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Particulate carbon, nitrogen and phosphorus stoichiometry of south west Florida waters

Susan Mary Murasko University of South Florida

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Particulate Carbon, Nitrogen and Phosphorus Stoichiometry of

South West Florida Waters

by

Susan Mary Murasko

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science College of Marine Science University of South Florida

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> Date of Approval: March 25, 2009

Keywords: West Florida Shelf, Redfield Ratio, nutrient limitation, phytoplankton, *Karenia brevis*

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ACKNOWLEDGMENTS

 I would like to thank my committee members, Dr Gabriel Vargo, Dr. Cynthia Heil and Dr. Ted VanVleet, for their support, patience and encouragement throughout this endeavor. I would also like to thank Merrie Beth Neely, Danyelle Ault, Julie Havens and Robyn Conmy for help with sampling, data analysis and data processing and also the crew of the R/V Suncoaster. Special thanks to my parents and Marco Nery for their love and support throughout this project.

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Susan Mary Murasko

ABSTRACT

 The southwestern Florida shelf marine environment has often been characterized as oligotrophic, yet these waters can support large, high biomass, persistent phytoplankton blooms, including blooms of the toxin producing dinoflagellate *Karenia brevis.* Little is known regarding which major nutrient potentially limits primary production in these waters as both inorganic nitrogen and phosphorus concentrations are often near the limits of analytical detection and it is difficult to estimate what percentage of the dissolved organic pool is available for phytoplankton uptake. To assess the nutrient status of phytoplankton populations on the southwest Florida shelf, this project examines the particulate nutrient stoichiometry of ambient phytoplankton assemblages from 1998-2000 as part of the ECOHAB: Florida Program.

 Particulate C, N, P concentrations and particulate ratios display a large range of values across the West Florida Shelf (WFS). The average particulate stoichiometry is well above the classic Redfield ratio with a geometric mean of 410C:56N:1P. Frequency percentages of particulate ratio values to total sample number binned according to potential nutrient limitation indicate that 39% (C:N) of the data have values suggesting N limitation and that from 88% (N:P) to 95%

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(C:P) of the data have values which suggest P-limitation. It is difficult to discern whether phytoplankton biomass is truly P-limited as related to the nutrient regime on the WFS or whether detrital contributions, which can potentially be large on this shallow shelf, are skewing the N:P and C:P ratios towards higher values. Errors which could potentially be related to the different methodologies of determining C, N and P concentrations must also be considered when interpreting the particulate nutrient ratios.

 The data were also analyzed as subsets to determine near-shore to offshore, latitudinal, seasonal, inter-annual and *K. brevis* bloom versus nonbloom trends. The near-shore to offshore transect indicates decreasing concentrations of particulate C, N, P concentrations and increasing C:N, N:P, C:P ratios with increasing distance offshore. Particulate nutrient concentrations and particulate ratio values are very similar between the Tampa Bay, Sarasota and Fort Meyers transects indicating that these latitudes are not spatially distinct with regards to these variables. There does not appear to be any relationship between the particulate C, N, P concentrations or C:N, N:P, C:P ratios and rainfall as indicated by Spearman Ranking Correlation coefficients. However, there does appear to be monthly trends across the shelf where peak particulate nutrient concentrations and particulate ratio values occur during the spring, summer and fall. The average particulate nutrient concentrations and ratios differ for each year as well as each *K. brevis* bloom which occurred during the study period.

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 In summary, the particulate C, N, P concentrations and particulate nutrient ratios vary both spatially and temporally on the WFS and are potentially related to the flexibility of phytoplankton uptake kinetics in response to the varying nutrient regimes of the WFS.

CHAPTER ONE

INTRODUCTION AND OBJECTIVES

The Biological Pump

The biological carbon is the sum of a suite of biological and physical processes that transport carbon from surface waters to the oceans interior. This mechanism plays an important role in the cycling of nutrients in the global open oceans and is largely mediated by phytoplankton production in the photic zone, export production rate of sinking particulate matter, remineralization rates at depth and upward eddy diffusion rates of dissolved inorganic nutrients back into the photic zone (Eppley and Peterson 1979; Karl et al. 2001). The dependence of each process on the other provides an effective feedback mechanism which ultimately drives the carbon (C) cycle and balances $CO₂$ flux between the atmosphere and the oceans over large time scales. In well lit surface waters the rates and intensities of these processes within the biological pump are influenced by the cycling and concentrations of nitrogen (N) and phosphorus (P) which are linked to the carbon cycle (Michaels et al. 2001) through biological production (Wu et al. 2000). However, at depth, the more refractory C can become decoupled from the N and P cycles as they are remineralized at faster rates and "net carbon sequestration" can take place (Christian et al. 1997; Karl et al. 2001).

In this manner, the biological pump serves to "fractionate" the distributions of the conservative elements (Mg, Na, Co) and those which are non-conservative or biologically active (e.g. C, N, P) and a distinct "biochemical circulation" of

nutrients is the result (Redfield et al. 1963). This is primarily because N and P are recycled between the dissolved and particulate pools on time scales much shorter than the mixing and residence time of waters in the basin (Harris 1986). These processes are critical in oligotrophic oceans, often supplying the only source of "new" nutrients into these systems for phytoplankton uptake and assimilation (Dugdale and Goering 1967). In this case, the cycle of biological production, remineralization of that production at depth and the return of nutrients to surface waters primarily control the stoichiometry of C:N:P found within both the dissolved and particulate pools in the open ocean (Karl et al. 2001). In coastal and shallow marine environments, controls on C:N:P stoichiometry becomes much more complex as nutrient pathways (i.e. sources and sinks) and ecosystem community structure become much more varied and dynamic.

The Redfield Ratio

The classic work of Alfred Redfield (1934, 1958, 1963) and Richard Fleming (1940), has provided scientists with a unifying concept of nutrient stoichiometry, which reflects the continuous recycling of N and P between the particulate organic matter (POM) and the dissolved inorganic pool in the ocean (Gieder and La Roche 2002). Redfield documented the constancy of plankton C:N:P and the N:P of deep ocean waters throughout the worlds oceans and more over, that the ratios of the two pools were similar to each other (Redfield 1958; Redfield et al. 1963). Based on previous works of C: N: P stoichiometry, Redfield and co-researchers empirically derived by averaging available data an elemental

ratio of 106:16:1, by atoms and is now termed the "classic Redfield Ratio" (Redfield 1933; Redfield 1958). The consistency of this ratio further suggests that the uptake and release of nutrients in the ocean tend to occur in specific proportions (Karl et al. 2001; Micheals et al. 2001). This observation led Redfield to the conclusion that the phytoplankton ultimately control the chemical constituents in the ocean by adjusting the N:P stoichiometry of the ocean by fixing atmospheric N to meet the metabolic needs of the plankton (Redfield 1933; Redfield et al. 1963; Hecky and Kilham 1988; Tyrell 1999; Falkowski 2000; Micheals et al. 2001). In an effort to describe nutrient distribution in seawater, Redfield et al. (1963) invoked two causative principals; 1) the constrained ("inherently regular") stoichiometry of the phytoplankton which results from physiological requirements for growth and 2) the dynamic stoichiometry that results from an equilibrium between the physical and biological processes which determine the concentration of elements present at any point in the sea. Falkowski (2000) describes the Redfield Ratio as "the result of nested processes that have a molecular biological foundation, but are coupled to biogeochemical process on large spatial and long temporal scales".

The Redfield Ratio has provided researchers with a general foundation on which has been based modeling efforts, laboratory experiments and field studies designed to understand nutrient dynamics and biogeochemical processes in aquatic environments (Menzel and Ryther 1964; Goldman et al. 1979; Hecky and Kilham 1988; Karl et al. 2001; Michaels et al. 2001; Falkowski 2000; Sterner et al. 2008). Based on the idea that phytoplankton assimilate C: N: P in specific

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proportions and that nutrients are recycled in the those same proportions, if the concentration of one element was known, it would be possible to calculate the concentrations of the other nutrients. General assumptions could also be made about nutrient cycling and recycling, primary production and export production (Michaels et al. 2001; Geider and La Roche 2002).

As research continued with the Redfield ratio as a guide, it became evident that under varying nutrient regimes, phytoplankton seem to only exhibit C:N:P in Redfield proportions when cells are growing at or near the maximum rate under conditions of nutrient sufficiency (Caperon and Meyer 1972; Droop 1974; Droop 1975; Goldman et al. 1979; Harris 1986; Hecky et al. 1993; Vaillancourt et al. 2003). Under these conditions, growth is balanced where "all cellular components increase exponentially at the same rate" and "cellular composition remains fixed" (Shuter 1979). Therefore, the stoichiometry of phytoplankton should be reflective of nutrient availability or limitation in both cultured and natural assemblages and can be employed to assess population dynamics as related to the concept of steady state (growth rate = uptake rate) versus exponential growth.

The application of algal stoichiometry concepts is potentially important to the understanding of nutrient cycling as it pertains to the biological pump, biogeochemical cycling, atmospheric and oceanic $CO₂$ exchange and algal growth management (Karl et al. 2001; Sterner et al. 2008).

Nutrient Limitation of Phytoplankton

The concept of a limiting nutrient was formulated in 1863 by an agricultural chemist, Justus von Leibig. His Law of the Minimum states the "growth of a plant is dependent on the amount of foodstuff which is presented to it in minimum quantity". Expressed more simply, Leibig's Law suggests that "growth rate is determined by the availability of the most limiting substance" (Tyrell 1999). The seminal work of Leibig has remained as an important central concept of ecology and oceanography. In this manner, Leibig has been considered to be the "founding father of Ecological Stoichiometry" (Sterner and Elser 2002). This limiting nutrient concept provides the basis for modern modeling strategies which relate nutrient limitation and phytoplankton growth. The Droop model (1974) is based on the premise that phytoplankton nutrient assimilation rates and related growth rates are determined by the internal nutrient stores of the organism and that nutrient limited growth is reflected in the particulate composition of the organism (Hecky and Kilham 1988; Geider and La Roche 2002). In contrast the Monad Model relates phytoplankton growth to external concentrations of dissolved nutrients (Hecky and Kilham 1988).

Over the decades, the concept of the "limiting nutrient" to phytoplankton growth has fueled many debates and inspired many research projects. The current dogma is that lakes and streams are predominately P-limited while oceans and estuaries are N limited (Goldman et al. 1979; Herbland et al. 1998). However there is much more evidence to support the former than the latter due to the complexities associated with the size, long residence times and variable

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boundary layer in the ocean (Hecky and Kilham 1988). Unlike in freshwater systems, where ecosystem wide experiments have been conducted (Sommer 1990; Hecky et al. 1993), marine system assessments are largely confined to culture and bottle experiments in determination of the limiting nutrient (Hecky and Kilham 1988). Hecky and Kilham (1988) and Smith (1984) suggest that these types of experiments have their limitations and results may not reflect processes that would occur in natural environments.

Is the ocean N-limited or P-limited? There are two schools of thought on this: the geochemist point of view is that P limits primary production, while the biologist point of view where N limits primary production in the ocean (Tyrell 1999). The geochemists argue that when nitrogen becomes limiting, nitrogen fixers can utilize the abundant supply of N_2 in the atmosphere to meet their requirements for growth. Remineralization of this new biomass releases dissolved N, replenishing the supply of N available for phytoplankton uptake (Redfield 1958; Tyrell 1999). In contrast, new inputs of P in the ocean are largely limited to coastal inputs or up-welled deep ocean water and are a function of physical processes rather than a function of the biology and thus their rate of supply cannot be replenished as readily. However, natural nutrient abundance data have shown that typically it is N that is in scarce supply relative to P (Tyrell 1999). It is also N additions that most often stimulate phytoplankton growth in nutrient bioassays conducted with oligotrophic waters (Goldman 1976; Hecky and Kilham 1988; Tyrell 1999). In theory it seems that P should limit primary production in the ocean but "in practice" it seems that N is the "master limiting

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nutrient" (Tyrell 1999). This may be related to timescale considerations where on geological time P limits production in the oceans, while on shorter scales, N limits production as related to the biology of the system.

Nutrient limited or non-nutrient limited growth of phytoplankton can be inferred by an examination of the C:N:P stoichiometry of the phytoplankton composition based on the concept that cellular C, N and P concentrations change in response to changing nutrient regimes (Nalewajko and Lean 1980). Fluxes of nutrients in the marine environment can be quite dynamic and are related to both biotic and abiotic processes. Biological controls are perhaps the most influential in this respect and include the strength of the biological pump as related to production and particle sinking velocities and the turnover times of N and P (Harris 1986) as related to the efficiency of the microbial loop and the intensity of grazing activity. Physical influences on nutrient availability tend to be more episodic as many processes which effect nutrient distributions are dependent on climate conditions such as upwelling events (wind), horizontal advection (wind), stratification (temperature and wind) and riverine inputs (precipitation). Other physical processes include nutrient movement along concentration differentials and redox conditions. In response to this everchanging environment, phytoplankton have adapted the ability to adjust the quantity of metabolic and storage components within the cell in order to sustain growth. As a result, the C: N ratio increases and the N: P ratio decreases during N limitation while the C: P and N: P ratios increase when P is limiting. The Redfield Ratio provides a numerical benchmark to make this determination

where N: P ratios greater than 16:1 implies P limitation and N: P ratios less than 16:1 are indicative of N limitation. Furthermore, particle C:P can be employed to "set constraints on carbon sequestration" (Micheals et al. 2001) and the particulate C:N ratio provides "a relative measure of growth rate" (Donaghay et al.1978) as a response to the nutrient status of the cell (Eppley et al. 1973). Phytoplankton compositional C: N: P ratios thus provide a simple and powerful tool to determine phytoplankton nutritional state as it relates to nutrient availability and growth (Eppley et al. 1973; Hecky 1993).

