

DISSOLVED ORGANIC MATTER CYCLING ON THE LOUISIANA SHELF:
IMPLICATIONS FOR THE FORMATION OF HYPOXIA

A Thesis

by

LI SHEN

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE

December 2011

Major Subject: Oceanography

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Approved by:

Chair of Committee,	Thomas S. Bianchi
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ABSTRACT

Dissolved Organic Matter Cycling on the Louisiana Shelf:
Implications for the Formation of Hypoxia (December 2011)

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Chair of Advisory Committee: Dr. Thomas S. Bianchi

Although there has been considerable work on the role of nutrient-derived (mostly nitrate) primary production in fueling hypoxia in northern Gulf of Mexico, very little is known about the relative importance of autochthonous versus allochthonous sources of dissolved organic matter (DOM). Moreover, even less is known about the importance of dissolved organic nitrogen (DON), a critical component of DOM (along with dissolved organic carbon (DOC)) in supporting hypoxia in this region. Most nitrogen in marine organisms exists in the form of amino acids. Changes in the spatial and temporal distribution of amino acids in the Mississippi River Plume have been shown to be important in the dynamic microbial cycling in the plume. In this study, concentrations of amino acids, DON and DOC were linked with hydrography data (e.g., dissolved oxygen (DO), salinity, temperature, fluorescence) to determine how these sources of DOM are related to seasonal and diurnal changes in hypoxia on the inner Louisiana shelf. The general working hypothesis of this work was that allochthonous and autochthonous sources of DOM on the Louisiana shelf have been largely underestimated in their role in fueling hypoxia in northern Gulf of Mexico.

A positive correlation between DOC, DON and fluorescence demonstrated that the main source of both DOC and DON was likely to be *in situ* phytoplankton production. Surface waters in the near-field showed this relationship more than at stations to the west where a sub-surface chlorophyll peak near the pycnocline may also provide a source of DOC and DON in bottom waters. Dissolved free amino acids (DFAA) always had relatively low concentrations at all water depths, which further supports prior work which has shown rapid cycling and high consumption rate of DFAA by heterotrophic bacteria. In addition to biotic controls, selective adsorption of DFAA likely contributed to the dominance of aspartic and glutamic acids at our stations. Hypoxia was generally observed in bottom waters in both spring and summer 2010. Dissolved oxygen generally revealed a negative correlation with nitrate+nitrite concentrations. Based on other work, one possible reason for such linkages may be from NH_4^+ released from dissimilatory nitrate reduction to ammonium (DNRA). Another possible reason may be the high degradation of labile DOM (such as DFAA) as shown by high respiration in bottom waters in prior work.

ACKNOWLEDGEMENTS

I would like to thank my committee chair, Dr. Bianchi, and my committee members, Dr. Chapman, Dr. Thornton, Dr. Amon, for their guidance and support for this research.

Thanks also go to my friends and colleagues and the department faculty and staff for making my time at Texas A&M University a great experience.

Finally, thanks to my mother and father for their encouragement and to my boyfriend for his patience and love.

NOMENCLATURE

MR	Mississippi River
AF	Achafalaya River
LDE	Large-river Delta-front Estuary
GOM	Gulf of Mexico
DO	Dissolved Oxygen
DOM	Dissolved Organic Matter
DOC	Dissolved Organic Carbon
DON	Dissolved Organic Nitrogen
DFAA	Dissolved Free Amino Acid
DCAA	Dissolved Combined Amino Acid
TDN	Total Dissolved Nitrogen
DIN	Dissolved Inorganic Nitrogen
TSM	Total Suspended Matter
POC	Particulate Organic Carbon
PN	Particulate Nitrogen

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CHAPTER I

INTRODUCTION

Occupying no more than 20% of the surface area of the world ocean, the continental margins play a significant role in the global-wide carbon and nitrogen biogeochemical cycles (Walsh, 1991). In particular, large-river delta front estuaries (LDEs) have been shown to be responsible for most carbon burial (ca. 80%) along continental margins (Bianchi and Allison, 2009, and references therein). Many of the LDEs have also been sites of significant anthropogenic change at the coastline as well as in the upper watershed (Milliman and Farnsworth, 2011, and references therein).

