L^{-1}) coming out of Atchafalaya Bay and was very low near Southwest Pass (<0.1 µM in March and <0.1-0.25 µM in May). Distributions of DOP were similar to P$_i$ in both months. DOP concentrations were 0.1-0.25 µmol L^{-1} along the shore and <0.1 µmol L^{-1} in deeper waters. TP was high near both river mouths, where it peaked at 2-3 µmol L^{-1}. Along the coast, TP was >1 µmol L^{-1} and 0.1-0.5 µmol L^{-1} in deeper waters. March distributions were similar to May.

NO$_x$:P$_i$ ratios ranged from <16 to >128 during March and were patchy in distribution. They were highest to the west of Southwest Pass and lowest near Atchafalaya Bay and at the southern most stations. In May, DIN:P$_i$ was highest along the coast, where it was always >32 (Fig. 4.4). The distribution of higher DIN:P$_i$ ratios was tight along the coastline. In both March and May, TN:TP was patchy but was often directly correlated with salinity. TN:TP values were higher than DIN:P$_i$ on the scale of the entire cruise, but contours of the two ratios were opposite in distribution at many of the same stations. TN:TP ratios topped 512 at some stations offshore and was >64 at
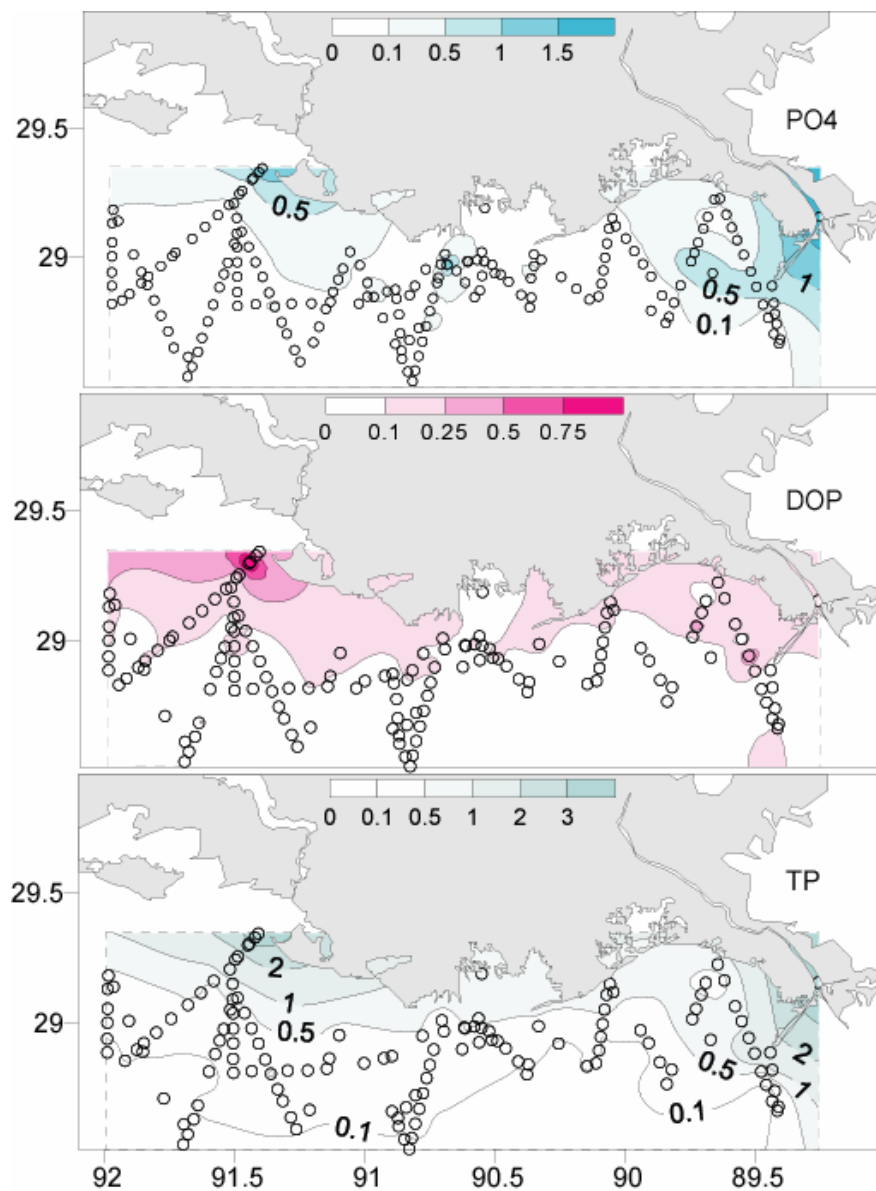
Figure 4.3. Contours of May 2004 P_i, DOP and TP, all concentrations in μM.
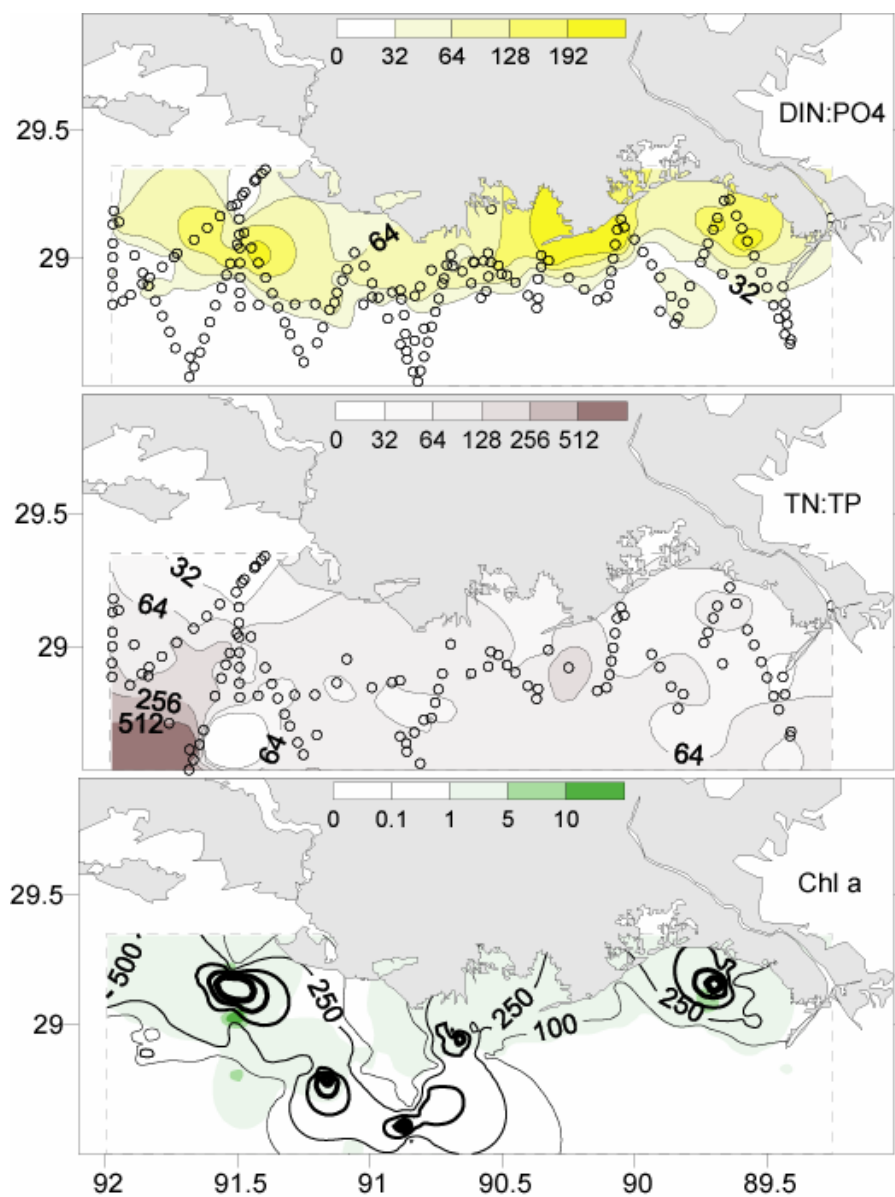
Figure 4.4. May 2004 DIN:P$_i$, TN:TP, Chl *a* concentrations (µg L^{-1}) and AP activity (nmol L^{-1} h^{-1}).

most of the other stations during March and May. TN:TP was lower near Atchafalaya

Bay than SWP for both cruises as well.

Chl a concentrations were 1-5 μmol L^{-1} at most stations (Fig. 4.4).

Concentrations <0.1 μg L^{-1} accompanied higher salinities. AP activities were much

higher in May than in March. In March, AP activity was lowest (<50 nmol L^{-1} h^{-1}) on the

eastern transects of the cruise, including near the Mississippi River. It was >50 nmol L^{-1}

h^{-1} across almost the entire western portion of the shelf. The maximum activity was 204

nmol L^{-1} h^{-1} but only two stations were >200 nmol L^{-1} h^{-1}. In May, activities topped 1000

nmol L^{-1} h^{-1} at some stations. At many stations, especially those nearest the two rivers,

contours of AP activity mirrored those of DIN:P_i in May. AP activity contours were

similar to Chl a as well, but there were two areas offshore where high AP activities were

not mirrored by high Chl a concentrations.

Conservative mixing plots indicate a substantial drawdown of inorganic nutrients

(DIN, P_i vs salinity) at all salinities sampled (Fig. 4.5). DIN:P_i values were clearly

highest at mid-salinites. In March, the peak was at salinities 25-33 as opposed to May,

when the peak was at salinities 15-25.

Inclusion of organic and particulate nutrients in the conservative mixing plots

causes the distributions of properties to fall closer to the conservative mixing line (Fig.

4.6). TN and TP are still drawn down at all salinities, but less so than inorganic nutrients.

TN:TP falls more along the conservative mixing line than DIN:P_i for both months. The

noise around the line increases with salinity. Above salinity 30, there is even distribution

about the conservative mixing line, indicating TN and TP are neither drawn down nor
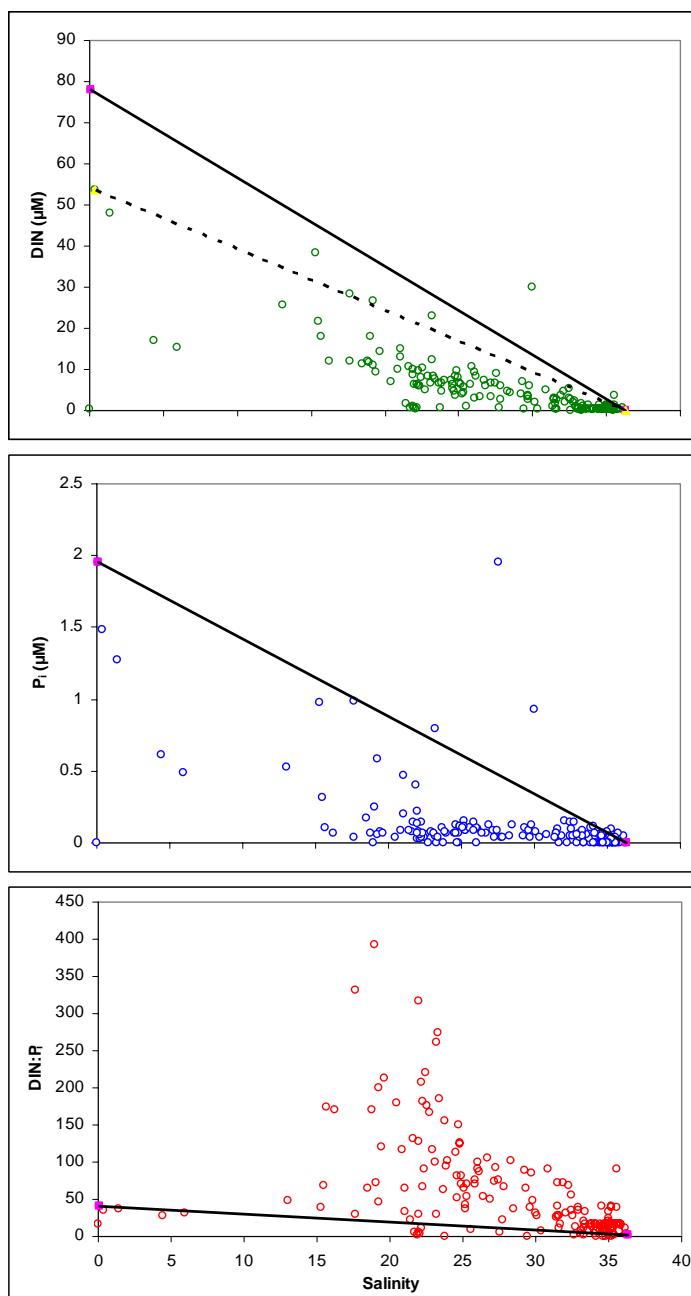
Figure 4.5. May 2004 DIN, P_i and DIN:P_i vs Salinity. Solid line indicates conservative mixing. 0 salinity station is Head of Passes, maximum salinity was taken from station with greatest salinity for the cruise. Dotted line in plot of DIN vs Salinity shows a low salinity end member of 0.341 salinity from near Achafalaya Bay instead of 0.123 at Head of Passes.
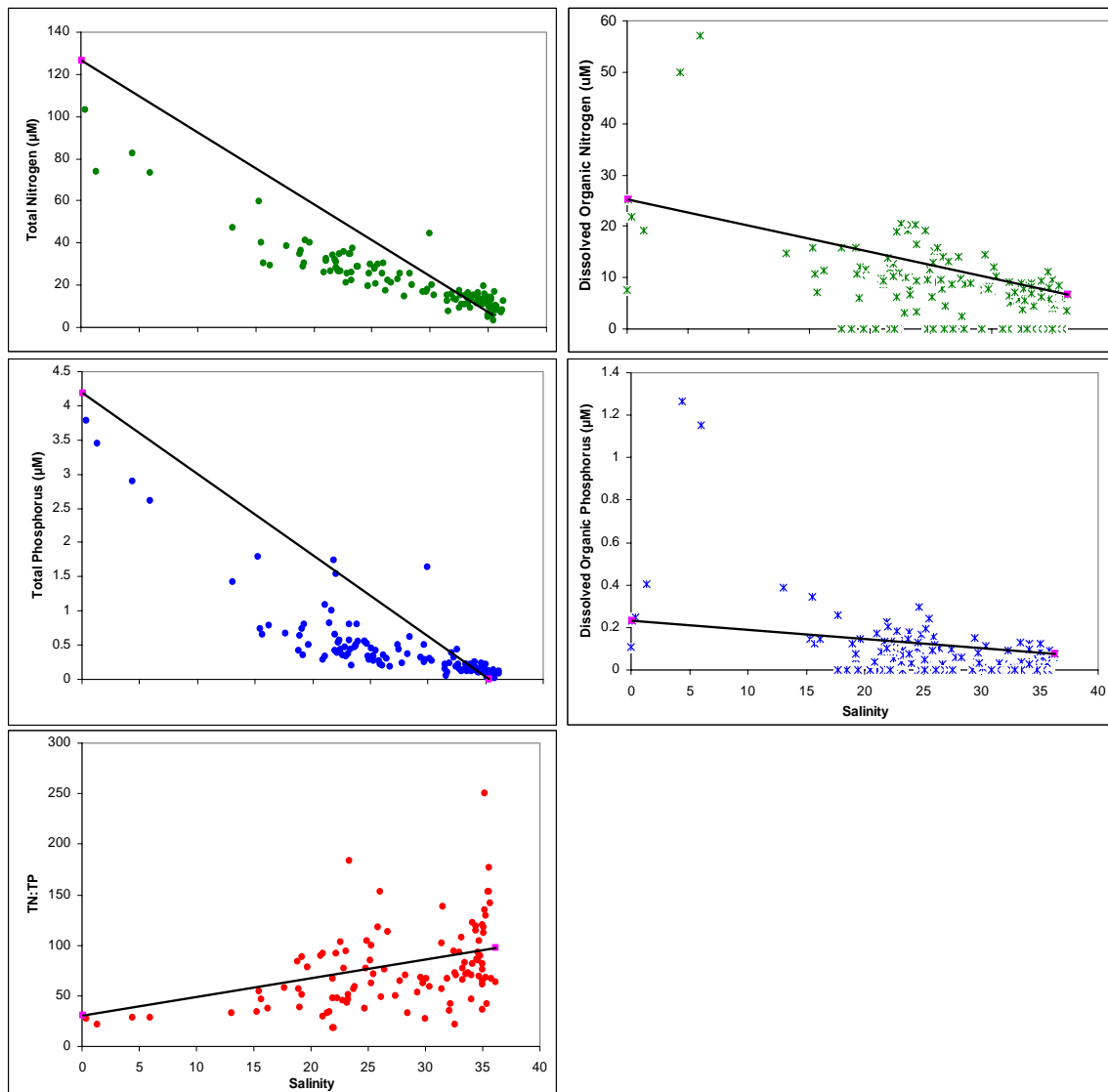
Figure 4.6. May 2004 TN, TP, TN:TP, DON and DOP vs Salinity. Solid line indicates conservative mixing. 0 salinity station is Head of Passes, maximum salinity was taken from station with greatest salinity for the cruise.

supplied at these salinities. There is an obvious increase in TN:TP with salinity. DON and DOP show only a small drawdown, and only at higher salinities.

In July, Mississippi discharge had been very high for a month prior to the cruise and was higher than the mean for this time of year. This resulted in lower salinities seen on the shelf than the two previous cruises (Fig. 4.7). Salinity was <30 at almost all the stations despite stations further south on this cruise than the other two (further from the rivers). There is an eastward shift of the low salinity contours from both rivers, indicating eastward currents as a result of westerly winds.

DIN, as well as all other nutrients measured, was higher than the March and May cruises (Fig. 4.7). Concentrations were highest near Southwest Pass (>50 μmol L^{-1}) and Atchafalaya Bay (>25 μmol L^{-1}). Near the coast, DIN was almost always 10-25 μmol L^{-1}. Distributions of DIN near the river mouths were very similar to salinity. DOC was highest during July. It topped 600 μM at a few stations near SWP and was >300 at many stations on the shelf. There was not an enhancement of DOC from the Atchafalaya River during this cruise. DON was highest at Southwest Pass where it was >20 μmol L^{-1}. Almost the entire rest of the shelf had DON concentrations of 10-20 μmol L^{-1}. TN was >100 μmol L^{-1} near the mouth of the Mississippi and >50 μmol L^{-1} at almost a quarter of the stations, but these higher concentrations were all near Southwest Pass. TN decreased on an east to west basis but was never <10 μmol L^{-1}.

P_i contours mirrored those of DIN (Fig. 4.8). Concentrations were >2 μmol L^{-1} closest to the two rivers. South of Atchafalaya Bay, P_i was 1-2 μmol L^{-1} at many stations and was >0.1 μmol at almost wall of the stations during this cruise. DOP was often less than P_i at the same stations and was >0.1 μmol L^{-1} near both rivers. TP was >3 μmol L^{-1}

near Southwest Pass and >2 µmol L^{-1} near Atchafalaya Bay. Concentrations were >0.5 µmol L^{-1} at most of the stations and only fell below 0.1 µmol L^{-1} at a few stations.

In July 2004, the higher DIN:P$_i$ ratios were located almost exclusively on the eastern part of the Louisiana shelf (Fig. 4.9). Except for one small region with a few stations, DIN:P$_i$ was <32 at all the stations south of Atchafalaya Bay and on the western portion of the Louisiana shelf. A majority of the stations near the Mississippi were 64-128. TN:TP contours were similar to DIN:P$_i$ but with a slightly higher magnitude.

Chl a concentrations were 1-5 µg L^{-1} across most of the shelf (Fig. 4.9). They were lower (<1 µg L^{-1}) in the southwest corner of the shelf and >5 µg L^{-1} near Southwest Pass. AP activity during this cruise was high again. Activities were >500 nmol L^{-1} h^{-1} at many stations on the eastern portion of the shelf. On the western portion of the shelf, AP activity was nearly absent minus two hot spots at the southern end of the mapped area. Contours of P$_i$ and AP activity were very much opposite to each other during this cruise.

Almost all the DIN fell below the conservative mixing line during July 2004 (Fig. 4.10). Nearly 20% of the P$_i$ stations were above the line, as opposed to March and May, where they were all below the line. The conservative mixing line for DIN:P$_i$ had a positive slope in July 2004. The peak in DIN:P$_i$ ratios occurred between salinities 10-25, but it was not as obvious as the other two cruises.