The Nutrients

The major nutrients that are required by all phytoplankton for growth are carbon, nitrogen and phosphorus. In the worlds oceans these elements continually cycle between the dissolved inorganic, dissolved organic and particulate organic (both living and non-living particles) pools on timescales of minutes to days to thousands of years and are driven by the biogeochemical processes both large and small that keep these elements continually cycling. It is the size of the nutrient pool (storage capacity) and the rates of movement between these pools (turnover rate) rather than the absolute amounts of nutrients that are more important to understanding the roles of these biogeochemical processes as they relate to carbon sequestration over geological time or to global nutrient budgets or to "ecosystem function" and local nutrient availability (Harris 1986). On local spatial scales it is the availability of N and P that ultimately regulate phytoplankton growth rate, biomass and bloom duration (Vargo et al.

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2008). Dugdale and Goering (1967) divided nitrogen into two forms, "new N" or "regenerated N". "New" N enters the system from an external source and thus can contribute to new biomass (growth). "Regenerated" N originates within a system (eg. zooplankton grazing and excretion and bacterial degradation) and can only maintain the present biomass, not produce new biomass (Dugdale and Goering 1967).

All in all, "for natural populations to exist their cellular growth rate must exceed or equal losses to dilution, sedimentation, physiological death and grazing" and "cellular growth rates are a function of nutrient supply" (Harris, 1986).

Carbon

In the marine environment, speciation within the dissolved inorganic carbon pool is related to pH, alkalinity and temperature which results in an equilibrium distribution between the $CO_{2(aq)}$, bicarbonate (HCO₃⁻) and carbonate ions (Harris 1986). The form of carbon within this pool that is available for biological uptake is dissolved $CO₂$ which is in equilibrium with atmospheric concentrations and can enter the oceans directly or by way of photosynthetic activity (Harris 1986). As a result of this endless source, dissolved inorganic carbon is found in much greater concentrations than the other essential nutrients and is rarely considered to be the limiting nutrient in marine waters. Although C is a bioactive element, its relative abundance results in longer turnover times in surface waters on time scales similar to physical processes and therefore C can

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be considered to behave more conservatively than those of N and P (Harris 1986).

The refractory nature of a portion of the dissolved organic C pool often results in its decoupling from the more labile N and P nutrient pools. Remineralization rates of N and P occur on significantly shorter time scales than for C, and often take place in shallower water column depths (Christian et al.1997; Hopkinson et al. 1997). This is related to the high N and P requirements of the microbial community and its preferential remineralization of N and P relative to C, and results in increasing C:N and C:P ratios of dissolved organic matter (DOM) with depth (Christian et al. 1997). The flexibility (deviation from the Redfield Ratio) of the stoichiometry within the DOM pool is largely responsible for the oceans ability to store C.

Nitrogen

The nitrogen (N) cycle is very complex; many oxidation states of N exist as gains and losses of electrons to N compounds readily occur. The inorganic dissolved pool of N (DIN) in the aqueous environment includes the reactive forms $NO₃$, NO₂, NH₄⁺, which are the preferred species for phytoplankton uptake, and dissolved N_2 gas which is only available to a special group of organisms known as nitrogen fixers.

Terrestrial sources of dissolved N, including effluent from municipal waste water treatment plants, industry and agriculture which enter the system via ground waters and rivers are important to coastal processes. In the open ocean,

 $in-situ$ regeneration and higher trophic level digestion and excretion, N_2 fixation, upwelling and eddy diffusion across the thermocline provide the majority of N available for phytoplankton (Harris 1986). In oxygenated surface waters, nitrogen conversion is primarily the result of biological assimilation, grazing activity and heterotrophic bacterial regeneration within the euphotic zone (Harris 1986). These processes result in the release of NH_4^+ (ammonification) and the potentially bio-available components of the dissolved organic pool of N (DON) which are urea and amino acids (McCarthy 1980; Bronk and Ward 1999; Cochlan and Bronk 2001; Glibert et al. 2004). In environments where concentrations of NO₃⁻ and NH₄⁺ are low, it has been shown that urea could be a significant source of N to primary producers (Antia et al. 1991; Joint et al. 2001). Turnover times of DIN can be expected to be longer than for DIP as DON is more refractory than DOP (Walsh et al. 2006) and N "must undergo changes in oxidation state before metabolism" (Harris 1986).

Nitrification, denitrification and N_2 fixation are also biologically mediated processes that play a very important role in N cycling and therefore N availability. Nitrification is an oxygen requiring process where a suite of bacterial decomposers oxidize NH₄⁺ to NO₂⁻ to NO₃⁻ thus returning nitrogen into the preferred species for phytoplankton uptake. This pathway of $NO₃$ regeneration occurs quickly in both the water column and in oxygenated sediments and is in part responsible for the low concentrations of NH_4^+ and NO_2^- in marine waters (Harris 1986). Denitrification occurs in the absence of oxygen where facultative anaerobic bacteria reduce nitrates to gaseous nitrogen (Chempedia.com) and

"represents a substantial loss of biologically available N from the ocean (Ganeshram et al. 2002)". The balance between nitrification and denitrification is related to the flux of organic matter into bottom waters where increased flux means increased decomposition efforts resulting in oxygen depletion and increased denitrification and vice versa. N₂ fixation is the process in which "N₂ gas is combined, via the enzyme nitrogenase, with free hydrogen molecules to produce NH_4^+ as the stable end product" (Chempedia.com) and is carried out by bacteria or the blue-green algae referred to as cyanobacteria. This provides an important mechanism converting N from an unlimited source (atmosphere) into new biomass which upon decomposition provides a potential N source for non- N_2 fixing phytoplankton. It has specifically been linked to *K*. *brevis* bloom initiation and duration in oligotrophic Gulf waters (Lenes et al. 2001; Walsh and Steidinger 2001; Vargo et al. 2008).

Phosphorus

The phosphorus (P) cycle is less complex compared to the nitrogen cycle because phosphorus primarily exists as the (ortho-)phosphate ion $PO₄³$ in both the aqueous environment and as cellular constituents (Harris 1986). In marine waters, the largest reservoir of P is typically within the particulate pool followed by DOP and the lowest concentrations are usually found within the DIP pool (Valiela 1995). The paucity within the DIP pool is not only the result of phytoplankton uptake, but may be a result of the ease in which P complexes with other particles. P readily forms insoluble compounds with some metals under

aerobic conditions which than sink out of the water column and become stored in the sediments (Valiela 1995).

Sources of P to coastal areas are primarily terrogenous in origin and carried into marine environment through riverine inputs, "direct discharge from industry and domestic sewage, surface runoff, erosion, leaching and groundwater transports and release from anaerobic sediments" (Anonymous 1994-1995). In contrast, in the open ocean, P is predominantly supplied by *insitu* regeneration via zooplankton excretion, grazing and the cycling of the microbial loop and also periodic upwelling events (Nalewajko and Lean 1980). Turnover times of P can be quite rapid on the order of minutes to days depending on nutrient concentrations and P pool distributions (Nalewajko and Lean 1980).

Phytoplankton primarily utilize orthophosphate for their metabolism and to manufacture cellular components, i.e. mainly phospholipids and nucleic acids (ribosomal RNA). PO_4^{3-} can be directly absorbed into the cell (Rivkin and Swift 1980), and no oxidation or reduction reactions are required for these processes (Harris 1986). This is an energy dependent reaction which requires energy supplied from respiration or photosynthesis (Nalewajko and Lean 1980). However, studies show that P uptake can become saturated at low light levels when P is replete and that P uptake rates can be similar in both the light and dark phases (Nalewajko and Lean 1980).

Some phytoplankton have the ability to take advantage of the large DOP pool by producing alkaline phosphatase, an extracellular enzyme that hydrolyzes organic monophosphate esters, releasing P that is available for assimilation by

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the cell (Perry 1974; Rivkin and Swift 1980; Graneli et al. 1999). An additional mechanism for P incorporation by phytoplankton has been suggested by Sanudo-Wilhelmy et al. (2004), where P that has been abiotically adsorbed or "scavenged" by phytoplankton cell surfaces can than be internalized by way of a "two-step kinetic process". As yet it is unknown whether this process contributes significantly to the internal stores of P or just confounds phytoplankton stoichiometry studies which consider only total cellular P (Sanudo-Wilhelmy et al. 2004).

The rate of P uptake is determined by the internal cellular P concentration of the phytoplankton (Fuhs et al. 1972) and the concentration and the N:P ratio of available nutrients. P uptake typically follows Michaelis-Menten kinetics (Nalewajko and Lean 1980). Algal cells which are P deficient have rapid assimilation rates when first given sufficient P and uptake rates than decrease as cell P content increases (Healy and Hendzel 1980). When P is available in excess, phytoplankton have the ability to store P as polyphosphates in the cytoplasm and vacuoles of the cell, allowing for continued algal growth in the event that P becomes limiting (Nalewajko and Lean 1980).

Scope of this Study

The primary purpose of this study is to assess the nutrient status of the natural phytoplankton populations on the Southwestern Florida shelf by comparing the particulate stoichiometry of carbon:nitrogen:phosphorus ratios of these assemblages to the Redfield Ratio of 106C:16N:1P. A secondary analysis of this data set will include the comparison of cross shelf transects (near-shore to offshore), latitudinal transects (north to south), the wet versus dry season, interannual (1998-2001) and bloom versus non-bloom conditions of *Karenia brevis* and *Trichodesmium.*

CHAPTER TWO

WEST FLORIDA SHELF STUDY AREA

Physical description

The semi-enclosed western continental shelf of Florida is broad (extending 200km to the west) and relatively shallow due to a gently sloping topography (Yang and Weisberg 1998) with isobaths that generally parallel the coastline (Weisberg et al. 2000). The wide width of the WFS allows for the characterization of different regions as defined by distinctly different momentum balances (Weisberg et al. 2009). The near shore region is part of the inner shelf and is directly impacted by estuaries where salinity related baroclinicity influences circulation (Weisberg et al. 2005, 2009). The inner shelf (landward of the 50m isobath) is mostly affected by local wind forcing (Weisberg et al. 2000) and can be characterized by interacting surface and bottom Ekman layers (Weisberg et al. 2009). The mid-shelf (seaward of 50m isobath) is where "along shelf momentum balance is in pure surface Ekman layer balance" and bottom stress is negligible (Weisberg et al. 2009). This region can experience flows which are opposite to those of the inner shelf as influenced by the partial closure of the WFS by the Florida Keys (Weisberg et al. 2005). The outer shelf represents the transition between the shelf and deep ocean processes. The WFS is wide enough so that the inner shelf and outer shelf do not overlap (Weisberg et al. 2009). The circulation patterns within the eastern Gulf of Mexico are the primary drivers of material flux across and within these regions of the

WFS shelf and are primarily a result of isobath and coastline geometries, winds and buoyancy fluxes (He and Weisberg 2002; Weisberg et al. 2005, 2009), bounding Gulf waters and the Loop Current.

The region experiences basically two seasons typical of a subtropical climate. Based on rainfall data (www.coaps.fsu.edu), the winter or dry season typically extends from October to May, with the summer or wet season from June to September. In response to shifts of the subtropical high pressure belt and associated changes in wind stress, seasonal patterns of shelf water circulation occur as well (Weisberg et al. 1996; Yang and Weisberg 1998). A brief and general summary of Yang and Weisberg (1998) is presented at this time. During the winter season, prevailing winds are from the north/northwest which results in a drop of coastal sea level as surface waters move westward. At this time, there are two opposing jets along the coast, one flowing south from the north and the other flowing north from the south, which meet during March and October near the west-central Florida shelf. The mid shelf region is dominated by a strong northwestward jet along the 50m isobath. These winter conditions induce coastal upwelling, mid-shelf downwelling and a well-mixed water column. In contrast, prevailing winds in the summer are from the south/southeast and coastal sea surface elevation rises. Gulf circulation is somewhat simpler at this time, with only a single northwestward flowing coastal jet along the entire west coast. The shelf region is now dominated by downwelling conditions and the strong jet along the 50m isobath disappears. During both seasons, the shelf break is

predominately influenced by northwestward moving topographic waves which results in alternating upwelling and downwelling conditions in this region.

Due to low background inorganic nutrient concentrations (Heil 2000), this system is generally considered to be oligotrophic (Vargo et al. 2004; Bisset et al. 2005; Heil et al. 2007). Despite this characterization, the area has supported large and persistent blooms of diatoms (Neely et al. 2004), cyanobacteria (e.g. *Trichodesmium* spp), (Lenes et al. 2001) and the dinoflagellate *Karenia brevis* (Vargo et al. 2004). The source of nutrients which fuel this primary production is currently unknown and much research is underway to gain insights into this enigma (Vargo et al. 2008).

Nitrogen and Phosphorus Sources

Primary production in the SW Florida coastal zone is influenced by new nutrients entering the Gulf of Mexico via numerous rivers and tributaries which drain into the Tampa Bay and Charlotte Harbor estuaries and the gated flow of the Caloosahatchee River which periodically receives the overflow of Lake Okeechobee. The nutrient loads associated with these watersheds originate from residential development, industry, agriculture, cattle ranching and the Miocene Hawthorne phosphatic deposits (Heil et al. 2007). The "sandy soils, conductive aquifers and permeable coastal sediments" of these watersheds are conditions conducive to submarine ground water discharge into coastal waters which can carry nutrient loads with concentrations similar to riverine inputs (Kroeger et al. 2006). These sources tend to carry greater loads of inorganic

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phosphorus than inorganic nitrogen and the estuaries within the study area are generally considered to be N-limited or P-enriched, with low DIN:DIP ratios (Wang et al. 1999; Heil et al. 2001; Vargo et al. 2001, 2008). Other nutrient inputs to coastal waters include overland runoff, discharge from storm water systems, wastewater treatment plants, industrial and domestic point sources (Wang et al. 1999; Poor et al. 2001).