The Gulf of Mexico (GOM) receives its largest freshwater input from the Mississippi-Atchafalaya system in its northern coastal regions. The Mississippi River system is the major nitrogen source of the northern GOM and is believed to be strongly linked with the annual development of the hypoxic zone (Turner and Rabalais, 1991; Scavia *et al.*, 2003 and references therein). More specifically, this system discharges approximately 0.96, 0.78 and 0.07 Tg N y⁻¹ of nitrate, organic nitrogen and ammonium to the northern GOM, respectively (Turner and Rabalais, 1991; Dagg and Breed, 2003). These nitrogen (N) inputs have been clearly influenced by land-use activities (e.g., fertilizer application, effluent from animal feedlots, and municipal runoff from bordering cities along the river) (Dale *et al.*, 2010).

Nitrate concentrations, typically > 100 μM, are generally positively correlated with freshwater discharge (Bratkovich *et al.*, 1994; Lohrenz *et al.*, 1999). While much

This thesis follows the style of *Geochimica Et Cosmochimica Acta*.

of the interest on N cycling in the Mississippi River Plume has been focused on dissolved inorganic nitrogen (DIN), little attention has been given to the cycling and composition of dissolved organic nitrogen (DON) (Gardner *et al.*, 1996, 1997; Grace and Bianchi, 2010).

1.1 The Organic Matter Cycle in LDE Coastal Regions

The main sources of DOM in estuaries are terrigenous materials, biogenic matter and sediment resuspension. DOM cycling is significantly affected by the inorganic nutrient concentrations, especially nitrogen, phosphorus, and silicon which are actively consumed by the phytoplankton (Ducklow and Steinberg, 2001). As the major components of DOM, the cycling of DOC and DON are of great importance in understanding the biogeochemical dynamics of coastal DOM. In coastal regions, the dominant sources of organic carbon (OC) are derived from marine phytoplankton and riverine/estuarine inputs from algae and terrestrially-derived OC. Coastal zones, especially Large-river Delta-front Estuaries (LDEs), act as active interfaces between terrestrial and coastal ocean environments (Bianchi and Allison, 2009). Large amounts of DOM are transported to the coastal ocean by major rivers via the deltaic regions (Duan and Bianchi, 2007; Bianchi and Allison, 2009; Bourgoin and Tremblay, 2010).

The interactions between bacteria and DOM play a major role in the global carbon cycle (Amon and Fitznar, 2001). Past work has shown that phytoplankton is a major source of DOM for heterotrophic bacteria in the Mississippi River Plume (Cotner and Gardner, 1993). Other studies have shown that as much as 60% of primary production passes through heterotrophic bacteria (Ducklow *et al.*, 1993; Cole *et al.*,

1988). Much of the DOC consumed by bacteria has been shown to be primarily composed of neutral sugars and DAA (Bourgoin and Tremblay, 2010). The rapid uptake of labile DOC results in relatively low concentrations of DOC in the ocean and the background DOM is usually composed of low reactive material (Keil and Kirchman, 1991).

Nitrogen sources to the coastal ocean are controlled by riverine inputs, atmospheric inputs, as well as sediment fluxes (Paerl *et al.*, 2002). Fresh water inputs are the dominant sources to coastal estuaries (Smullen *et al.*, 1982; Peierls *et al.*, 1991). The flux of organic nitrogen (ON) to estuaries is commonly split 50% between particulate and dissolved organic nitrogen (PON and DON) (Tappin, 2002; Berman and Bronk, 2003). The transport of ON is also governed by particle-water interactions (Henrichs and Sugai, 1993). Inorganic forms of N are utilized by phytoplankton and ultimately converted to POM (Verity, 2002). A close correlation between phytoplankton biomass and total nitrogen was shown by Nielsen *et al.* (2002). At the same time, N fixed into biomass undergoes complicated biogeochemical cycling during which the form of N is reversibly converted between inorganic ions and organic molecules. Coastal N could also be released in the form of N₂ gas during denitrification or ammonia assimilation (Jaffe, 2000) and anammox (Neubacher *et al.*, 2011). The distribution of organic and inorganic forms of N is critical in understanding coastal productivity and many of the problems associated with hypoxic regions.