For both TN and TP, almost all of the data points fall below the conservative mixing line (Fig. 4.11). TN:TP displayed a positive conservative mixing line with data points evenly scattered on both sides of the line. DON fell mostly below the conservative mixing line, indicating some drawdown. DOP was not selectively drawn down at any salinity.
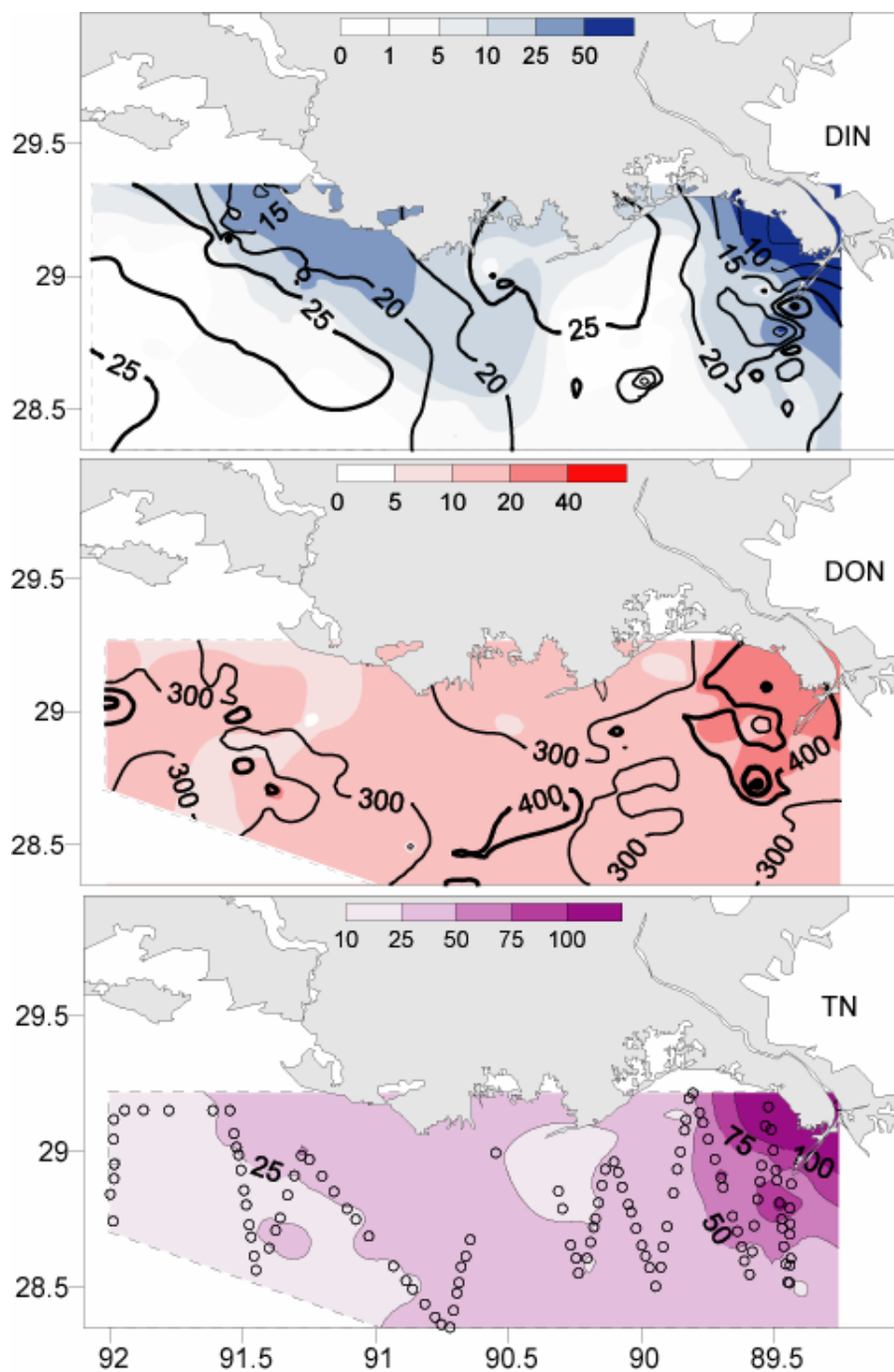
Figure 4.7. July 2004 DIN, DON and TN contours, all concentrations in μM. Contours of salinity (lines only) overlay DIN contours (colors only, no lines) and contours of DOC (μM, lines only) overlay DON contours (colors only, no lines).
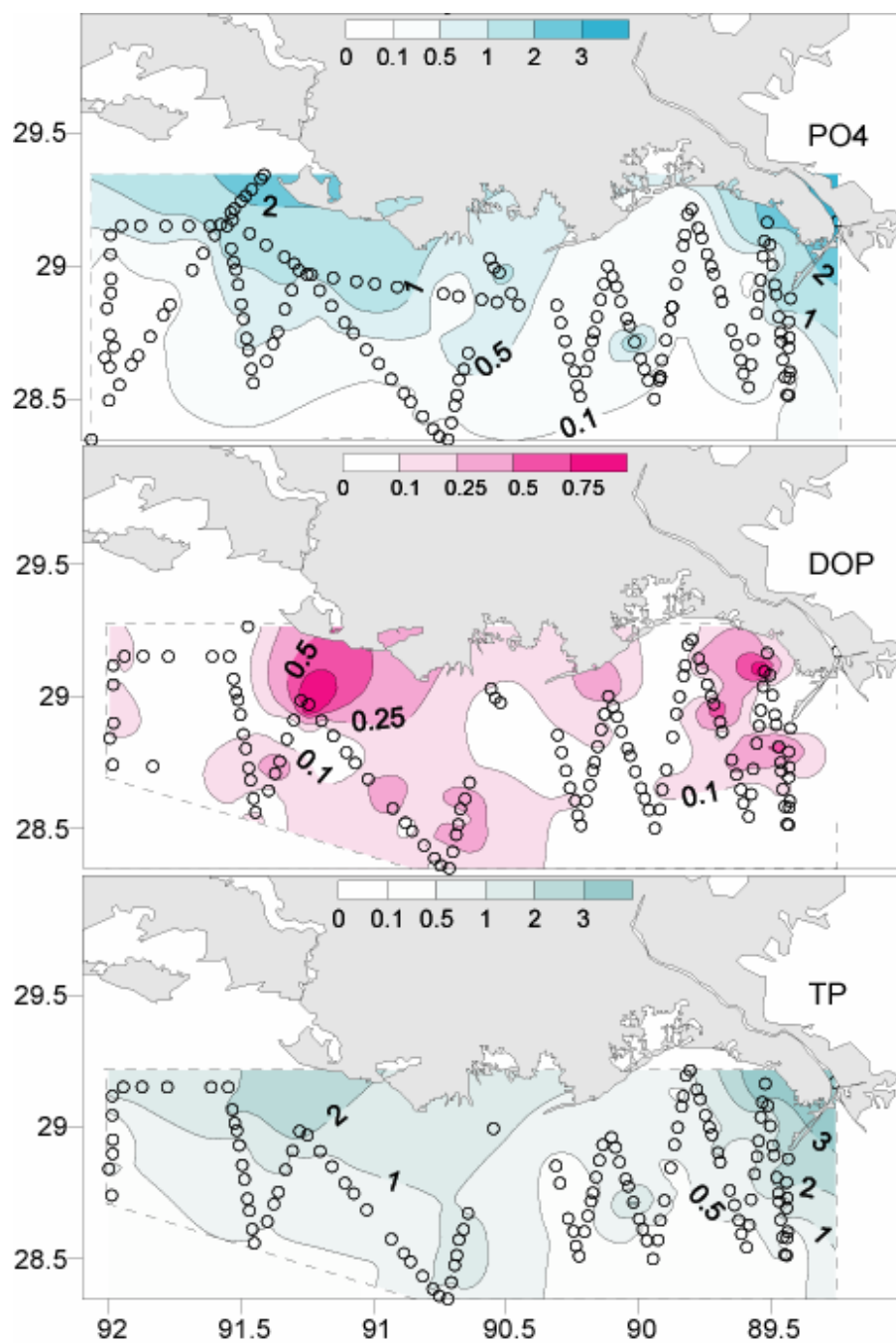
Figure 4.8. Contours of July 2004 P_i, DOP and TP, all concentrations in μM.
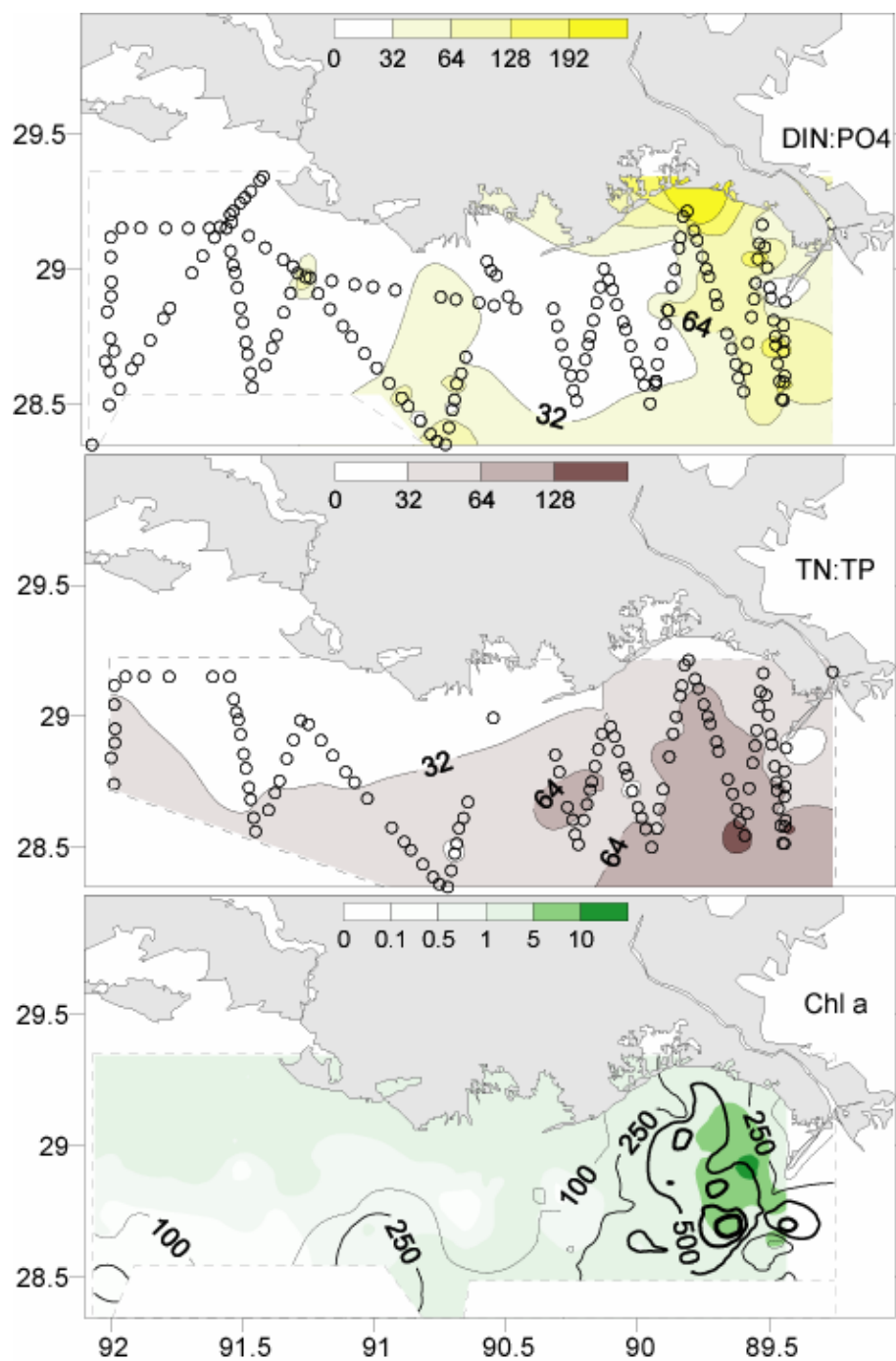
Figure 4.9. July 2004 DIN:P$_i$, TN:TP and Chl a concentrations (μg L^{-1}). Contours of AP activity (nmol L^{-1} h^{-1}, lines only) overlay the Chl a contours (no lines, colors only).
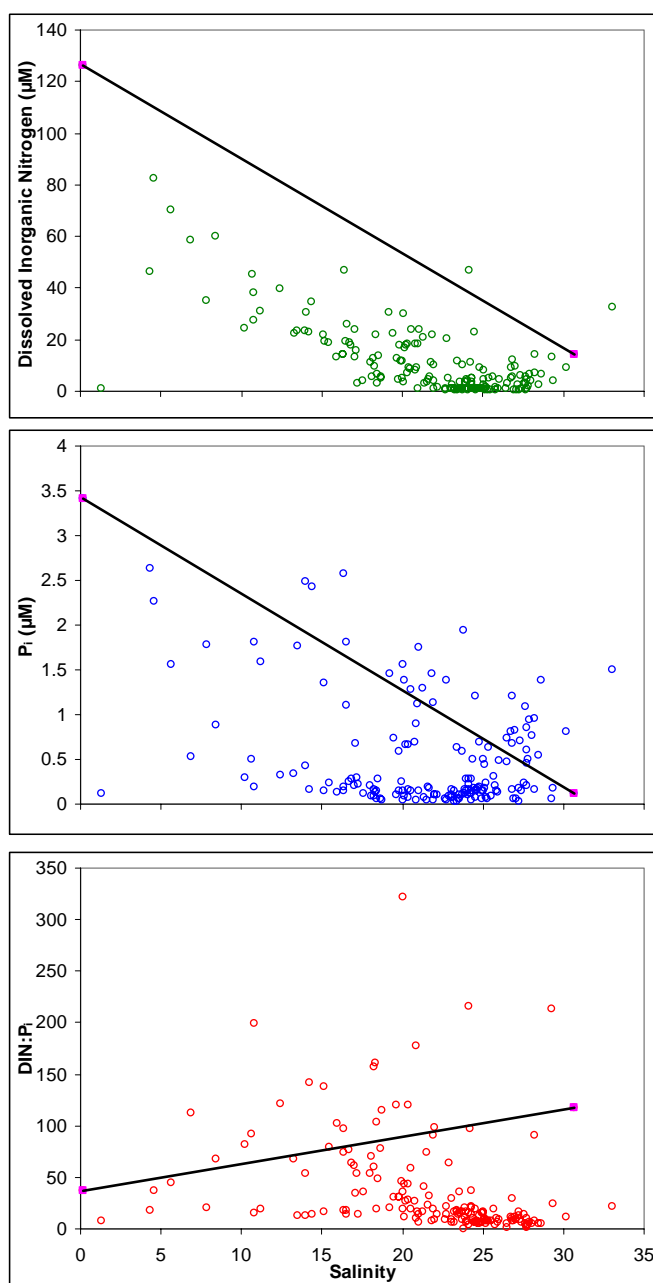
Figure 4.10. July 2004 DIN, P_i and DIN:P_i vs Salinity. Solid line indicates conservative mixing. 0 salinity station is Head of Passes, maximum salinity was taken from station with greatest salinity for the cruise.
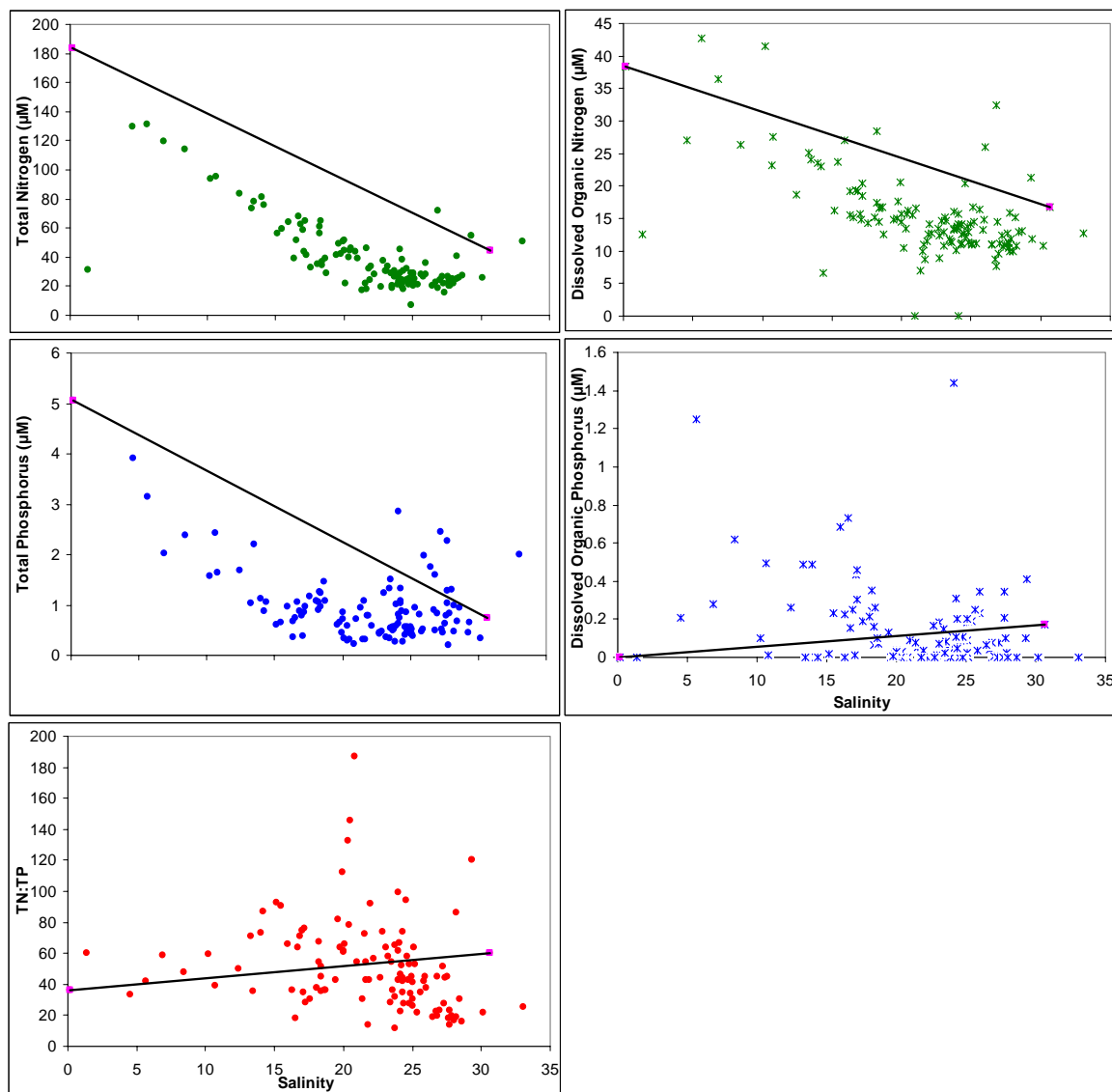
Figure 4.11. July 2004 TN, TP, TN:TP, DON and DOP vs Salinity. Solid line indicates conservative mixing. 0 salinity station is Head of Passes, maximum salinity was taken from station with greatest salinity for the cruise.

4.4 Discussion

This work examined distributions of all available pools of nutrients during spring and summer months on the Louisiana continental shelf. The study area is subject to annual bottom water hypoxia as a result of riverine influenced eutrophication (Rabalais et al. 2002a), making it essential to understand what drives this hypoxia. By looking at every fraction of the nutrient pools, we are able to draw a more complete picture of nutrient cycling and eutrophication in the area and predict what analyses should be done, and also those that are not necessary for making management predictions in the future.

In 2001, mean DIN on the shelf was 4-5 times higher in March and May and nearly 3 times higher in July than it was our 2004 cruises (Sylvan et al. 2006). These authors also found lower P_i concentrations in the same area than in 2004, averaging 0.56 µM in March and ~0.085 µM in May and July. However, in 2001, the highest discharge occurred in March, not July, as it did in 2004. The highest inorganic nutrients on the shelf during both years were measured following the period of greatest discharge, which more commonly occurs in the spring than the late summer, as it did in 2004 (Figure 4.1). Due to the higher DIN and lower P_i measured in 2001, DIN:P_i ratios were much higher in 2001 (Sylvan et al. 2006), although the mean for the 2004 cruises was 44 (Table 4.1), which is still indicative of P limitation. Chl *a* concentrations on the shelf were much higher in 2001 as well, and AP activities were ~40% higher.

A likely difference between these two years is the pattern of Mississippi discharge. The mean discharge volume between March and July was 23,011 m^3 sec^{-1} and 23,354 m^3 sec^{-1} for 2001 and 2004, respectively. While these are very similar, there was an extremely high peak during March in 2001, resulting in an exceptionally large nutrient

Table 4.1. Mean and median values of measured parameters during the three cruises in 2004. One ANOVA was run for each parameter. Different letters within each parameter denote significant differences ($p < 0.01$) between the months for that parameter determined by univariate posthoc pairwise comparisons using Tukey adjusted least-squares means. Identical letters indicate no significant differences between months.

	3/04 Mean	3/04 Median	5/04 Mean	5/04 Median	7/04 Mean	7/04 Median
DIN	4.98 (148)[a]	2.69	5.52 (170)[a]	2.16	12.46 (166)[b]	5.84
P_i	0.200 (148)[a]	0.068	0.132 (170)[a]	0.060	0.528 (166)[b]	0.210
DIN:P_i	33 (148)[a]	20	60 (170)[b]	35	38 (166)[a]	17
Si	9.61 (148)	8.01	8.31 (170)	3.54	18.50 (166)	10.15
DOC	145.0 (145)[a]	133.8	199.7 (133)[b]	191.7	342.8 (124)[c]	333.9
DON	8.75 (145)[a]	7.82	9.97 (133)[a]	8.14	15.39 (129)[b]	13.91
TDN	13.80 (145)	10.70	16.36 (130)	11.65	26.82 (129)	18.30
DOP	0.060 (140)[a]	0.031	0.097 (132)[ab]	0.058	0.133 (123)[b]	0.050
POC	75.04 (127)	69.68	48.08 (162)	40.64	106.1 (116)	91.53
PON	8.02 (127)	6.58	5.84 (162)	5.11	13.89 (116)	11.96
TN	22.17 (126)[a]	17.46	22.35 (120)[a]	16.46	40.97 (116)[b]	30.72
POP	0.167 (131)	0.107	0.248 (131)	0.133	0.422 (120)	0.345
TP	0.398 (130)[a]	0.233	0.477 (130)[a]	0.280	0.971 (118)[b]	0.797
TN:TP	102.0 (125)[a]	82.42	99 (113)[a]	70	50.86 (115)[b]	44.69
Chl a	1.23 (157)[a]	0.84	1.61 (176)[ab]	1.09	2.07 (184)[b]	1.45
APA	61.2 (139)[a]	56.4	216 (163)[b]	88.5	192 (184)[b]	82.6
AmpA	NA	NA	NA	NA	79.7 (177)	52.3

load on the shelf in the early spring, fueling the extreme biomass we saw during the spring and summer that year. In 2004, the peak in discharge was only 75% as high as 2001, and it occurred in three bursts, the longest of which was mid-June through mid-July, just prior to our July cruise (Fig. 4.1). The moderately high discharge during this time period, which was greater than average, resulted in the highest nutrients and biomass seen during the 2004 cruises. It seems that the discharge in the preceding month or more directly influences the current nutrient and biomass concentrations on the shelf. Supporting this theory, residence time on the entire Louisiana and Texas shelf for freshwater from the Mississippi is 3 months (Dinnel & Wiseman 1986). Clearly the nutrients poured onto the shelf can produce biomass for months following their appearance on the shelf, provided they are not exhausted.

Statistical analyses of differences between the three cruises also indicate that the difference in discharge is largely responsible for the differences seen between months (Table 4.1). Mean DIN, P_i, DON, TN, TP, and TN:TP were all statistically the same in March and May, which were different from July. DOC was statistically different each month.

DOP was higher coming out of the Atchafalaya River for both March and May and in July as well, although slightly offset to the east of the river mouth, than at Southwest Pass. This is likely for two reasons. First, the flow is much slower coming through Atchafalaya Bay than Southwest Pass. This allows for collection of organic matter while the water passes through the shallow Atchafalaya Bay. At Southwest Pass, however, the water enters onto the shelf without a chance to interact with any shallow plant life, and therefore does not collect DOP. Secondly, water in the Atchafalaya River

passes over shallow swamps along its journey to the open Gulf. DOP is released into the river in these swamps by submerged vegetation, elevating organic nutrient concentrations in the water.

Converse to DOP contours, DON is higher coming out of the Atchafalaya than the Mississippi only in May. This may be due to a higher bioavailability of DON than DOP, allowing it to be utilized by phytoplankton and bacteria in the Atchafalaya River before it reaches the Gulf. The faster discharge rate in the Mississippi prevents utilization of much of the DON before it reaches the Gulf, resulting in higher DON concentrations exiting Southwest Pass. This latter argument indicates an internal source of DON in both rivers that is not utilized in the Mississippi before reaching the Gulf. (Lopez-Veneroni & Cifuentes 1994) found DON on the Louisiana continental shelf varied directly with river discharge. Highest concentrations (10-40 μM) occurred in the spring and the lowest concentrations (8-14 μM) occurred in the winter in 1992.

One argument against P-limitation on the Louisiana shelf is that cells can use organic P (Boesch 2004) and therefore DIN:P_i ratios are not important. DIN:P_i ratios were elevated near the rivers and along the coasts in March and May, and were very high near the Mississippi River in July. Mean DIN:P_i was highest in May (Table 4.1), the time when hypoxia is forming. TN:TP ratios take into account all possible utilizable nutrient sources, and therefore, may allow a more complete assessment of nutrient limitation. Mean TN:TP ratios were higher than DIN:P_i ratios during all three cruises, indicating that P limitation may actually be more severe than thought from inorganic ratios alone. An analysis of multiple datasets of DIN:P_i and TN:TP ratios indicated that the latter is a more

useful measure of nutrient limitation, and that a TN:TP ≥50 indicates P limitation (Guildford & Hecky 2000). Using this criterium, P was limiting on all three cruises.

Another argument against P-limitation points to a P supply from the sediments, especially during periods of hypoxia, due to sulfate reduction and the release of P from sulfate-P complexes. However, bottom water P measurements on the shelf indicate no source of DOP from the sediments or transported from deeper waters (Rinker & Powell 2006).

Contour patterns of DIN:P_i were often opposite to those of TN:TP. The former are typically high near the rivers and lower at higher salinities. TN:TP in the river is near Redfield (Turner et al. 2006) and, therefore, close to 16 at the river mouths. However, riverine particulate phosphate sinks when it enters ocean waters (Fox et al. 1985), which results in lower TP at higher salinities, and as a result, higher TN:TP ratios at higher salinities as well. The higher TN:TP ratios than DIN:P_i, in combination with the low DOP concentrations seen during these cruises indicate that phytoplankton in this area are likely not able to use DOP to relieve P stress or support significant excess growth in combination with the unutilized N after P_i is drawn down. Finally, DOP distributions do not differ from conservative mixing, indicating no drawdown of DOP (Figs. 4.6 and 4.11). Therefore, DOP is likely not used as a huge source of P for phytoplankton on the Louisiana shelf.

Some investigators have used DIN:TP ratios for assessing nutrient limitation for this area (Rabalais et al. 2002b, Dodds 2006). Based on data from in the Mississippi, before its water reaches the Gulf, P was not considered limiting. One reason for using DIN:TP, rather than TN:TP or DIN:P_i, is the poor correlation between TP and P_i in the

river due to the high particulate P load in riverine waters. The correlation between TN and DIN is much better (Dodds 2006). Therefore, DIN:TP ratios may be more valuable in the river. Even so, the availability of particulate P to breakdown by phytoplankton and bacteria remains a relevant unknown for determining the bioavailability of the particulate P pool. We compared total nutrients to inorganic nutrients from our cruises to see if the correlations from the rivers were the same in ocean water (Fig. 4.12). In our samples, the correlation between TN and DIN was basically the same as that between TP and P_i. The relationship between TP and P_i was much better than in the river, and therefore we conclude that TN:TP ratios on the shelf are more accurate than DIN:TP and possibly more accurate than DIN:P_i as well. However, given the extra effort required to measure total nutrients than inorganics alone, the regression between total and inorganic nutrients indicates that DIN:P_i ratios are indeed useful in marine waters and may be used as an indicator of nutrient stress. It should also be noted that autochthonous OC production in the Mississippi River contributes only 12% of the total labile OC on the shelf, and only 4% of the carbon demand for the annual bottom water hypoxia (Green et al. 2006). Therefore, the production that occurs within in the river, where DIN:TP values are near Redfield, has little affect on hypoxia and it is the nutrient ratios on the shelf that are more important to understanding and controlling hypoxia. TN:TP and DIN:TP ratios on the shelf are therefore more useful measures of nutrient limitation for the production that drives hypoxia than DIN:TP in the river.

Alkaline phosphatase (AP) is an ectoenzyme found in gram negative bacteria and some phytoplankton. A protein in the pho regulon, it cleaves inorganic P from organic P-esters when environmental P_i becomes low (Torriani-Gorini 1994). The pho regulon

consists of a high affinity P transport system that is not transcribed when environmental P_i is replete and is induced when it is low, making AP an excellent indicator of P-limitation. When AP activity, as measured by a simple fluorescence assay, is high, this is an indication of P limitation. When it is low, P is not considered to be limiting. Taken together, nutrient concentrations, $DIN:P_i$ ratios and AP activity provide excellent evidence for the presence or lack of P limitation.
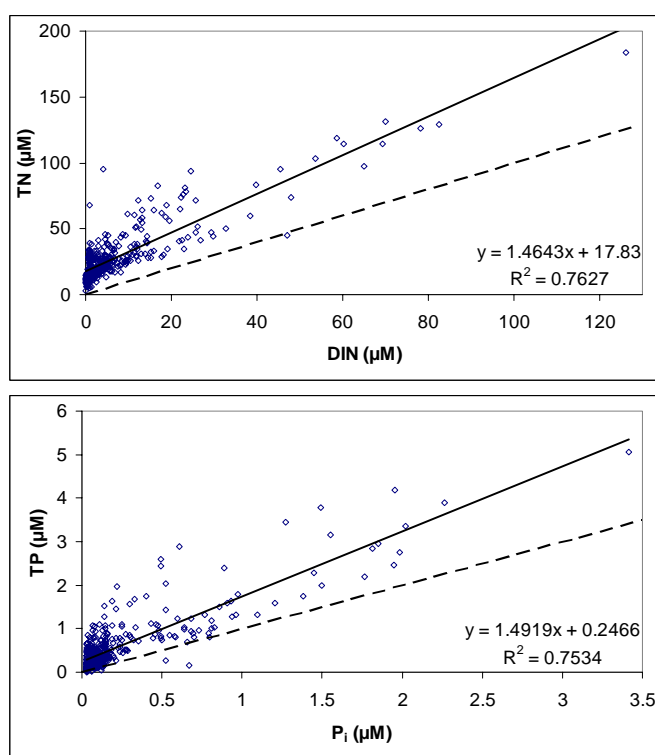
Figure 4.12. Total and dissolved inorganic N and P concentrations from all stations during this study. Dashed line is a 1:1 relationship (perfect correspondence between dissolved inorganic and total) and solid line is best fit relationship, as defined by equation at bottom right of each plot.

The presence of AP activity indicates that cells are able to use P-esters (C-O-P bond) as a source of P for growth. P-esters comprise 75% of marine high molecular weight (HMW) DOP, while phosphonates (C-P bond) make up the remaining 25% (Clark et al. 1998), and these can not be hydrolyzed by AP. Some *Synechococcus* have a gene that codes for phosphonates (Palenik et al. 2003), but as of yet, no strains have been shown to express it. *Trichodesmium* are the only phytoplankton so far proven to utilize phosphonates as a sole source of P for growth (Dyhrman et al. 2006), indicating that this portion of the HMW DOP may be highly refractory for most phytoplankton. HMW DOP comprises, on average, 35% of the DOP pool (Benitez-Nelson 2000). Therefore, excluding phosphonates as a source of bioavailable DOP, AP was capable of utilizing approximately 0.016, 0.025 and 0.035 μmol DOP L^{-1} in March, May and July, respectively, for growth. If you add this pool of potentially bioavailable DOP to P_i, it reduces $DIN:P_i$ ratios to 23, 35 and 22 for March, May and July, respectively. To date, knowledge about the composition and bioavailability of the LMW DOP pool is woefully inadequate, but it can be assumed that some portion of that pool is bioavailable as well, providing additional material for P utilization. Still, this would add, at most, 0.030, 0.046, and 0.067 μM P if the entire pool was bioavailable, which is not likely. It would appear that the DOP pool can aid in alleviating P stress, however, our estimate of bioavailable DOP is liberal, and these ratios do not consider lability of the DON pool.