 As anthropogenic activity continually increases on Florida's west coast, atmospheric deposition should potentially be an important source of new N but not P, to the coastal marine environment. A study conducted by Poor et al. (2001) found that average total wet and dry deposition of nitrogen (NH $_4^+$, HNO₃, $NO₃$) to the Tampa Bay estuary during 1996-1999 contributed approximately 22.0% of the nitrogen to this region. Data collected at the Mote Marine Lab and the Gandy Bridge during 2000-2002 had deposition rates of N and P that were 1- 2 orders of magnitude lower than estuarine inputs and were not significant sources of nutrients to coastal zones primarily due to dilution effects (Vargo et al. 2008).

The shallow southwestern Florida shelf supports a diverse autotrophic and heterotrophic benthic community and as such, benthic flux of remineralized N and P out of the sediments into the water column could be an important source of nutrients to this system (Vargo et al. 2008). Modeled values of benthic flux report that ammonia flux rates are more significant relative to P fluxes out of the sediment (Vargo et al. 2008). Wang et al. (1999), reports that the release of $NH₃$ and $PO₄³$ from the sediments in Tampa Bay exceeded all external loads.

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Nutrient flux out of the Tampa Bay and Charlotte Harbor estuaries and the Caloosahatchee River can be an important source of TN and TP to coastal marine waters, especially when river inputs are high during the late summer and fall. During this time, tributaries of both Tampa Bay and Charlotte Harbor have high concentrations of silica (see Froelich et al. 1985, Vargo et al. 1991). Therefore, Si concentrations can be used as a non-conservative indicator for estuarine discharge into the coastal zone. Inorganic $PO₄³$ and DOP are elevated at the 10m isobath and show a distinct seasonal pattern that coincides with river flow (Vargo et al. 2008). When estimates of N and P within the daily volume of water flowing out of the Tampa Bay and Charlotte Harbor estuaries and subsequent dilution calculations are considered, estuarine outflows are generally "confined to the areas immediately offshore of the estuary" (Vargo et al. 2008).

The inner west Florida shelf experiences periodic upwelling events where interacting surface and bottom Eckman layers move deeper nutrient rich waters shoreward across isobaths as part of an Ekman-Geostrophic adjustment to wind forcing along the coast (Weisberg et al. 2000). At the shelf break, nutrient rich slope waters are occasionally upwelled (reaching the 30m isobath) in response to intrusions of the Loop current onto the outer shelf of the Gulf of Mexico and local wind events (Heil et al. 2001; Vargo et al. 2008). Although this water rarely reaches the surface, the entrained nutrients could potentially fuel near bottom diatom populations which develop during summer stratification (Heil et al. 2001). This mechanism indirectly provide nutrients to surface water as the remineralization products of this biomass eventually reach the photic zone

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through vertical mixing in the fall (Vargo et al. 2008). Across shelf transport of upwelling waters provides an important albeit sporadic source of new nutrients to the photic zone and creates an effective link between shelf break and near shore nutrient sources (He and Weisberg 2002).

Moving seaward, away from coastal influences, the balance between the phytoplankton uptake from the soluble pool and regeneration of the nutrient from the particulate pool becomes an increasingly important factor regulating production in these oligotrophic waters. N_2 fixation by cyanobacteria, metabolic activity of grazers (zooplankton and flagellates) and *in situ* regeneration (microbial loop) are the likely biological processes recycling nutrients in GOM offshore waters. Blooms of *Trichodesmium* spp. blooms periodically occur within 75 km of the west coast of Florida and have been linked to the wind driven Saharan dust events which deposit large amounts of iron to Gulf waters during the summer months (Lenes et al. 2001, 2008). Iron is a critical component of nitrogenase, the enzyme responsible for N_2 fixation. Therefore, iron has the potential to limit N_2 fixation in offshore environments (Lenes et al. 2001) but typically not in coastal environments where iron is delivered into the marine environment via rivers (Ingle and Martin 1971). *Trichodesmium* ssp. has been reported to excrete inorganic N and P as well as DON (Lenes et al. 2001, 2008; Mullholland et al. 2004; Glibert and Bronk 1994). In turn, these "new" sources of N and P would potentially become available to other cells including the harmful algae *K. brevis* (Mullholland et al. 2004; Glibert and Bronk 1994; Havens 2004).

Summary of Nitrogen and Phosphorus Distributions

The Tampa Bay and Charlotte Harbor estuaries are characterized by low DIN concentrations (less than 0.5 μ M) and high DON concentrations with values measured in 2001 of ~44-56 µM (Vargo et al. 2008). A study conducted by Heil et al. during the dry season of 2003 has shown that the inorganic N pool is typically dominated by NH₄⁺ and is found in the highest concentrations at the mouth of Tampa Bay and inside Charlotte Harbor, an area which also exhibits the greatest concentration of DON (Heil et al. 2007). Coastal standing stocks of DIP and DOP are of similar magnitude and show seasonal peaks in the late summer and fall as related to increase river flow during this time (Vargo et al. 2008). The Caloosahatchee River had higher average concentrations of TN and TP relative to Tampa Bay and Charlotte Harbor during 1998-2001.

Typically offshore (greater than the 10m isobath) concentrations of DIN and DIP are low, ranging from ~0.02-0.2 µM and ~0.025-0.24 µM respectively. Such values are in contrast to concentrations of organic $N \sim 8-14$ µM and organic P ~0.2-0.5 µM which are present at much higher concentrations (Vargo et al. 2008). I refer the reader to Vargo et al. (2008), Walsh et al. (2006) and Heil et al. (2007) for a more detailed description of the nutrient distribution on the West Florida Shelf.

CHAPTER THREE METHODOLOGY

Sampling

The Florida Ecology and Oceanography of Harmful Algal Blooms (ECOHAB) program was a multi-institutional collaboration, multi-agency (National Science Foundation, National Oceanic and Atmospheric Administration, Environmental Protection Agency) project examining the dynamics of the Florida *Karenia brevis* Red Tide which consisted of several major components. As part of the hydrological ECOHAB component, monthly field surveys were conducted aboard the R/V Suncoaster, from June 1998 through December 2001 in the Southwestern Gulf of Mexico off the coast of Florida. The study site was determined in relation to where *K. brevis* was usually first observed, which is ~27º N latitude between Tampa Bay and Charlotte Harbor (Walsh et al. 2006) (Figure 1)

Three East to West transects were sampled monthly from 1998 to 2001, 1) outside the mouth of Tampa Bay (St. Petersburg), 2) Sarasota and 3) Fort Meyers. Stations were sampled synoptically approximately every 9.2 kilometers out to the 50m isobath along all transects over a 4 day period. The stations along the Sarasota transect were extended out to the 200m isobath.

Seawater samples were obtained from 12L Niskin bottles attached to an aluminum-framed rosette/CTD package which also provided continuous vertical profiles of chlorophyll fluorescence, temperature, salinity and density. Surface

hydrologic data were collected from a deck mounted underway flow through

Figure 1. Map of ECOHAB: Florida study area and station locations.

system where surface temperature, salinity, chlorophyll fluorescence, density, particle scattering and light transmission data matched with latitude and longitude. Therefore the surface data provided the ability to construct surface maps of all parameters.

Chemical and Biological Measurements

For Chlorophyll a (Chl *a*) analysis, 250 ml of whole seawater was filtered onto 25mm Whatman GF/F filters in duplicate. The filtration chimney was rinsed with 0.2 µm filtered seawater, then the GF/F filter was folded in half and immersed in 10 ml of methanol contained in a 10 ml plastic centrifuge tube, vortexed for approximately 2 seconds, capped and frozen at -15 ºC. Immediately prior to analysis, samples were then allowed to equilibrate to room temperature and centrifuged for 10 minutes at 80 rpms. The fluorescence of the resultant supernatant was determined using a Turner 10AU fluorometer and Chl *a* and phaeopigments content were determined as given by Holm-Hansen et al.1965).

For analysis of particulate phosphate, 500 ml of seawater was pre-filtered using 153 µm mesh to eliminate large zooplankton and than filtered onto replicate pre-combusted (450º C for 2.5 hours) 25mm GF/F filters and frozen in fired (450º C , 2.5 hours) scintillation vials at -15 ºC. The samples were subsequently processed following the Solorzano and Sharp (1980) method and particulate phosphate concentrates were measured on a Beckman spectrophotometer.

To determine particulate carbon and nitrogen, seawater was pre-filtered using a 153 µm mesh to eliminate large zooplankton and filtered in duplicate onto a pre-combusted (450º C, 2.5 hours) 15mm GF/F filter using a sample volume which gave the filter adequate color for the analysis. The filter was than treated with 2-3ml of 10% HCl in filtered seawater to remove inorganic carbon, rinsed

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with filtered sea water then placed in fired foil (450º C, 2.5 hours),frozen at -20 ºC, followed by lyophilization and storage at -20º C over desiccant. Particulate carbon and nitrogen were measured by high temperature combustion/oxidation of a whole filter using a Carla Erba Elemental Analyzer.

Karenia brevis was counted live within 3 hours of sampling. One ml samples were placed in a glass well plate and the number of *K. brevis* cells was determined using an Olympus dissecting microscope.

Trichodesmium spp concentration was determined by filtering between 1-4 L of seawater onto a 47mm Whatman GF/F filter. The filter was than placed in a 47mm plastic Petri dish. The number of individual trichomes and colonies (puffs and tufts) were counted on ship using an Olympus dissecting microscope.

Monthly precipitation data were obtained from http://www.coaps.fsu.edu for Tampa Bay, Fort Meyers and Sarasota areas. Data from these sites were then averaged to provide an overall area precipitation average.

Particulate Nutrient Ratio Calculations

The mass of particulate carbon and nitrogen values were calculated from the combustion of replicate filters so average C:N ratios and accompanying standard deviation for that ratio could be determined. Particulate phosphate however, was determined by a different method, and therefore the mass of particulate carbon, nitrogen and phosphate were first averaged for each station, with N: P and C: P ratios calculated without the statistical application of standard deviation. All particulate ratios presented are molar ratios as determined by the equation: [(Mass (mg)/Volume filtered (L) * 1000)/Formula Weight].

Statistical Methodology

Data were statistically analyzed using SigmaPlot (version 11). Data were compiled in Microsoft Excel and imported into SigmaPlot. Kolmogorov-Smirnov goodness of fit analysis and skewness and kurtosis Z scores were used to assess the distribution of the data. A Spearman Rank Order Correlation was performed on all particulate nutrient concentration and calculated nutrient ratio data as well as Chl a data.Spearman Rank Order Correlation is a nonparametric test that computes the correlation coefficient to quantify the relationship between two variables without specifying dependent and independent variables. This test was performed on data where the residuals are not normally distributed and/or have non-constant variances. This test is based on ranks rather than arithmetic means.

To analyze nutrient data for potential detrital contribution and parameter relationships, data were also analyzed using simple linear regressions in SigmaPlot. Results of linear regressions were used to produce scatter plots of the residuals and normal probability distribution of the residuals and observed versus predicted values.

Central Tendency Analyses were also performed on log transformed and non-transformed particulate nutrient concentration and calculated particulate ratio

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data using Excel. Central Tendency Analyses provided the mean, geometric mean (Gmean), minimum (min), maximum (max) and median.

CHAPTER 4

RESULTS AND DISCUSSION

Complications to the Interpretation of Particulate Nutrient Stoichiometry

Particulate nutrient concentration quantifies how much C, N and P is in the particulate pool at a given time or place and should primarily be related to the physical processes of nutrient delivery. Theoretically surface particulate ratios should be related to phytoplankton biomass and reflect phytoplankton uptake and growth dynamics as related to nutrient availability. Particulate C, N and P are useful to include when discussing particulate nutrient ratios as these values can help explain why a ratio changes concentration in relation to the elements that comprise that ratio. However, interpreting *in situ* particulate nutrient data and particulate nutrient stoichiometry is challenging because it is often unknown exactly what comprises the particulate nutrient fractions being measured. For this study, particulate nutrients are operationally defined as the total particulate material that is in the size range from 0.7 µm to 153 µm.

It is known that the detrital component of the particulate pool varies in both quantity and chemical composition (Menzel and Ryther 1964; Sharp et al. 1980; Valiela 1985; Hecky et al. 1993; Hessen et al. 2003) and that the contribution of detrital nutrients can confound nutrient stoichiometry interpretation. In oligotrophic waters where phytoplankton biomass is low, the detrital contribution can be large (Harris 1986), but potentially has a similar particulate stoichiometry

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to phytoplankton as turn over rates of both fractions are rapid (Hecky et al.1993). In contrast, in coastal environments where phytoplankton biomass is higher, detrital contributions can become less important as living cells contribute a greater portion to the particulate pool (Steele and Baird 1961; Harris 1986). However, the chemical composition has more potential to vary due to inputs from sources other than phytoplankton including decaying submerged vegetation (e.g. seagrass), macro-algae, resuspension of bottom material and terrestrial sources which have higher proportions of particulate C and N relative to P than those of phytoplankton cells (Hecky et al. 1993). Without other complimentary analysis, whether the particulate nutrient ratios are truly reflective of living phytoplankton cellular material is unknown.

Another aspect of this study which complicates data interpretation concerns the potential for the underestimation/overestimation of particulate P relative to the underestimation/overestimation of particulate C and N due to the different methodologies used for each (See Chapter 3). If the method for measuring particulate C and N concentration either overestimates or underestimates C and N values concurrently, the C:N ratio would remain the same. However, the complication arises when interpreting N:P and C:P ratios. The underestimation/overestimation of either particulate C and N or P would not be expected to be of the same magnitude or possibly the same direction and could significantly skew the particulate N:P and C:P ratios leading to erroneous conclusions.

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It should be mentioned that sampling was continuous from June 1998 through December 2000 and resumed in April of 2001 through December 2001. This could potentially bias the data when calculating the mean, ranges and median of the particulate constituents and ratios as this was not taken into consideration at this time.

General Particulate Nutrient and Nutrient Ratio Distributions on the SW Florida Shelf

Surface particulate nutrient data collected over the sampling period from 1998-2001 displayed a large range for each element (Table 1). Particulate C ranged form 1.05 to 503.20 µM (geometric mean=20.82±0.69), particulate N ranged from 0.05 to 330.88 µM (geometric mean=2.85±1.08) and particulate P ranged from 0.001 to 0.071 µM (geometric mean=0.05±0.91). Particulate N concentrations displayed the greatest variability, encompassing 4 orders of magnitude. The spread of particulate nutrient concentrations values across the wide range are not normally distribution and are heavily skewed toward higher values (Figure 2).