Most nitrogen in marine organisms exists in the form of amino acids (Capone *et al.*, 2008). Dissolved amino acids (DAA) in sea water approximately contribute 10%

of the total dissolved organic nitrogen (Dittmar *et al.*, 2001) and particulate amino acids (PAA) accounted for $49 \pm 20\%$ of total nitrogen in seawater on average (Behrends and Liebezeit, 1999). Dissolved amino acids account for the major fraction of labile organic nitrogen in the ocean and are essential to the overall nitrogen cycle in marine ecosystems. Their low molecular weight and high N:C ratio make them an ideal nitrogen source for bacteria (Amon and Benner, 1994). Consequently, the uptake rate of DAA by the microbial community is fast, resulting in a low concentration of DAA in coastal waters (Fuhrman, 1990; Mulholland *et al.*, 2002). However, DAA are important indicators for elucidating the relationship between coastal organic matter and biomass, as they are widely involved in the nitrogen cycling. For example, DAA could be generated through hydrolysis of high molecular weight organic matters such as protein. The degradation of phytoplankton cells also releases DAA. On the other hand, ammonium is generated from dissolved free amino acids (DFAA) under certain conditions. Heterotrophic bacteria could take up ammonium as a nitrogen source and convert it to biomass. The bacterial mediation of ammonium and DFAA conversion was shown to be important in the Mississippi River Plume (Gardner *et al.*, 1993).

1.2 Study Site: The Mississippi/Atchafalaya River LDE

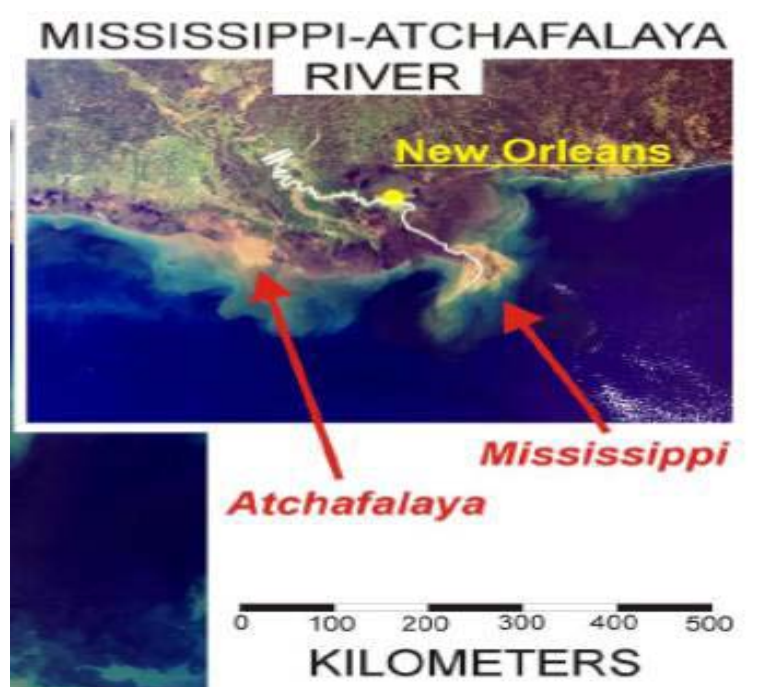


Figure 1. Map of Mississippi-Atchafalaya LDEs (Bianchi and Allison, 2009).

Discharges from the Atchafalaya/ Mississippi River system (Fig. 1) contribute approximately 94% of the freshwater on the Texas Louisiana shelf (Bianchi *et al.*, 1997). This river system also represents an important source of organic matter and nutrients for the northern GOM (Trefry *et al.*, 1994; Wiener *et al.*, 1998). It accounts for most of the terrestrially-derived sedimentary organic carbon input to the GOM, which results in the GOM receiving a relatively higher proportion of terrestrial inputs when compared with other U.S. coastal margins (Hedges and Parker, 1976; Trefry *et al.*, 1994). Recent work has shown there are significant gradients of DOC and dissolved lignin from local

marshes to shallow shelf regions where frequent hypoxia occurs in the northern GOM (Bianchi *et al.*, 2009). However, further work is needed to better link DOM inputs, both autochthonous and allochthonous, with the occurrence of hypoxia events in the GOM.