AP activity displayed a hyperbolic relationship to P_i concentrations (Fig. 4.13). Activities were high when P_i was <0.30 μM, and low when P_i was >0.30 μM. This relationship was not evident with DOP. There were few stations where DOP was >0.40 μM, but it seems that there was not as dramatic a decrease in AP activity at higher DOP

concentrations. These field measurements confirm the use of AP as an indicator of P limitation which is induced under low P_i concentrations but is unresponsive to the concentrations of its substrate, DOP. While heterotrophic bacteria can use the carbon hydrolyzed from AP substrates, the presence of the DOC does not appear to have induced AP here. Plots of AP activity vs DOC show no correlation (data not shown). Contours of P_i and AP activity tend to be somewhat opposite, although there can be a biomass effect so that even when P_i is high, moderate to high AP activity may still be present. Our July contours are an excellent example of the expected relationship between P_i and AP activity and indicate that AP expression coupled with nutrient data can be a powerful indicator of P-limitation in field samples.
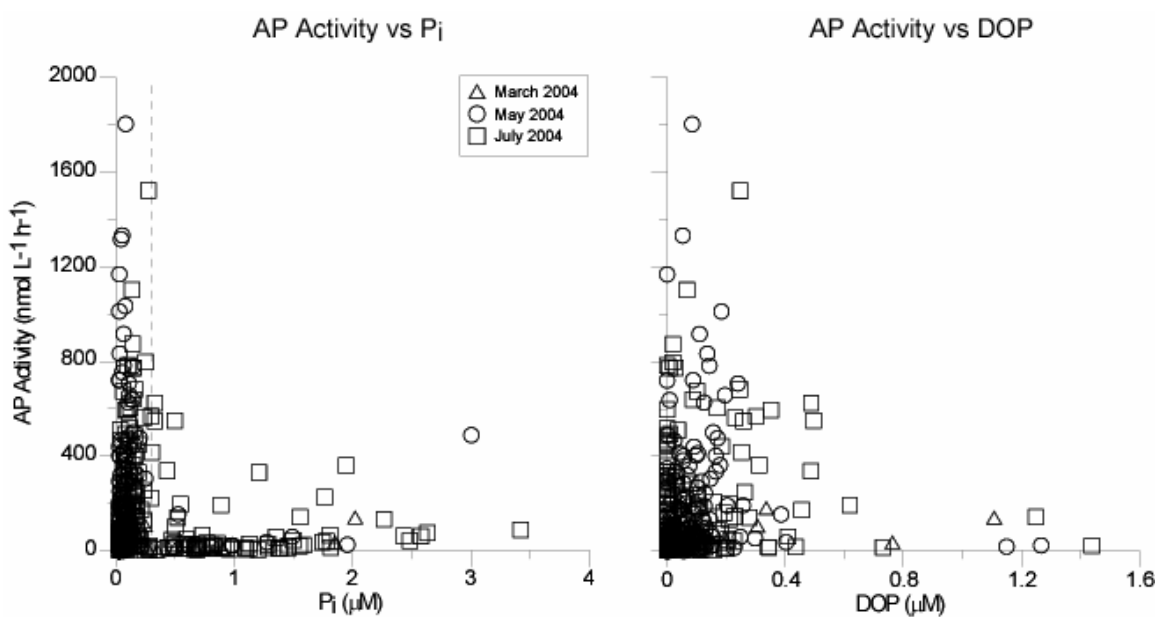
Figure 4.13. AP Activity vs P_i (left) and DOP (right) concentrations for all stations during 2004 cruises. The legend is the same for both plots. The dotted line indicates 0.30 μM P_i.

While measurement of AP activity has proved useful for detection of P-limitation in bulk water samples, it remains a black box measurement. The AP activity derived from the assay represents the entire phytoplankton and bacterial communities, combined. There is no distinction between functional groups or species. This is important because phytoplankton and bacteria can be differentially limited in some systems (Sundareshwar et al. 2003), and it would be useful to be able to discern at the least between the two groups and also more specifically between groups of phytoplankton or bacteria, if possible. Future studies focused on methods for separating AP activity into different functional groups would advance our understanding of P-limitation and stress in aquatic environments.

Past work has shown that there is an enrichment of dissolved organic carbon (DOC) at intermediate salinities in the GOM, likely supplied by blooms of phytoplankton at these salinities (Benner & Opsahl 2001). This study found DOC concentrations >300 μM in the Mississippi River and a decrease with salinity to <100 at full salinity during four cruises between 1990 and 1993, similar to our results, except for higher values in the river during our July cruise. In July 1993, DOC decreased steadily with increasing salinity (Pakulski et al. 2000). Highest values were ~440 μM DOC and the lowest concentrations, in full salinity seawater, was ~100 μM, slightly lower than our measured values in July 2004. Concentrations were similar in both rivers and plumes. Similar values were seen during two cruises to both river plumes in June 2000 and April 2001, but DOC was higher in the spring (April) then the summer (June), when discharge is lower (Chen & Gardner 2004).

Only a few prior studies investigated DON or DOP in this region, and these studies measured a limited number of stations in or near the rivers. DOP ranged from <0.10-0.30 in the Atchafalaya River and <0.10-0.20 in the Mississippi River and its plume in May 1992 (Kim 1996). Pakulski *et al.*(2000) found near zero DOP concentrations in the Atchafalaya River and a peak in concentrations at low salinity in the plume of 0.37 μM during July 1993. DOP decreased steadily with salinity to slightly under 0.20 μM at salinity 26. These values are similar to those found during July 2004. The same study found DON concentrations ranging from ~10-23 μM and ~15-26 μM in the Mississippi and Atchafalaya Rivers and plumes, respectively.   There was no correlation between concentration and salinity for DON. Conversely, we found higher DON near the Mississippi in July, but distributions were similar to those in July 1993 during our May cruise. DOP in the lower Mississippi River was 0.5-0.6 μM during April and November 1999 (Sutula et al. 2004). In one of the few complete studies of DOP in the MRP, concentrations ranged from >2.0 μM at Head of Passes to <0.3 μM (the detection limit for this study) at most stations with salinity ≥30 during March and October 2002 (Rinker & Powell 2006). These authors found little difference in DOP concentrations between the two cruises. Interestingly, DIN:P_i ratios from this study showed many stations with ratios >16 in March but all stations <16 in October, during the lowest annual discharge. DON:DOP ratios showed little variation between the two cruises.

The eutrophication seen on the Louisiana shelf is not unique, similar conditions exist now or did in the recent past in Chesapeake Bay, the northwest shelf of the Black Sea, the Neuse River estuary, and the Pearl River estuary in China (Yin et al. 2000, Mee

2001, D'Elia et al. 2003, Paerl et al. 2004). The Patuxent River in Maryland was one of the first river basins in the United States where nutrient control strategies were developed in response to anthropogenic induced eutrophication (D'Elia et al. 2003). Symptoms of eutrophication included significant increases in nutrient load and Chl *a* concentrations in tandem with decreased bottom water O_2 concentrations, primarily resulting from a twenty-fold increase in population in the watershed and the coincident increase in sewage. Dual controls of N and P here have seemingly prevented further degradation of the system, although it will take more time to see if they lead to any significant improvements in water quality. The neighboring Choptank River, also a tributary to Chesapeake Bay, has seen increased levels of eutrophication in recent years as a result of increasing agriculture in its watershed, as opposed to population increase, but the end result of increased nutrients, Chl *a* and bottom water hypoxia are the same (Fisher et al. 2006). The nutrient controls in the Chesapeake indicate that nutrient controls can have a positive affect, but lawmakers must insist more drastic controls for real results to occur.

The northwest shelf of the Black Sea is host to the discharge from several large rivers, including the Danube, with a watershed including seventeen countries (Mee 2001). Like the Mississippi, agricultural and livestock runoff in the region led to eutrophication and summertime bottom water anoxia. Shifts in dominant phytoplankton and zooplankton species also resulted from the ecosystem alteration (Mee, 2001 and references therein). In the 1990s, as a result of the economic collapse of the former Soviet Union, nutrient inputs to the rivers that empty feed the shelf decreased dramatically and a reprieve in anoxia was evident. This is another promising example where nutrient reductions yielded increased water quality, but there is some worry that as the area recovers economically,

the current improvements may prove transient. A recent look at the system indicated springtime P limitation due to high nitrogen loads at mid-salinities in the region and summertime N limitation as discharge, and therefore N loading, decreased (Ragueneau et al. 2002). This analogous situation to the Louisiana shelf points to a need for dual nutrient control for successful reduction of summertime anoxia on the Black Sea shelf.

The Neuse River estuary in North Carolina, USA, is an example of the dangers of single nutrient reductions as well as the success of dual nutrient controls (Paerl et al. 2004). Here, reductions in P alone in an effort to reduce algae blooms in P limited estuarine waters resulted in transport of unused N downstream to N limited waters, causing algae blooms downstream rather than upstream. Implementation of N reductions to complement the P controls provided promising preliminary results and highlighted the need for reductions in both N and P to effectively combat eutrophication. Experiments showed seasonal P limitation in the Pearl River in China near Hong Kong, but efforts to reverse the trend of eutrophication here are absent (Yin et al. 2000).

It is clear from this and earlier work on the Louisiana shelf that P limits the amount of biomass during the spring and early summer as a result of excessive N loading. Therefore, dual controls of N and P appear to be the best solution to mitigating eutrophication here. This is in agreement with the management strategies employed in Chesapeake Bay and the Neuse River estuary. A recent review, focusing on N reductions, suggested the combination of three management strategies: 1. reduction of N fertilizer use through more careful application and reduction of extra, or insurance, fertilizer application, 2. creation of targeted riparian zones and wetlands to remove nutrients from groundwater before it reaches the Mississippi River, and 3. management of

planned river diversions through swamps near the river delta to remove nutrients from the water before it reaches the Gulf (Mitsch et al. 2001). While these practices would certainly reduce the amount of N reaching the Gulf, they are quite ambitious and even so, neglect P controls. Also, N reduction targets are easier said than done. Even in the Chesapeake, which is a much smaller basin, the targeted reductions of 40% have been met with actual reductions of only <20% (Fisher et al. 2006). Luckily, P loads are more easily reduced than N loads through point source treatment plants, especially from sewage (Conley 2000). The Task Force, whose purpose it is to develop and implement strategies to reduce hypoxia in the Gulf, decided that a 30% reduction in N load would be necessary to reduce the size of the annual hypoxic zone to <5000 km^2 (Force 2001). A recent reassessment of this document indicated that P reductions would also be necessary and called for N reductions closer to 40%. Given the magnitude of the problem, along with opposition from parties who value their financial interests over environmental activism, it may be years before we see an improvement in water quality on the Louisiana shelf.

We measured inorganic, organic and particulate nutrient distributions as well as Chl *a* and AP activities on the Louisiana continental shelf during the spring and summer of 2004. Our results provide important data for guiding the decisions of policy makers. The inorganic nutrient and Chl *a* distributions bolster results from previous work indicating P limitation of phytoplankton biomass in the spring and early summer (Sylvan et al. 2006). Data from TN and TP distributions indicated phytoplankton are indeed P limited. DOP and TP distributions did not reveal a source of P large enough to rescue phytoplankton from P limitation. The P limitation here is driven by excess N loading and

dual nutrient control strategies are likely necessary to help mediate the annual bottom water hypoxia. The anthropogenically induced eutrophication on the Louisiana shelf is not unique and restoration of water quality in other areas such as Chesapeake Bay and the Black Sea indicate that dual nutrient controls can indeed instill positive change when intelligently implemented.

5.0 Diversity and Biogeography of the gene *pstS* in Marine *Synechococcus spp.*

Abstract

42 clones of *pstS*, the gene encoding the periplasmic phosphate binding protein of the Pho regulon, were isolated from marine *Synechococcus* in the Gulf of Mexico and Sargasso Sea. Sequences from the same samples were most closely related and diversity was positively correlated with nutrient level in the samples. This pattern held up when previously sequenced samples from other locations were incorporated into our dataset.

5.1 Introduction

Phosphorus (P) can limit phytoplankton biomass in parts of the ocean, making a complete understanding of how phytoplankton assimilate P vital to our knowledge of the global carbon cycle. Phosphate (PO_4^{3-}) is the most desirable form of P to microbes, but dissolved organic phosphorus (DOP) may be utilized by species that have genes enabling them to do so when PO_4^{3-} concentrations are low (Dyhrman et al. 2007). *pstS* is a periplasmic gene that encodes the phosphate binding protein of the Pho regulon, a system of genes induced by low environmental PO_4^{3-} concentrations, which collectively enable cleavage of PO_4^{3-} from phosphate esters and import of the released PO_4^{3-} into the cell (Torriani-Gorini 1994).

pstS is found in cyanophages (Sullivan et al. 2005) as well as phytoplankton and gram negative bacteria. A recent metagenomics study found *pstS* to be more common in two samples from the Pacific Ocean than two samples from the Atlantic Ocean, where PO_4^{3-} concentrations are generally lower, indicating *pstS* may be lost or gained in genomes depending on local PO_4^{3-} availability (Rusch et al. 2007). We sampled diversity

of *pstS* in *Synechococcus* species at three stations, two on the eutrophic Louisiana shelf and one in the oligotrophic Sargasso Sea at the Bermuda Atlantic Time Series (BATS) station.

5.2 Materials and Methods

Samples from the Gulf of Mexico (GOM) were collected from over the side of the boat with a bucket that was first rinsed three times with sample water. Water was filtered onto 0.2 μm Sterivex filters (Millipore) using a Cole-Parmer peristaltic pump and acid washed Teflon tubing. Filtrate was collected for five minutes and then the Sterivex cartridge was sealed at the bottom with clay and at the top with an autoclaved plastic screw cap, after which the cartridge was immediately dropped into liquid nitrogen. The sample from the BATS station was collected with a Niskin bottle and filtered the same as the GOM samples. Following the cruise, the samples were transferred from liquid nitrogen to a -80° C freezer. DNA was extracted with the PUREGENE Genomic DNA Isolation Kit (Gentra Systems) using the manufacturer's instructions. *pstS* genes were amplified using the primers Syn_pstS f (5'-GATYTAYCAGCGYTGGTT-3') and Syn_pstS r (5'CCGATCTTGTTCACAGC-3'). The PCR protocol was: 1 cycle of 94˚C for 10 minutes, 25 cycles of 94 ˚C for 1 minute, 50˚C for 1 minute and 72˚C for 1 minute, concluding with a final step of 72˚C for 10 minutes. PCR products were cloned using TOPO TA Cloning Kit for Sequencing (Invitrogen) and clones were screened by digestion with AluI at 37˚ for 4 hours before comparison of banding patterns by electrophoresis. Further sequences were obtained from the CAMERA database's Global Ocean Sampling (GOS) project samples (http://camera.calit2.net) using BlastX against

known *pstS* sequences. Alignments were made using protein sequences in ClustalX and phylogenies were built in Mr. Bayes from 293 unique sites (Ronquist & Huelsenbeck 2003).

5.3 Results and Discussion

We amplified 42 unique *pstS* sequences from three samples. Eleven sequences with ≥97% identities to known genomic strains were considered the same as the genomic sequences and excluded from our phylogenetic analysis. In a recent study comparing genomes of wild strains of *Arabidopsis thaliana* with that of the sequenced lab grown strain, there was an average of 4% difference between the reference genome and the others, and a sequence polymorphism approximately every 180th base (Clark et al. 2007). *A. thaliana* has a compact genome for a higher plant, indicating this level of variation may also occur in *Synechococcus* species, making a 97% cutoff reasonable. Twelve unique sequences with <97% identities to known sequences were identified in the CAMERA database.

The *pstS* sequences showed geographical patterns (Fig 1). *Synechococcus* WH8102 dominated the sequences from the Sargasso Sea. Eleven of twelve sequences recovered from the Sargasso Sea were most similar to this species, and nine of those shared ≥97% identities to WH8102. However, only four of thirty sequences from the GOM showed highest similarity to WH8102, one with ≥97% identities. The sequences isolated that most resembled *Synechococcus* RS9917 were almost exclusively from the GOM, except for 8 sequences collected near the Galapagos Islands, on the equator in the eastern Pacific. Within the GOM samples, the sequences from GOM st.30 (MRP plume

samples in Fig. 1) grouped in a cluster on the tree, and most of those from GOM st.102 (shelf samples in Fig. 1) also grouped tightly, although there are a few scattered in other branches of the tree. While our sequences may show PCR bias towards sequences from some species, the sequences from the GOS database were generated using shotgun sequencing, which does not have PCR bias. Therefore, we conclude that the geographical patterns seen in our samples are real. Although *Synechococcus* is a globally distributed species, there do appear to be regions where some species are more common than others.

In a sub-sample of the GOS dataset, abundance of *pstS* sequences were greater in *Prochlorococcus marinus* and *Pelagibacter ubique* in waters with less PO_4^{3-} (Rusch et al. 2007). We found more diversity in waters with greater PO_4^{3-}. Metadata for the samples is in Table 1. PO_4^{3-} concentrations, Chl *a* concentrations and AP activity in our three samples, in ascending order is BATS<GOM102<GOM30. The number of different sequences according to closest BlastX hit was 2, 3 and 6 in the BATS, GOM102 and GOM30 samples, respectively. This indicates that there may be a connection between higher diversity and higher PO_4^{3-} as well. This is not surprising, and likely related to increased diversity with greater resources (or nutrients). At sites considered oligotrophic, there was less diversity in the *pstS* gene than more eutrophic sites. This is true of the microbial community in general.

Measurement of alkaline phosphatase (AP) activity, the pho regulon enzyme commonly assayed for in environmental samples, has proved useful in detection of P-stress, but it remains a black box measurement. The AP activity derived from this assay represents the combined phytoplankton and bacterial communities (Dyhrman et al. 2007).

Phytoplankton and bacteria can be differentially limited in some systems (Sundareshwar et al. 2003) so it is important to be able to discern between the two groups and also more specifically between groups of phytoplankton or bacteria, if possible. Whereas AP appears to be poorly conserved, and therefore a poor target for PCR studies, *pstS* has conserved regions and is amenable to isolation from environmental samples, as shown here, making it a good candidate to probe multiple groups or species for P-stress.

This work is an initial step towards creating a molecular taxonomic assay for environmental P-stress. Our study indicates that *pstS* would be a good candidate gene to use on a microarray for expression, where positive expression would be indicative of P-stress. Combining data from sequenced genomes and the CAMERA database, it is now possible to build a virtual clone library from which to include sequences on an array. This study also revealed previously unknown sequence diversity of *pstS* in marine *Synechococcus*, as well as regional dominance of specific sequences in different geographical samples.
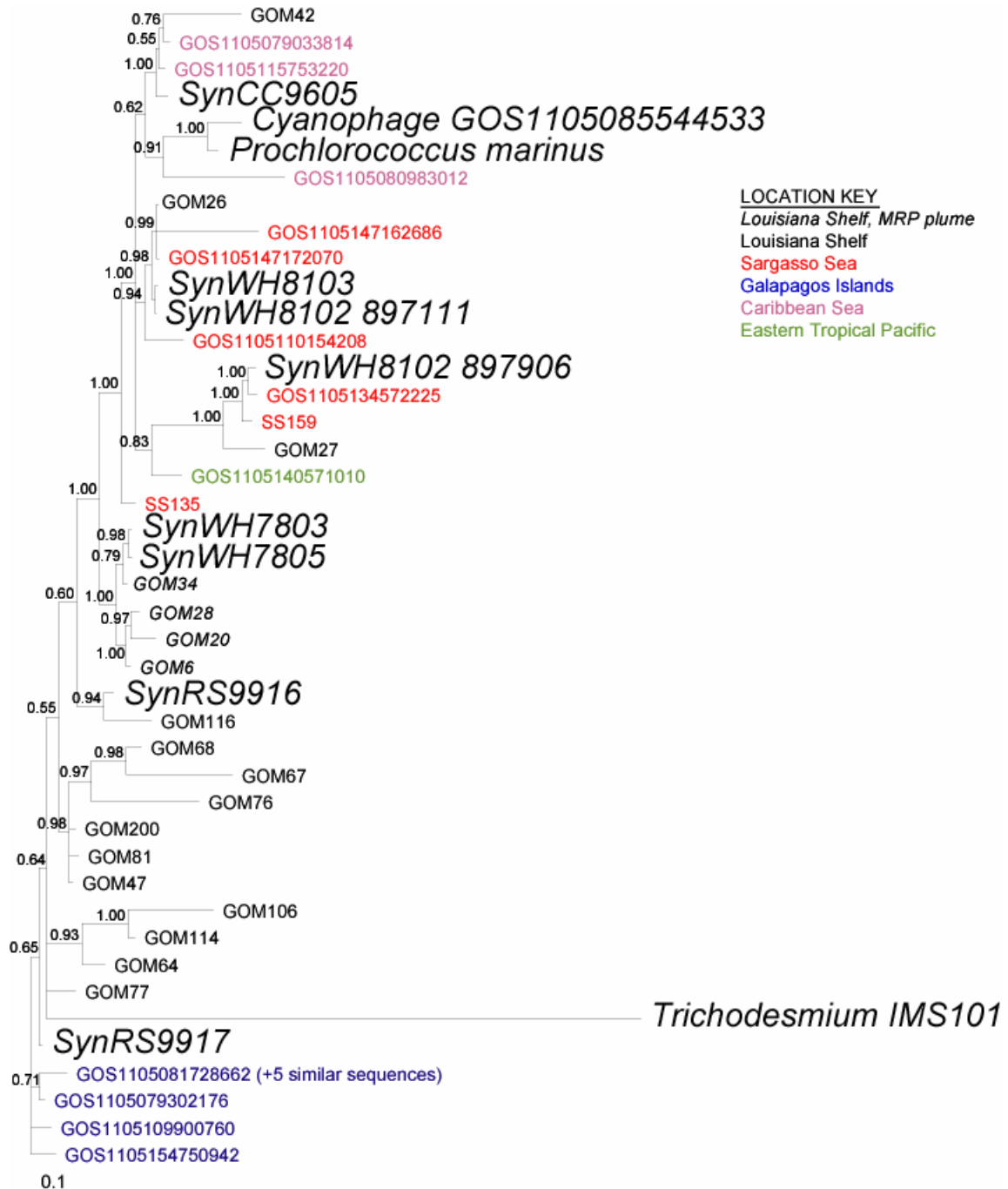
Fig 5.1. Bayesian tree based on *pstS* sequences from *Synechococcus spp.* *P. marinus* and cyanophage genes were included as close relatives to close relatives to *Synechococcus* and *Trichodesmium* IMS101 was included as an outgroup. GOM (Gulf of Mexico) and

SS (Sargasso Sea) samples were sequenced during this study, GOS sequences are from the CAMERA database. A gamma rate substitution model was used. Numbers at nodes indicate posterior probability values as determined by Mr. Bayes.

Table 5.1. Station data for samples where DNA was collected. Latitude is in ˚N, longitude is in ˚W, DIN, DON, TN, P_i, DOP and TP are in µmol L^{-1}, Chl a is in µg L^{-1}, and APA (alkaline phosphatase activity) is in nmol L^{-1} h^{-1}. bd= below detection.

Station	Date	Latitude	Longitude	DIN	DON	TN	P_i	DOP	TP	Chl a	APA
GOM 30	17 July 04	28.6468	89.6214	11.602	20.598	50.5771	0.253	0.020	0.4508	3.3987	18.54
GOM 102	19 July 04	28.4117	90.7073	6.639	14.4630	34.2335	0.064	0.158	0.9652	2.6435	9.33
BATS	19 May 06	31.75	64..1667	bd	bd	bd	0.001	0.126	0.144	0.074	9.13

6.0 Conclusion

In this dissertation, three approaches to studying nutrient limitation in phytoplankton were applied to the Louisiana continental shelf in an effort to understand the causes of eutrophication there and elucidate ideas for possible management strategies. FRRf is now a commercially available technology, enabling a growing number of scientists to use it in their experiments. This work was the first to use FRRf to investigate P-limitation in the field. The results were very successful in the incubation experiments, and less clear cut in the mapping work. Phytoplankton underwent and increase in F_v/F_m and p and a decrease in σ_{PSII} and τ_{Qa} in incubations with P added but not in those with the addition of N alone. Coupled with an increase in Chl a concentrations in response to P additions, this is strong evidence for P-limitation in the MRP. FRRf results were less clear when used to map phytoplankton response to eutrophication across the shelf, but DIN:P_i ratios, Chl a concentrations and AP activities were indicative of P-limitation on the shelf. This was the first investigation of how the four FRRf parameters measured interact with each other over a large area of the ocean. The heterogeneous nature of the area sampled and rapid response time of FRRf parameters are a likely reason for the low correlations between FRRf parameters and basic water parameters. It would be great to see more studies like this and Moore et al. (2003, 2005) that compare multiple FRRf parameters on the shelf. FRRf has proven useful to study changes as a result of environmental perturbation in oligotrophic waters (Boyd & Abraham 2001, Behrenfeld et al. 2006, Benitez-Nelson et al. 2007) and its aspects remain optimistic in waters like the Louisiana shelf, but more studies will be necessary to pinpoint its strengths and weaknesses in a heterogeneous regime.

The three cruises in 2004 provided a wealth of data on nutrient cycling on the Louisiana shelf. Altogether, 400-500 samples of each parameter were measured, providing an excellent picture of riverine impact on nutrient distributions. This work illustrated that in this area, high $DIN:P_i$ ratios are mirrored by even higher TN:TP ratios. While AP activities were high, DOP, the substrate for AP, was commonly lower than P_i, indicating that the DOP pool is unlikely to alleviate P-limitation in this area. These three cruises expanded on the work of Sylvan et al. (2006) and bolstered the overall conclusion that P limits phytoplankton biomass on the Louisiana shelf during the spring and early summer. This P limitation occurs during the period of hypoxia formation as a result of excess N loads delivered by the rivers, indicating that controls of both N and P are necessary to reduce the size of the hypoxia. Partly as a result of the FRRf work and that of Sylvan et al. (2006), the task force to reduce hypoxia in the Gulf of Mexico will suggest drastic reductions of N **and** P in the Mississippi River in the update to their original action plan, which suggested only cuts to N loads. While there are certainly more questions that need to be answered about the biogeochemistry of this area, including addressing the possibility of P release from hypoxic/ anoxic sediments and the possibility of offshore P sources, there is certainly enough data available to start taking action

Multiple new *Synechococcus spp. pstS* sequences were found in samples from the GOM and Sargasso Sea. This indicates that there may be strains of *Synechococcus spp.* still unknown or possibly that this gene is very diverse between within species. Using sequences from my work and the CAMERA database from around the world, it seems that this gene is conserved geographically. This study provided a suite of DNA

sequences that can be used in expression studies as an assay for P-limitation in *Synechococcus*. One could make a microarray with these and sequences from other organisms to test for taxonomic differences in response to P-limitation as a logical next step for this work.

Eutrophication and bottom water hypoxia are serious environmental problems on the Louisiana continental shelf as well as many other estuaries worldwide. The work presented here is of interest for both basic science and remediation of these problems. It is my hope that this work and other studies like it will allow policymakers to implement successful programs for remediation of these problems.

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Appendix

Metadata from July 2002, March 2004, May 2004 and July 2004 cruises. Included from each cruise is nitrate + nitrite (NO_x), ammonium, dissolved inorganic nitrogen ($DIN = NO_x + NH_4^+$), and inorganic phosphate (P_i) concentrations, chlorophyll a (Chl a) concentrations, and alkaline phosphatase (AP) activities. Metadata from the 2004 cruises includes total dissolved phosphorus (TDP), dissolved organic phosphorus ($DOP = TDP - P_i$), particulate phosphorus (PP), total phosphorus ($TP = PP + TDP$), total dissolved nitrogen (TDN), dissolved organic nitrogen ($DON = TDN - DIN$), particulate nitrogen (PN), total nitrogen ($TN = PN + TDN$), silicate (Si), dissolved organic carbon (DOC), particulate carbon (PC) and suspended particulate matter (SPM) in addition to the above parameters. Fast repetition rate fluorometry parameters measured during July 2002 are included where measured. All nutrient concentrations are in μM, Chl a is in $\mu g\ L^{-1}$, AP activity is in $nmol\ L^{-1}\ h^{-1}$, SPM is in $mg\ L^{-1}$, F_v/F_m and p are dimensionless, σ_{PSII} is in $\mathring{A}^2$ quanta^{-1}, and τ_{Qa} is in μsec.