A variety of tests performed for normality of the untransformed and natural log transformed data including Kolmogorov-Smirnov goodness of fit, skewness and kurtosis Z-scores, confirmed that surface particulate C, N and P values were not normally distributed. Results of statistical analysis showed that particulate C (normal log transformed) was the most normally distributed variable of all the parameters presented, only failing to conform to kurtosis or the "peakedness" test

Table 1. Central tendency and ranges for the surface particulate nutrient concentrations (±S.D.) sampled from June 1998 through December 2001. All units are in (µM).

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of the distribution. This suggests that particulate C concentrations across the shelf are less inclined to have extreme values relative to particulate N or P. This seems to make sense in that the potential for the more biologically active elements, N and P, to vary is much greater than the potential for C to vary. It is also interesting to note that particulate N has a frequency distribution which is different from particulate C and P, which share a similar distribution. This may be related to biological processes or the sensitivity of the elemental analyzer in detecting N at low concentrations.

Interestingly, the right tails of these distributions are comprised entirely of samples collected adjacent to the mouths of Tampa Bay and Charlotte Harbor or along the 10 m isobath for which some stations had *Karenia brevis* concentrations greater than 1,000 cells/L (Figure 2). This implies that contributions from coastal inputs and *K. brevis* biomass has a large influence particulate nutrient stoichiometry at this isobath and seem to be responsible for

Figure 2. Histogram of surface particulate nutrient A) carbon, B) nitrogen, and C) phosphorus concentrations sampled from June 1998 through December 2001. The red bars identify concentration bins that are comprised entirely of samples collected from the 10m isobath. The hashed lines indicate a change in scale. All units in $µM$.

Figure 3. Relationship between surface particulate C, N and P and Chl *a* (Figs. A, B,C) or *K. brevis* concentrations (Figs. D, E, F) in samples comprising the bins from histogram Fig. 2, indicating samples from the 10m isobath.

the high values which occur with low frequency relative to non-coastal stations or non-bloom conditions on the WFS. A shared spatial distribution justifies the validity of these numbers, and excludes their potential exclusion based solely on the fact that they lie outside the range of most of the data. Particulate C and P values show no linear relationship to Chlorophyll *a* (Chl *a*) (Figure 3) with R^2 =0.0004 for C and R^2 = 0.0305 for P. The lack of a relationship may be the result of detrital contributions influencing the particulate stoichiometry of coastal stations, despite the high biomass associated with near shore stations and bloom conditions. However, there does seem to be a positive linear relationship between C (R²=0.9990), N (R²=0.5608) and P (R²=0.4350) with *Karenia brevis* cell concentration (Figure 3) which provides justification to include those data points in the analysis. It appears that particulate C, N and P concentrations increase with increasing *K. brevis* concentration as biomass increases.

The surface particulate C, N and P molar ratios collected over the sampling period from 1998-2001 also displayed a large range of values across the WFS (Table 2). Particulate C:N ranged from 0.09-98.82 (geometric mean=7.69±0.97), N:P ranged from 0.59-789.08 (geometric mean=54.60±0.96) and C:P ranged from15.13-4431.17 (geometric mean=407.48±0.82).

The surface particulate molar ratios of C:N, N:P and C:P are not normally distributed as given by the failure to pass Kolmogorov-Smirnov goodness of fit,

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Table 2. Central tendency and ranges of surface particulate nutrient ratios sampled from June 1998 through December 2001.

skewness and kurtosis Z-scores tests for normality (Figure 4). The large range in the data requires these histograms to be presented on two scales to accommodate those samples of higher values but less frequency (see caption Figure 4). It is interesting to note that the data for the particulate N:P and C:P ratios (Fig 4, B and C) display a more normal distribution when considering the bulk of the data (N:P bins 10 to 100 and C:P bins 50 to 1000) relative to the bulk of the nutrient constituents (C, N and P) and the C:N ratio.

<u>36 - John Stein, amerikansk skriuwstrate</u> The large range in the particulate nutrient constituents is evidence of the wide variety of processes on the WFS which can potentially influence nutrient inputs and availability for phytoplankton uptake. These include: proximity to coastal inputs, N_2 fixation, upwelling events, vertical structure of the water column (e.g. thermal stratification), wind events, salinity fronts, hydrography of different regions and seasonality. These processes, along with the ability of phytoplankton to adapt to the nutrient regime of their environment, may be responsible for the wide range within the particulate ratios over space and time.

Figure 4. Histogram of surface particulate nutrient ratios A) C:N, B) N:P and C) C:P sampled from June 1998 through December 2001. Hash marks indicate a change in bin for A) from 2 to 4, B) from 10 to 100 and C) from 50 to 1000

This could also explain in part, the non-normal distribution of this data set, where the values comprising the right tail of both histograms (Figure 2, 3) could potentially be related to more infrequent events such as phytoplankton blooms, large detrital contributions to coastal stations as a result of increased river flow or pulsed nutrient inputs in response to climatic forcing (e.g. wind events).

Variability of particulate nutrient ratios is not confined to the WFS. Studies of natural phytoplankton assemblages conducted by Karl et al. (2000, 2001) at station ALOHA and BATS and a review of the GEOSECS data by Micheals (2001) have indicated that nutrient stoichiometries based on *in situ* samples are not constant and can vary substantially. Phytoplankton culture experiments also have shown that phytoplankton exhibit flexible particulate stoichiometry in response to different nutrient and light regimes (Rhee 1974, 1978; Epply et al. 1974; Goldman et al. 1979; Perry 1976; Goldman 1986).

The West Florida Shelf from June 1998 through December 2001 had a geometric mean particulate C:N:P stoichiometry of 332:77:1 (Table 2), which is very different from the classic Redfield ratio of 106:16:1 (Redfield 1934, 1958) or the more recent work of Montegut-Copin and Montegut-Copin (1983) who report a global average of 103:16.1:1. The geometric mean of 7.69 for the surface particulate C:N ratio is close to the Redfield ratio of 6.66 and the global average of 7.70 reported by Bertilsson et al (2003) (Table 2). However particulate N:P and C:P have geometric means of 54.60 and 407.48 respectively, and do not compare with other values found in the literature for natural phytoplankton assemblages (Table 3) nor to the Redfield ratios of N:P and C:P of 16 and 106

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respectively. The closest values in the literature to the current WFS results are those reported for P-limited phytoplankton culture experiments (Table 4). Reported N:P and C:P ratios of marine phytoplankton grown in P limited cultures are well above the Redfield ratio. *Prochlorococcus*, *Synechococcus* and *Thalassiosira pseudonana* are part of the phytoplankton assemblage found in WFS waters and reported N:P values ranged from 61.1 to 109.0 and C:P values ranged from 464.0 to 779.0 when grown under P-limited conditions (Perry 1976;Bertillsson et al. 2003; Wawrik and Paul 2004). These findings suggest that on average, the WFS seemed to be predominately P-limited during the sampling period.

Surface particulate nutrient ratios have been binned according to categories derived from their potential nutrient status (no limitation with values close to Redfield, nutrient limited and severely nutrient limited) (Figure 5) as suggested by Hecky et al. (1993), Downing (1997), Tyrell (1999) and Grieder and La Roche (2001). 43.4% of the data are near Redfield proportions for C:N and are either not nutrient limited or growing at their maximal rates, while 26.4% of the data are N-limited and 11.9% are severely N-limited. 18.3% fall into the category of C-limitation; however this is most likely due to light limitation. The N:P ratios have only 9.7% of the data near Redfield, with 40.4% suggesting Plimitation and 48.2% suggesting severe P-limitation. The ratio of C:P have 83.76% of the data categorized as severely P-limited and only 2.32% are near the Redfield Ratio. The fact that 86% of the N:P and 94.87% of the C:P nutrient

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Table 3. Literature summary of *in situ* particulate nutrient ratios. Values presented are the average, with the range given in parentheses if available.

Table 3. (Continued).

N.A.: not applicable; E.Z.: Euphotic zone; M.L.: Mixed Layer; *from literature review; **January; ***April; # value for field collected *Trichodesmium*; ^{##} August; [±] May; maximum value; [&]Diatom bloom; [¥]Geometric mean

Table 4. Literature summary of particulate nutrient ratios from phytoplankton cultures. Values presented are the average, with the range given in parentheses if available.

Table 4. (Continued).

__ E.G: Exponential growth;*****species not indicated; ******10% growth rate; ***50% growth rate; # 90% growth rate; ##µ=0.041h-1; $^{\texttt{+}}$ µ=0.017h^{,1}; $^{\texttt{\$}}$ µ=0.0085h $^{\texttt{-1}}$

Figure 5. Histogram of surface particulate nutrient ratios A) C:N, B) N:P and C) C:P sampled from June 1998 through December 2001. The data are binned according to potential nutrient limitation as indicated by Redfield proportions of 106C:16N:1P. The % contribution of each bin to total samples is indicated as a % above the bar.

ratios are well above the expected Redfield ratio further suggests that the WFS was largely P-limited over the course of the sampling period.

Although the world's oceans are thought to be primarily N-limited, there appears to be some systems which at times exhibit P-limited conditions. Data from the North Pacific subtropical gyre suggests that this system has shifted from an N-limited environment to a P-limited environment over the past two decades, as evidenced by enhanced N_2 fixation and relatively high N:P ratios of the particulate pool (Karl et al. 2000). Similar findings are reported for the northwestern Atlantic (Sargasso Sea), western and north-eastern tropical Atlantic, western sub-tropical Atlantic and eastern Atlantic (Angola Basin) (Herbland et al. 1998; Ammerman et al. 2003). Carlson and Graneli (1999) suggest that P can limit productivity in the northern Adriatic Sea, as P stimulated phytoplankton growth in bioassay experiments. The Mediterranean Sea is another marine environment which appears to be a P-controlled system (Berland et al. 1980). Inorganic nutrient concentrations, together with incubation experiments, suggest that the southeastern Mediterranean is strongly P-limited (Krom et al. 1991) and high pulse uptake capacity and subsaturated uptake in phytoplankton suggest P deficiency during the summer in the northwest Mediterranean (Thingstad et al. 1998).

P-limitation can result when there are greater inputs of "new" N (*sensu stricto* Dugdale and Goering 1967) relative to P sources (e.g. from N₂ fixation) or by low inorganic P availability relative to inorganic N. A study by Zehr (2002**)** has shown that N_2 fixation by picoplankton could be a major, previously overlooked,

source of new N in oligotrophic oceanic environments, in addition to N supplied by *Trichodesmium*. Both types of cyanobacteria are found on the WFS. The presence of *Trichodesmium* on filters was not noted during sampling. However, the $N₂$ fixing picocyanobacteria may still have contributed significantly to samples. M. Mullholland (pers. comm.) has measured $N₂$ fixation in <2.0 µm fraction on the WFS, suggesting that $N₂$ fixing picoplankton are present in this system. P-limitation on the WFS could also possibly be related to the physical properties of P compounds. Phosphorus has a tendency to adhere to other particles (Harris 1986; Sanudo-Wilhelmy et al. 2004) and thus could potentially sink out of the photic zone, become sequestered in the sediments and therefore made unavailable for remineralization in surface waters (Harris 1986). To partially explain why the eastern Mediterranean exhibits P-limited conditions, Krom et al. (1991) has suggested that Saharan Dust which has a high affinity for dissolved PO_4^{3} , could effectively remove this nutrient as it sinks though the water column. The WFS also receives atmospheric deposition of Saharan Dust and may in part explain some of the findings in this study. However, this is unlikely given the shallow depth of the WFS and the strong influence of wind driven circulation in the region (Mitchum and Sturges 1982). Van Mooy et al. (2006, 2009) have demonstrated the ability of picocyanobacteria to substitute non-P membrane lipids for phospholipids in environments where P sources are scarce. This would skew phytoplankton C:N:P stoichiometry away from the Redfield ratio and increase cellular C and N relative to P, but allow phytoplankton to still meet their metabolic needs in the face of low dissolved P concentrations. These

organisms are some of the dominant species on the WFS and this mechanism could potentially explain the low concentrations of particulate P seen across the shelf. Further confounding plankton stoichiometry interpretation is the idea presented by Sanudo-Wilhelmy (2004) of a pool of P which adheres to the external structure of phytoplankton cells, but is not internalized into cellular components. Although interesting, this does not help explain why particulate P concentrations are so low on the WFS.

The idea that the WFS is primarily P-limited seems unlikely, as DIN:DIP ratios are generally low and suggest N-limitation (Heil et al. 2007). Furthermore, zooplankton excretion can be an important source of regenerated N and especially P to the WFS. It has been estimated that zooplankton excretion could potentially supply all the P required to support *K. brevis* populations of 10⁶ cells/L (Vargo et al. 2008). However DON:DOP ratios are generally high (Heil et al. 2007) and support the conclusions drawn from the particulate nutrients. Alkaline phosphatase activity (APA) has been detected across the shelf and suggests that phytoplankton are utilizing DOP, which can be a response to a P-limited conditions. It has also been suggested that *Trichodesmium* populations can draw down inorganic and organic stocks of P, leading to P-limitation within the bloom (Sanudo-Wilhelmy et al. 2001; Lenes et al. 2008).

The fact that 48% of the N:P and 84% of the C:P ratios suggesting severe P-limitation, presents a bit more of a conundrum. Explanations may very well lie within the methodology. It is possible that the molybdenum blue method (see Methods section) underestimates particulate P concentrations where the

potential for P to adhere to the glass scint vial or filter during processing does exist. It is also probable that some cellular material was lost during the filtration process due to cell breakage, which would have a larger effect on particulate P than C or N values as this element is found in lower concentrations within the cells. Another possibility is that corrections for the filter contributions (filter blanks) may be high due to contamination or other hidden factors. It has also been suggested that P uptake by zooplankton with high P demands could result in P limitation of the surrounding waters (Hessen et al. 2003). As these grazers were filtered out during the sampling process, they could potentially represent a missing portion of the particulate P pool.