1.3 Possible Linkages with DOM and Hypoxia in Gulf of Mexico

Hypoxia is defined as the phenomenon that occurs when dissolved oxygen (DO) concentrations reach below $63 \mu\text{mol L}^{-1}$, which is equal to 1.4 mL L^{-1} (Diaz and Rosenberg, 2008; Bianchi *et al.*, 2010). The annual occurrences of hypoxia in the northern GOM bottom waters (west of the Mississippi delta) begin in late spring and summer (Renaud, 1986). The region of hypoxia varies every year from 8,000 to 9,000 km^2 during 1985-1992 (Rabalais *et al.*, 2007) to almost 19,000 km^2 during 2006 to 2008 (Diaz and Rosenberg, 2008). In fact, sustained hypoxia in the GOM is the largest hypoxic region in the western hemisphere (Rabalais *et al.*, 2002).

The number of areas where hypoxia has been found globally has doubled every 10 years for the past four decades because of anthropogenic nutrient enrichment and elevated productivity (Diaz and Rosenberg, 2008; Zhang *et al.*, 2010). Since the global population has been increased dramatically during the latter half of the 20th century, a large amount of anthropogenic N fertilizer has been loaded into rivers and estuaries from soils and sewage (Bianchi, 2007; Diaz and Rosenberg, 2008, and references therein). As a result, enhanced *in situ* primary productivity and organism population promote oxygen consumption and hypoxia occurs when the consumption of DO is faster than it can be replenished by vertical mixing through a stratified water column (Wei *et al.*, 2007; Diaz and Rosenberg, 2008). It is widely agreed that biological processes are the key in

controlling hypoxia events within the near-field of the Atchafalaya/Mississippi River discharge regions (Rabalais *et al.*, 2007). However, other physical processes, such as stratification and seasonal changes in currents and winds may play an important role in determining the persistence and distribution of hypoxia in both near-field and far-field western regions of the Louisiana shelf (Rowe and Chapman, 2002; Hetland and DiMarco, 2007; Bianchi *et al.*, 2011). Hypoxia also affects local C and N cycling in a profound way which is reflected in both the change of productivity and the shift of biochemical reaction pathways (Bianchi *et al.*, 2010). For instance, it was demonstrated that secondary productivity in the Baltic Sea was reduced by 30% under the influence of hypoxia (Diaz and Rosenberg, 2008).

Further work on the role of DAA in both organic and inorganic nitrogen cycling is needed to better understand the mechanisms of hypoxia formation in the GOM. Thus, the objectives of the study were to determine:

1) How the changes in the spatial and temporal distribution of bulk parameters such as salinity, TSM, DOC, TDN, DON, POC, PN as well as DFAA in the Mississippi-Achafalaya River Plume correlate with low DO concentrations in bottom water and their role in fueling hypoxia in the northern GOM;

2) How the concentrations of amino acids, DON and DOC link with hydrography data (e.g., DO, salinity, temperature, fluorescence) and how these sources of DOM are linked to seasonal and diurnal changes in hypoxia on the inner Louisiana shelf;

3) The role of total DFAA and individual DFAA distributions as a linkage between the DOM pool and microbial loop due to the rapid cycling and high

consumption rate. All of these objectives will be used to better understand the linkages between DOM cycling and hypoxia in the LDE region.

CHAPTER II

METHOD

2.1 Sample Collection and Processing

Seawater samples were collected and analyzed for DOC, TDN, DAA, POC, TSM, PAA analyses, as well as all other hydrography data, during two 5-day research cruises (NOAA-funded “Mechanisms Controlling Hypoxia [MCH] in the Mississippi/Atchafalaya LDE) during 6-11 April 2010 and 15-20 August 2010 on the *R/V Pelican*. The 3 stations labeled AB5, 10B, and 8C are shown in Figure 2.