A1.1 July 2002 Metadata, Part 1

Station	Longitude	Latitude	Salinity	NO_x	$NH_4^\pm$	DIN	P_i
1	-88.9559	29.1265	24.22	6.44	1.63	8.07	0.35
3	-88.9058	29.24	29.64	0.07	0.2	0.27	0.14
4	-88.8104	29.2058	29.67	1.105	0.16	1.265	0.3
5	-88.7114	29.1667	26.56	0.88	0	0.88	0.18
6	-88.6551	29.1456	28.04	0.09	0.11	0.2	0.3
9	-88.8644	29.0418	32.92	0.02	0	0.02	0.06
10	-88.9591	28.994	28.49	1.14	0	1.14	0.26
11	-88.972	28.9249	29.28	0.63	0	0.63	0.029
13	-89.2041	28.8983	20.20	10.37	0.12	10.49	0.03
14	-89.31	28.8646	14.01	57.08	1	58.08	0.81
15	-89.3857	28.8167	29.61	10.36	0	10.36	0.029
17	-89.5209	28.7317	33.82	0.81	0	0.81	0.029
18	-89.5822	28.7817	26.38	12.04	0	12.04	0.08
19	-89.5597	28.8584	10.98	95.49	0.44	95.93	1.77
20	-89.5376	28.9334	15.89	24.55	0.23	24.78	0.029
21	-89.52	28.9925	18.06	19.78	1.34	21.12	0.029
22	-89.5029	29.0584	14.82	36.22	0.25	36.47	0.18
23	-89.4883	29.101	16.44	19.45	1.82	21.27	0.029
24	-89.5616	29.0573	18.97	13.07	0.33	13.4	0.029
25	-89.6125	29.0005	20.02	12.33	1.23	13.56	0.32
26	-89.6445	28.9459	19.35	9.69	0.41	10.1	0.029
27	-89.6706	28.9011	12.71	66.16	0.26	66.42	0.4
28	-89.6912	28.8658	13.98	40.51	0.45	40.96	0.15
29	-89.7095	28.8475	15.91	30.62	0.12	30.74	0.25
30	-89.7318	28.8058	19.32	15.97	0.64	16.61	0.029
31	-89.7506	28.7748	36.13	0.29	0	0.29	0.09
32	-89.7565	28.8304	19.14	23.55	0.29	23.84	0.029
33	-89.7621	28.8813	15.49	28.73	0.13	28.86	0.029
34	-89.7681	28.9348	14.08	40.67	0.08	40.75	0.029
35	-89.7749	28.9957	15.40	31.4	0.17	31.57	0.09

Station	Longitude	Latitude	Salinity	NO$_x$	NH$_4^{+}$	DIN	P$_i$
36	-89.7808	29.0398	15.23	30.99	0.43	31.42	0.029
37	-89.7867	29.0931	20.27	2.65	0	2.65	0.09
38	-89.793	29.1515	20.25	3.92	0.29	4.21	0.03
39	-89.7994	29.2096	18.30	11.32	0	11.32	0.029
40	-89.8022	29.2556	8.76	51.35	0.71	52.06	0.43
41	-89.8239	29.2108	8.82	19.35	0.08	19.43	0.029
42	-89.8519	29.1519	8.80	0.95	0.37	1.32	0.07
43	-89.8793	29.0942	8.78	13.97	0	13.97	0.029
44	-89.9073	29.035	8.77	19.64	0.33	19.97	0.05
45	-89.9321	28.9829	8.76	22.3	0	22.3	0.029
46	-89.9538	28.9491	8.76	17.28	0.77	18.05	0.029
47	-89.9665	28.9195	21.23	13.55	0	13.55	0.029
48	-89.9935	28.8619	31.59	2.17	0	2.17	0.37
50	-90.045	28.7528	34.75	0.57	0	0.57	0.029
51	-90.0614	28.7029	35.70	0.38	0	0.38	0.029
52	-90.0846	28.6522	36.05	0.59	0	0.59	0.029
53	-90.1051	28.6496	36.11	0.41	0	0.41	0.029
54	-90.1063	28.6973	36.03	0.71	0	0.71	0.029
55	-90.1075	28.749	35.00	0.4	0	0.4	0.029
56	-90.1091	28.8174	33.67	0.49	0	0.49	0.029
57	-90.1101	28.8525	33.66	0.41	0	0.41	0.12
58	-90.112	28.909	33.53	0.51	0	0.51	0.029
59	-90.1058	28.9549	33.16	0.71	0	0.71	0.029
60	-90.1143	29.0021	28.55	3.99	0	3.99	0.029
61	-90.1154	29.0242	27.20	8.68	0.14	8.82	0.029
62	-90.1175	29.0719	21.82	16.29	0.38	16.67	0.029
63	-90.1201	29.0981	20.16	14.13	0.29	14.42	0.2
64	-90.148	29.0536	22.45	12.61	0.11	12.72	0.029
65	-90.1746	29.0104	30.31	2.52	0	2.52	0.029
66	-90.2012	28.9681	32.08	0.67	0.19	0.86	0.029
67	-90.2311	28.9204	31.94	0.32	0	0.32	0.04
68	-90.2578	28.8776	32.04	0.52	0	0.52	0.029
69	-90.2773	28.8466	32.55	0.36	0.36	0.72	0.029
70	-90.3048	28.8516	33.23	0.55	0.05	0.6	0.029
71	-90.335	28.8948	31.69	0.45	0.19	0.64	0.23
72	-90.7272	29.3071	24.28	6.22	0.47	6.69	0.029
73	-90.404	28.9936	20.84	10.16	0.69	10.85	0.029
74	-90.4276	29.0138	21.52	10.26	0.67	10.93	0.029
75	-90.4663	28.9608	21.24	9.5	0.4	9.9	0.029
76	-90.5052	28.9064	28.64	1.73	0.54	2.27	0.07
78	-90.5815	28.8002	26.89	4.39	0.97	5.36	0.08
79	-90.6302	28.7326	29.39	0.39	0.24	0.63	0.029
80	-90.6638	28.6857	32.90	0.91	0.65	1.56	0.029
82	-90.6889	28.7617	28.88	1.36	0.63	1.99	0.029
83	-90.6975	28.7988	27.74	4.01	0.59	4.6	0.029
84	-90.7072	28.8493	25.17	6.86	1.3	8.16	0.029
85	-90.7174	28.9016	22.52	6.54	1.5	8.04	0.029
86	-90.7278	28.9547	22.40	6.94	1.53	8.47	0.04
87	-90.7352	28.9935	21.46	1.54	1.15	2.69	0.029

Station	Longitude	Latitude	Salinity	NO$_x$	NH$_4^\pm$	DIN	P$_i$
88	-90.7643	28.9532	22.41	5.14	1.12	6.26	0.029
89	-90.7951	28.9096	22.90	6.5	1.13	7.63	0.029
90	-90.8326	28.8586	23.32	6.6	1.65	8.25	0.21
91	-90.8598	28.8195	24.00	6.96	1.23	8.19	0.18
92	-90.8843	28.7858	25.45	5.77	1.48	7.25	0.13
93	-90.9103	28.7491	26.48	2.09	0.76	2.85	0.029
94	-90.9375	28.7103	25.51	4.41	1.45	5.86	0.12
95	-90.9673	28.6681	26.02	2.93	0.81	3.74	0.26
96	-90.9978	28.6246	31.00	1.27	0	1.27	0.17
97	-91.0257	28.5846	35.09	0.67	0	0.67	0.25
98	-91.0492	28.6084	35.47	0.44	0	0.44	0.22
99	-91.0912	28.6543	32.11	0.74	0	0.74	0.11
100	-91.1376	28.7053	27.66	2.02	0	2.02	0.04
101	-91.1819	28.754	25.25	3.69	0	3.69	0.08
102	-91.2172	28.794	25.64	3.61	0.1	3.71	0.1
103	-91.2585	28.839	25.82	2.05	0	2.05	0.17
104	-91.3037	28.888	26.48	1.55	0	1.55	0.029
105	-91.3478	28.936	27.59	0.61	0	0.61	0.27
106	-91.3922	28.9842	21.77	7.64	1.35	8.99	0.029
107	-91.418	29.0126	21.37	4.98	0.2	5.18	0.18
108	-91.4627	29.0606	20.28	8.04	0.52	8.56	0.3
109	-91.5034	29.1046	21.16	2.81	0	2.81	0.029
110	-91.5484	29.1532	21.58	5.68	0.76	6.44	0.029
111	-91.573	29.1684	21.57	4.39	0.69	5.08	0.029
112	-91.6018	29.1165	22.53	2.02	0.32	2.34	0.03
113	-91.6304	29.0665	28.72	1.18	0	1.18	0.16
114	-91.6601	29.015	31.52	0.42	0	0.42	0.03
115	-91.6889	28.9646	29.95	2.55	0	2.55	0.17
116	-91.6992	28.9457	30.08	2.69	0.24	2.93	0.09
117	-91.7397	28.8762	31.53	1.59	0	1.59	0.15
118	-91.7713	28.8207	34.88	0.49	0	0.49	0.18
119	-91.7963	28.7774	34.39	0.31	0	0.31	0.05
120	-91.821	28.7341	34.55	0.45	0	0.45	0.45
121	-91.8439	28.7285	34.56	0.22	0	0.22	0.08
122	-91.8929	28.765	34.87	0.49	0	0.49	0.07
123	-91.9416	28.8012	35.71	0.24	0	0.24	0.18
124	-91.9851	28.8337	35.56	0.62	0	0.62	0.13
125	-92.0406	28.8752	33.40	0.83	0	0.83	0.3
127	-92.1234	28.9367	33.86	0.43	0	0.43	0.16
128	-92.1801	28.9791	34.48	0.61	0	0.61	0.03
129	-92.2346	29.0194	33.76	0.45	0	0.45	0.029
130	-92.2906	29.0613	33.62	0.7	0	0.7	0.04
131	-92.3435	29.1006	31.89	0.32	0	0.32	0.18
132	-92.4027	29.1444	28.24	0.52	0.05	0.57	0.14
133	-92.4845	29.2052	25.44	1.42	0	1.42	0.08
134	-92.5297	29.2422	25.01	1.88	0	1.88	0.029
135	-92.5308	29.3053	25.26	1.73	0	1.73	0.029
137	-92.5328	29.4098	25.70	1.32	1.56	2.88	0.08
138	-92.5341	29.4744	18.68	10.73	0.61	11.34	0.57

Station	Longitude	Latitude	Salinity	NO$_x$	NH$_4^\pm$	DIN	P$_i$
139	-92.5352	29.5303	6.83	78.52	0.25	78.77	1.97
140	-92.5256	29.5072	7.03	61.13	0.59	61.72	1.71
141	-92.4988	29.4536	17.28	18.37	0.35	18.72	1.17
143	-92.4778	29.404	24.85	1.48	0.69	2.17	0.029
144	-92.4545	29.3453	25.66	6.15	0	6.15	0.029
145	-92.4059	29.2344	24.80	1.79	0	1.79	0.19
146	-92.3248	29.1779	26.22	0.69	0.2	0.89	0.14
147	-92.2121	29.1195	25.83	0.74	0.18	0.92	0.11
148	-92.0909	29.0902	23.66	0.85	0.48	1.33	0.09
149	-92.0598	29.0834	18.91	6.42	0.63	7.05	0.029
150	-91.9224	29.0497	30.82	1.28	6.66	7.94	0.24
151	-91.7989	29.0196	31.63	0.87	0	0.87	0.29
152	-91.7171	29.0012	30.08	0.61	1.16	1.77	0.029
153	-91.5804	28.9665	27.74	0.89	0.29	1.18	0.23
154	-91.4679	28.9599	28.53	0.86	0.36	1.22	0.029
155	-91.3515	28.9544	26.55	1.08	0.37	1.45	0.18
156	-91.2189	28.9468	21.53	2.79	1.01	3.8	0.22
157	-91.0826	28.9485	20.61	0.24	0.23	0.47	0.06
158	-90.9437	28.953	23.64	5.42	0.32	5.74	0.03
159	-90.8275	28.9572	22.89	5.77	6.8	12.57	0.029
160	-90.7056	28.965	22.09	6.14	1.83	7.97	0.21
161	-90.5854	29.022	21.36	5.17	0.58	5.75	0.029
mean			**25.17**	**8.28**	**0.44**	**8.72**	**0.15**
median			*25.68*	*2.09*	*0.17*	*2.65*	*0.05*

A1.2 July 2002 Metadata, Part 2

Station	DIN:P$_i$	Chl a	AP Activity	F$_v$/F$_m$	σ$_{PSII}$	p	τ$_{Qa}$
1	23.06	38.32					
3	1.93	6.26		0.3395	282.21	0.20938	691.24
4	4.22	12.45					
5	4.89	17.49					
6	0.67	15.92	52.38				
9	0.33	0.56	13.34				
10	4.38	10.78	74.92				
11	21.72	3.73	22.76	0.3598	214.9333	0.18	344
13	349.67	37.90	55.88	0.3201	221.9	0.122	543
14	71.70	12.45	0.00	0.3129	214.3	0.1667	592.6667
15	357.24	21.76	0.00	0.3124	208.9	0.1237	475.6667
17	27.93	7.99	0.00	0.3066	192.325	0.1258	409.75
18	150.50	21.05	21.04	0.2959	202.7	0.207	564.3333
19	54.20	13.57	0.76	0.3131	196.625	0.1193	502
20	854.48	22.66	22.76	0.3114	210.8	0.166	502
21	728.28	14.90	22.72				
22	202.61	20.21	7.70				
23	733.45	18.13	23.14	0.4788	206.7195	0.381927	467.9024
24	462.07	13.23	30.61				
25	42.38	11.50	92.52				
26	348.28	15.14	30.88				
27	166.05	23.68	54.24				
28	273.07	25.65	67.64	0.474705	196.359	0.389179	448.3846
29	122.96	28.30	13.45	0.465226	198.4516	0.388	427.5806
30	572.76	36.60	53.77	0.429238	217.3269	0.333692	394.5385
31	3.22	0.90	60.17	0.395244	195.0306	0.310444	443.0833
32	822.07	41.44	28.49				
33	995.17	38.03	50.41				
34	1405.17	38.03	26.94				
35	350.78	23.90	24.30				
36	1083.45	51.78	30.67				
37	29.44	18.87	6.44				
38	140.33	12.93	21.81	0.391012	226.2326	0.230465	484.5814
39	390.34	14.20					
40	121.07	24.68	28.16	0.4788	215.3	0.411	379
41	670.00	26.81	11.72	0.447	207.7333	0.363	385.6667
42	18.86	15.51	30.38	0.4005	228.7333	0.2977	395
43	481.72	18.06	41.37	0.403	255.4	0.2923	424.6667
44	399.40	18.42	37.36	0.4167	231.3667	0.246	416
45	768.97	27.03	64.79	0.4699	208.6333	0.3713	392
46	622.41	25.58	35.40	0.4651	212.7333	0.3793	406
47	467.24	25.99	103.35	0.4657	197.9333	0.3597	446.6667
48	5.86	3.50	22.87	0.4669	193.1	0.369	459
50	19.66	0.38	5.45	0.3848	170.1667	0.346	437.6667
51	13.10	0.18	4.88	0.3893	170.2	0.4003	353.6667
52	20.34	0.16	84.38				
53	14.14	0.12	125.78	0.3841	162.8	0.339	377

Station	DIN:P$_i$	Chl a	AP Activity	F$_v$/F$_m$	σ_{PSII}	p	τ_{Qa}
54	24.48	0.12	28.54	0.3878	163.2	0.296	482
55	13.79	0.23	1.29	0.3874	175.6	0.3497	423
56	16.90	0.18	0.02	0.3885	173.05	0.337	416.5
57	3.42	0.19	1.71	0.3873	179.35	0.3468	446.25
58	17.59	0.20	0.63	0.3931	179.3667	0.3307	422
59	24.48	1.33	14.23	0.3847	177.525	0.3628	468.5
60	137.59	8.45	146.80	0.4374	205.6333	0.3477	412.6667
61	304.14	17.76	193.11				
62	574.83	21.36	153.55	0.4896	212.3	0.371	440
63	72.10	14.42	83.03	0.491	220.4333	0.397	461.6667
64	438.62	22.18	92.49				
65	86.90	4.00	14.58				
66	29.66	1.01	8.78				
67	8.00	0.63	5.11	0.371057	212.2738	0.327976	552.9048
68	17.93	0.39	94.10	0.2548	237.9212	0.403273	248.1212
69	24.83	0.37	133.18	0.363028	277.002	0.26132	320.84
70	20.69	0.42	56.08				
71	2.78	0.54	26.63				
72	230.69	9.28	220.53	0.327181	258.5979	0.253042	473.6667
73	374.14	13.83	241.92				
74	376.90	15.51	274.14				
75	341.38	12.60	295.06				
76	32.43	2.83	322.11				
78	67.00	4.59	122.11				
79	21.72	0.86	82.57				
80	53.79	0.73	25.95				
82	68.62	0.95	98.09	0.330332	311.84	0.27736	665.28
83	158.62	6.11	102.98	0.367097	252.3515	0.290364	368.0303
84	281.38	4.10	251.06	0.397279	241.9917	0.270333	352.1667
85	277.24	5.20	523.98	0.35045	254.1643	0.29	457.0714
86	211.75	4.96	138.96				
87	92.76	12.28	135.61	0.3797	223.65	0.3443	354.5
88	215.86	5.53	127.58				
89	263.10	4.87	91.00				
90	39.29	4.29	134.71				
91	45.50	4.08	74.61	0.3595	267.4	0.386	483
92	55.77	4.89	79.72				
93	98.28	2.78	99.15				
94	48.83	1.92	87.84	0.4158	259.2	0.201	454
95	14.38	2.63					
96	7.47	2.41	120.60				
97	2.68	0.45	509.98	0.2336	287.8	0.366	2129
98	2.00	0.42	796.18				
99	6.73	1.84	429.54				
100	50.50	1.43	1.78				
101	46.13	3.28	1.36				
102	37.10	3.63	2.38				
103	12.06	3.95	3.85				
104	53.45	2.31	244.90				

Station	DIN:P$_i$	Chl a	AP Activity	F_v/F_m	σ_{PSII}	p	τ_{Qa}
105	2.26	11.80	727.82				
106	310.00	10.19	716.19				
107	28.78	9.42	383.95				
108	28.53	8.25	58.43				
109	96.90	10.16	98.47				
110	222.07	9.21	91.03				
111	175.17	17.23	125.98				
112	78.00	6.55	311.47				
113	7.38	6.78	180.91				
114	14.00	3.23	131.27				
115	15.00	2.33	383.98				
116	32.56	0.10	236.81				
117	10.60	1.46	563.11				
118	2.72	0.82	671.87				
119	6.20	0.67	285.26				
120	1.00	0.82	12.08				
121	2.75	0.63	12.45				
122	7.00	0.86	0.00				
123	1.33	0.15	33.10				
124	4.77	0.38	196.83				
125	2.77	1.02	417.27				
127	2.69	0.67	62.51				
128	20.33	0.46					
129	15.52	0.77	21.87				
130	17.50	0.79	26.56				
131	1.78	1.39	134.58				
132	4.07	3.37	407.70				
133	17.75	5.96					
134	64.83	6.95	201.66				
135	59.66	6.06	206.92				
137	36.00		119.77	0.4525	256.2	0.355	405.5
138	19.89	8.51	22.78	0.4504	234.6	0.309	379
139	39.98	24.66	79.98	0.4378	206.8	0.317	449.6667
140	36.09	11.96	17.62	0.4362	210.75	0.3605	412
141	16.00	9.30	122.96	0.4523	241.9667	0.307	388
143	74.83	9.47	63.46	0.4543	244.35	0.3505	405.5
144	212.07	4.82	191.00				
145	9.42	5.38	369.17				
146	6.36	2.69	374.10				
147	8.36	6.26	361.76				
148	14.78	8.91	151.48				
149	243.10	4.49	535.71	0.3085	227.45	0.2305	348
150	33.08	1.78	236.98				
151	3.00	0.95	70.00	0.3279	257	0.444	445
152	61.03	0.89	121.74	0.2944	195.95	0.0865	614.5
153	5.13	3.77	263.22				
154	42.07	2.46	214.50				
155	8.06	3.71	345.64				
156	17.27	4.38	185.52	0.295614	280.6429	0.359	477.5714

Station	DIN:P_i	Chl a	AP Activity	F_v/F_m	σ_{PSII}	p	τ_{Qa}
157	7.83	5.74	372.82	0.372477	280.0462	0.312462	358.3846
158	191.33	5.97	204.74	0.402152	226.5148	0.295778	403.8889
159	433.45	2.62	76.72	0.301389	259.8778	0.134778	549.5556
160	37.95	2.82	173.54	0.394645	231.0273	0.189455	477.4545
161	198.28	5.78		0.388838	251.8769	0.233077	453.7692
mean	**146.35**	**9.11**	**138.56**	**0.39**	**222.45**	**0.30**	**469.24**
median	*36.09*	*5.29*	*79.85*	*0.39*	*215.30*	*0.32*	*440.00*

A2.1 March 2004 Metadata, Part 1

Station	Latitude	Longitude	Salinity	P_i	TDP	DOP	PP	TP
1_2	29.0955	-89.2794	0.17	2.176			1.255	
2	28.9054	-89.4329	0.22	1.983	1.967	0	0.7667	2.7497
3	28.6892	-89.4039	34.91	0.657	0.085	0	0.0409	0.6979
4_2	28.6409	-89.3993	35.41	0.052	0	0	0.0696	0.1216
5	28.6861	-89.4186	34.50	0.03				
6	28.7332	-89.4376	31.33	0.055	0.053	0	0.0821	0.1371
7	28.7785	-89.4557	30.06	0.07	0.12	0.05	0.1933	0.3133
8	28.8266	-89.4752	28.52	0.112				
9	28.8735	-89.4941	19.20	0.904	0.956	0.052	0.6394	1.5954
10	28.926	-89.5152	21.35	0.834				
11_2	28.9581	-89.5283	26.16	0.496	0.468	0	0.296267	0.792267
12	29.002	-89.546	24.29	0.793	0.823	0.03	0.075867	0.898867
13	29.0497	-89.5653	24.19	0.27	0.301	0.031	0.2228	0.5238
14	29.0969	-89.5842	25.67	0.067	0.089	0.022	0.271533	0.360533
15	29.1456	-89.6041	25.99	0.224	0.388	0.164	0.173533	0.561533
16	29.1824	-89.6186	26.01	0.135	0.234	0.099	0.378533	0.612533
17_2	29.2474	-89.6453	27.18	0.237	0.547	0.31	0.237667	0.784667
18	29.1808	-89.6737	25.88	0.191	0.273	0.082	0.4848	0.7578
19	29.1274	-89.6946	25.73	0.079	0.139	0.06	0.38205	0.52105
20	29.0744	-89.7139	25.70	0.058	0.137	0.079	0.5388	0.6758
21	29.0149	-89.7376	25.28	0.041	0.103	0.062	0.34415	0.44715
22	28.9578	-89.7582	24.20	0.131	0.291	0.16	0.54465	0.83565
23_2	28.8776	-89.7935	25.70	0.351	0.453	0.102	0.2702	0.7232
25	28.779	-89.8297	30.12	0.213	0.143	0	0.1315	0.2745
26	28.763	-89.8443	30.77	0.113	0.056	0	0.1018	0.1578
27	28.7081	-89.8615	33.62	0.099	0.033	0	0.0723	0.1053
28_2	28.6352	-89.8917	35.70	0.03	0.041	0.011	0.0246	0.0656
29	28.6973	-89.9104	34.63	0.107	0.071	0	0.054867	0.125867
30	28.7611	-89.9272	32.90	0.062	0	0	0.123067	0.123067
31	28.8231	-89.9438	31.12	0.523	0.079	0	0.1904	0.2694
32	28.8873	-89.9608	28.86	0.03	0.104	0.074	0.370667	0.474667
33_2	28.9227	-89.9768	27.96	0.03	0.109	0.079	0.439533	0.548533
34	28.9789	-89.9952	25.99	0.058	0.182	0.124	0.3338	0.5158
35	29.0363	-90.0145	26.23	0.054	0.178	0.124	0.556333	0.734333
36	29.0953	-90.0341	24.88	0.045	0.068	0.023	0.3662	0.4342
37_2	29.1413	-90.0495	24.73	0.062	0.146	0.084	0.455267	0.601267
38	29.097	-90.0594	24.60	0.074	0.212	0.138	0.247667	0.459667
39	29.039	-90.0701	26.24	0.046	0.128	0.082	0.4958	0.6238
40	28.9801	-90.0808	26.89	0.247	0.553	0.306	0.5526	1.1056
41	28.9139	-90.0932	27.55	0.03	0.129	0.099	0.253667	0.382667
42_2	28.8186	-90.1122	29.77	0.043	0.078	0.035	0.210667	0.288667
43	28.7729	-90.1217	30.94	0.03	0.068	0.038	0.125133	0.193133
44	28.7157	-90.1316	33.54	0.03	0	0	0.0912	0.0912
45	28.6454	-90.1439	35.27	0.03	0.042	0.012	0.033133	0.075133
46_2	28.5941	-90.1531	35.92	0.03	0	0	0.098333	0.098333
47	28.6373	-90.1845	34.07	0.03	0.0655	0.036	0.0772	0.1427