The detrital contribution to the particulate pool is variable both in its chemical structure and quantity. It has been suggested by Menzel and Ryther (1964) that one approach to correcting particulate nutrient data for detrital contributions is to regress particulate nutrients against another and Chl *a* and the particulate nutrient ratios against Chl *a*. This type of analysis was not appropriate when applied to the entire data set. The parameters (nontransformed data and natural log transformed data) do not share a linear relationship, slope of the regression did not predict the mean, residuals are not normally distributed (normal probability plot), scatter plots of residuals showed structure and predicted versus observed values were not linear.

The inability to correct for the detrital contribution to the particulate pool could potentially result in the largest error within the data set. The C:N:P ratios of benthic marine plants (seagrass and macroalgae) are more depleted in P relative

to C and N than phytoplankton and have a median atomic ratio of 700:35:1 (Atkins and Smith 1983). These plants are a major component of the benthos within the shallow WFS and could contribute significant detrital material to the water column influencing the particulate ratios of this study. Upon the decomposition of organic matter, P is utilized more rapidly than N and C (Menzel and Ryther 1964) and if detrital contributions were large during the sampling period, this could also skew the particulate nutrient ratios towards less P relative to C and N, potentially resulting in the extreme values of the N:P and C:P ratios seen on the WFS during the study period. Karl et al. (2001) noted that during the summer and fall at station ALOHA there was an increase of non-living particulate matter, which was accompanied by an increase of particulate N but not particulate P. This resulted in elevated particulate N:P ratios during that period. This observation further supports the idea that a lack of particulate P in detrital matter can skew particulate ratio interpretation to P-limitation, at least during times of high phytoplankton production.

Spearman Rank Order Correlation show that all the particulate nutrient parameters (C, N, P and Chl *a*) have positive correlation coefficients and therefore tend to increase together. The particulate nutrients all have similar correlation coefficients of approximately 0.500 (Table 5), indicating that these parameters are related to some degree. C and N are weakly associated with Chl *a* and have similar correlation coefficients of 0.330 and 0.316 respectively. The variables with the strongest relationship to Chl a is particulate P (r_s =0.752), further supporting the idea that particulate P concentrations may have a stronger

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association with live cells as the turnover time of P is much faster than turnover times for C or N.. This, and the high particulate N:P and C:P ratios suggests that, as in fresh water systems, P controls biomass.

Table 5. Summary of Spearman Rank Order Correlation coefficients (r_s) for surface particulate C (μ M), N (μ M), P (μ M) concentrations, particulate nutrient ratios and Chl *a* (µg/L) sampled from June 1998 through December 2001.

Spearman Ranking Correlation Coefficients for the particulate nutrients as related to the particulate ratios give some interesting results (Table 5). The results indicate that the C:N ratios are more associated with N (r_s = -0.711) than C (r_s =0.160). The negative sign of this coefficient is due to the fact that N is the denominator of the ratio, so as N increases the C:N ratio decreases and vice

versa. The results also indicate that the C:P ratios are more related to P (r_s = -7.21) than C $(r_s = 0.110)$. This supports the premise that particulate C concentrations are more constant across the shelf relative to the more variable particulate N and P concentrations. This is reasonable as C is not considered to be a limiting nutrient on the WFS. Particulate N (r_s = 0.519) also seems to be more related to the N:P ratio than P (r_s = -0.389) and could reflect the greater potential for inorganic N sources to vary across the WFS as a result of N_2 fixing activity.

The lack of strong relationships of the variable pairs presented in Table 5, is expected, as this data set includes the results of all stations sampled across the WFS for each month in each year. Environmental processes at each isobath in each month over each year would be expected to vary and this variance would be reflected in the stoichiometry of the particulate nutrients. In short, the scale of the sampling approach used in this study might be too broad to discern individual factors influencing particulate nutrient ratios.

Spatial Considerations

Near-Shore to Offshore Trends

 It is reasonable to assume that different circulation patterns and associated nutrient concentrations within each region of the WFS would influence phytoplankton uptake rates of C, N and P, and therefore different particulate concentrations and ratios across these zones. Underlying this assumption and further confounding data interpretation, is the probability that both phytoplankton populations and detritus are transported onto different regions of the shelf via wind and currents (e.g. via the bottom Ekman layer, see Weisberg et al. 2009), and their nutrient stoichiometries may be more reflective of their origin or transit path rather than present location. Thus particulate nutrient composition of phytoplankton may be indicative of cell history and transport as well as present nutrient availability and limitation.

The relationships of the average surface particulate nutrients and ratios at each sampled distance offshore are well described by polynomial functions (Figure 6). The surface particulate C, N and P show surprisingly similar curves but of different magnitudes. This suggests that a similar regulating mechanism may be fundamentally acting on all three nutrients but to varying degrees. There is an initial decline in concentration from the 10m isobath (0 km offshore) out to the 30m isobath (~50 km offshore), where concentrations become level before decreasing again at the shelf break (~200km offshore). It is interesting to note

Figure 6. Average of surface particulate nutrient concentrations (Figures A, B,C) and partFigure 17. Scatter plots of surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations at the 10m isobath of the Tampa Bay, Sarasota and Fort Meyers stations during the wet season (pink) and dry season (blue) sampled from June

that Lester et al. (2008) has shown that the 30m isobath is a transition zone where the zooplankton community contains mixed populations of coastal and offshore species. This isobath appears to also be a transition zone from high particulate nutrient concentrations to low concentrations. Therefore, it seems possible that the particulate nutrient concentrations are driving zooplankton assemblages via regulation of food supply. The mean surface particulate ratios of C:N, N:P and C:P also share similar curves but instead steadily increase to a maximum value ~125km offshore and than decrease slightly at the 200m isobath.

Particulate C, N and P across the WFS display a wide range of concentrations (µM) from the coast to the shelf break, with the greatest variability found at the coastal stations (Figure 7). This is expected as these stations are directly impacted by estuarine and riverine inputs, where nutrient and detrital fluxes are more dynamic. In contrast, the C:N and C:P molar ratios (Figure. 7) exhibit greater scatter at distances greater than 50km from the coast. This suggests a decoupling of processes regulating particulate C from those regulating particulate N and P with distance offshore which can occur under nutrient limiting conditions. It has been shown that phytoplankton will store C when other nutrients are found in short supply (Fuhs et al. 1972). This could also be related to changes in the contribution of detrital material to the particulate concentration. Detrital material is composed of recalcitrant C, which could contribute a greater portion to the particulate as phytoplankton biomass decreases off-shore. In contrast, the range of particulate N:P ratios exhibit less

Figure 7. Influence of distance from shore on surface particulate C, N, P concentrations (Figures A, B,C) and particulate nutrient ratios C:N, N:P, C:P (Figures D, E, F) sampled from June 1998 through December 2001.
scatter across the shelf, perhaps related to the diminishing inorganic supply of both nutrients with increasing distance from coastal inputs.

To compliment other similar studies of the ECOHAB data set (Havens 2004; Lester 2005; Ault 2006) and to resolve particulate nutrient distributions, the data was partitioned into subsets by isobath (Table 6). The 10m isobath are those stations sampled closest to the coast and are directly impacted by estuarine and riverine fluxes. The 30m isobath, located in the middle of the inner shelf region, seems to represent a transition zone from coastally influenced water to more oligotrophic waters, where particulate nutrient concentrations remain constant. The 50m isobath is a transitional location from the inner shelf to the mid shelf and the 200m isobath located at the shelf break is associated with the transition between the shelf and the deep water processes (Weisberg et al. 2005, 2009).

From the coastal stations out to the 200m isobath, there is a decrease in the average particulate C (μ M) of 67% and a decrease in particulate N (μ M) and P (µM) of 76% and 90% respectively (Table 6). This trend reflects the influence of estuarine sources of inorganic nutrients and detrital material on the particulate nutrient pool, while the particulate nutrient pool further offshore reflect the oligotrophic conditions associated with this region. This decreasing trend is reflected in a similar decrease in Chl *a* concentration from the coastal region out to the 200m isobath (Figure 8).

Average surface particulate (C:N:P) nutrient stoichiometries are well above the Redfield Ratio at the 10m, 30m, 50m and 200m isobaths (Table 7).

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Table 6. Central tendency and ranges for the surface particulate nutrient concentrations and particulate nutrient ratios sampled from June 1998 through December 2001 at the 10m, 30m, 50m and 200m isobaths.

Figure 8. Relationship between surface Chl *a* concentration and distance from shore. The curve includes data sampled from June 1998 through December 2001.

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The most balanced nutrient conditions are found at the 10m isobath where average C:N:P=232:55:1. The ratios steadily increased with distance offshore to an average C:N:P ratio of 773:134:1 at the 200m isobath. Particulate C increases dramatically from the near shore to the off shore stations relative to particulate P and supports the hypothesis that either the phytoplankton could be storing C in excess to P or there is increasing detrital contributions with a greater portion of refractory C relative to P with increasing distance from the coast. The abundance of picocyanobacteria (*Synecococcu*s and *Prochlorococcus*) increases with distance offshore and these populations can have very high C:P ratios when P-limited (Table 4). Therefore, it is possible that the stoichiometry of a potentially P-limited picocyanobacteria assemblage could also be a factor contributing to the increasing C:P ratio with distance from the coast. Although particulate N increases from the 10m isobath to the 200m isobath relative to P, the increase is not as great when compared to particulate C (Table 7). This further supports the

hypothesis that N_2 fixation can be a very important process occurring on the WFS and also that nutrients have the potential to be recycled at different rates.

All the particulate nutrient ratios increase with distance from shore but the C:N ratio displays a fairly constrained range across the isobaths (8.63-16.90) in comparison to N:P (52.86-148.22) and C:P (260.07-880.59) (Table 6). The mean particulate C:N ratio increased by 49% from the near-shore stations along the10m isobath to the100m isobath (Table 6). This may be related to the slightly greater decrease of particulate nitrogen relative to carbon with distance offshore as inorganic N sources most likely decrease relative to inorganic C out on the shelf. The average ratio of particulate N:P increases by 64% from the 10m isobath out to the 100m isobath (Table 6) and could be related to sources of "new" N contributed to shelf waters by N_2 fixers and the relative lack of coincident new" P with increasing distance from the coast. The largest increase from the coastal stations to the 100m isobath is exhibited by the mean particulate C:P ratios which increase by 70% (Table 6). The average particulate nutrient ratios all show a decrease in values after the 100m isobath out to the 200m isobath, where C:N shows an 18% decrease, N:P decreases by 14% and P declines by 12%. This decrease could be in response to surface fronts at shelf break supplying regenerated nutrients to the primary producers, potentially reducing conditions of nutrient limitation.

Scatter plots suggest that particulate N:P and C:P ratios at the 10m isobath are distinct from those found at the 30m, 50m and 200m isobaths (Figure 9) and particulate C:N ratios are not distinct at any of the sampled isobaths. It is

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Figure 9. Scatter plots of surface particulate C, N and P concentrations at the 10m isobath (blue), 30m isobath (red), 50m isobath (green) and 200m isobath (turquoise) sampled from June 1998 through December 2001.

interesting to note that most of the variance within the C:N ratio is related to changes in particulate N rather than particulate C. Although the mean C concentrations decrease seaward of the coast (Table 6, Figure 7), it appears that particulate C concentrations are not as related to isobath spatial distributions as particulate N and P concentrations.

 Spearman Rank Order Correlation coefficients suggest that particulate C, N and P are most related at the 10m isobath with r_s values of C and N= 0.643, N and $P= 0.567$ and C paired with $P= 0.574$ followed by the 200m isobath where C and N have an r_s = 0.392, N and P = 0.338 and C paired with P = 0.521 (Table 8). Nutrient inputs from the estuaries at the 10m isobath and upwelled regenerated nutrients from deep waters at the 200m isobath could potentially be responsible for the correlation between particulate C, N and P. Phytoplankton populations might be less nutrient limited at the 10 and 200m isobaths, where nutrient uptake could be based more on cellular requirements rather than adapting nutrient uptake kinetics to nutrient availability, which tends to de-couple particulate C, N and P relationships. In contrast, the r_s values for particulate C, N and P at the 30m and 50m isobaths suggest that there is no relationship between these constituents. As these regions are primarily driven by regenerated nutrients, it is possible that particulate C, N, P relationships become decoupled in response to greater nutrient limitation

Spearman Ranking Order Correlation coefficients suggest that at all isobaths, the C:N and especially N:P ratios are most related to particulate N concentrations when compared to the r_s of C:N with C and N:P with P (Table 8).

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This suggests that the potential for particulate N to vary in concentration across the shelf is greater than either particulate C or P. It is interesting to note that the r_s of the paired variables C, C:N and P, N:P suggest that these variables are not related at the 10m isobath or the 200m isobath but are somewhat related at the 30m and 50m isobaths. The results are similar when considering C, C:P, but there is a weak correlation at the 10m and 200m isobath and a relatively strong relationship at the 30m and 50m isobath. It appears that the influence of particulate C on the C:N and especially the C:P ratio, are strongest in regions that are less productive, where detrital contributions could comprise a larger portion of the particulate pool. The strong correlation of C with C:P relative to the C:N at the 30m and 50m isobaths could be related to the lack of inorganic P inputs resulting in less cellular P and therefore particulate C would be expected to dominate this ratio. In contrast, the C:N ratio at the 30m and 50m isobath should be related to both additional particulate N inputs due to N_2 fixation and particulate C. The correlation between the paired variables of N with C:N, N with N:P and P with C:P does not change with distance from shore, and implies that the influence of N on the C:N and N:P ratios and the influence of particulate P on the C:P ratios remains similar across the shelf.