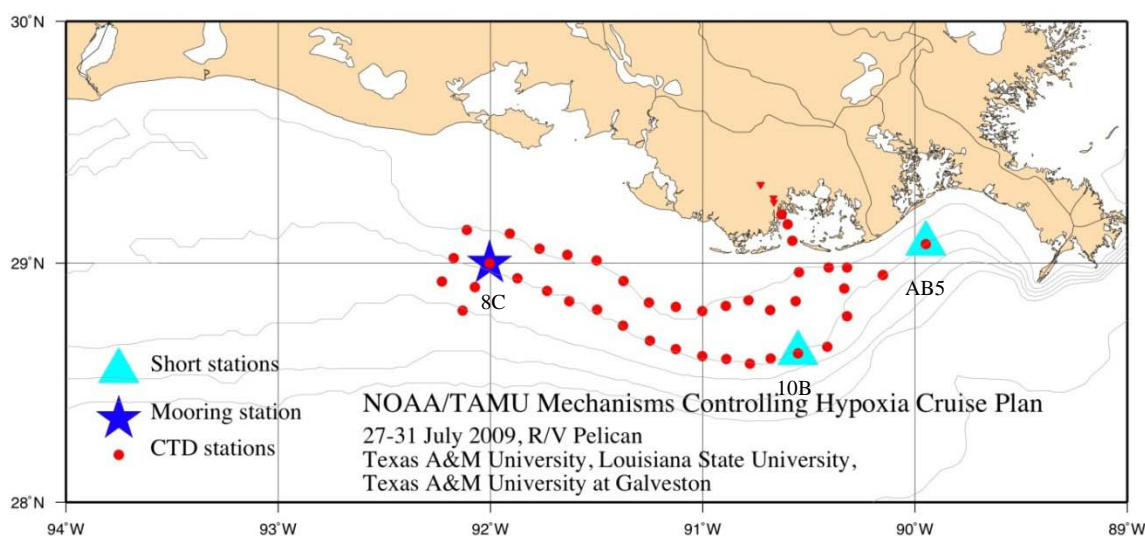


Figure 2. Locations at 3 anchor process stations along the 20 m isobaths in the northern GOM. The two light blue triangles are Stations AB5 and 10B and the one blue star Station 8C. also serves as a mooring station.

Physical water column hydrography data, which includes salinity, temperature, DO, and fluorescence were collected using a CTD at 0, 6, 12, 18, 24 h during each 24 h station = 5 cycles per 24 h.

Twenty-four-hour DOC, POC, TDN, TSM, and DAA duplicate samples were collected from CTD/rosette casts from three depths —surface, middle (the chlorophyll maximum depth) and bottom at 0, 6, 12, 18, 24 h intervals during each 24 h period = 5 cycles per 24 h. Approximately 2 L of seawater were filtered through 47 mm (in diameter) 0.7 μm (nominal pore size) pre-combusted (450°C, 4h) Whatman glass-fiber filters (GF/F) for DOC and DAA samples. DOC and DAA water samples were collected on board by gravity filtration with acid cleaned (2 N HCL) silicone rubber tubing (directly from the Niskin Bottles) using pre-combusted GF/F filters in an acid-cleaned polysulfone filtration cartridge. DOC and DAA samples were immediately stored frozen onboard at -20°C in pre-combusted 40 mL amber vials, which were sealed with acid washed Teflon-topped septa and plastic screw tops. POC, TSM and PAA samples were collected by filtering 0.5 to 2 L of seawater on pre-combusted 25 mm (diameter) 0.7 μm (nominal pore size) pre-combusted GF/F filters with a vacuum pump (at ≤ 5.0 psi to avoid filtration artifact). Filters for POC, TSM and PAA were folded in half and placed in combusted aluminum foil envelopes. All the GF/F filters for TSM were pre-weighed in the lab. After filtration, all filters were labeled and immediately stored frozen onboard at -20°C.