Station	Latitude	Longitude	Salinity	P_i	TDP	DOP	PP	TP
48	28.6974	-90.2156	31.67	0.032	0.082	0.05	0.103933	0.185933
49	28.7631	-90.2448	29.14	0.03	0.053	0.023	0.056133	0.109133
50_2	28.8146	-90.2682	28.41	0.03	0.026	0	0.166733	0.192733
51	28.9021	-90.3062	27.38	0.037	0.053	0.016	0.1548	0.2078
52	28.9589	-90.3326	26.80	0.03	0.107	0.077	0.0898	0.1968
53_2	29.0145	-90.3557	25.18	0.03	0.138	0.108	0.0716	0.2096
54	28.9612	-90.3695	26.53	0.079	0.139	0.06	0.0884	0.2274
55	28.8931	-90.3883	27.91	0.03	0.155	0.125	0.0742	0.2292
56	28.8266	-90.4065	29.49	0.03	0.043	0.013	0.0782	0.1212
57_2	28.7902	-90.4167	30.07	0.038	0.108	0.07	0.0616	0.1696
58	28.7291	-90.4346	30.69	0.085	0.175	0.09	0.023667	0.198667
59	28.6665	-90.4562	31.72	0.102	0.236	0.134	0.032667	0.268667
60	28.6065	-90.4769	32.64	0.069	0.084	0.015	0.020333	0.104333
61_2	28.5359	-90.5056	34.29	0.03	0	0	0.0178	0.0178
62	28.6243	-90.5433	33.17	0.03	0.07	0.04	0.029733	0.099733
63	28.6834	-90.5676	31.76	0.03	0.142	0.112	0.032533	0.174533
64_2	28.7808	-90.6111	30.73	0.061	0.254	0.193	0.025133	0.279133
65	28.836	-90.6318	30.25	0.034	0.044	0.01	0.062467	0.106467
66	28.8946	-90.6555	27.83	0.131	0.194	0.063	0.107467	0.301467
67	28.9526	-90.6792	26.91	0.041	0.125	0.084	0.126133	0.251133
68_2	29.0162	-90.7083	26.98	0.156	0.264	0.108		
69	28.941	-90.7241	26.95	0.047				
70	28.8774	-90.7401	27.06	0.043	0.074	0.031	0.053733	0.127733
71	28.8085	-90.7574	27.64	0.1	0.295	0.195	0.0626	0.3576
72_2	28.7674	-90.7684	28.01	0.096	0.065	0	0.105267	0.170267
73	28.6995	-90.7862	28.86	0.03	0.025	0	0.098267	0.123267
74	28.6351	-90.8017	29.99	0.03	0.104	0.074	0.065267	0.169267
75	28.5743	-90.8163	34.26	0.057	0.054	0	0.0594	0.1134
76_2	28.5236	-90.8307	35.10	0.03	0	0	0.053533	0.053533
77	28.5799	-90.8559	34.14	0.045				
78	28.6449	-90.8835	29.70	0.05	0.02	0	0.0744	0.0944
79_2	28.7154	-90.9123	29.00	0.079	0.049	0	0.1088	0.1578
80	28.7982	-90.9548	27.40	0.067	0.112	0.045	0.131333	0.243333
81	28.8566	-90.9779	26.98	0.099	0.138	0.039	0.1118	0.2498
82	28.9244	-91.0046	27.13	0.134	0.177	0.043	0.0538	0.2308
83	28.9602	-91.0291	26.17	0.123	0.117	0	0.1808	0.2978
84	29.0244	-91.047	25.45	0.095	0.076	0	0.227933	0.303933
85	29.0312	-91.0641	25.35	0.076	0.087	0.011	0.2224	0.3094
86	29.0427	-91.0517	25.28	0.142	0.2075	0.0655	0.327133	0.534633
87	28.971	-91.0924	26.10	0.058	0.066	0.008	0.2032	0.2692
88	28.9295	-91.1298	26.68	0.084	0.149	0.065	0.134867	0.283867
89	28.8645	-91.148	27.59	0.095	0.013	0	0.142133	0.155133
90	28.8034	-91.1652	27.99	0.076	0.032	0	0.202	0.234
91	28.7964	-91.1688	28.08	0.03	0.072	0.042	0.195933	0.267933
92	28.7405	-91.1838	29.46	0.11	0.164	0.054	0.0674	0.2314
93	28.6777	-91.2009	31.09	0.122	0.018	0	0.034067	0.052067
94	28.6064	-91.2203	33.87	0.03	0	0		
95_2	28.5343	-91.2406	32.42	0.059	0	0		
96	28.556	-91.256	32.33	0.056	0.068	0.012		

Station	Latitude	Longitude	Salinity	P_i	TDP	DOP	PP	TP
97	28.614	-91.281	32.62	0.05	0.124	0.074		
98	28.6727	-91.3061	32.61	0.081	0.138	0.057		
99	28.732	-91.3297	30.64	0.052	0.014	0		
100_2	28.8293	-91.3717	28.86	0.076	0.115	0.039		
102	28.9551	-91.4261	27.71	0.131	0.153	0.022		
103	29.0132	-91.4514	27.47	0.126	0.177	0.051	0.075867	0.252867
104	29.0696	-91.4762	25.34	0.167	0.279	0.112	0.060667	0.339667
105_2	29.1151	-91.4962	24.30	0.145	0.481	0.336	0.058867	0.539867
106	29.0627	-91.5148	26.57	0.097	0.15	0.053	0.087333	0.237333
107	29.0041	-91.5355	29.22	0.131	0.144	0.013	0.045133	0.189133
108	28.9512	-91.5533	30.41	0.079	0.186	0.107	0.134267	0.320267
109	28.905	-91.5689	30.68	0.127	0.067	0	0.038667	0.105667
110	28.8524	-91.587	31.86	0.03	0	0	0.071867	0.071867
111_6	28.8348	-91.5935	32.29	0.114				
112	28.8016	-91.6096	32.89	0.051	0.049	0		
113	28.7512	-91.6255	30.25	0.062	0.2	0.138	0.053867	0.253867
114	28.6976	-91.6424	30.52	0.07	0.085	0.015	0.042	0.127
116	28.592	-91.6795	34.45	0.03	0	0	0.060867	0.060867
117	28.5379	-91.6958	35.82	0.059	0	0	0.031533	0.031533
118_2	28.6105	-91.7346	34.64	0.032	0	0	0.034267	0.034267
119	28.6821	-91.7639	32.15	0.045	0.08	0.035	0.0532	0.1332
120	28.7443	-91.7897	30.57	0.03				
121_2	28.7712	-91.8048	30.58	0.065	0.021	0	0.178133	0.199133
122	28.8285	-91.8318	30.07	0.03	0	0	0.115667	0.115667
123	28.884	-91.8542	29.59	0.09	0.145	0.055	0.155533	0.300533
124	28.9456	-91.8782	30.50	0.05	0.057	0.007	0.210933	0.267933
125_2	29.0101	-91.9079	30.86	0.052	0.0355	0	0.126	0.1615
126	29.0652	-91.9346	30.17	0.03	0.162	0.132	0.125867	0.287867
127	29.1383	-91.9633	26.70	0.081	0.017	0	0.224	0.241
128	29.1912	-91.9842	26.20	0.03	0.113	0.083	0.1798	0.2928
129	29.212	-91.9973	26.46	0.03	0.134	0.104	0.244667	0.378667
130	29.1254	-91.9968	27.16	0.111	0.151	0.04	0.175867	0.326867
131	29.0638	-91.9968	29.67	0.105	0.073	0	0.215133	0.288133
132	29.0086	-91.9971	29.72	0.133	0.24	0.107	0.1286	0.3686
133	28.9443	-91.9972	29.68	0.098	0.16	0.062	0.0774	0.2374
134	28.8967	-91.9972	30.60	0.03	0.1225	0.0925	0.069	0.1915
135_2	28.8838	-91.9982	30.79	0.103	0.153	0.05	0.082267	0.235267
136	28.8398	-91.9976	31.19	0.079	0.11	0.031	0.025133	0.135133
137	28.7878	-91.9975	32.12	0.036	0	0	0.071067	0.071067
138	28.7319	-91.9975	32.14	0.069	0.111	0.042	0.029533	0.140533
139	28.6891	-91.9974	32.36	0.079	0.088	0.009	0.041067	0.129067
140_2	28.6361	-91.9962	34.21	0.036	0	0	0.030533	0.030533
141	28.6903	-91.9515	33.76	0.077	0.068	0	0.031533	0.099533
142	28.7352	-91.9147	33.28	0.67	0.09	-0.58	0.074933	0.164933
143	28.7779	-91.8775	31.04	0.03	0.047	0.017	0.029	0.076
144	28.8512	-91.8155	29.77	0.082	0.065	0	0.088333	0.153333
145	28.9077	-91.7698	30.92	0.064	0	0	0.131733	0.131733
146_2	28.9562	-91.7288	31.55	0.083	0.009	0	0.0782	0.0872
147	29.0017	-91.6923	30.05	0.043	0	0	0.110333	0.110333

Station	Latitude	Longitude	Salinity	P$_i$	TDP	DOP	PP	TP
148_2	29.0577	-91.6481	28.76	0.104	0.135	0.031	0.2422	0.3772
149	29.1262	-91.5952	25.94	0.072	0.054	0	0.166133	0.220133
152	29.2663	-91.4784	16.17	2.02	3.128	1.108	0.239267	3.367267
153	29.3205	-91.4295	3.70	1.849	2.6125	0.7635	0.3488	2.9613
Mean			**28.76**	**0.15795**	**0.179504**	**0.05607**	**0.167237**	**0.35022**
median			*29.63*	*0.068*	*0.1035*	*0.031*	*0.107467*	*0.2327*

A2.2 March 2004 Metadata, Part 2

Station	NO$_x$	TDN	DON	PN	TN	DOC	PC
1_2	69.242	101.7	32.458	12.9104762	114.610476	332.1	148.933333
2	65.018	91.7	26.682	5.75428571	97.4542857	213	96.3777778
3	15.337	26.8	11.463	0.91238095	27.712381	151.3	39.8666667
4_2	0.106	6.9	6.794	1.91238095	8.81238095	92.5	34.6
5	0.105	6.7	6.595			107.4	
6	2.509	11	8.491	3.31809524	14.3180952	111.1	81.8666667
7	6.308	15.2	8.892	5.83428571	21.0342857	129.5	88.5333333
8	7.805	15.5	7.695			137	
9	29.226	43.7	14.474	3.32571429	47.0257143	361.5	58.1555556
10	25.824	40.3	14.476			204	
11_2	14.684	24.9	10.216			124.8	
12	19.151	31.8	12.649	3.22857143	35.0285714	158.3	40.4444444
13	15.996	26.9	10.904	6.47047619	33.3704762	181.95	71.1777778
14	5.986	16.8	10.814	13.2285714	30.0285714	165.1	119.777778
15	6.912	20.3	13.388	11.487619	31.787619	188.8	94.2444444
16	3.788	16.6	12.812	9.38095238	25.9809524	185.3	81.1111111
17_2	2.874	16.9	14.026	11.7238095	28.6238095	176.1	89.1111111
18	4.529	18.1	13.571	12.3771429	30.4771429	171	107.555556
19	4.558	15.5	10.942	14.3809524	29.8809524	155	101.577778
20	4.81	14.3	9.49	14.9542857	29.2542857	149.9	115.222222
21	5.322	15.2	9.878	6.23238095	21.432381	147.3	71.7777778
22	13.821	23	9.179	7.8552381	30.8552381	139.1	81.6666667
23_2	14.549	24.7	10.151	3.30666667	28.0066667	145.2	46.8
25	2.731	11.7	8.969	6.04	17.74	358.4	63.5333333
26	1.447	9.3	7.853	7.61142857	16.9114286	107.5	76.2444444
27	0.338	6.8	6.462	5.84380952	12.6438095	98.7	62.2
28_2	0.148	6.3	6.152	0.65371429	6.95371429	83.3	48.0444444
29	0.291	5.6	5.309	0.55571429	6.15571429	99.7	27.1
30	0.323	6.4	6.077	4.81028571	11.2102857	105.8	51.3866667
31	0.802	7.5	6.698	5.85942857	13.3594286	130.6	46.0133333
32	2.875	10.7	7.825	10.16	20.86	125.9	96.7666667
33_2	4.081	11.7	7.619	83.2342857	94.9342857	127.6	73.7333333
34	7.712	17	9.288	10.24	27.24	145.2	139.1
35	3.594	12.9	9.306	14.0757143	26.9757143	142.9	139.916667
36	4.957	15	10.043	10.8308571	25.8308571	161.7	110.146667
37_2	5.199	18.6	13.401	9.38742857	27.9874286	157.4	91.3866667
38	5.299	20.1	14.801	18.4114286	38.5114286	173.8	173.466667
39	2.404	11.3	8.896	22.1371429	33.4371429	150.3	220.133333
40	1.306	18.1	16.794	20.0228571	38.1228571	204.2	194.4
41	2.111	12.9	10.789	10.1728571	23.0728571	135.4	116.65
42_2	2.943	12.2	9.257	9.43085714	21.6308571	126.7	82.0266667
43	1.824	10.6	8.776	8.296	18.896	112.1	71.7866667
44	0.279	8.1	7.821	5.672	13.772	100.2	60.7866667
45	0.081	6.7	6.619	5.26171429	11.9617143	89.9	44.8133333
46_2	0.088	5	4.912	4.28914286	9.28914286	82.3	41.96
47	0.167	6.2	6.033	5.10514286	11.3051429	91.1	69.56
48	1.088	8	6.912	8.17828571	16.1782857	116.1	90.6

Station	NO$_x$	TDN	DON	PN	TN	DOC	PC
49	3.144	10.1	6.956	8.79085714	18.8908571	116.4	77.6266667
50_2	4.056	13.5	9.444	8.192	21.692	139.5	75.4533333
51	3.667	11.9	8.233	9.31542857	21.2154286	136.6	83.6
52	3.711	14.6	10.889	11.024	25.624	147.6	102.706667
53_2	3.635	12.4	8.765	12.5714286	24.9714286	175.1	102.586667
54	3.976	14.8	10.824	9.992	24.792	168.3	101.853333
55	3.704	12.1	8.396	8.25028571	20.3502857	159.1	85.2266667
56	2.555	9.8	7.245	7.64914286	17.4491429	148.9	76.0533333
57_2	2.277	11.8	9.523	8.62057143	20.4205714	130.7	76.32
58	2.266	9.6	7.334	6.584	16.184	127.3	70.0666667
59	1.222	8.8	7.578	7.816	16.616	128.2	73.24
60	1.106	8.1	6.994	7.01028571	15.1102857	123.7	61.9066667
61_2	0.128	7.9	7.772	6.16685714	14.0668571	101.2	57.2666667
62	0.172	6.8	6.628	7.03657143	13.8365714	112.2	64.4133333
63	0.6	8.2	7.6	7.37942857	15.5794286	125.7	69.56
64_2	0.83	12.2	11.37	12	24.2	139.3	101.813333
65	0.919	57.5	56.581	10.6148571	68.1148571	123.3	87.6933333
66	2.334	11.5	9.166			170.7	
67	2.947	6.6	3.653	10.5908571	17.1908571	146.3	114.493333
68_2	1.745	13.2	11.455			159.5	
69	3.857	13	9.143			161.1	
70	2.736	10.2	7.464			146.8	
71	2.382	16.5	14.118	10.9485714	27.4485714	164.9	107.226667
72_2	1.181	9.5	8.319	4.54171429	14.0417143	93.5	41.24
73	1.985	25.7	23.715	7.25142857	32.9514286	119.4	66.08
74	1.548	9.1	7.552	7.29142857	16.3914286	125.2	64.9333333
75	0.102	7.4	7.298	3.47085714	10.8708571	98.4	34.6266667
76_2	0.121	6.5	6.379	2.51428571	9.01428571	86.3	38.32
77	0.116	5.5	5.384			102.2	
78	1.489	9.5	8.011	4.896	14.396	112.7	51.4666667
79_2	1.564	10.4	8.836	4.52914286	14.9291429	124.3	53.9333333
80	2.774			7.00228571			79.3733333
81	2.897	13.3	10.403	9.25942857	22.5594286	159.9	87.9066667
82	2.534	12.6	10.066	8.92685714	21.5268571	152.4	87.2533333
83	4.778	16.8	12.022	8.61371429	25.4137143	157.9	72.8133333
84	5.046	14.7	9.654	9.52	24.22	145.8	73.4533333
85	5.445	15	9.555	10.4994286	25.4994286	150.5	86.3466667
86	5.331	15.9	10.569	10.1097143	26.0097143	154.6	93.9066667
87	4.768	12.8	8.032	7.11428571	19.9142857	140.7	69.44
88	3.604	12.5	8.896	4.94285714	17.4428571	161.5	53.7333333
89	1.517	12.1	10.583	9.19657143	21.2965714	136.9	80.72
90	1.626	12.2	10.574	8.21371429	20.4137143	132.8	69.5333333
91	1.75	9.1	7.35	6.89828571	15.9982857	129.6	83.5733333
92	0.987	9.1	8.113	5.34514286	14.4451429	138.7	51.52
93	0.369	9.3	8.931	5.77714286	15.0771429	126.7	59.4933333
94	0.081	6.5	6.419			121.1	
95_2	0.859	8.4	7.541			129.8	
96	0.05	7.2	7.15			116.7	
97	0.05	7.5	7.45			126	

Station	NO$_x$	TDN	DON	PN	TN	DOC	PC
98	0.094	6.5	6.406			115.2	
99	0.336	8.4	8.064			119.9	
100_2	1.28	11.5	10.22			144.8	
102	2.548	10.7	8.152			146.3	
103	1.026	11.2	10.174	5.20914286	16.4091429	151.8	69.68
104	2.092	14.1	12.008	6.04114286	20.1411429	183.8	85.48
105_2	0.915	11.9	10.985	10.7108571	22.6108571	201.3	105.173333
106	1.581	12.8	11.219	7.88914286	20.6891429	157.1	79.36
107	1.809	11.1	9.291	5.19657143	16.2965714	133.8	54.8133333
108	0.726	9.4	8.674	4.81371429	14.2137143	144.6	58.64
109	0.895	9.5	8.605	5.85257143	15.3525714	124	47.8533333
110	0.179	8.6	8.421	5.184	13.784	111.6	47.4
111_6	0.137						
112	0.5	7.6	7.1			131.1	
113	1.89	11.9	10.01	4.11542857	16.0154286	443.1	47.7866667
114	1.502	10.8	9.298	4.19771429	14.9977143	132.5	52.16
116	0.218	8.9	8.682	0.74605714	9.64605714	110.7	41.4666667
117	0.129	6.3	6.171	2.50857143	8.80857143	85.3	31.28
118_2	0.26	7.4	7.14	3.512	10.912	88	44.9733333
119	0.933	10	9.067	3.38857143	13.3885714	109.4	34.0933333
120	1.589						
121_2	1.416	10.3	8.884	3.024	13.324	113.8	39.56
122	1.504	9.2	7.696	4.99085714	14.1908571	124.1	65.6666667
123	1.671	10	8.329	5.53714286	15.5371429	134.6	56.48
124	0.753	8.3	7.547	5.69028571	13.9902857	112.2	63.8666667
125_2	0.75	7.9	7.15	4.85257143	12.7525714	104.2	54.28
126	0.485	8.6	8.115	6.24914286	14.8491429	135.6	67.4933333
127	0.919	11.8	10.881	6.38628571	18.1862857	156.6	69.92
128	0.644	9.5	8.856	8.536	18.036	171.9	76.8
129	0.651	9.6	8.949	6.91771429	16.5177143	161.9	71.1066667
130	1.008	10.2	9.192	8.12342857	18.3234286	175.2	72.5866667
131	2.269	12.5	10.231	4.97942857	17.4794286	124.4	50.28
132	1.99	10.7	8.71			131.5	
133	1.691	9.7	8.009	4.84228571	14.5422857	130.2	50.3066667
134	1.24	9.1	7.86	5.02514286	14.1251429	122.6	44.6533333
135_2	1.278	8.6	7.322	4.79885714	13.3988571	124.4	46.28
136	1.482	9.5	8.018	3.72457143	13.2245714	111	32.9466667
137	0.847	7.2	6.353	4.304	11.504	101.3	43.84
138	0.895	9.7	8.805	2.848	12.548	152.05	32.2533333
139	0.832	7.9	7.068	2.25142857	10.1514286	130.6	31.5466667
140_2	0.352	6.6	6.248	2.44	9.04	94	34.56
141	0.547	6.4	5.853	2.43657143	8.83657143	96.6	33.7066667
142	0.604	9.3	8.696	2.64571429	11.9457143	113	35.7333333
143	1.403	8.9	7.497	2.75314286	11.6531429	114.5	39.44
144	1.582	11.3	9.718	4.10628571	15.4062857	129.9	42.44
145	1.925	10	8.075	5.84114286	15.8411429	126	57.28
146_2	0.22	7.3	7.08	5.12457143	12.4245714	209.4	43.6133333
147	0.921	10.4	9.479	7.08571429	17.4857143	162.9	56.28
148_2	1.738	10.8	9.062	8.87542857	19.6754286	154.6	81.2533333

Station	NO$_x$	TDN	DON	PN	TN	DOC	PC
149	1.386	11.8	10.414	7.98285714	19.7828571	178.2	74.2266667
152	11.451	32.5	21.049	27.94	60.44	317.5	268.9
153	25.751	44.2	18.449	27.2190476	71.4190476	324.5	242.888889
mean	**3.9725203**	**13.80207**	**9.778393**	**8.01762925**	**22.1169574**	**144.9903**	**75.0368329**
median	*1.5855*	*10.7*	*8.805*	*6.584*	*17.464286*	*133.8*	*69.68*

A2.3 March 2004 Metadata, Part 3

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl *a*	AP Activity
1_2	33.818	31.82077		70.6666667	0.5083575	
2	33.62	32.7877	35.44179	39	0.2178675	
3	33.62	23.34399	39.70824	30.6666667	0.1016715	32.38
4_2	0.591	2.038462	72.47024	32.6685	0.058098	32.62
5	0.591	3.5		16	0.3340635	54.44
6	6.159	45.61818	104.4354	9.33333333	0.9150435	63.35
7	10.709	90.11429	67.13784	15.3333333	0.2469165	32.32
8	13.593	69.6875		11.3333333	0.4793085	18.77
9	33.023	32.32965	29.47581	25.3333333	0.116196	8.04
10	33.196	30.96403		21.3333333	0.522882	4.87
11_2	22.936	29.60484		14.6666667	0.842421	6.1
12	26.733	24.15006	38.96971	-0.6666667	0.726225	5.24
13	24.853	59.24444	63.70843	8	2.294871	8.46
14	17.375	89.34328	83.28931	10.6666667	4.4590215	
15	4.242	30.85714	56.60861	6.66666667	2.382018	
16	bd	28.05926	42.41557	16.6666667	3.921615	
17_2	17.867	12.12658	36.47894	15.3333333	5.4466875	
18	13.942	23.71204	40.21792	6.66666667	3.5004045	
19	14.371	57.6962	57.34757	9.33333333	5.577408	
20	15.198	82.93103	43.28838	9.33333333	5.054526	
21	3.536	129.8049	47.93108	7.33333333	4.5752175	
22	27.824	105.5038	36.92364	13.3333333	3.9361395	
23_2	28.475	41.45014	38.72603	10.33	1.5250725	0
25	7.411	12.8216	64.62659	6.66666667	2.178675	30.06
26	4.967	12.80531	107.17	12.6666667	2.149626	69.4
27	1.542	3.414141	120.0742	10	0.784323	53.81
28_2	0.786	4.933333	106.0017	7.33333333	0.203343	0
29	1.407	2.719626	48.90663	12	0.2759655	47.78
30	2.748	5.209677	91.09116	6.5	1.132911	37.42
31	5.023	1.533461	49.58956	3.2	0.203343	
32	11.0875	95.83333	43.94663	8.8	0.2759655	
33_2	12.984	136.0333	173.0693	4.8	2.643459	26.06
34	18.158	132.9655	52.81117	7.5	2.120577	13.42
35	15.459	66.55556	36.73497	9.6	3.5294535	37.59
36	15.811	110.1556	59.49069	6	2.0479545	52.6
37_2	16.648	83.85484	46.54745	5	1.2345825	63.9
38	15.901	71.60811	83.78121		0.9440925	64.36
39	12.886	52.26087	53.60235		1.74294	108.6
40	12.485	5.287449	34.4816	8.4	2.42075	108.13
41	10.797	70.36667	60.29492	6.4	1.4088765	98.93
42_2	9.094	68.44186	74.93369	10	0.813372	18.54
43	7.368	60.8	97.83914	10	0.813372	36.43
44	2.659	9.3	151.0088	10.4	0.4212105	26.68
45	1.228	2.7	159.2065	12.8	-0.087147	28.25
46_2	0.708	2.933333	94.46586	12.6	0.029049	3
47	1.69	5.566667	79.22315	7.2	0.6826515	43.92
48	5.203	34	87.01122	6.8	1.655793	90.61
49	9.865	104.8	173.0989	4.4	1.045764	42.39
50_2	11.838	135.2	112.5493	9.4	0.8859945	26.58

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl a	AP Activity
51	12.817	99.10811	102.0954	5.2	2.556312	59.75
52	14.036	123.7	130.2033	10.8	2.8322775	51.74
53_2	16.173	121.1667	119.1385	8.7	3.3261105	84.58
54	14.681	50.32911	109.0237	2	2.585361	68.9
55	13.132	123.4667	88.78833	11.2	2.1641505	67.7
56	9.642	85.16667	143.9698	7.6	2.1641505	70.53
57_2	8.932	59.92105	120.4043	12.4	1.917234	56.36
58	7.905	26.65882	81.46309	5.2	1.16196	
59	5.264	11.98039	61.84615	15.2	1.4669745	
60	3.75	16.02899	144.827	11.2	1.132911	
61_2	0.646	4.266667	790.2729	11.6	0.726225	
62	1.779	5.733333	138.7357	11.6	1.016715	29.7
63	4.086	20	89.26334	10.4	1.394352	28.97
64_2	6.096	13.60656	86.69692	16.2	1.0893375	33.05
65	6.424	27.02941	639.7764		2.352969	49.58
66	12.612	17.81679		8	3.9361395	47.96
67	13.296	71.87805	68.45311	10.4	2.8322775	62.58
68_2	13.511	11.1859		8.4	0.9731415	81.71
69	14.492	82.06383		4	2.4255915	74.19
70	13.839	63.62791		9.2	2.3384445	63.57
71	13.354	23.82	76.75775	8	2.4255915	58.18
72_2	6.809	12.30208	82.46896	16.7	1.0312395	71.83
73	8.488	66.16667	267.3182	6	0.522882	85.1
74	6.407	51.6	96.8379	12.4	0.232392	48.76
75	0.227	1.789474	95.86294	37.6	0.1597695	26.53
76_2	0.25	4.033333	168.3864	7.6	0.058098	6.66
77	0.791	2.577778		10.8	0.261441	34.66
78	6.389	29.78	152.5	-7.6	0.261441	57.88
79_2	8.053	19.79747	94.608	4.4	0.9440925	71.44
80	12.594	41.40299		5.6	0.203343	76.28
81	15.836	29.26263	90.30996	4.8	0.7407495	74.39
82	13.209	18.91045	93.27061	7.2	0.4212105	69.62
83	13.256	38.84553	85.33819	2.4	0.319539	85.55
84	12.042	53.11579	79.68853	7.6	0.261441	107.91
85	16.169	71.64474	82.41574	14	0.464784	106.92
86	12.764	37.54225	48.64963	12.4	0.4793085	111.79
87	12.328	82.2069	73.9758	4	0.842421	110.42
88	11.431	42.90476	61.44736	3.2	1.510548	110.74
89	10.541	15.96842	137.2791	3.6	0.522882	128.07
90	9.95	21.39474	87.2381	3.2	0.1888185	109.07
91	9.543	58.33333	59.70995	11.8	0.3340635	107.6
92	11.804	8.972727	62.42499	4.4	0.0145245	129.96
93	3.482	3.02459	289.5738	8	0.0726225	127.19
94	0.74	2.7		8.8	0.1016715	49.73
95_2	3.986	14.55932		8	0.029049	9.63
96	2.564	0.892857		7.2	0.1307205	34.32
97	0.671	1		6.8	0.232392	62.85
98	1.141	1.160494		0.8	0.7697985	129.84
99	4.072	6.461538		4.4	1.0893375	147.37
100_2	8.115	16.84211		9.6	1.8446115	192.89
102	9.143	19.45038		3.2	1.539597	118.66