At each isobath, the frequency of surface particulate nutrient ratios were binned into categories of near Redfield, nutrient limited and severe limitation (Figures 10-12 see figure captions for explanations of individual categories for each ratio). The frequency distribution of the C: N ratio at the 0, 30, 50 and 200m isobaths remain constant in each category across the shelf, with

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approximately 50% of the data near to the Redfield Ratio (Figure 10, Table 9). In

contrast, the N: P ratio decreased from 26% of the data near to Redfield at the

10m isobath to 3% near Redfield at the 200m isobath, (Figure 11, Table 9)

Table 8. Summary of Spearman Rank Order Correlation coefficients (r_s) for surface particulate C (μ M), N (μ M), P (μ M) concentrations and particulate nutrient ratios at the 10m (N=106), 30m (N=103), 50m (N=101) and 200m (N=32) isobaths sampled from June 1998 through December 2001.

and the C:P decreased from 8% near Redfield at the 10m isobath to 0% at the 30, 50 and 200m isobaths (Figure 12, Table 9). At the 10m isobath 23% of the N:P data was indicative of severe P-limitation; this percentage increased to 65% at the 200m isobath. The same trend is found in the C:P ratio, where 50% of the data at the 10m isobath could be considered severely P-limited, which increased to 92% at the 30m isobath and 100% out at the 200m isobath. These results

C:N

Figure 10. Histograms of surface particulate C:N binned according to nutrient limitation as indicated by Redfield proportions (106C:16N) for the A) 10m isobath, B) 30m isobath, C) 50m isobath, D) 100m isobath and E) 200m isobath. C-limitation is indicated by 0-4, near Redfield proportions by 4-10, N-limitation by 10-20 and severe N-limitation by 20+. The data include samples collected from June 1998 through December 2001. Note that the frequency distribution scale for the 200m isobath has been changed to a maximum of 15 due to a decrease in the number of samples at this site.

Figure 11.) Histograms of surface particulate N:P binned according to nutrient limitation as indicated by Redfield proportions (16N:1P) for the A) 10m isobath, B) 30m isobath, C) 50m isobath, D) 100m isobath and E) 200m isobath. N-limitation is indicated by 0-10, near Redfield proportions by 10-20, P-limitation by 20-50 and severe P-limitation by 50+. The data include samples collected from June 1998 through 2001. Note that the frequency distribution scale for the 200m isobath has been changed to a maximum of 30 due to a decrease in the number of samples at that site.

Figure 12.) Histograms of surface particulate C:P binned according to nutrient limitation as indicated by Redfield proportions (106C:1P) for the A) 10m isobath, B) 30m isobath, C) 50m isobath, D) 100m isobath and E) 200m isobath. C-limitation is indicated by 0-90, near Redfield proportions by 90- 122, P-limitation by 122-212 and severe P-limitation by 212+. The data include samples collected from June 1998 through December 2001. Note that the frequency distribution scale for the 100 km and 200m isobaths have been changed to a maximum of 30 due to a decrease in the number of samples at these sites.

support the hypothesis that P limitation increases with distance offshore, but do not support the idea of a decrease in P limiting conditions at the 200m isobath (Table 7) that is suggested by mean N:P and C:P values. These data also strongly suggests that N-limitation does not increase with distance off shore,

Table 9. Frequency percentage (%) of surface particulate nutrient ratio values to total sample number within different isobaths with considerations to the Redfield Ratio and nutrient limitation.

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*for C:N values, C-limited was 0-4, Near Redfield was 4-10, N-limited was 10-20, Severe N-limitation was greater than 20; **for N:P values, C-limited was 0-10, Near Redfield was 10-20, P-limited was 20-50, Severe P-limitation was greater than 50; ***for C:P values, C-limited was 0-90, Near Redfield was 90-122, Plimited was 122-212, Severe P-limitation was greater than 212

consistent with the idea that pelagic nitrogen fixation is a very important process in the oligotrophic waters of the WFS.

The trend for increasing particulate N:P ratios across the shelf, could result from a decreasing supply of inorganic P or an increasing supply of new N relative to P due to nitrogen fixation. Either explanation or a combination of both are plausible, as new sources of P away from coastal sources are restricted to inputs from deeper waters and nitrogen fixation is known to occur in offshore oligotrophic waters. The process of nitrogen fixation can contribute to a draw down in PO4 concentration, as this process itself requires P.

Latitudinal Trends

Heil et al (2007) demonstrated a relationship between particulate N:P ratios and latitude in the coastal area between Tampa Bay to Florida Bay, which they hypothesized was related to the different nutrient inputs from various riverine sources along this gradient. The current study included three onshoreoffshore sampling transects which originated from Tampa Bay, Sarasota Bay and Fort Meyers. Each transect was sampled out to the 50m isobath, which allows for analysis of latitudinal trends. In this section the particulate nutrient data were partitioned into north (Tampa Bay) to south (Fort Meyers) transect subsets to examine potential trends.

Central tendency measures of the particulate nutrient data, organized by latitude (Table 10), suggest that surface particulate nutrient concentrations and ratios were very similar along the Tampa Bay, Sarasota and Fort Meyers transects. The geometric mean of N:P and C:P ratios decreased from the northern Tampa Bay to the southern Fort Meyers by 19% and 9% respectively, suggesting a weak trend of decreasing P-limitation along this gradient. The geometric mean of the C:N ratio increased by 10%, suggesting a weak trend of increasing N limitation towards the south. Stoichiometry calculations using the geometric mean support this as Tampa Bay has a C:N:P of 527:71:1, Sarasota 383:49:1 and Fort Meyers 383:44:1 (Table 11). All particulate C:N:P stoichiometries are above the classic Redfield Ratio which suggests P-limiting conditions along all three transects however.

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Table 10. Central tendency measures and ranges of surface particulate nutrient concentrations and particulate nutrient ratios for the Tampa Bay, Sarasota and Fort Meyers transects. The data include all stations sampled out to the 50m isobath for each transect from June 1998 through December 2001.

when the particulate ratios are considered and binned according to nutrient

deficiency or sufficiency, the distribution percentages do not support a

Table 11. Surface particulate nutrient stoichiometry based on the geometric mean and median of the Tampa Bay, Sarasota and Fort Meyers transects. The data include all stations sampled out to the 50m isobath and at the 10m isobath for each transect.

trend of decreasing P limitation nor increasing N-limitation from Tampa Bay to Fort Meyers (Figure 13, Table 12). Fort Meyers has the highest percentage of data distributed within the near Redfield bin for all particulate ratios with 53% of C:N, 13% of N:P and 3%of C:P in this category (Table 12). The Fort Meyers station is influenced by nutrient inputs from Charlotte Harbor and the Calossahatchee River which have greater fluxes of TN and TP compared to both Tampa Bay and Sarasota Bay (Vargo et al. 2008)and could potentially explain this observation. The lack of strong trends is not surprising, as the factors

Figure 13. Histogram of surface particulate A) C:N, B) N:P and C) C:N ratios sampled from June 1998 through December 2001 binned according to potential nutrient limitation as indicated by Redfield proportions of 106C:16N:1P. Tampa Bay (blue), Sarasota (red) and Fort Meyers (green) transects.

influencing the particulate C:N:P ratios across the distances of the entire transect

are most likely to be similar regardless of the small changes in latitude.

However, each transect point of origin is influenced by a different riverine system

and drainage basin, so the particulate nutrient data at the 10m could potentially

reflect these different influences. In times of high river flow the 30m isobath

Table 12. Frequency percentage (%) of surface particulate nutrient ratio values to total sample number within different transects with considerations to the Redfield Ratio and nutrient limitation. Each transect includes all station data from the 10m isobath to the 50m isobath.

*for C:N values, C-limited was 0-4, Near Redfield was 4-10, N-limited was 10-20, Severe N-limitation was greater than 20; **for N:P values, C-limited was 0-10, Near Redfield was 10-20, P-limited was 20-50, Severe P-limitation was greater than 50; ***for C:P values, C-limited was 0-90, Near Redfield was 90-122, Plimited was 122-212, Severe P-limitation was greater than 212

could be potentially influenced by coastal processes but will not be considered at this time (Vargo et al. 2008).

At the 10m isobath, Sarasota has the lowest concentration of average particulate nutrients and Chl *a* concentrations (Ault 2006) compared to Tampa Bay (Table 13) and Fort Meyers. Sarasota Bay does not have the large river systems influencing its adjacent coastal stations, as does the Tampa Bay transect (Manatee River) and the Fort Meyers transect (Charlotte Harbor and Caloosahatchee River), but instead is fed by small creeks. Therefore, it seems likely that dissolved nutrient or detrital inputs to the coastal stations of Tampa Bay and Fort Meyers would be larger resulting in greater particulate C, N and P concentrations relative to Sarasota Bay. Tampa Bay has the highest concentration of average particulate C (Gmean=40.71µM) and P (Gmean=0.23µM). The tributaries which enter Tampa Bay and Charlotte Harbor drain the Hawthorn phosphatic deposits yet; inorganic P concentrations at the mouth of Tampa Bay are greater than at the mouth of the Caloosahatchee River (Vargo et al. 2008). This could potentially be a contributing factor to the high particulate P concentration at the 10m isobath of the Tampa Bay transect. Fort Meyers has the greatest average concentration of particulate N (Gmean=41.09µM) (Table 13) at the 10m isobath and is 74% greater than the Tampa Bay station and 89% greater than the Sarasota station at the 10m isobath. The Caloosahatchee River has a higher total nitrogen flux compared to Tampa Bay and supports this observation (Vargo et al. 2008).

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Table 13. Central tendency measures and ranges of surface particulate nutrient concentrations and nutrient ratios of Tampa Bay, Sarasota and Fort Meyers transects. The data include all stations sampled at the 10m isobath for each transect from June 1998 through December 2001.

The Gmean C:N ratio for Sarasota (7.8) and Fort Meyers (7.39) are very similar while Tampa Bay (4.97) is below the Redfield Ratio (Table 13). This implies that at the 10m isobath of the Tampa Bay transect, phytoplankton cells are not limited by N (Figure 14). This is unexpected as it is well known that phytoplankton biomass is limited by N inside the Tampa Bay estuary (Walsh et al. 2006; Vargo et al. 2008). However, a DIN/PO₄ ratio of 5.7 at the mouth of the estuary (Walsh et al. 2006) suggests that N-limiting conditions could potentially be restricted to the inside of Tampa Bay. Further confounding this study, are the Gmean particulate N:P ratios at the 10m isobath which are: 40.19 for Tampa Bay, 29.59 for Sarasota and 33.16 for Fort Meyers. This implies that all three coastal stations are potentially limited by P (Table 11, Table 13, Figure 14). The Gmean of the particulate C:P ratios also imply P-limitation at these stations (Table 11, Table 13). However, the DIN: PO_4 at these stations are all below the Redfield ratio (Walsh 2006) and do not support the hypothesis drawn from the particulate nutrient data. There must either be a significant pool of particulate P that was not accounted for while sampling (i.e. zooplankton), a significant sink of inorganic P other than phytoplankton uptake (abiotic or biotic processes) or the method for particulate P determination underestimated P concentrations.

Spearman Ranking Correlation coefficients indicate that there is better correlation between the Particulate C, N and P concentrations at the 10m isobath of Tampa Bay and Fort Meyers stations then at the Sarasota station (Table 14). This supports the hypothesis that the hydrology of the region (i.e. the larger riverine systems influence on the Tampa Bay and Fort Meyers regions and the

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Figure 14. Histogram surface particulate A) C:N, B) N:P and C) C:N ratios sampled at the 10m isobath from June 1998 through December 2001 binned according to potential nutrient limitation as indicated by Redfield proportions of 106C:16N:1P. Tampa Bay (blue), Sarasota (red) and Fort Meyers (green) transects.

Table 14. Summary of Spearman Rank Order Correlation coefficients (rs) for surface particulate C (μ M), N (μ M), P (μ M) concentrations and particulate nutrient molar ratios at Tampa Bay (N=37), Sarasota (N=35), Fort Meyers (N=33) at the 10m isobath sampled from June 1998 through December 2001.

smaller freshwater systems influencing the Sarasota regions) could potentially influence the particulate nutrient concentrations and the relationships between the particulate constituents. However, the correlation coefficients indicate that correlation decreases between particulate C and N and the ratios C:N, N:P, C:P from Tampa Bay south to Fort Meyers at the 10m isobath. The decoupling of N to the C:N and N:P ratio could potentially be related to the decrease of inorganic N concentrations from Tampa Bay to Fort Meyers (Walsh 2006). In response to lower inorganic N concentrations, adjusted phytoplankton uptake ratios could be responsible for this trend. The particulate C:N ratio does support increasing Nlimited growth from Tampa Bay to Fort Meyers (Figure 14).

Temporal Considerations

Seasonal Trends

Particulate nutrient concentrations and nutrient ratios should be influenced by the seasonal patterns of climatology, ocean circulation, sea surface temperature and stratification as the varying influences of these parameters ultimately control the nutrient regime available to phytoplankton. The rainy

Figure 15. The monthly average rainfall at Tampa Bay, Sarasota and Fort Meyers for each month from 1998-2001. Data are from Florida State University. http://www.coaps.fsu.edu/climate_center/prcpdat.

season in southern Florida typically lasts from June to September and the dry season from October to May (Figure 15). The rainy season coincides with the along shore current flowing from the south to north and increased sea surface temperature which in deeper waters can result in the thermal stratification of the water column. During the dry season, the along shore currents flow from the north to the south and sea surface temperature decreases.

Scatter plots of all (the entire data set) the particulate C, N and P from the wet season and the dry season do not show any notable differences between the two data sets (Figure 16). The Gmean of the particulate C, N and P concentrations support this observation, as there is little difference in the concentrations between the two seasons (Table 15). However, the range of particulate C and N concentrations are greater during the dry season than during the wet season. This result seems counterintuitive; logic suggests that there would be greater flux of particulate detrital material during times of high river flow giving rise to a larger range of concentrations within the particulate pool.