2.2 Analytical Procedures

2.2.1 Dissolved Organic Carbon and Total Dissolved Nitrogen Analyses

Both DOC and TDN measurement were performed on a Shimadzu TOC-V_{csH/csn}, using high-temperature catalytic oxidation (HTCO) and chemiluminescence, respectively (Guo *et al.*, 1994; Sharp *et al.*, 2002). All DOC samples were auto-injected

(80 μ L) using a ASI-V automatic sample injector, and dissolved inorganic carbon has been removed by 2 N HCl. Sample analyses of both DOC and TDN were performed with a precision of approximately $\pm 3\%$ (on the basis of the standard deviation). External DOC and TDN standards were prepared using potassium hydrogen phthalate and potassium nitrate, respectively, and all DOC and TDN measurements were corrected for instrument blanks. Coefficients of variation from duplicate DOC and TDN samples (5-7 injections) were usually on the order of $< 8\%$. Concentrations of DON were obtained by subtracting dissolved inorganic nitrogen (DIN) from TDN. All DIN analyses were made using an automated Lachat Nutrient Analyzer at the Geochemical and Environmental Research Group (GERG) at TAMU.

2.2.2 Particulate Organic Carbon and Total Suspended Matter

Both POC and TSM sample filters were freeze-dried for 24 h using a Millrock Freeze-drier. TSM sample filters were then immediately weighed using an analytical balance. POC sample filters were acidified with 12 N HCl vapor in a desiccator for 24 h to remove inorganic carbon according to methods by Hedges and Stern (1984). Filters were then sealed in silver capsules and placed in a 96-well tray for bulk total nitrogen and POC analyses – using a ACS 4010 Elemental Analyzer in TAMU Stable Isotope Geosciences Facility, TX, US.

2.2.3 Amino Acid Analysis

Amino acids were analyzed by reverse-phase high-performance liquid chromatography (HPLC) system, using a modification of the pre-column *o*-phthaldialdehyde (OPA) derivatization technique (Lindroth and Mopper 1979; Lee *et al.*,

2000). The HPLC system consists of a Dionex GP50 gradient pump and a RF2000 fluorescence detector (excitation at 330 nm and emission at 418 nm). All DFAA samples were auto-injected (40 μ L) using a Dionex ASI-100 refrigerated auto-sampler. Separation was accomplished with an apHera C₁₈ Reversed-phase Column (5 μ m, 250 \times 4.6 mm) fitted with an Econosphere guard column at a flow rate of 1.0 mL min.⁻¹. A binary gradient of 0.05 M sodium acetate with 5% tetrahydrofuran (pH adjusted to 5.5 with acetic acid) (Eluent A) and HPLC grade methanol (Eluent B) was used. The gradient began at time zero with 22% B, ramped to 60% over 40 min. and finally to 100% B at 50min., where it remained isocratic for an additional 10 min. to wash out all the components in the system. And then it went back to initial gradient (22% B) at 60 min. and kept running this gradient for another 10 min. to balance the pressure and start the next sample with the same condition. Individual amino acids were quantified on the basis of individual amino acids standards (Sigma Chemical Company) and corrected for individual responses from a standard amino acid mix (Pierce Standard-H). The standard deviation of individual amino acids ranged from 18% for arginine to 2% for threonine. Detection limits for individual amino acids ranged from 0.5 nM (valine) to 5 nM (glycine) with an average of 1.7 nM for all amino acids measured. For DFAA analysis, samples were injected by the auto-sampler directly after reaction with OPA for 2 min. Coefficients of variation from duplicate DFAA samples were usually in the order of 10%.

2.3 Statistical Analyses and Data Processing

Statistics were performed using the SPSS statistical package. Correlation analysis was performed using a Spearman Rank Correlation coefficient, statistically significant differences analysis was determined using a One-way ANOVA (two tails, $\alpha=0.05$). Means are reported with a 95% confidence interval. Figures were graphed using OriginPro (Version 7.5).

CHAPTER III

RESULTS

3.1 Spatial Distribution

3.1.1 Water Column Hydrography Data

Water column hydrography data, which includes salinity, temperature, DO, and fluorescence, were collected by CTD at 0, 6, 12, 18, 24 hr during each 24 hr station = 5 cycles per 24 h.