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl *a*	AP Activity
103	6.704	8.142857	64.89247	2.4	1.510548	143.72
104	13.222	12.52695	59.29679	9.6	2.0479545	75.19
105_2	13.609	6.310345	41.8823	14.4	2.933949	182.51
106	7.76	16.29897	87.17335	20	1.946283	204.66
107	8.013	13.80916	86.16446	7.6	1.278156	125.68
108	3.872	9.189873	44.38087	11.2	1.191009	82.77
109	6.142	7.047244	145.2925	18	1.1764845	97.02
110	2.327	5.966667	191.7996	13.2	1.074813	105.19
111_6	0.907	1.201754		12	1.016715	82.68
112	13.261	9.803922		9.6	0.842421	87.7
113	7.053	30.48387	63.08598	10	0.5664555	61.68
114	7.105	21.45714	118.0922	13.6	0.551931	41.09
116	1.567	7.266667	158.4785	15.2	0.029049	9.68
117	1.095	2.186441	279.3416	26.4	0.0726225	2.74
118_2	1.584	8.125	318.4436	11.2	0.1307205	1.44
119	4.413	20.73333	100.5148	15.2	0.0726225	6.68
120	6.943	52.96667		13.2	0.232392	19.63
121_2	6.597	21.78462	66.90994	14.1	0.377637	6.78
122	7.221	50.13333	122.6875	14	0.2469165	29.24
123	7.04	18.56667	51.69857	10	0.232392	32
124	4.425	15.06	52.21555	6.8	0.726225	81.06
125_2	4.566	14.42308	78.96329	14.6	0.813372	85.65
126	9.152	16.16667	51.58341	10.8	0.900519	35.24
127	10.312	11.34568	75.46177	10.8	0.929568	64.02
128	10.1	21.46667	61.59836	12.8	0.6826515	116.11
129	9.625	21.7	43.62072	60	1.016715	95.05
130	9.509	9.081081	56.05781	12.4	1.191009	80.45
131	9.287	21.60952	60.66437	8.8	1.1183865	15.89
132	7.077	14.96241		18	0.3631125	17.7
133	6.949	17.2551	61.25647	10.8	0.174294	27.15
134	6.638	41.33333	73.76054	15.6	0.3340635	6.8
135_2	5.917	12.40777	56.95179	15.2	0	0
136	5.593	18.75949	97.86313	12.4	0.232392	
137	4.061	23.52778	161.8762	15.6	0.116196	8.11
138	8.372	12.97101	89.28843	11.2	0.1016715	5.37
139	3.832	10.53165	78.6526	10	0.087147	8.82
140_2	1.805	9.777778	296.0699	20	0.0726225	4.4
141	2.344	7.103896	88.78002	10	0.087147	9.06
142	3.101	0.901493	72.42753	14	0.1016715	8.72
143	6.812	46.76667	153.3308	15.2	0.1597695	20.65
144	6.292	19.29268	100.4758	12.8	0.6536025	42.6
145	7.077	30.07813	120.2516	8.4	1.2636315	44.55
146_2	1.877	2.650602	142.4836	18.4	0.987666	62.1
147	4.795	21.4186	158.4808	24	1.365303	86.25
148_2	7.244	16.71154	52.16179	14.8	2.004381	89.63
149	11.76	19.25	89.86761	9.2	2.8613265	106.21
152	27.233	5.668812	17.94928	100	0.406686	141.55
153	18.88	13.92699	24.11746	94.67	0.1888185	37.13
mean	**9.60787**	**33.79822**	**102.508**	**12.84**	**1.176844341**	**59.12392308**
median	*8.013*	*20.3667*	*82.4157*	*10.33*	*0.842421*	*54.125*

A3.1 May 2004 Metadata, Part 1

Station	Latitude	Longitude	Salinity	PO4	TDP	DOP	PP	TP
1-2	29.1567	-89.2575	0.12	1.96	2.19	0.23	2.00	4.19
4-2	28.8899	-89.4411	29.99	0.93	0.89	0.00	0.72	1.64
5	28.8238	-89.4336	21.05	0.47	0.32	0.00	0.63	1.09
7	28.7825	-89.4302	22.12	0.08				
8	28.7437	-89.424	31.66	bd	0.03	0.03	0.07	0.10
9	28.683833	-89.4101	31.58	0.04	0.04	0.00	0.01	0.05
10	28.6676	-89.41405	0.00	bd	0.11	0.11	0.05	0.16
11	28.7046	-89.4342	35.35	bd	0.07	0.07	0.02	0.09
12	28.766633	-89.4568	35.11	0.03	0.03	0.00	0.05	0.08
13	28.8174	-89.4761	32.10	0.15	0.12	0.00	0.23	0.38
14	28.8869	-89.5014	15.29	0.97	1.12	0.15	0.66	1.78
15	28.9459	-89.5236	13.06	0.53	0.91	0.39	0.51	1.42
16-2	29.0096	-89.5508	19.06	0.25	0.19	0.00	0.49	0.73
17	29.0662	-89.5764	17.67	0.04	0.29	0.26	0.37	0.67
18	29.1151	-89.5971	19.44	0.08				
19	29.1651	-89.6176	18.81	0.07	0.20	0.13	0.21	0.41
20	29.2266	-89.6428	15.67	0.10	0.23	0.13	0.42	0.65
21	29.2236	-89.6637	18.45	0.17				
22	29.1558	-89.6894	19.21	0.06	0.11	0.05	0.24	0.34
23	29.1107	-89.7062	19.66	0.07	0.21	0.14	0.30	0.51
24	29.0569	-89.7262	15.49	0.32	0.67	0.35	0.07	0.74
25	29.0179	-89.741	19.25	0.59	0.66	0.08	0.14	0.80
26	28.9842	-89.7536	17.67	0.99				
27	28.9388	-89.6705	23.21	0.80	0.50	0.00	0.01	0.81
28	28.8915	-89.7944	32.45	0.15				
29	28.8248	-89.8198	32.50	0.05	0.06	0.01	0.12	0.18
30	28.7702	-89.8387	32.24	bd	0.09	0.09	0.22	0.31
31-2	28.746333	-89.8512	35.28	0.07				
32	28.7947	-89.9082	35.82	0.04				
33	28.8531	-89.8654	32.97	bd	bd	0.00	0.12	0.12
34-2	28.9264	-89.9084	34.53	bd	0.05	0.05	0.08	0.13
35	28.9745	-89.9399	35.03	0.05	0.09	0.04	0.05	0.14
36	29.0241	-89.9731	34.80	0.05				
37	29.0729	-90.0055	27.19	0.09				
38-2	29.1206	-90.0444	23.23	0.05	0.14	0.09	0.42	0.56
39	29.1511	-90.0571	16.22	0.07	0.22	0.15	0.58	0.79
40	29.1104	-90.0704	18.93	bd	0.13	0.13	0.51	0.64
41	29.0535	-90.0782	21.93	0.03	0.15	0.12	0.50	0.65
42	28.9987	-90.0858	31.47	0.04	bd	0.00	0.18	0.22
43	28.9492	-90.0926	34.98	0.04	bd	0.00	0.05	0.09
44	28.8981	-90.0996	36.14	0.05	0.10	0.05	0.02	0.11
45-2	28.8495	-90.1107	36.18	bd	0.06	0.06	0.03	0.09
46	28.8372	-90.1462	35.73	bd	0.06	0.06	0.07	0.13
47	28.8786	-90.1959	35.56	0.03				
48-2	28.9243	-90.2546	35.17	bd	bd	0.00	0.04	0.04
49	28.9904	-90.3315	23.30	bd	0.15	0.15	0.30	0.44
50-6	29.011	-90.3597	20.44	0.04				

Station	Latitude	Longitude	Salinity	PO4	TDP	DOP	PP	TP
51	28.9664	-90.3595	24.61	0.12				
52	28.9193	-90.3719	33.82	0.10				
53	28.8446	-90.3706	33.43	bd	0.04	0.04	0.07	0.11
54-2	28.807	-90.3765	34.41	bd	0.04	0.04	0.06	0.10
55	28.8557	-90.4096	34.43	0.06	0.03	0.00	0.04	0.11
56	28.9062	-90.4578	31.89	0.05	0.08	0.03	0.16	0.24
57-2	28.9341	-90.4891	26.15	0.10	0.21	0.12	0.15	0.36
58	28.972	-90.5221	22.59	0.06	0.16	0.10	0.19	0.35
59	28.984	-90.5508	20.88	0.09	0.12	0.04	0.17	0.29
60	28.9286	-90.56	26.70	0.07	0.10	0.03	0.09	0.19
61	28.8719	-90.5694	31.65	0.10				
62	28.8462	-90.5891	34.15	0.07				
63	28.9025	-90.6253	29.37	0.11	0.10	0.00	0.21	0.32
64-2	28.9488	-90.6598	21.61	0.08				
65	29.0124	-90.7029	21.08	0.20	0.37	0.17	0.14	0.34
66	28.973333	-90.7192	22.31	0.15				
67	28.9217	-90.7288	26.08	0.10				
68-2	28.9016	-90.7343	25.89	0.15	0.30	0.16	0.07	0.22
69	28.8427	-90.74933	31.48	0.07	0.10	0.03	0.08	0.15
70	28.7925	-90.7617	32.56	0.09	0.03	0.00	0.34	0.43
71	28.7346	-90.776	32.74	0.14	0.15	0.01	0.01	0.15
72-3	28.6753	-90.79037	33.84	bd	bd	0.00	0.11	0.11
73	28.6188	-90.805	34.65	bd	bd	0.00	0.16	0.16
74	28.5639	-90.8186	35.29	0.09	0.13	0.04	0.03	0.12
75-2	28.522	-90.8283	35.15	bd	0.06	0.06	0.04	0.04
76	28.5593	-90.8472	35.82	bd	0.09	0.09	0.01	0.01
77	28.6086	-90.8693	33.73	0.03	0.02	0.00	0.18	0.21
78	28.6659	-90.895	33.57	0.06	0.07	0.01	0.13	0.19
79-2	28.7662	-90.9426	31.53	0.07				
80	28.8478	-90.9786	26.85	0.12				
81	28.9022	-91.0023	24.93	0.11				
82-2	28.9698	-91.0324	24.77	0.07				
83	29.0213	-91.0699	22.03	0.22				
84	28.9561	-91.0974	24.90	0.12	0.28	0.17	0.17	0.29
85-2	28.9145	-91.1154	25.16	0.15				
86	28.8673	-91.1354	27.44	0.09	0.19	0.10	0.32	0.51
87	28.8007	-91.1637	29.22	0.04				
88	28.732	-91.1895	33.08	0.07				
89-2	28.6717	-91.2114	34.81	0.04	0.02	0.00	0.10	0.14
90	28.5975	-91.2625	34.98	0.06	0.06	0.00	0.06	0.12
91	28.6427	-91.2837	34.97	0.08	0.08	0.00	0.09	0.16
92-2	28.705	-91.314	34.63	0.04	0.09	0.06	0.13	0.23
93	28.7501	-91.334	32.61	0.05	bd	0.00	0.16	0.21
94	28.8092	-91.3601	28.49	0.12	0.19	0.07	0.43	0.62
95	28.8632	-91.3822	25.32	0.08	0.14	0.06	0.20	0.34
96	28.9245	-91.4074	22.91	0.07	0.10	0.03	0.24	0.33
97	28.9817	-91.4346	22.46	0.04	0.09	0.06	0.35	0.44
98	29.0403	-91.4613	22.19	0.03	0.12	0.09	0.26	0.38
99	29.099	-91.4887	22.28	0.03	0.17	0.14	0.37	0.54

Station	Latitude	Longitude	Salinity	PO4	TDP	DOP	PP	TP
100	29.0533	-91.5159	23.11	0.07	0.11	0.04	0.26	0.37
101	28.9794	-91.5415	23.38	0.04	0.11	0.07	0.09	0.20
102	28.9355	-91.5565	25.29	0.08	0.14	0.06	0.14	0.27
103	28.8843	-91.5741	34.71	0.06	0.07	0.01	0.06	0.13
104-2	28.8172	-91.598	35.58	bd	0.04	0.04	0.02	0.06
105	28.7526	-91.619	35.17	0.05				
106	28.6892	-91.641	35.04	bd	0.11	0.11	0.01	0.12
107	28.6357	-91.65637	35.41	bd	0.06	0.06	0.01	0.07
108	28.5786	-91.6795	35.69	bd	0.06	0.06	0.02	0.07
109	28.54	-91.6968	35.55	bd	bd	0.00	0.01	0.01
110	28.6163	-91.69447	35.36	bd	0.00	0.00	0.00	0.00
111-2	28.6513	-91.75	35.37	bd				
112	28.7149	-91.772	35.76	0.06	bd	0.00	0.02	0.02
113	28.7758	-91.7993	34.96	bd				
114	28.8346	-91.8256	35.14	bd				
115-3	28.8933	-91.8518	35.52	0.04	0.07	0.02	0.04	0.11
116	28.9431	-91.8743	34.82	bd				
117	29.0106	-91.9054	33.15	0.04	0.05	7.00	0.08	0.13
119-2	29.1405	-91.9644	24.78	bd	0.09	0.09	0.24	0.33
120	29.1833	-91.9841	25.52	0.11	0.35	0.24	0.07	0.42
121	29.1321	-91.9874	25.22	0.11	0.31	0.20	0.02	0.33
122	29.0574	-91.9875	33.31	0.08	0.20	0.13	0.01	0.21
123-2	29.0037	-91.9882	34.11	bd	0.13	0.13	0.01	0.13
124	28.942	-91.9892	35.17	0.04	0.07	0.04	0.03	0.10
125	28.89	-91.989	35.58	bd	0.03	0.03	0.02	0.05
126	28.8208	-91.9889	35.23		0.14			
127-2	28.8344	-91.9495	36.31	bd	0.08	0.08		
128	28.8585	-91.9206	35.29	0.03	0.09	0.06	0.02	0.11
129-2	28.9009	-91.8752	35.07	bd	0.09	0.09	0.04	0.13
130	28.9261	-91.8482	35.02	bd	0.12	0.12	0.09	0.21
131	28.9665	-91.7999	34.14	bd	0.10	0.10	0.07	0.17
132	29.0041	-91.7548	27.75	0.03				
133-2	29.0187	-91.7435	26.04	bd	0.12	0.12	0.08	0.20
134	29.0717	-91.679	23.81	bd	0.17	0.17	0.32	0.49
135-2	29.1177	-91.6289	23.78		0.18	0.18	0.33	0.51
136-2	29.1629	-91.5798	22.78	bd	0.18	0.18	0.28	0.46
137-2	29.2019	-91.5365	22.16	0.06				
138	29.2445	-91.4968	21.67	0.15	0.28	0.13	0.72	1.00
139	29.2991	-91.4484	5.96	0.49	1.64	1.15	0.96	2.60
140	29.3285	-91.4217	1.37	1.28	1.68	0.40	1.76	3.44
141-2	29.3436	-91.40825	0.34	1.49	1.74	0.25	2.05	3.78
142	29.3055	-91.4429	4.41	0.61	1.88	1.27	1.02	2.90
143	29.2562	-91.4865	21.88	0.40	0.63	0.23	1.11	1.74
144	29.2079	-91.5173	22.01	0.14	0.34	0.20	1.19	1.53
145	29.151802	-91.5072	21.44	0.08	0.17	0.09	0.65	0.81
146	29.0918	-91.507	22.33	0.07	0.18	0.11	0.39	0.57
147-2	29.0393	-91.5058	21.93	0.07	0.17	0.10	0.25	0.42
148	28.9811	-91.5048	24.71	bd	0.30	0.30	0.21	0.51
149	28.9254	-91.5047	30.14	0.08	0.09	0.01	0.21	0.30

Station	Latitude	Longitude	Salinity	PO4	TDP	DOP	PP	TP
150	28.8659	-91.5051	30.36	0.04	0.16	0.12	0.10	0.26
151	28.8125	-91.5039	34.60	0.05	0.08	0.03	0.07	0.15
152	28.8191	-91.4338	33.28	0.08	0.01	0.00	0.13	0.22
153	28.8215	-91.03563	34.70	bd				
154	28.8215	-91.2956	27.80	0.04	0.10	0.06	0.13	0.23
155	28.8221	-91.2185	26.42	0.06	0.17	0.10	0.13	0.29
156	28.8285	-91.1453	25.81	0.08	0.18	0.09	0.09	0.27
157	28.502267	-91.0676	27.23	0.04			0.13	
158	28.8493	-91.0022	29.66	0.09	0.13	0.04	0.12	0.25
159	28.8685	-90.926	29.83	0.13	0.16	0.03	0.13	0.29
160-2	28.876	-90.8951	28.30	0.05	0.10	0.06	0.26	0.36
161	28.8409	-90.8906	31.38	0.04				
162	28.7797	-90.8808	33.32	0.05				
163	28.7066	-90.8761	33.40	bd				
164-3	28.6405	-90.8716	34.72	bd	0.00	0.00	0.16	0.16
165	28.6807	-90.8406	34.06	0.12	0.14	0.03	0.03	0.17
166	28.7277	-90.8047	34.08	bd	0.10	0.10	0.16	0.25
167	29.2964	-90.8099	32.90	0.06				
168-2	28.8543	-90.8398	30.88	0.06				
169	28.8895	-90.8197	29.46		0.15	0.15		
170	28.954	-90.7776	29.71	0.04	0.12	0.08	0.37	0.49
171	28.9708	-90.6952	27.52	1.95	0.19	0.00	0.24	0.43
172-2	28.9861	-90.6167	25.10	0.10	0.15	0.05	0.30	0.45
173	28.9825	-90.6146	24.50	0.06	0.17	0.10	0.39	0.56
174	28.9381	-90.5105	24.58	0.07	0.20	0.13	0.36	0.56
175	28.9892	-90.5786	23.70	0.11	0.25	0.15	0.21	0.47
176	29.19	-90.5501	24.00	0.07	0.10	0.03	0.45	0.55
177	29.0202	-90.562	23.85	0.07	0.15	0.08	0.65	0.80
mean			**27.81**	**0.13**	**0.22**	**0.15**	**0.25**	**0.48**
median			*29.66*	*0.06*	*0.12*	*0.06*	*0.14*	*0.28*

A3.2 May 2004 Metadata, Part 2

Station	NO_x	NH_4^+	DIN	TDN	DON	PON	TN	DOC	POC
1-2	77.49	0.65	78.14	103.30	25.16	22.96	126.26	281.29	220.06
4-2	28.20	1.64	29.83	37.10	7.27	7.44	44.54	144.09	64.22
5	14.58	0.58	15.16	23.90	8.74	8.477	32.38	154.47	60.20
7	bd	0.29	0.29			5.203			44.35
8	bd	bd	bd			4.415		183.5	33.76
9	bd	bd	bd	5.70	5.20	1.869	7.57	97.9	23.56
10	bd	bd	bd	8.00	7.50	0	8.00	157.8	13.60
11	bd	bd	bd			2.402		151.5	20.10
12	bd	bd	bd	6.80	6.30	3.05	9.85	93.2	25.53
13	4.34	0.43	4.77	10.40	5.63	2.91	13.31	110.2	21.20
14	35.87	2.44	38.31	54.07	15.76	5.854	59.92	233.75	57.14
15	22.72	2.99	25.71	40.38	14.67	6.627	47.01	198.7	50.54
16-2	16.22	1.62	17.84	23.79	5.95	4.742	28.53	141.67	35.22
17	10.99	0.95	11.94	27.70	15.76	10.87	38.56	253.12	72.01
18	9.45		9.45			6.983			53.29
19	9.42	2.54	11.95	27.69	15.74	6.822	34.51	217.9	45.58
20	16.26	1.82	18.08	25.14	7.06	5.381	30.52	154	44.93
21	11.25		11.25			7.38			54.77
22	9.39	1.61	10.99	23.14	12.15	7.22	30.36	215.7	59.91
23	13.05	1.23	14.28	25.94	11.67	14.07	40.01	189.2	80.65
24	20.64	1.16	21.80	32.40	10.60	7.992	40.39	219.2	59.05
25	24.38	2.36	26.74	37.17	10.43	3.964	41.14	228.8	51.20
26	28.48		28.48			8.733			67.06
27	21.53	1.48	23.01	32.97	9.96	1.773	34.74	210.1	38.09
28	4.68	0.58	5.26			5.04			36.80
29	2.84	bd	2.84	11.80	8.96	5.33	17.13	153	9.13
30	2.07	bd	2.07	7.80	5.73	5.33	13.13	111.8	9.13
31-2	0.85		0.85			5.31			8.96
32	bd		0.50			2.894			24.13
33	1.05	bd	1.05	6.90	5.85	3.943	10.84	100.1	26.92
34-2	1.22	bd	1.22	8.10	6.88	2.895	11.00	117.1	26.32
35	0.50	0.42	0.92	4.98	4.07	0	4.98	111.4	53.51
36	0.12	0.17	0.29			3.218			23.22
37	6.53		6.53			5.698			53.06
38-2	11.81	0.45	12.27	19.92	7.66	5.95	25.87	175.8	67.12
39	10.29	1.58	11.87	23.26	11.38	5.95	29.21	203	58.50
40	10.98	0.79	11.77	22.50	10.73	13.91	36.41	190.35	86.34
41	9.70	0.43	10.13	20.40	10.27	10.61	31.01	200.6	76.96
42	2.63	0.10	2.73	9.30	6.57	3.045	12.35	93.1	39.73
43	1.00	0.35	1.35	5.40	4.05	0.323	5.72	84.7	17.76
44	bd	0.53	0.53	3.99	3.46	3.234	7.23	62.7	20.94
45-2	bd	0.13	0.13	6.40	6.27	1.962	8.36	120.6	17.26
46	bd	bd	0.50	6.50	6.00	1.9	8.40	136.7	17.02
47	0.85	0.35	1.21			1.629			17.26
48-2	1.06	0.14	1.21	5.90	4.70	4.83	10.73	88.1	37.39
49	7.64	0.57	8.21	15.00	6.79	7.502	22.50	151.1	54.16
50-6	7.04		7.04			9.759			63.51

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PON	TN	DOC	POC
51	6.26		6.26			9.515			60.11
52	1.33		1.33			3.792			28.46
53	0.70	0.30	0.99	5.40	4.41	3.795	9.20	78.7	26.56
54-2	bd	bd	bd	7.70	7.20	3.964	11.66	140.5	27.83
55	0.47	bd	0.47	8.40	7.93	3.671	12.07	146.7	23.81
56	3.08	0.57	3.65	10.70	7.05	5.02	15.72	109.3	32.22
57-2	7.18	1.01	8.19	12.70	4.51	4.411	17.11	113.7	47.48
58	9.07	1.36	10.43	30.90	20.47	5.129	36.03	316.1	56.12
59	8.60	1.28	9.88	19.60	9.72	6.377	25.98	213.4	51.57
60	6.65	0.79	7.44	16.20	8.76	5.122	21.32	196	35.26
61	2.66		2.66			2.89			18.93
62	bd		bd			2.828			21.35
63	5.32	1.56	6.87	14.40	7.53	2.678	17.08	168.8	38.80
64-2	9.09	1.47	10.55			6.177		240.1	49.08
65	10.59	2.44	13.03	22.50	9.47	8.757	31.26	194.7	73.46
66	8.21	1.55	9.76			7.287			52.34
67	7.85	1.40	9.25			4.816			40.48
68-2	8.35	2.15	10.50	18.32	7.82	7.277	25.60	165	51.34
69	2.09	0.78	2.87	12.10	9.23	3.138	15.24	191.3	23.60
70	2.03	0.54	2.57	6.40	3.84	2.848	9.25	98.9	19.58
71	1.22	0.62	1.84	7.40	5.56	3.349	10.75	140.6	27.80
72-3	bd	bd	bd			6.18		203.2	43.03
73	0.49	bd	0.49			4.087		220.6	27.11
74	bd	0.23	0.23	6.63	6.40	1.555	8.19	160.5	43.65
75-2	bd	bd	bd			1.555		221.7	16.80
76	bd	bd	bd			4.211		228.7	26.90
77	bd	bd	bd	8.30	7.80	7.04	15.34	125.2	42.27
78	bd	bd	bd	7.77	7.27	5.582	13.36	191.7	35.67
79-2	1.77		1.77			7.095			40.80
80	6.02		6.02			7.924			41.73
81	7.90		7.90			9.622			55.14
82-2	8.20		8.20			7.275			115.34
83	6.41		6.41			11.29			68.50
84	7.78	1.91	9.69	21.20	11.51	8.398	29.60	233.8	46.11
85-2	6.50		6.50			10.35			63.93
86	5.13	1.48	6.61	16.40	9.80	8.858	25.26	247.4	50.88
87	3.91		3.91			10.41			62.87
88	bd	bd	bd	9.00	8.50	6.087	15.09	151.1	39.63
89-2	bd		bd	7.10	6.60	5.391	12.49	134.7	34.62
90	bd	0.17	0.17	9.86	9.70	4.457	14.32	212	30.17
91	bd	0.29	0.29	7.10	6.81	5.448	12.55	216.5	30.45
92-2	bd		bd	11.70	11.20	7.605	19.31	244.45	49.73
93	bd	0.07	0.07	7.80	7.73	7.253	15.05	148.5	46.52
94	3.83	0.55	4.38	13.50	9.12	6.8	20.30	197.2	47.80
95	5.11	0.61	5.72	14.90	9.18	5.805	20.71	199.8	38.59
96	7.28	1.16	8.44	18.40	9.96	7.246	25.65	226.5	46.66
97	6.92	1.00	7.92			10.34			69.30
98	5.50	0.72	6.22	25.22	19.00	9.402	34.62	282	57.94
99	5.38	0.76	6.14			9.902		270.2	65.76