Despite the similar range of the particulate constituents during the wet and dry period, the Gmean of the molar ratios suggest that there might be a difference in how these constituents are incorporated into phytoplankton cells potentially based on nutrient availability. The Gmean of the C:N ratio during the wet season is 6.77 and implies balanced growth while the C:N ratio during the dry season is 8.44 which suggests that N could potentially become limiting during that time. In contrast, the Gmeans of both N:P and C:P suggest conditions of greater P-limitation during the wet season. This is again counterintuitive as dissolved P inputs would be expected to be greater during times when river flow is highest. When considering specifically the influence of rainfall on the particulate nutrients and ratios, it is reasonable to assume that the stations that

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Figure 16. Scatter plots of surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations during the wet season (pink) and dry season (blue) sampled from June 1998 through December 2001.

Table 15. Central tendency measures and ranges of surface particulate nutrient concentrations and nutrient ratios of the wet season (June to September) and the dry season (October to May). The data include all stations sampled from June 1998 through December 2001.

are directly influenced by estuaries should reflect the changes in dissolved nutrient concentrations and availability and detrital materials associated with changes in river flow. When only the average particulate nutrient data from the Tampa Bay, Sarasota and Fort Meyers stations at the 10m isobath are considered, the particulate C,N and P concentrations are still similar during both the wet and the dry period and the widest range of particulate concentrations remain during the dry period (Figure 17, Table 16). The dry period still has C:N values above the Redfield ratio but the N:P and C:P ratios are very similar during the wet and dry season where values in both cases are suggestive of Plimitation. Spearman Ranking Correlation Coefficients indicate that there is no correlation between any possible paired particulate variables and rainfall.

Analyzing the data binned as the wet or dry season may have been too broad a classification and subtle trends were not recognized. To analyze the data on a finer scale of temporal resolution, the particulate nutrient concentrations and nutrient ratios were plotted against month

Plots of all particulate C, N, P and of the particulate nutrient ratios, indicate that there is a wide range of values for each month, most noticeably from June to October (Figure 18, 19). However, average particulate nutrient concentrations for each month suggest that there may be seasonal trends within the wet and dry seasons that are not only associated with rainfall, but with other process as well (Figure 20). The particulate nutrient concentrations seem to indicate that similar processes are influencing C and P and these processes could potentially be different during the wet and dry periods (Figure 20). The particulate N curve displays a similar curve to particulate C and P during the dry season, suggesting these concentrations might be linked to processes potentially driving particulate C and P concentrations. However, during the wet season, particulate N concentrations increase linearly from June to October appearing independent from the curve of the C and P concentrations. Thus, a different set of processes

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P (µM)

Figure 17. Scatter plots of surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations at the 10m isobath of the Tampa Bay, Sarasota and Fort Meyers stations during the wet season (pink) and dry season (blue) sampled from June 1998 through December 2001.

Figure 18. Relationship between month and surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations sampled from June 1998 through December 2001.

Figure 19. Relationship between month and surface particulate ratios A) C:N, B) N:P and C) C:P sampled from June 1998 through December 2001. .

Table 16. Central tendency measures and ranges of surface particulate nutrient concentrations and nutrient ratios of the wet season (June to September) and the dry season (October to May). The data include the averaged data of the Tampa Bay, Sarasota and Fort Meyers stations at the 10m isobath sampled from June 1998 through December 2001.

may be acting on particulate N during the wet period. Average C:N and N:P ratios do not exhibit the strong seasonal patterns of the particulate C, N, P concentrations and C:P ratios (Figure 21). The monthly average C:N ratios

Figure 20. Monthly average surface particulate C (blue), N (pink) and P (green) concentrations sampled from June 1998 through December 2001.

suggest decreasing N-limitation from February to October and the monthly average N:P ratios suggest increasing P-limitation during this time period. This could potentially be related to increasing N_2 fixation during these months which would alleviate N-limitation and compound P-limiting conditions. It is interesting that the C:P curve is practically identical to the curves of particulate C and P concentrations. In contrast, the C:N and N:P curves are somewhat different in comparison with particulate C and N concentrations. This suggests that phytoplankton C:P uptake ratios might be more straightforward and more related to the physical processes controlling nutrient availability while C and N and N and P uptake ratios seems more complex and potentially more related to phytoplankton adaptation strategies concerning nutrient uptake. The processes which influence the average monthly ratios should potentially be different across the shelf (e.g. coastal processes versus offshore processes). Therefore, to

Figure 21. Relationship between month and average surface particulate ratio A) C:N, B) N:P and C) C:P sampled from June 1998 through December 2001.

assess the seasonal influence on the particulate nutrients and ratios across the WFS, it is necessary to combine spatial and temporal perspectives.

The monthly averaged particulate C, N and P curves at the 10m isobath (Figure 22A) are surprisingly similar to the average curves (Figure 20). The particulate C, N and P concentrations track very well at the 10m and 30m and to some degree, at the 50m and 200m isobaths as well. This suggests that there may be a fundamental process or set of processes driving the particulate nutrient pool across the shelf. Although the basic patterns are retained, the curves of particulate C, N and P begin to shift with each seaward isobath and suggest that with distance offshore the relationship between particulate C, N and P decreases.

The curves of the particulate C, N and P concentration all exhibit increases in concentrations during the spring, early summer and fall at all isobaths presented (Figure 22, 23). There does seem to be a seasonal influence on the particulate nutrient constituents that is not simply due to rainfall, but may be related to the seasonal change in flow regime on the WFS and probably other processes not revealed in this study.

During the spring, increased day length could potentially increase phytoplankton productivity, resulting in the increase of particulate C, N and P (Figure 23) during this time of the year. The peaks in the curves of particulate C, N and P (Figure 23) during the summer at the 10m and 30m isobaths could potentially be related to the "first flush" of runoff associated with the start of the rainy season, when detrital material, degradation products and anthropogenic

Figure 22. Monthly average surface particulate C, N and P concentrations at the A) 10m, B) 30m, C) 50m and D) 200m isobaths sampled from June 1998 through December 2001. Particulate C (blue), particulate N (pink) and particulate P (green).

Figure 23. Monthly average surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations along different isobaths sampled from June 1998 through December 2001. 10m isobath (blue), 30m isobath (red), 50m isobath (green) and the 200m isobath (turquoise).

nutrient sources built up during the dry period are discharged into the marine environment at higher concentrations during the rest of the rainy season. At the 50m and 200m isobaths it should be expected that this trend is more related to ocean circulation patterns as increased (or decreased) riverine nutrient inputs should not influence this region of the shelf. In situ regeneration within the photic zone of regions that become thermally stratified could also be responsible for increased particulate nutrient concentrations. The peaks in the curves of particulate C, N and P (Figure 23) during the fall could potentially be related to the fall water column turnover event where cooler temperatures result in the break down of thermal stratification in the water column, resulting in the upward diffusion of nutrients increasing phytoplankton production and the observed increase in particulate nutrient concentrations. In the fall, along shore currents revert back to the north to south flow pattern and could potentially influence particulate C, N and P concentrations at this time of the year. The dips that often follow the peaks might be a result of the draw down of nutrients after periods of increased growth and would result in a decrease of nutrients in the particulate pool.

During the dry season, the particulate C:N ratio at all isobaths have similar curves with peak values occurring in February, followed by another peak in May and the lowest values occurring in October (Figure 24A). This suggests that similar processes may be acting on the particulate C:N ratio across the shelf during that period. Ocean circulation patterns are known to reverse during May and October and might be a contributing factor to the more N limiting conditions

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Figure 24. Monthly average surface ratios A) C:N, B) N:P and C) C:P along different isobaths sampled from June 1998 through December 2001. 10m isobath (blue), 30m isobath (red), 50m isobath (green) and the 200m isobath (turquoise).

during the spring and less N-limiting conditions during the fall. At the 10m and 30m isobaths this pattern could possibly be related to rainfall where the spring peak may be related to the first flush of nutrients at the start of the rainy season and the low concentrations in October results as a lack of river flow. The first heavy rainfall would be expected to bring large loads of detrital C into the estuaries and coastal zones thereby elevating the C:N ratio. The high C:N values that occur in February could be related to carbon over-consumption (Fuhs 1972) as inorganic nutrient concentrations are known to decrease during the winter months. For all hypotheses presented, it is difficult to determine if the C:N ratios are more influenced by particulate N or particulate P as both of these concentrations decrease in February and May (Figure 23A, 23B) and increase in October. During the rainy season the particulate C:N curves at all isobaths exhibit a different trend compared to the dry season. This suggests that processes contributing to the C:N ratio across the shelf may be different during wet and dry seasons. More over, the curves at the10m and 30m isobath are similar and the curves at the 50m and 200m isobaths are somewhat similar to each other (Figure 24A) and implies that from June to September the processes contributing to the particulate C:N values found within the inner shelf could be different than processes contributing to offshore particulate C:N values. The particulate C:N ratios at the 10m and 30m isobaths steadily declines throughout the wet season and could be related to the potential increase in concentrations of inorganic N due to increased river flow during the summer months or perhaps N_2 fixers are responding to an increase in iron availability deposited as Saharan

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dust. It is also possible that detrital C materials become less important after the "first flush" of the rainy season contributing to this trend by reducing particulate C concentrations (Figure 23A). Explanations for the rise in the average particulate C:N ratios at the 50m and 200m isobaths during July and September are not as readily available and may be related to summer circulation patterns within the offshore region.

The particulate N:P ratio exhibits a general trend of increasing P-limitation from February to July across the WFS as particulate N:P values steadily increase from the lowest values in February to higher values in July (Figure 24B). From August to November the curve of the 10m isobath exhibits a different trend when compared to the surprisingly similar curves at 30m, 50m and 200m isobaths exhibited throughout all months (Figure 24B). Particulate N:P values at the 10m isobath increase throughout the wet season indicating conditions of continually increasing P-limitation into September. In contrast, the particulate N:P ratios farther offshore decrease in value during August and September, indicating decreasing P-limitation during the late summer. This implies that during the summer and fall, processes driving the coastal particulate N:P ratios are different from those processes influencing particulate N:P ratios farther offshore. However, which processes contributing to the trend of increasing P-limitation at the 10m isobath and decreasing P-limitation at the 30m, 50m and 200m isobaths during the late summer are difficult to explain. During the wet season, inorganic P concentrations along the coast increase as the flow of rivers draining Hawthorne phosphatic deposit increase. This should result in a decrease of the

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particulate N:P ratio during the rainy season as coastal phytoplankton should not, in theory, be limited by P. It is possible that a large portion of the inorganic P is taken up within the estuaries and therefore not available to coastal populations, but does not explain why the N:P ratio increases from May to September. It is unclear why the offshore stations appear to become less P-limited during the late summer months than during July. N₂ fixation rates offshore should increase during the late summer, increasing particulate N concentrations relative to particulate P at the 30m, 50m, and 200m isobath. However, this trend is observed during the month of October. It is interesting to note that average C:N and N:P values generally exhibit opposite trends at all isobaths in all months, which implies that particulate N may be driving both ratios on the WFS during the wet and dry periods. These ratios display seasonal trends which are potentially related to changing circulation patterns, thermal regimes, biological processes (i.e. of N2 fixation by *Trichodesmium* populations in late summer), and rainfall (10m and 30m isobaths). Despite the relatively constant values of the average particulate N concentrations (Figure 20, 23B), it seems likely that seasonal processes affect the mechanisms by which particulate N is partitioned into cellular material to a greater degree than particulate C.

The particulate C:P ratio lacks some of the structure seen in both the C:N and N:P curves, most notable at the 10m isobath (Figure 24C), which implies that this ratios may be less seasonally dependent than ratios which include particulate N. However, throughout the wet season the particulate C:P ratios at both the 10 and 30m isobath decline and could potentially be related to increased

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inorganic P concentrations associated with increased river flow. Based on the hypothesis when discussing trends of the N:P ratio, this trend seems more likely to be related to a decrease in particulate C after the "first flush".

Inter-annual Trends

The primary controls on the particulate nutrients and ratios would be expected to be the same throughout the study period, however, inter-annual differences in the inorganic nutrient regimes that would be reflected in phytoplankton C:N:P stoichiometry. Wind events of various direction, strength and duration which result in upwelling/downwelling conditions would be expected to alter inorganic nutrient concentrations throughout the years, as would the variability in rainfall (Figure 15).

Geometric means of particulate P concentrations across the shelf are relatively constrained throughout the study period, while average particulate C and N concentrations have lower average concentrations during 1998 and 2001 and greater average concentration during 1999 and 2000 (Table 17). This could potentially be related to different environmental conditions on the WFS during 1998/2001 and 1999/2000.

99 - Paul Barbara, política estadounidense de 1990.
1990 - Paul Barbara, política español de 1990.
1990 - Paul Barbara, política estadounidense de 1990. The geometric means of particulate C:N (14.01) and N:P (32.38) during 1998 suggest that this year was the most N-limited and the least P-limited compared to 1999-2001 (Table 17, 18). This seems to be related to the very low concentrations of particulate N (1.93 uM) from June to December of that year rather than an increase in particulate P or C (Table 17). This could be related to

Table 17. Central tendency measures and ranges of surface particulate nutrient concentrations and nutrient ratios from sampled from June 1998 through December 2001. The data only include the months of June to December for each year in order to directly compare the study years.

Table 18. Surface particulate nutrient stoichiometry based on the mean and geometric mean. The data only include the months of June to December for each year in order to directly compare the study years.

a deep water upwelling event which occurred during the spring and into the fall of 1998 (Vargo et al. 2008). Weisberg et al. 2005 observed that during this period, "Complimentary deep ocean and local forcing led to anomalous stratification and circulation where the thermocline stayed strong into July even up to the beach and cold water outcrops were observed in satellite images" The upwelled nutrient rich water could have the effect of preferentially sustaining non- N_2 fixing organisms which have lower half saturation constants allowing them to outcompete N_2 -fixers for the available nutrients. N_2 fixing organisms typically have cellular concentrations enriched in N relative to P compared to non-Nitrogen fixers, which might explain why the average particulate N values and N:P ratio are lower, but the C:P ratio are higher in 1998 compared to other years within this study (Table 17, 18).