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PON	TN	DOC	POC
100	5.82	0.84	6.66	25.86	19.20	9.123	34.98	308.1	59.20
101	6.86	0.77	7.63	28.03	20.40	9.225	37.25	258.3	55.68
102	4.07	0.40	4.47	19.57	15.10	7.953	27.52	264.3	52.14
103	bd	bd	bd	7.50	7.00	6.262	13.76	189.7	37.39
104-2	bd	bd	bd	6.10	5.60	3.758	9.86	183	23.51
105	bd	bd	bd	8.00	7.50	6.064	14.06	178.5	31.03
106	bd	bd	bd	6.40	5.90	3.618	10.02	189.2	20.49
107	0.07	bd	0.07			3.139	3.14	195.5	0.00
108	bd	bd	bd	6.90	6.40	3.212	10.11	173.1	19.95
109	bd	bd	bd	6.50	6.00	3.19	9.69	173.3	18.99
110	bd	bd	bd	6.20	5.70	0	6.20	184.9	23.58
111-2	bd	bd	bd			2.995			21.66
112	bd	0.45	0.45	6.40	5.95	3.221	9.62	174.1	21.97
113	0.73	bd	0.73			3.423			19.89
114	bd	bd	bd	7.60	7.10	4.815			27.75
115-3	3.21	0.59	3.81	12.10	8.29	4.451	16.55	132.8	20.62
116	bd	0.00	0.50	7.10	6.60	5.278			28.66
117	bd	0.18	0.18	7.30	7.13	6.575	13.87	207	40.47
119-2	3.27	0.49	3.76	13.40	9.64	11.88	25.28	277.5	66.14
120	0.35	0.72	1.07	17.00	15.93	12.97	29.97	277.1	77.73
121	3.36	0.78	4.13	17.00	12.87	11.28	28.28	255	73.33
122	bd	0.14	0.14	9.10	8.96	7.416	16.52	158.6	48.65
123-2	bd		bd	9.80	9.30	6.256	16.06	198.6	37.50
124	bd	1.43	1.43	8.63	7.20	5.201	13.83	229.9	24.62
125	bd	bd	bd	9.00	8.50	0	9.00	189.2	24.80
126		bd	bd	6.50	6.00	6.683	13.18	241.1	22.54
127-2	bd	0.08	0.08	6.70	6.62	5.819	12.52	140.9	22.46
128	bd	bd	bd	7.50	7.00	6.878	14.38	203.8	25.60
129-2	bd	0.54	0.54	7.10	6.56	6.98	14.08	188.2	22.46
130	bd	bd	bd	6.60	6.10	7.176	13.78	165.8	26.17
131	bd	bd	bd	6.91	6.41	6.943	13.85	158.8	32.05
132	0.78		0.78			11.99			61.32
133-2	2.67	0.33	3.00	17.04	14.04	13.39	30.43	227.4	77.28
134	3.96	0.73	4.68	14.10	9.42	14.49	28.59	324.4	91.33
135-2		0.61	0.61	17.10	16.50	11.5	28.60	222.7	65.26
136-2	4.33	0.68	5.01	8.06	3.05	13.02	21.08	108.9	71.07
137-2	bd	0.59	0.59	6.76	6.18	20.02	26.79	115.7	137.81
138	bd	0.68	0.68	12.40	11.72	21.53	33.93	263.7	189.21
139	13.68	1.56	15.24	72.30	57.06	0.824	73.12	607.9	15.76
140	45.59	2.27	47.86	67.00	19.15	6.613	73.61	401.8	42.43
141-2	51.72	1.86	53.58	75.50	21.93	27.5	103.00	376.8	282.59
142	14.51	2.40	16.90	66.80	49.90	15.87	82.67	489.5	139.72
143	bd	0.86	0.86	13.60	12.74	18.23	31.83	279.4	164.72
144	bd	0.65	0.65	11.01	10.36	16.81	27.82	232	175.41
145	1.14	0.69	1.83	15.70	13.87	10.94	26.64	320.3	105.15
146	4.88	1.08	5.96	16.90	10.94	9.87	26.77	249.2	79.25
147-2	7.68	0.90	8.59	18.85	10.27	9.133	27.99	255.2	61.56
148	2.03	2.49	4.52	14.04	9.52	5.244	19.28	158.3	36.10
149	2.11		2.11	14.21	12.11	5.597	19.81	263.2	47.00

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PON	TN	DOC	POC
150	bd	0.30	0.30	10.50	10.20	4.79	15.29	185.1	31.56
151	bd	bd	bd	7.10	6.60	6.695	13.79	195.7	42.55
152	1.23	0.45	1.68	9.90	8.22	4.228	14.13	126.5	28.87
153	bd	0.38	0.38	8.50	8.12	6.974	15.47		42.93
154	2.21	0.58	2.79	11.40	8.61	3.481	14.88	186.2	27.49
155	2.55	0.89	3.45	16.50	13.06	5.916	22.42	258.2	45.74
156	5.27	1.08	6.34	15.90	9.56	NF		260.2	NF
157	1.77	1.57	3.34	17.30	13.96	5.595	22.89		43.21
158	2.46	0.95	3.41	11.50	8.09	5.425	16.92	207.4	31.74
159	4.65	1.40	6.05	14.20	8.15	3.792	17.99	183.8	27.15
160-2	3.91	0.75	4.66	13.50	8.84	11.99	25.49	185.1	63.65
161	0.98	bd	0.98			11.99			63.65
162	bd	bd	bd	7.50	7.00	3.999	11.50		22.87
163	bd	bd	bd			3.359		246.4	28.36
164-3	bd	bd	bd	6.40	5.90	4.736	11.14		32.28
165	bd	bd	bd	7.90	7.40	4.177	12.08	174.2	27.92
166	bd	bd	bd	6.70	6.20	4.866	11.57		27.97
167	1.88	0.35	2.23			7.406			46.00
168-2	3.95	1.10	5.05						
169		0.34	0.34	14.80	14.46			179.9	
170	3.23	0.35	3.58	11.50	7.92				
171	8.60	0.53	9.13	11.60	2.47			225.6	
172-2	6.23	0.46	6.69	13.00	6.31				
173	6.85	0.42	7.27					264.5	
174	5.17	0.25	5.42	24.62	19.20			250	
175	6.83		6.83	27.23	20.40			315.7	
176	6.79	0.40	7.19					247.5	
177	6.13	0.68	6.81	10.06	3.25			115.1	
mean	**5.35**	**0.65**	**5.93**	**16.36**	**9.97**	**6.674**	**23.20**	**199.74**	**48.08**
median	*2.16*	*0.46*	*2.73*	*11.65*	*8.14*	*5.836*	*17.08*	*191.7*	*40.64*

A3.3 May 2004 Metadata, Part 3

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl a	AP Activity
1-2	65.70	39.97	30.14	108.8	0.67	
4-2	24.61	32.11	27.09	14	0.32	
5	17.60	32.60	29.67	7.6	1.51	
7	1.38	3.71		8.5	0.23	
8	1.10	16.67			0.23	
9	bd	11.36	137.79		0.06	
10	bd	16.67	48.80	0	0.03	6.84
11	bd	16.67		3.6	0.06	7.45
12	1.25	15.15	117.26		0.22	12.91
13	5.57	31.38	35.14		0.49	13.71
14	41.66	39.33	33.62	21.2	0.41	21.73
15	27.04	48.87	33.05	4.8	2.57	154.25
16-2	22.18	71.64	38.86	3.2	3.09	304.98
17	24.08	331.67	57.90	2.8	2.57	192.82
18	22.24	121.21		4.4	1.87	429.23
19	23.68	170.73	83.80	3.6	1.34	98.67
20	19.75	173.87	46.92	9	2.21	627.40
21	22.56	65.02		1.2	3.73	325.02
22	21.13	199.82	88.41	0.8	3.36	1333.04
23	24.81	213.10	78.61	12	6.07	782.72
24	25.74	68.13	54.76	12.8	5.84	
25	30.03	45.71	51.44	6.67	3.06	
26	20.35	28.91		11.52	0.28	23.74
27	23.71	28.79	43.08	8	0.78	17.61
28	6.69	35.78			0.29	
29	3.06	55.71	93.76	4.8	0.51	59.17
30	1.93	69.07	42.11	0.8	0.64	79.31
31-2	1.04	12.19		1.2	0.06	91.99
32	bd	13.89			0.20	53.47
33	1.21	34.97	92.60	0	0.33	61.42
34-2	1.10	40.53	86.10		0.32	
35	0.97	19.91	35.76	7.27	0.15	10.84
36	2.23	6.40		13.2	0.26	16.66
37	11.47	73.34			2.75	51.92
38-2	23.20	260.96	46.05	1.6	2.92	55.68
39	24.61	169.60	36.84	5.2	2.86	79.43
40	25.84	392.43	56.96	1.2	4.33	120.96
41	24.89	316.59	47.47	5.2	4.24	140.36
42	5.81	71.82	56.40	2.4	1.15	68.83
43	1.81	33.68	61.07	0.8	0.17	47.88
44	0.66	11.30	62.91	3.2	0.06	30.96
45-2	0.65	4.40	97.68		0.06	27.41
46	0.87	16.67	66.67	2.4	0.04	38.24
47	1.29	38.90		2.8	0.06	12.66
48-2	0.80	40.17	249.92	3.57	0.10	28.56
49	18.65	273.60	50.98	3.6	2.53	133.02
50-6	15.15	180.44		1.6	2.93	180.70
51	12.86	51.28			2.31	104.59
52	3.33	12.95		1.2	0.49	38.55

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl a	AP Activity
53	bd	33.13	82.25	0.8	0.15	42.67
54-2	bd	16.67	118.70	0.8	0.15	84.16
55	1.25	7.74	114.81	3.6	0.23	71.49
56	5.60	71.55	66.82	6.8	0.55	33.04
57-2	13.22	86.18	48.19	5.2	1.47	43.11
58	16.54	176.71	102.94		2.19	269.10
59	15.67	116.25	88.90	8	2.66	184.74
60	15.28	104.80	113.60	6.4	1.34	153.86
61	3.79	27.67		0	0.52	69.91
62	0.87	7.14		5.2	0.19	388.03
63	11.80	64.23	53.37	5.6	0.71	348.89
64-2	16.03	131.93		8.4	2.66	1034.66
65	21.77	64.82	92.15	8.8	2.06	476.44
66	14.22	66.36		9.6	2.14	779.73
67	13.43	91.53		6.8	1.76	479.35
68-2	14.51	70.97	117.20	62.4	1.44	501.32
69	3.51	41.00	102.27	4	0.49	17.18
70	1.45	27.29	21.51	20	0.38	292.69
71	bd	12.96	70.07	24.4	0.55	637.84
72-3	bd	16.67		0	1.13	720.43
73	2.93	0.16			0.58	489.20
74	1.32	2.54	68.10	17.2	0.67	172.50
75-2	1.13	16.67		6.4	0.09	154.07
76	bd	16.67		4.4	0.04	75.67
77	bd	16.67	71.91	1.2	1.41	1169.02
78	bd	8.20	70.94	2	0.55	197.14
79-2	2.78	27.29		12.8	0.78	128.88
80	12.00	49.72		0.4	0.68	46.66
81	14.19	70.51			1.02	124.52
82-2	18.32	124.26			0.83	30.65
83	19.32	29.53		4	0.97	18.81
84	16.89	81.41	103.64	1.2	0.90	335.99
85-2	17.64	42.21		12	1.16	446.82
86	10.97	75.07	49.71	4.8	1.34	403.08
87	6.84	88.95		6.4	1.22	1316.81
88	0.62	7.46		0.4	1.44	
89-2	2.36		89.95	4	0.46	
90	0.57	2.67	120.55	4	0.25	
91	1.45	3.82	76.30	2.4	0.28	
92-2	0.52	13.89	85.06	4.8	0.61	215.19
93	bd	1.62	71.98	2.8	0.78	14.13
94	6.86	36.48	32.77	2	2.05	132.23
95	8.68	69.73	61.72	0.8	1.92	284.58
96	18.26	117.18	76.97	4	1.31	297.35
97	13.12	219.89		2.8	2.61	401.24
98	10.32	207.17	91.21	4.8	2.56	722.09
99	9.75	180.65		7.5	3.43	834.13
100	7.86	99.40	94.24	9.5	1.98	414.87
101	11.46	186.02	183.78	6.4	2.16	319.74
102	4.99	53.18	100.14	4.8	2.06	382.72
103	bd	7.81	104.49	5.2	0.51	77.93

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl a	AP Activity
104-2	bd	16.67	152.36	3.6	0.07	42.84
105	bd	10.20		4.8	0.10	32.31
106	bd	16.67	81.85		0.06	12.70
107	0.58	2.40	41.91	4.8	0.01	9.21
108	0.69	16.67	141.62	5.2	0.03	0.14
109	0.77	16.67	821.18	1.2	0.03	0.12
110	0.60	16.67	1631.58	8.8	0.01	0.10
111-2	bd	16.67		2.8	0.06	0.23
112	bd	7.13	490.86	2.8	0.04	0.30
113	1.05	24.20		10	0.09	0.49
114	bd	16.67		30	0.07	0.44
115-3	6.61	90.62	153.25	27.6	0.12	465.69
116	bd	16.67		35.2	0.17	187.13
117	bd	4.17	107.78	37.6	1.02	35.80
119-2	bd	125.33	76.64	4	3.41	440.78
120	bd	9.72	71.60	2	4.21	708.00
121	1.14	36.58	84.75	7.2	3.28	658.36
122	bd	1.83	77.32	32.4	0.74	189.20
123-2	bd		122.38	57.6	0.42	15.26
124	bd	38.73	134.31		0.06	10.02
125	0.68	16.67	176.70	0.4	0.03	15.27
126					0.03	15.93
127-2	bd	2.63			0.01	13.68
128	bd	16.13	128.75	2.8	0.03	7.66
129-2	bd	17.87	112.04		0.06	13.01
130	bd	16.67	64.82	0	0.17	39.62
131	bd	16.67	81.61	3.2	0.70	68.47
132	0.60	23.06		0.8	1.86	252.32
133-2	2.99	99.87	152.78	1.2	2.32	293.82
134	5.32	156.10	58.93	7.2	2.90	402.22
135-2			56.49	6	1.77	362.71
136-2	6.96	166.97	45.79	5.2	3.14	1012.10
137-2	7.84	10.64		32	5.61	754.55
138	9.62	4.72	33.86	38.8	5.00	30.42
139	14.21	31.09	28.10	10.4	1.37	18.44
140	41.70	37.53	21.39	51.2	1.25	36.97
141-2	33.38	35.98	27.21	144	1.31	59.74
142	7.27	27.76	28.54	48	1.23	23.79
143	9.09	2.15	18.28		3.99	13.54
144	10.55	4.74	18.14	21.33	5.08	192.10
145	4.31	21.82	32.72	26.67	4.71	1803.79
146	8.55	90.30	46.98	4.5	3.20	916.96
147-2	10.56	128.16	66.64	6	26.84	412.98
148	3.13	150.67	37.77	7.2	2.24	53.53
149	1.96	27.04	67.16	7.6	2.51	157.23
150	bd	7.39	58.90	4.8	1.83	100.32
151	bd	10.00	92.34	8.8	7.03	69.80
152	1.88	20.45	65.26	8.4	1.79	116.45
153	bd	12.77		2	0.44	72.21
154	1.29	66.40	64.01		1.95	223.30
155	2.92	53.83	76.19		2.12	180.52

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl a	AP Activity
156	8.27	75.51		9.6	2.27	158.72
157	3.18	92.67		6	1.19	88.46
158	3.57	39.20	67.89	6.4	1.54	95.99
159	10.87	47.61	62.23	4.4	0.96	51.75
160-2	12.01	101.30	70.29	6.4	1.19	70.54
161	1.13	25.10		5.2	1.23	83.00
162	bd	10.87		2.8	0.52	100.70
163	bd	16.67		5.6	0.29	98.52
164-3	bd	16.67	68.61	0	1.05	59.39
165	bd	4.35	69.89	1.6	0.62	78.74
166	bd	16.67	45.86	4	0.45	99.20
167	5.58	38.48		0.8	1.25	53.97
168-2	12.09	90.23		2	2.32	38.65
169				1.6	3.04	60.61
170	7.49	85.29		3.6	1.25	49.00
171	12.29	4.67		0.4	1.47	26.40
172-2	12.31	64.91		4	3.66	175.61
173	17.41	113.66		2.8	3.25	174.87
174	13.26	80.85		2.8	4.04	243.66
175	18.10	63.82		3.2	3.75	304.60
176	19.00	101.28		1.2	4.18	336.92
177	14.40	94.57		1.2	3.92	360.54
mean	**8.31**	**60.10**	**99.13**	**99.127**	**99.13**	**99.13**
median	*3.54*	*35.37*	*69.89*	*69.89*	*69.89*	*69.89*

A4.1 July 2004 Metadata, Part 1

Station	Salinity	Latitude	Longitude	P_i	TDP	DOP	PP	TP
2-2	0.18	29.1691	-89.2575	3.42	2.31	0.00	1.63	5.05
3-2	33.04	28.8786	-89.4349	1.50	1.44	0.00	0.55	1.99
4	10.66	28.79	-89.4405	0.50	0.99	0.50	1.44	2.43
5-2	30.66	28.7316	-89.4389	0.12	0.29	0.17	0.45	0.74
6	18.35	28.6931	-89.4407	0.14	0.20	0.07	1.06	1.27
7-2	21.55	28.6035	-89.4366	0.05	0.10	0.05	0.20	0.31
8	20.82	28.5796	-89.4387	0.05	0.01	0.00	0.19	0.23
9-2	20.11	28.5138	-89.4412	0.08	0.07	0.00	0.25	0.33
10	19.63	28.5162	-89.4477	0.11	0.06	0.00	0.50	0.60
11	20.40	28.583	-89.4554	0.08	0.11	0.03	0.47	0.58
12	16.71	28.6483	-89.4633	0.25	0.40	0.16	0.65	1.06
13-2	29.30	28.7172	-89.4689	0.06	0.16	0.10	0.29	0.45
14	12.41	28.7489	-89.4715	0.33	0.59	0.26	1.09	1.68
15	8.42	28.8093	-89.4786	0.89	1.51	0.62	0.88	2.39
16-2	26.84	28.8925	-89.4886	1.21	0.67	0.00	0.39	1.60
17	13.47	28.9298	-89.4931	1.76	0.71	0.00	0.43	2.19
18	10.23	29.0036	-89.5021	0.30	0.40	0.10	1.16	1.57
19-2	6.85	29.0801	-89.5113	0.52	0.80	0.28	1.23	2.03
20	4.56	29.1638	-89.5215	2.26	2.47	0.21	1.43	3.90
21	5.64	29.0935	-89.5326	1.56	2.80	1.25	0.35	3.15
22	10.77	29.0372	-89.5382	0.19	0.20	0.01	1.43	1.64
23-2	21.62	28.9469	-89.5466	0.19	0.19	0.00	0.88	1.07
24	14.20	28.8879	-89.5525	0.16	0.06	0.00	0.71	0.87
25	13.29	28.8219	-89.5617	0.33	0.82	0.49	0.22	1.04
26-2	15.44	28.7251	-89.5752	0.24	0.47	0.23	0.18	0.65
27-2	28.21	28.6293	-89.582	0.16	0.09	0.00	0.32	0.47
28	20.51	28.5448	-89.5918	0.15	0.11	0.00	0.17	0.31
29	20.33	28.5952	-89.6119	0.16	0.15	0.00	0.14	0.30
30-2	19.95	28.6468	-89.6214	0.25	0.27	0.02	0.18	0.45
31	16.82	28.7041	-89.6378	0.28	0.52	0.25	0.36	0.88
32	17.15	28.7598	-89.656	0.30	0.60	0.30	0.25	0.85
33-2	15.14	28.8666	-89.6917	0.14	0.16	0.02	0.44	0.60
34	13.98	28.9025	-89.6996	0.43	0.92	0.49	0.19	1.11
35	15.93	28.9706	-89.7227	0.13	0.81	0.68	0.16	0.97
36	16.33	28.9996	-89.7326	0.19	0.07	0.00	0.49	0.68
37	17.04	29.0445	-89.7477	0.21	0.23	0.01	0.56	0.78
38-2	18.25	29.1055	-89.7673	0.16	0.41	0.25	0.50	0.90
39	18.22	29.1422	-89.7802	0.08	0.43	0.35	0.61	1.05
40	20.00	29.214	-89.8053	0.04	0.07	0.04	0.78	0.85
41	24.22	29.1943	-89.8208	0.12	0.09	0.00	0.62	0.74
42-2	21.67	29.1166	-89.831	0.18	0.13	0.00	0.15	0.32
43	20.02	29.0774	-89.8371	0.15	0.18	0.03	0.55	0.73
44	19.77	28.998	-89.8522	0.15	0.15	0.01	0.50	0.66
45	21.00	28.9332	-89.8644	0.15	0.24	0.09	0.48	0.72
46-1		28.8457	-89.8786	0.10				
46-2	21.96	28.8457	-89.8786	0.10	0.07	0.00	0.26	0.36
47	23.04	28.7963	-89.8876	0.16			0.48	

Station	Salinity	Latitude	Longitude	P_i	TDP	DOP	PP	TP
48	23.22	28.7217	-89.9025	0.15	0.21	0.06	0.37	0.58
49	23.10	28.6465	-89.9176	0.10	0.29	0.19	0.18	0.47
50-1	23.55	28.5834	-89.9232	0.10				
50-2	23.86	28.5834	-89.9232	0.11				
51	22.19	28.5717	-89.9263	0.10	0.03	0.00	0.40	0.50
53	22.88	28.5005	-89.9458	0.08	0.09	0.01	0.42	0.51
54-2	24.32	28.57	-89.9683	0.12	0.10	0.00	0.30	0.42
55	1.34	28.6127	-89.9838	0.12	0.05	0.00	0.41	0.52
56	23.73	28.6522	-89.9978	0.10	0.04	0.00	0.37	0.47
57	23.77	28.7149	-90.0197	1.95	0.09	0.00	0.51	2.45
58-2	25.05	28.7751	-90.0384	0.14	0.23	0.09	0.45	0.68
59	24.94	28.8031	-90.0484	0.15	0.08	0.00	0.49	0.64
60	25.82	28.8674	-90.072	0.14	0.18	0.04	0.45	0.64
61-2	27.20	28.9224	-90.0872	0.18	0.14	0.00	0.34	0.52
62	28.44	28.9606	-90.1022	0.55	0.17	0.00	0.30	0.85
63	29.38	28.9999	-90.1206	0.17	0.58	0.41		
64	27.59	28.9327	-90.1353	0.24	0.10	0.00	0.35	0.59
65	25.95	28.8739	-90.1479	0.14	0.37	0.23	0.27	0.63
66-3	24.72	28.8095	-90.1609	0.17	0.28	0.11	0.29	0.57
67	24.01	28.7504	-90.1726	0.11	0.12	0.02	0.14	0.26
68	23.99	28.7193	-90.1794	0.14	0.13	0.00	0.25	0.39
69	24.09	28.6638	-90.1911	0.16	0.11	0.00	0.27	0.43
70-2	24.62	28.6041	-90.2042	0.15	0.14	0.00	0.27	0.41
71	23.90	28.5109	-90.2245	0.16	0.07	0.00	0.10	0.26
72	25.18	28.5496	-90.2364	0.24	0.16	0.00	0.23	0.47
73-2	25.10	28.605	-90.2456	0.18	0.36	0.18	0.09	0.45
74	24.58	28.6532	-90.2658	0.16	0.21	0.05	0.13	0.34
75	24.48	28.7182	-90.2809	0.18	0.12	0.00		
76	24.77	28.7876	-90.297	0.19	0.18	0.00	0.20	0.39
77-2	27.38	28.8527	-90.3121	0.15	0.23	0.08	0.13	0.36
89	30.15	28.9937	-90.5479	0.81	0.81	0.00	0.37	1.18
97	19.45	28.6731	-90.644	0.73	0.86	0.13	0.11	0.97
98-2	17.06	28.612	-90.6612	0.68	1.12	0.44	0.12	1.24
99	16.32	28.5734	-90.6785	0.15	0.37	0.23	0.70	1.07
100-2	17.55	28.5146	-90.6865	0.11	0.30	0.19	0.79	1.09
101	17.22	28.4763	-90.6945	0.22	0.67	0.46	0.79	1.46
102	18.40	28.4117	-90.7073	0.06	0.22	0.16	0.74	0.97
103	18.09	28.3489	-90.7204	0.08	0.30	0.21	0.65	0.95
104-2	18.71	28.3603	-90.7531	0.05	0.12	0.07	0.68	0.80
105	18.66	28.387	-90.7763	0.07	0.17	0.10	0.91	1.08
106	18.43	28.4356	-90.8155	0.15	0.41	0.26	0.41	0.82
107-2	21.37	28.4901	-90.8611	0.08	0.15	0.08	0.41	0.56
108	21.91	28.5215	-90.8862	0.04	0.08	0.03	0.49	0.57
109	24.27	28.5755	-90.9337	0.14	0.45	0.31	0.11	0.57
110	26.80	28.6331	-90.9803	0.17				
111	25.64	28.6861	-91.0266	0.30	0.56	0.25	0.25	0.80
112-2	25.06	28.7478	-91.0752	0.50	0.52	0.02	0.22	0.74
113	24.78	28.7876	-91.1088	0.69	0.69	0.00	0.21	0.91
114	23.73	28.8504	-91.1577	0.58	0.64	0.06	0.19	0.83

Station	Salinity	Latitude	Longitude	P_i	TDP	DOP	PP	TP
115	23.43	28.9081	-91.2026	0.64	0.79	0.15	0.24	1.03
116-2	24.11	28.969	-91.2502	0.22	1.66	1.44	0.32	1.98
117	16.54	28.9842	-91.28	1.81	2.55	0.73	0.31	2.85
118	26.73	28.9099	-91.3069	0.81	0.85	0.04	0.16	1.01
119	27.01	28.8381	-91.3327	0.83	0.83	0.00	0.21	1.04
120-2	27.74	28.7533	-91.3602	0.46	0.80	0.35	0.08	0.88
121	25.99	28.7078	-91.3773	0.48	0.83	0.34	0.13	0.95
122	24.11	28.6425	-91.4019	0.28	0.33	0.05	0.18	0.51
123-4	23.96	28.5607	-91.4513	0.29	0.40	0.11	0.10	0.50
124	24.32	28.6128	-91.4589	0.28	0.32	0.05	0.19	0.51
125-4	24.35	28.683	-91.4697	0.49	0.70	0.20	0.14	0.83
126	25.36	28.7283	-91.4768	0.64	0.83	0.19	0.16	0.99
127-4	25.07	28.8017	-91.4882	0.44	0.64	0.20	0.15	0.79
128	26.83	28.8556	-91.4966	0.68	0.76	0.08	0.18	0.94
129-3	27.29	28.9307	-91.5082	0.70	0.63	0.00	0.17	0.80
130	27.89	28.9865	-91.5169	0.94	0.96	0.02	0.32	1.27
131-2	28.22	29.0147	-91.5252	0.96	0.88	0.00	0.35	1.31
132	21.81	29.0653	-91.5342	1.45	1.16	0.00	0.83	2.28
133-2	28.62	29.1508	-91.5497	1.38	0.78	0.00	0.37	1.75
134	27.66	29.1507	-91.6141	1.09	0.93	0.00	0.24	1.33
135	26.50	29.1507	-91.6934	0.73				
136	27.68	29.1507	-91.7798	0.86	0.81	0.00	0.64	1.49
137-2	28.01	29.1517	-91.875	0.77	0.73	0.00	0.55	1.32
138	27.71	29.1514	-91.9459	0.60	0.80	0.21	0.43	1.24
139	26.47	29.1172	-91.9874	0.48	0.54	0.06	0.52	1.06
140	24.29	29.0444	-91.9878	0.04	0.15	0.11	0.29	0.44
141-2	24.91	28.9518	-91.9854	0.06			0.20	0.20
142	22.70	28.8986	-91.9863	0.04	0.21	0.17	0.24	0.45
143	23.56	28.8411	-92.0005	0.06	0.15	0.09	0.40	0.55
144	23.50	28.7411	-91.9896	0.06	0.09	0.02	0.26	0.34
145-2	26.92	28.6565	-92.0091	0.06				
146	22.64	28.6964	-91.9746	0.05				
147-2	27.06	28.6207	-91.9902	0.06				
148	25.16	28.3479	-92.0589	0.07				
149	25.26	28.4953	-91.9931	0.06				
150	25.49	28.5539	-91.9538	0.08				
151-2	27.27	28.6291	-91.9087	0.03				
152	23.26	28.664	-91.8839	0.03			0.25	
153	23.06	28.7353	-91.8385	0.08	0.15	0.07		
154-2	24.52	28.8161	-91.7891	0.08				
155	23.41	28.8549	-91.764	0.03				
157	27.69	28.9851	-91.6803	0.20				
158	25.77	29.0481	-91.6397	0.20				
159-2	20.87	29.1164	-91.5957	0.90				
160	15.12	29.1563	-91.5739	1.35				
161	7.84	29.2009	-91.5357	1.78				
162	10.79	29.2433	-91.4978	1.81				
163-2	14.02	29.288	-91.4574	2.48				
164	4.35	29.3273	-91.4229	2.63				

Station	Salinity	Latitude	Longitude	P_i	TDP	DOP	PP	TP
165-2	16.38	29.3426	-91.4109	2.57				
166	14.39	29.2637	-91.4798	2.43	2.24	0.00		
167-2	20.12	29.2159	-91.5218	1.38				
168	11.20	29.1737	-91.5295	1.59				
169	16.50	29.1221	-91.465	1.10				
170	20.94	29.0788	-91.4029	1.12				
171-2	24.51	29.0345	-91.3348	1.20				
172	21.27	29.0089	-91.2978	1.29				
173	21.89	28.9676	-91.2327	1.13				
174	20.55	28.9555	-91.1511	1.28				
175-3	21.04	28.942	-91.0643	1.75				
176	20.07	28.9333	-90.9951	1.55				
177	19.20	28.9211	-90.9105	1.46				
179-2	18.02	28.896	-90.7382	0.21				
180	18.49	28.8862	-90.6811	0.29				
181-3	19.79	28.8744	-90.5938	0.58				
182	20.23	28.8639	-90.5362	0.66				
183-3	20.80	28.8538	-90.4552	0.69				
184	20.35	28.8977	-90.4827	0.66				
185-3	22.73	28.9757	-90.5276	1.39	1.07	0.00		
186	27.78	29.0282	-90.5633	0.50	0.60	0.10		
mean	**21.34**			**0.528**	**0.504**	**0.133**	**0.422**	**0.971**
median	*22.88*			*0.205*	*0.303*	*0.048*	*0.3447*	*0.797*

A4.2 July 2004 Metadata, Part 2

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PN	TN	DOC	PC
2-2	125.86	0.37	126.23	164.60	38.37	19.02	183.62	357	180.33
3-2	31.88	0.75	32.63	45.40	12.77	5.06	50.46	474	65.17
4	44.66	0.72	45.38	68.50	23.12	26.56	95.06	413.2	180.93
5-2	12.85	1.41	14.25	31.00	16.75	13.22	44.22	338.8	108.16
6	21.49	0.63	22.12	38.70	16.58	26.40	65.10	406.2	202.53
7-2	2.30	1.24	3.54	13.50	9.96	8.66	22.16	227.7	61.63
8	7.74	0.46	8.19	23.70	15.51	20.01	43.71	319.1	144.13
9-2	3.34	0.22	3.55	14.10	10.55	7.76	21.86	240.8	70.23
10	12.52	0.44	12.96	28.00	15.04	21.39	49.39	304.7	160.40
11	9.22	0.05	9.27	25.00	15.73	19.91	44.91	327	254.38
12	18.37	0.59	18.96	38.40	19.44	29.27	67.67	315	241.73
13-2	12.01	1.18	13.19	34.40	21.21	20.18	54.58	401.44	138.13
14	36.43	3.33	39.76	58.50	18.74	24.97	83.47	345.1	168.00
15	58.33	1.86	60.19	86.60	26.41	27.55	114.15	423.64	177.07
16-2	8.96	3.26	12.22	44.70	32.48	26.81	71.51	350.08	179.33
17	19.06	4.41	23.47	47.50	24.04	30.46	77.96	419.26	203.20
18	22.48	2.00	24.48	66.00	41.53	27.57	93.57	396.9	165.47
19-2	56.28	2.45	58.72	95.10	36.38	24.05	119.15		140.40
20	80.42	2.01	82.42	109.40	26.98	19.97	129.37	453.4	129.37
21	67.62	2.45	70.06	112.80	42.74	18.64	131.44	509.8	129.75
22	35.46	2.50	37.96	65.60	27.64			472	
23-2	1.48	2.96	4.44	15.40	10.96	30.31	45.71	191.8	208.00
24	21.49	1.26	22.75	45.70	22.95	29.98	75.68	400.45	201.60
25	20.81	1.50	22.31	47.50	25.19	26.08	73.58	438.2	175.73
26-2	15.86	2.86	18.72	42.50	23.78	16.80	59.30	670.7	123.35
27-2	9.30	4.84	14.14	29.40	15.26	11.49	40.89	322.7	85.36
28	7.62	0.92	8.54	24.70	16.16	21.07	45.77	355.5	139.73
29	6.09	0.89	6.98	20.40	13.42	19.79	40.19	353.8	130.08
30-2	10.72	0.88	11.60	32.20	20.60	18.38	50.58	339.8	130.16
31	16.28	1.34	17.63	36.80	19.17	25.35	62.15	395.9	162.27
32	15.07	0.79	15.86	36.30	20.44	28.25	64.55	405.9	189.33
33-2	17.04	2.45	19.49	35.70	16.21	20.18	55.88	417.2	138.13
34	22.12	1.13	23.24	46.80	23.56	34.72	81.52	497.34	218.40
35	11.53	1.68	13.21	40.20	26.99	23.93	64.13	449.94	168.27
36	13.39	0.85	14.24	33.50	19.26			353.1	
37	12.37	0.75	13.12	28.80	15.68	29.60	58.40	345.07	198.00
38-2	9.33	0.37	9.70	38.10	28.40	23.11	61.21	414.2	163.33
39	11.98	0.76	12.74	30.10	17.37	26.48	56.58	360.8	181.20
40	11.33	0.57	11.90	26.40	14.50	25.45	51.85	302.1	196.53
41	11.11	0.28	11.38	22.40	11.02	16.24	38.64	286.9	129.57
42-2	2.24	3.42	5.66	14.30	8.64	3.34	17.64	193.3	34.96
43	4.72	0.58	5.31	21.00	15.69	23.78	44.78	343.5	182.40
44	3.93	0.59	4.52	22.20	17.68	19.74	41.94	405.5	181.07
45	0.50	0.51	1.01	17.60	16.59	21.63	39.23	371.15	174.40
46-1	4.96	5.01	9.97						
46-2	0.50	0.38	0.88	15.00	14.12	18.22	33.22	311	159.60
47	0.50	0.42	0.92	13.90	12.98	16.22	30.12	291.8	142.53

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PN	TN	DOC	PC
48	0.50	0.36	0.86	15.50	14.64	18.37	33.87	292.9	150.67
49	0.50	0.39	0.89	16.00	15.11	14.35	30.35	313.8	146.53
50-1	2.32	1.22	3.54						
50-2	1.21		1.21						
51	1.17	0.34	1.51	14.30	12.79	13.99	28.29	256.7	103.20
53	4.56	0.65	5.21	19.90	14.69	17.76	37.66	360.6	134.80
54-2	1.98	0.47	2.45	16.60	14.15	14.18	30.78	261.8	112.29
55	0.50	0.41	0.91	13.50	12.59	18.08	31.58	263.4	136.13
56	0.50	0.31	0.81	16.80	15.99	13.85	30.65	421.2	119.07
57	0.50	0.22	0.72	13.90	13.18	13.83	27.73	266.2	118.21
58-2	2.12	0.35	2.46	13.70	11.24	14.45	28.15	261.4	118.59
59	0.50	0.40	0.90	15.10	14.20	13.74	28.84	349.1	107.27
60	1.00	0.49	1.49	14.70	13.21	11.83	26.53	286.1	92.28
61-2	1.61	0.71	2.32	14.70	12.39	12.09	26.79	426.4	84.12
62	1.57	0.87	2.44	15.30	12.86	10.43	25.73	363.3	87.20
63	4.14	0.14	4.28	16.20	11.92			197.1	
64	2.25	0.99	3.24	15.90	12.66	10.45	26.35	401.1	81.43
65	0.50	0.44	0.94	15.70	14.76	12.61	28.31	297.1	104.21
66-3	0.50	0.46	0.96	14.80	13.84	9.78	24.58	297.9	83.17
67	0.50	0.37	0.87	14.70	13.83	11.13	25.83	333.9	94.87
68	0.50	0.41	0.91	14.50	13.60	9.32	23.82	358.8	80.65
69	0.50	0.19	0.69	16.40	15.71	12.29	28.69	295.3	92.04
70-2	0.50	0.43	0.93	13.20	12.27	10.86	24.06	277.2	79.24
71	2.87	0.47	3.34	16.70	13.36			249.1	
72	0.84	0.48	1.32	15.80	14.48	9.11	24.91	277.4	67.57
73-2	0.78	0.78	1.56	18.30	16.74	10.40	28.70	449.8	72.12
74	0.50	0.63	1.13	21.50	20.37	10.89	32.39	527.7	79.04
75	0.50	0.54	1.04	13.80	12.76			359	
76	0.50	0.54	1.04	14.00	12.97	6.81	20.81	302.3	51.75
77-2	0.50	0.40	0.90	11.80	10.91	3.99	15.79	262	40.95
89	5.45	3.79	9.23	20.10	10.87	5.69	25.79	258.9	43.41
97	18.04	4.41	22.45	37.30	14.85	3.90	41.20	381.6	36.73
98-2	19.53	4.32	23.85	38.60	14.75	4.84	43.44	374	47.32
99	10.47	3.77	14.24	29.70	15.46	9.46	39.16	377.67	74.11
100-2	2.56	1.42	3.98	18.30	14.32	14.90	33.20	370.74	96.64
101	2.02	0.99	3.01	21.46	18.46	19.74	41.20	414.10	115.73
102	5.21	1.43	6.64	21.10	14.46	13.13	34.23	356.81	96.37
103	4.40	1.45	5.85	20.99	15.14	14.45	35.44	420.19	91.03
104-2	4.13	1.61	5.74	18.29	12.55	10.44	28.73	356.97	82.51
105	3.67	1.39	5.05	21.88	16.83	17.02	38.90	400.36	102.64
106	1.57	1.34	2.91	19.71	16.80	17.11	36.82	338.10	133.25
107-2	1.96	1.09	3.04	10.00	6.96	7.29	17.29	175.3	57.16
108	2.79	1.13	3.92	16.40	12.48	8.18	24.58	280.7	72.03
109	3.00	2.19	5.19	19.10	13.91	4.91	24.01	266.00	51.35
110	3.87	1.00	4.87						
111	5.17	0.47	5.63	22.10	16.47	5.93	28.03	292.1	51.05
112-2	5.37	2.53	7.90	18.90	11.00	3.53	22.43	328.91	38.63
113	5.47	3.60	9.07	20.40	11.33	4.53	24.93	293.24	49.39
114	5.77	4.19	9.95	23.40	13.45	2.88	26.28	302.7	32.71

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PN	TN	DOC	PC
115	6.68	5.12	11.79	23.70	11.91	5.06	28.76	359.90	50.13
116-2	43.07	3.90	46.97	36.40	0.00	8.64	45.04	351.73	69.12
117	20.29	5.82	26.10	41.20	15.10	10.64	51.84	376.8	85.17
118	5.70	3.62	9.32	18.00	8.68	4.91	22.91	276.2	43.05
119	5.79	3.68	9.47	19.00	9.53	5.03	24.03	243.1	39.21
120-2	2.95	1.79	4.74	14.60	9.86	5.59	20.19	287.1	48.05
121	3.15	1.28	4.43	30.50	26.08	5.45	35.95	445.8	42.84
122	2.31	1.84	4.15	18.30	14.15	5.14	23.44	292.6	41.47
123-4	2.36	2.24	4.60	14.80	10.20	6.62	21.42	296.6	46.56
124	1.82	1.89	3.71	14.90	11.19	2.95	17.85	321.8	38.03
125-4	3.24	1.70	4.93	16.10	11.17	6.71	22.81	379.2	53.89
126	3.36	1.81	5.16	16.30	11.14	5.16	21.46	305.6	44.45
127-4	1.77	2.72	4.50	15.50	11.00	5.18	20.68	476	44.67
128	3.42	2.23	5.65	13.30	7.65	5.32	18.62	284.9	49.07
129-3	3.99	2.24	6.23	16.80	10.57	5.03	21.83	218.2	50.52
130	2.33	4.04	6.37	18.20	11.83	6.71	24.91	593.61	54.76
131-2	3.60	3.64	7.24	18.00	10.76	6.69	24.69	274.4	54.32
132	10.20	1.11	11.31	22.90	11.60	9.01	31.91	303.77	71.76
133-2	6.71	0.14	6.86	20.00	13.14	7.37	27.37	271.33	60.39
134	2.87	2.96	5.83	17.20	11.37	6.45	23.65	331.6	62.69
135	1.59	1.70	3.29	14.20	10.91			251.9	
136	2.38	0.44	2.81	13.20	10.39	7.43	20.63	245.1	75.47
137-2	3.41	0.61	4.02	13.90	9.88	8.24	22.14	309.6	66.36
138	0.50	0.31	0.81	11.90	11.09	10.17	22.07	264.66	90.28
139	0.53	0.26	0.79	11.80	11.01	8.44	20.24	240.92	70.01
140	0.50	0.43	0.93	13.40	12.47	5.99	19.39	559.8	62.52
141-2	0.50	0.36	0.86			6.90	6.90		70.64
142	0.50	0.36	0.86	13.30	12.44	6.32	19.62	305.4	68.27
143	0.50	0.45	0.95	12.20	11.25	7.73	19.93	332.6	68.25
144	0.50	0.40	0.90	12.40	11.50	6.20	18.60	309.9	60.19
145-2	0.50		0.50	15.00	14.50			NO ACID	
146	0.50		0.50	14.00	13.50			NO ACID	
147-2	0.50		0.50	11.60	11.10			NO ACID	
148	0.50		0.50						
149	0.50		0.50						
150	0.65		0.65						
151-2	0.50		0.50						
152	0.50		0.50						
153	1.34	0.96	2.30	13.10	10.80			260.8	
154-2	0.50		0.50						
155	0.50		0.50						
157	0.50		0.50						
158	0.73		0.73						
159-2	9.00		9.00						
160	21.76		21.76						
161	35.17		35.17						
162	27.30		27.30						

Station	NO$_x$	NH$_4^+$	DIN	TDN	DON	PN	TN	DOC	PC
163-2	30.33		30.33						
164	46.18		46.18						
165-2	46.86		46.86						
166	31.60	3.02	34.63	41.20	6.58			397.8	
167-2	16.64		16.64						
168	30.97		30.97						
169	19.58		19.58						
170	18.20		18.20	16.60	0.00			NO ACID	
171-2	23.11		23.11						
172	21.03		21.03						
173	21.85		21.85						
174	23.90		23.90						
175-3	24.17		24.17						
176	30.09		30.09						
177	30.53		30.53						
179-2	11.08		11.08						
180	13.93		13.93						
181-3	17.61		17.61						
182	18.07		18.07						
183-3	18.13		18.13						
184	18.13		18.13						
185-3	19.78	0.45	20.23	29.10	8.87			287.7	
186	1.71	0.43	2.14	18.10	15.96			NO ACID	
mean	**11.31**	**1.48**	**12.46**	**26.82**	**15.39**	**13.89**	**40.97**	**342.81**	**106.09**
median	*4.2695*	*0.96*	*5.8365*	*18.3*	*13.91*	*11.96*	*30.72*	*333.9*	*91.53*

A4.3 July 2004 Metadata, Part 3

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl *a*	AP Activity
2-2	135.03	36.95	36.37	69		90.02
3-2	38.40	21.78	25.35	18	0.17	44.86
4	47.65	91.50	39.06	10.4	7.67	551.05
5-2	1.34	117.80	59.84	5.2	2.08	605.33
6	23.97	161.45	51.41	8.8	4.63	1103.10
7-2	0.63	73.71	72.53	3.6	0.74	87.01
8	0.50	178.13	186.90	7.2	3.67	469.82
9-2	0.50	43.88	66.18	7.6	1.02	198.93
10	1.79	119.97	81.83	6.8	1.60	291.25
11	0.50	120.40	77.99	8	3.04	313.99
12	15.97	76.77	63.97	10.4	8.28	1.52
13-2	1.01	212.76	120.49	10	1.38	675.66
14	35.19	120.85	49.67	11.6	7.12	548.52
15	64.70	67.86	47.80	10	6.39	193.89
16-2	15.13	10.12	44.83	7.2	3.63	331.39
17	48.95	13.31	35.56	7.2	3.27	226.58
18	13.92	81.86	59.70	8	4.94	223.54
19-2	35.53	112.28	58.75	7.2	4.50	142.13
20	57.14	36.42	33.18	6.4	4.21	133.33
21	26.28	45.06	41.69	11.6	4.36	143.68
22	19.67	198.73			5.66	331.39
23-2	1.04	23.25	42.80	10.8	11.04	448.22
24	6.02	142.19	86.97	9.2	11.04	487.03
25	2.81	67.20	70.82	9.2	6.75	625.17
26-2	3.14	78.98	90.84	7.2	1.96	563.38
27-2	3.12	90.06	86.15	6.8	2.95	166.03
28	0.50	58.87	145.78	6.8	2.89	320.35
29	0.50	43.07	132.92	5.2	2.06	275.96
30-2	0.75	45.86	112.19	8.4	3.40	797.79
31	3.98	63.87	70.69	7.2	7.26	1522.95
32	0.70	53.04	75.84	8.8	6.65	569.08
33-2	1.01	138.22	93.11	8	6.65	874.07
34	0.54	53.68	73.18	9.2	9.59	338.46
35	4.53	102.40	66.20	7.2	4.24	
36	3.98	74.18			5.81	
37	4.93	61.59	74.55	9.6	6.25	
38-2	6.12	60.62	67.65	6.4	3.56	683.10
39	6.21	157.22	54.09	7.6	4.14	595.85
40	5.18	321.57	60.96	8.4	3.78	511.04
41	4.34	97.30	52.29	6.8	3.20	317.95
42-2	1.32	31.64	54.31	1.2	0.44	28.62
43	0.59	35.85	61.51	5.6	2.98	774.38
44	1.18	31.17	63.75	7.2	3.05	773.77
45	0.50	6.76	54.30	7.2	2.83	640.85
46-1	2.36	98.69				
46-2	2.05	8.46	92.12	6.4	1.89	784.06
47	5.03	5.90		6.4	1.96	405.03
48	1.30	5.88	58.01	6.4	1.60	232.40
49	2.60	8.56	64.09	4.8	1.38	442.38

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl a	AP Activity
50-1	0.71	36.15		9.6	1.53	532.88
50-2	0.50	10.89		4.4	1.67	377.61
51	0.50	14.53	56.58	4.4	1.60	276.70
53	0.50	64.31	73.76	4.4	1.67	493.13
54-2	0.50	20.61	73.82	5.2	1.31	458.56
55	0.85	7.69	60.24	5.2	0.87	517.71
56	2.64	8.39	65.33	5.2	1.16	597.29
57	7.68	0.37	11.30	5.2	1.45	360.80
58-2	7.16	17.11	41.28	4.8	1.60	189.09
59	6.04	6.07	44.92	3.6	1.23	263.74
60	6.42	10.32	41.67	3.2	1.53	233.52
61-2	6.56	12.72	51.21	3.6	1.45	242.99
62	7.73	4.47	30.33	3.6	2.25	197.70
63	14.39	24.75		6.4	3.34	61.08
64	9.07	13.72	44.93	3.6	1.67	129.40
65	8.91	6.74	44.69	4	1.31	147.02
66-3	4.43	5.49	43.08	4	0.80	188.82
67	2.13	8.30	99.18	3.6	0.80	222.91
68	4.08	6.42	61.33	4.4	0.87	204.14
69	0.50	4.39	66.62	4	0.87	146.59
70-2	0.61	6.29	58.08	4	1.05	261.06
71	0.50	20.49		7.2	1.55	232.54
72	0.50	5.51	52.82	3.6	1.70	255.79
73-2	0.61	8.84	63.98	4.4	0.78	75.70
74	0.50	7.08	94.39	4	0.81	149.92
75	0.50	5.85		2.8	0.81	143.06
76	7.26	5.34	53.21	3.2	0.42	59.91
77-2	3.01	6.05	44.18	2.8	0.46	44.77
89	19.26	11.41	21.89	3.6	1.28	13.94
97	39.75	30.67	42.43	7.2	0.52	15.80
98-2	42.34	34.97	35.14	4.8	0.61	17.27
99	42.64	97.51	36.57	5.6	2.67	42.99
100-2	22.91	35.83	30.50	2.8	3.22	161.14
101	28.45	13.91	28.27	4.4	3.51	173.90
102	16.78	103.73	35.47	4	2.64	208.07
103	15.24	70.45	37.42	2	1.54	197.77
104-2	12.77	114.86	36.09	2.4	1.83	201.49
105	10.45	77.74	36.01	3.2	2.06	237.55
106	7.70	19.37	45.05	4	2.32	247.85
107-2	6.38	40.59	30.75	4	1.48	285.90
108	6.70	91.09	42.99	3.6	1.51	277.03
109	7.01	36.54	42.28	0.4	0.73	363.20
110	7.16	29.00		0.8	0.87	400.99
111	15.41	18.52	34.97	5.2	1.10	416.98
112-2	17.10	15.80	30.30	3.2	0.64	101.66
113	19.70	13.09	27.53	3.6	0.93	26.88
114	17.99	17.13	31.65	4.4	0.84	29.36
115	19.14	18.48	28.00	6.4	1.02	27.28
116-2	38.39	216.47	22.78	18	1.83	22.08
117	44.36	14.40	18.19	14.8	1.05	15.16
118	20.72	11.52	22.66	6.8	1.10	25.12

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl *a*	AP Activity
119	50.57	11.46	23.13	4	1.25	23.44
120-2	14.42	10.41	22.84	4.8	0.41	14.68
121	15.39	9.18	37.77	2.4	0.38	16.30
122	9.85	14.82	46.10	2.8	0.26	15.04
123-4	12.71	16.13	42.62	2.4	0.20	3.54
124	12.32	13.45	35.00	1.6	0.17	14.80
125-4	18.47	9.98	27.37	4	0.55	9.18
126	22.22	8.09	21.68	2.8	0.76	11.30
127-4	15.81	10.17	26.10	4.4	0.46	15.32
128	28.10	8.29	19.88	3.6	0.58	21.90
129-3	30.49	8.86	27.37	3.2	0.09	12.82
130	32.95	6.81	19.55	4.4	1.39	12.16
131-2	31.79	7.53	18.84	6.4	0.76	7.36
132	40.45	7.79	14.00	12	1.28	11.18
133-2	39.02	4.97	15.67	10.8	0.87	8.64
134	31.16	5.33	17.77	9.2	1.34	15.57
135	27.52	4.49		7.6	1.57	67.72
136	32.84	3.28	13.80	10	2.50	31.47
137-2	34.64	5.23	16.77	7.6	2.67	34.63
138	24.69	1.36	17.85	6.4	3.83	49.16
139	22.36	1.66	19.03	3.6	2.44	45.92
140	5.99	22.12	44.41	6.4	1.45	57.01
141-2	3.68	15.36	34.21	0.4	0.87	85.32
142	6.27	22.13	44.06	1.2	0.99	90.46
143	12.09	15.52	36.43	1.2	0.58	63.32
144	9.78	14.55	54.06	2	0.41	77.34
145-2	8.94	7.81		1.6	0.52	70.10
146	9.84	9.43		1.6	0.46	82.47
147-2	5.11	8.47		1.6	0.23	176.92
148	4.47	7.04		2.8	0.29	165.89
149	1.16	7.94		4.4	0.29	348.48
150	3.21	7.88		2.4	0.35	187.69
151-2	1.49	16.67		6.4	0.12	97.07
152	4.82	16.67		4.8	0.35	182.30
153	7.20	28.78		4.4	0.41	89.05
154-2	3.98	6.67		2.4	0.76	56.88
155	5.18	16.67		2.8	0.64	82.56
157	14.99	2.46			2.56	22.26
158	20.22	3.63		4.4	3.49	46.56
159-2	28.22	9.96			4.53	19.42
160	44.06	16.09			4.79	57.77
161	39.24	19.80			2.27	41.11
162	25.34	15.10			1.42	67.49
163-2	55.57	12.22			1.53	43.37
164	59.93	17.56			1.02	76.15
165-2	52.44	18.21			1.89	62.44
166	41.77	14.25		6.8	0.80	63.62
167-2	50.07	12.08		8	1.98	13.20
168	35.82	19.53		6	2.96	23.69
169	46.24	17.75		6.4	4.65	8.47
170	40.23	16.20		4	2.50	10.22

Station	Si	DIN:P$_i$	TN:TP	SPM	Chl *a*	AP Activity
171-2	46.60	19.24		4.8	1.80	5.78
172	41.76	16.32		4.4	1.54	15.59
173	43.10	19.36		3.2	0.64	30.51
174	46.35	18.64			0.52	27.97
175-3	50.62	13.85		2.8	0.78	37.08
176	58.78	19.39		2.4	0.58	20.75
177	59.64	20.92		1.6	0.81	21.89
179-2	28.54	53.53		3.2	0.61	52.38
180	36.28	48.89			0.96	20.45
181-3	35.75	30.26		3.2	0.46	9.75
182	36.89	27.38			0.46	7.55
183-3	35.63	26.42			0.70	6.32
184	36.35	27.47			0.46	11.31
185-3	42.91	14.58			1.05	8.88
186	34.06	4.33			3.02	30.27
mean	**18.50363**	**38.18106**	**50.85544**	**5.968919**	**2.0712411**	**207.88**
median	*10.152*	*17.1218*	*44.6885*	*4.8*	*1.45245*	*115.53*

Curriculum Vitae

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EDUCATION
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2004   M.S.   Oceanography, Rutgers University, New Brunswick, New Jersey
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PUBLICATIONS
Sylvan, JB, A Quigg, S Tozzi & JW Ammerman. (2007) Eutrophication induced
Phosphorus limitation in the Mississippi River Plume: Evidence from fast
repetition rate fluorometry. *Limnology and Oceanography*, **52 (6)**: 2679-2685.

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period of hypoxia formation. *Environmental Science and Technology*, **40 (24)**:
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Lee, SE, F Pâques, **J Sylvan**, & JE Haber. (1999) Role of yeast *SIR* genes and mating
type in directing DNA double strand breaks to homologous and non-homologous
repair paths. *Current Biology,* 9: 767-770.

TEACHING EXPERIENCE
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Fall 2000-   Introductory Oceanography Lab (Texas A&M University, College Station)
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