In contrast, 2000 has an average C:N:P stoichiometry indicative of the greatest P-limitation relative to the other sample years (Table 18). The average N:P and the C:P molar ratios of 177 and 763 are values which suggest conditions of severe P limitation (Table 17). These extremely high values seem to be more related to larger detrital contributions of refractory C and P during this year. It seems unlikely that N:P ratio values would reach 177 as a result of N_2 fixation processes alone. Hurricane Gordon, which affected the WFS during September, could certainly have contributed to an increase in detrital contributions to the particulate pools via both to heavier river flows due to increased rainfall and resuspension of particulates from the sediments as a result of increased wind activity. This hypothesis is supported in the curves of the particulate constituent concentrations (Figure 25) and particulate ratio values (Figure 26). During 2000, particulate C concentrations and the C:P ratio both increased dramatically in October and during November particulate N concentrations and the particulate N:P values also radically increased. Particulate P concentrations were only slightly elevated during those months and the C:N ratio does not increase in October or November. This is most likely due to the fact that detrital components are primarily composed of refractory particulate C and N and very little particulate P. The June–December periods of 1999 and 2001 have more similar particulate stoichiometries when compared to those of 1998 and 2000, especially the average particulate N:P ratios which are almost identical (Table 17, 18). Neither of these years had anomalous weather conditions, which might be responsible for the similarity of the particulate ratios.

Average values of particulate nutrient concentrations and nutrient ratios for all stations sampled each month of each year show pulsed increases/decreases

Figure 25. Monthly averages of surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations sampled from June through December of 1998 (blue), 1999 (red), 2000 (green) and 2001 (turquoise)..

Figure 26. Monthly averages of surface particulate nutrient A) C:N, B) N:P and C) C:P ratios for all stations sampled from June through December of 1998 (blue), 1999 (red), 2000 (green) and 2001 (turquoise).

during different months and the structure of the curves are very different for each year (Figure 25, 26). This supports the hypothesis that interannual physical and biological process are different for each year and result in a variety of particulate C, N, P concentrations and particulate ratio values within each year.

Particulate N and P concentrations as related to distance offshore all share very similar trends seaward of the 30m isobath (Figure 27). This implies that offshore processes influencing particulate N and P concentrations are similar from year to year on the WFS. The variability at the 10m isobath is most likely due to the variety of coastal processes which would be expected to vary with year. In contrast, the particulate C concentration curves tend to vary from year to year seaward of the 30m isobath, indicating that processes influencing particulate C concentration may not be as constrained as those acting on particulate N and P and could potentially be related to detrital contributions, C over-consumption or phytoplankton assemblage (i.e. picocyanobacteria) .

Although the particulate N and P concentrations are constrained, and potentially limited by physical processes seaward of the 30m isobath, the particulate ratios are much more variable with distance offshore from year to year (Figure 28). This is most likely related to the complexity of the processes involving phytoplankton uptake mechanisms, adaptive strategies and competition between species based on nutrient regimes that would be expected to change from June through December during each year of the study period.

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Figure 27. Average surface particulate A) carbon, B) nitrogen and C) phosphorus concentrations at each isobath sampled from June through December of 1998 (blue), 1999 (red), 2000 (green) and 2001 (turquoise).

Figure 28. Average surface particulate ratios A) C:N, B) N:P and C) C:P at each isobath for all stations sampled from June through December of 1998 (blue), 1999 (red), 2000 (green) and 2001 (turquoise).

Karenia brevis

Karenia brevis is the toxic dinoflagellate responsible for the large red tide blooms that occur with almost inter-annual regularity on the WFS. Because of the high cell biomass associated with these blooms, it would be expected that *K. brevis* blooms have a relationship with particulate nutrient stoichiometry on the SW Florida shelf. When *K. brevis* concentration ranges are binned in ranges (i.e. <1,000 cells/L, 1,000-10,000 cells/L, >10,000-100,000 cells/L and >100,000 cells/L) there is a difference in the ranges of the particulate nutrient ratios associated with each binned cell concentration. The ranges when there are no *K. brevis* cells present or in low concentrations are much larger for particulate C:N, N:P and C:P than when *K. brevis* is present in concentrations greater than 10,000 cells/L (Table 19).

Mean C:N, N:P, C:P and C:N:P ratios decrease as *K. brevis* cell concentration increase from 0 to >100,000 cells/L (Table 19, 20). This indicates that the particulate nutrient concentrations of high biomass populations are approaching the Redfield ratio and perhaps are not as nutrient limited as *K. brevis* populations of lower biomass and populations which do not include *K. brevis*. This trend may also potentially be related to a higher portion of live cells relative to detrital materials contributing to the particulate pool in blooms, which would result in lower C:N:P stoichiometry values. It should be mentioned that during the November 2000, particulate N values at five coastal stations where *K. brevis* cell concentrations were 1,000 cells/L, were anomalously high, larger than

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Table 19. Central tendency measures and ranges of surface particulate nutrient ratios of *K. brevis* concentration, cells/L (0 includes sample with no *K. brevis* detected, 1,000-10,000 includes regulatory limits for commercial shellfish bed closure, >10,000-10,0000 includes low bloom concentrations and >100,000 includes high bloom concentrations) sampled from June 1998 through December 2001. The stations with less than 1000 *K. brevis* are only those stations that had a record of *K. brevis* present at some point during the study period.

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*cells /L

Table 20. Average surface particulate C:N:P stoichiometry within *K. brevis* blooms from June 1998 through December 2001.

particulate C values for the same stations. These values could be related to a localized event at these coastal stations, (e.g. Hurricane Gordon) or the contamination of that particular set of samples. The nutrient sources which fuel these high biomass blooms are hypothesized to include at least six different sources (Havens et al. 2004; Heil et al. 2007: Vargo et al. 2008). The capability of *K. brevis* to potentially adjust to a variety of nutrient conditions is supported by the variety of particulate ratio values within four different blooms examined on the WFS during 1998-2001 (Table 21). In most cases, all 4 blooms had particulate

Table 21. Summary of average surface particulate nutrient ratios for each *K*. *brevis* bloom that occurred from June 1998 through December 2001.

Particulate Ratio	No Bloom*	1998-1999	1999-2000	2000	2001
C: N	15.22	14.57	7.52	4.60	9.03
N: P	90.22	24.15	61.15	321.98	38.43
C: P	445.92	292.13	441.80	529.58	293.67

*Includes only those stations which had *K. brevis* cells present at some point during the sampling period.

ratio values closer to Redfield values than the average particulate ratios of samples where *K. brevis* was not present. The blooms which occurred during 1998-1999 and 2001 seem to be less nutrient limited than the blooms which occurred during 1999-2000 and 2000. The longevity and the lower C:N, N:P and

Table 22. Particulate C, N and P content (SE) of *K. brevis* within blooms sampled from June 1998 through December 2001.

 $*$ 10⁴, $*$ data not reported, $**$ Wilson clone, low light is 24, medium light is 90 and high light is 160 μ E m⁻² sec^{-1,} # Wilson clone at exponential growth..

C:P ratios of the 1998-1999 *K. brevis* bloom could be related to the anomalous upwelling event that occurred during the spring and summer of that year.

The comparison of particulate C, N and P content of *K. brevis* cells during the different blooms supports the hypothesis that the ranges of particulate C, N and P concentrations decrease with increasing cell concentration and that *K. brevis* populations with concentrations >100,000 are growing more near to the Redfield ratio (Table 22). This could possibly be related to an increasing supply of regenerated nutrients within the bloom supplied by organisms which have succumbed to the effects of the brevetoxin*.*

The values of *in situ* particulate C and N concentrations within *K. brevis* blooms are greater than those reported for *K brevis* culture at a range of light levels (Shanley 1985) and during exponential growth (Heil 1985). These differences could potentially be related to detrital contributions to the particulate values in the marine environment. In contrast, particulate P concentrations are greater during the 1998-1999 and 2001 blooms but less during the 1999-2001 and 2000 blooms compared to cultured values of cells growing exponentially. Detrital contributions of particulate P would be expected to be less in the marine environment due to the rapid turnover times of P.

Summary

In situ particulate nutrient ratios are difficult to interpret for a variety of reasons. The method of sample collection is such that it was often unknown exactly what comprised the particulate fraction that were measured (i.e. live phytoplankton cells versus detrital material) as all material in the size range of 0.7µm to 153µm was analyzed. The different methods employed to determine particulate C, N and particulate P concentration could potentially skew resultant ratio values underestimating particulate P concentrations and resulting in the very high N:P and C:P values observed throughout the course of this study. Furthermore, the interpretation of *in situ* particulate ratios requires that the physical processes of nutrient delivery, microbial nutrient regeneration and the different uptake strategies employed by different groups of phytoplankton (i.e. N_2) fixers and non- N_2 fixers) must all be considered.

Particulate C, N, P concentrations and the particulate ratios of C:N, N:P and C:P of the entire data set display a wide range of values across the shelf, most likely related to the wide variety of physical and biological processes that occur both spatially and temporally on the WFS. The frequency distribution histogram of the data and Spearman Ranking Correlation coefficients indicate that particulate C concentrations are more conservative relative to particulate N and P concentrations, which probably have a greater potential to vary in response to changing nutrient regimes across the shelf. The frequency distributions of particulate C and particulate P are similar, but differ from distributions of particulate N concentrations. This suggests that processes acting

on particulate C and P concentrations may be different than those acting on particulate N concentrations, is most likely due to N inputs from N_2 fixation. Correlation coefficients suggest that particulate N concentrations drive the C:N and N:P ratios. The WFS from June 1998 through December 2001 had a geometric mean particulate C:N:P stoichiometry of 332:77:1 which is very different from the classic Redfield Ratio or values reported for natural phytoplankton in the literature, but similar to reported literary values for P-limited cultures. This implies that phytoplankton growth on the WFS seems to be predominately P-limited, which is driven by particulate N concentrations. In theory, P-limitation on the WFS could be due to: 1) populations of N_2 fixing *Trichodesmium* and picocyanobacteria providing new sources of N while concurrently drawing down inorganic P concentrations, 2) populations of picocyanobacteria substituting non-P membrane lipids for phospholipids resulting in non-Redfieldian ratios 3) inorganic P adsorption to deposits of Saharan dust during summer months, 4) underestimation of particulate P concentrations due to problems with the molybdenum blue method and 5) inability to correct for detrital C and N contributions to the particulate nutrient samples.

The relationship between average particulate C, N, P concentrations and distance offshore are well described by a polynomial functions and the similarity of the curves for the different nutrients suggest that there are similar regulating mechanisms acting on all three variables are related. There is an initial decline in average particulate C, N and P concentrations from the 10m isobath out to the 30m isobath where concentrations then become level out to the shelf break. The

30m isobath potentially represents a transition zone from a coastally influenced environment to a more oligotrophic environment. The relationship between average particulate ratios and distance can also be described by polynomial functions where values increase out to the 100m isobath than slightly decrease out to the 200m isobath. The greatest ranges in the particulate C:N and C:P ratios occur at distances greater than 50km offshore and implies a decoupling of processes regulating particulate C from both N and P with distance offshore as related to biological activity. This could be related to phytoplankton storing C in excess relative to N and P as nutrient availability decreases with distance offshore, or may be indicative of a change in the contribution of detrital materials as a result of decrease biomass in this region. The comparison of the geometric mean particulate nutrient stoichiometry (C:N:P) indicates that P-limitation increases with distance from the coast and is supported by frequency distribution histograms binned according to nutrient limitation.

The geometric means of the particulate C, N and P concentrations at the Tampa Bay, Sarasota and Fort Meyers along the entire transect (10m isobath to the 50m isobath are very similar but suggest a very weak trend of decreasing Plimitation and increasing N-limitation from the north to the south. When only considering these stations at the 10m isobath, Sarasota has the lowest concentrations of particulate C, N and P compared to the Tampa Bay and Fort Meyers stations. The C:P and N:P particulate ratios at the 10m isobath suggest that all three coastal stations are predominantly P-limited. Given the N-limited

environment of adjacent estuaries, this observation presents a bit of a conundrum.

Particulate C, N, P concentrations and particulate ratios are similar during the wet season (June-September) and the dry season (October-May). However, average particulate nutrient ratios indicate that phytoplankton growth could potentially be more N limited during the dry period and more P limited during the wet season in response to an increase of N_2 fixing populations during the summer and early fall. There do appear to be monthly trends within the wet and dry periods as well, where peaks in the particulate concentrations and ratios occur during the spring, summer and fall as phytoplankton populations adapt (i.e. N_2 fixers vs non- N_2 fixers) to the seasonal mechanisms of nutrient delivery (i.e. day length, circulation patterns, storms, river flow, thermal stratification/non stratification).

The particulate C, N, P concentrations and the particulate ratios differ on inter-annual scales. Though the basic physical processes throughout the years would not be expected to change, the strength and duration of these processes vary from 1998 through 2001 and could potentially be responsible for the fluctuations of the particulate C, N, P concentrations and ratios throughout the study period.

Particulate C:N:P stoichiometry within *K. brevis* blooms has a narrower range and appears to be growing closer to the Redfield ratio than particulate ratios where *K. brevis* is not present. This relationship strengthens with increasing cell concentration. Particulate C:N, N:P and C:P ratios do vary within

different blooms are most likely related to the different nutrient regimes associated within each bloom. The values of the particulate nutrient ratios within natural blooms are greater than that of cultured *K. brevis* cells. This difference is most likely related to detrital contributions within the marine environment and the nutrient replete conditions in culture experiments.

The particulate C, N and P concentrations and ratios vary both spatially and temporally and are often above the classic Redfield ratios as related to the flexibility in phytoplankton responses to varying nutrient regimes.

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APPENDICES

Appendix A: Particulate Carbon, Nitrogen and Phosphorus Concentrations and standard deviation (S.D.) from 1998-2000