The overall mean DO data for Stations AB5, 10B and 8C in April, were $3.68 \pm 2.56 \text{ mL L}^{-1}$, $4.39 \pm 1.58 \text{ mL L}^{-1}$ and $4.02 \pm 1.88 \text{ mL L}^{-1}$, respectively. And the mean DO data for each station in August were $2.96 \pm 1.02 \text{ mL L}^{-1}$, $3.44 \pm 1.01 \text{ mL L}^{-1}$ and $2.40 \pm 1.64 \text{ mL L}^{-1}$, respectively (Table 1). The lowest dissolved oxygen concentration was observed at Station 8C during the summer cruise. Mean DO values for surface, middle, and bottom waters were $6.29 \pm 0.73 \text{ mL L}^{-1}$, $3.76 \pm 1.61 \text{ mL L}^{-1}$ and $2.03 \pm 0.71 \text{ mL L}^{-1}$ in April, respectively, and $4.13 \pm 0.37 \text{ mL L}^{-1}$, $3.30 \pm 1.13 \text{ mL L}^{-1}$ and $1.37 \pm 0.89 \text{ mL L}^{-1}$ in August (Table 2). All three depths showed significant ($p < 0.05$, one-way ANOVA, two-tailed) differences in DO at all three stations, and the bottom layers always had the lowest DO value. Thus, the hypoxia mainly happened at bottom layers in August.

The salinity data had a significantly ($p < 0.05$, one-way ANOVA, two-tailed) increasing trend with depth and a significantly negative correlation with dissolved oxygen ($R = -0.8$, $n = 87$, $p < 0.01$) for all samples at all three stations. The mean salinities for Stations AB5, 10B and 8C in April were 30.50 ± 4.75 , 33.08 ± 1.36 and

Table 1 The mean values and standard deviations of parameters for each station at all three depths in April and August 2010.

Seasons	April 2010			August 2010			
Parameters	Stations	AB5	10B	8C	AB5	10B	8C
Salinity		30.50 ±4.75	33.08 ±1.36	32.84 ±1.40	32.29 ±2.96	30.93 ±4.14	31.79 ±3.58
DO (ml/L)		3.68 ±2.56	4.39 ±1.58	4.02 ±1.88	2.96 ±1.02	3.44 ±1.01	2.40 ±1.64
Fluorescence		0.52 ±0.51	0.25 ±0.14	0.26 ±0.14	0.19 ±0.20	0.10 ±0.02	0.22 ±0.18
TSM (mg/L)		18.05 ±11.75	7.27 ±3.33	9.72 ±6.82	6.25 ±4.08	1.54 ±0.94	2.67 ±2.23
TDN (µM)		ND	ND	ND	12.11 ±3.08	10.10 ±2.03	15.30 ±3.26
DOC (µM)		103.98 ±31.73	58.04 ±15.42	95.88 ±13.41	105.32 ±40.79	103.21 ±34.80	119.30 ±48.49
DON (µM)		ND	ND	ND	7.44 ±3.40	7.42 ±2.28	8.11 ±3.51
DFAA (nM)		381.9	261.6	280.5	328.2	249.7	257.5

Table 2 The mean values and standard deviations of parameters for each depth at all three stations in April and August 2010.

Seasons	April 2010			August 2010			
Parameters	Depth	Surface	Middle	Bottom	Surface	Middle	Bottom
Salinity		29.48 ±3.65	32.07 ±1.52	34.86 ±0.50	27.27 ±1.16	31.79 ±2.40	35.50 ±0.57
DO (ml/L)		6.29 ±0.73	3.76 ±1.61	2.03 ±0.71	4.13 ±0.37	3.30 ±1.13	1.37 ±0.89
Fluorescence		0.47 ±0.53	0.26 ±0.12	0.31 ±0.16	0.31 ±0.19	0.11 ±0.16	0.08 ±0.16
TSM (mg/L)		11.02 ±9.24	8.85 ±7.47	15.17 ±9.89	3.69 ±3.77	1.31 ±5.54	4.86 ±8.69
TDN (µM)		ND	ND	ND	11.67 ±1.51	10.43 ±2.63	15.14 ±4.13
DOC (µM)		101.37 ±34.32	86.59 ±26.07	72.82 ±17.32	155.79 ±27.80	92.78 ±24.81	80.09 ±17.04
DON (µM)		ND	ND	ND	10.77 ±1.23	7.07 ±1.92	5.11 ±1.87
DFAA (nM)		321.70	312.48	293.28	294.72	282.71	233.06

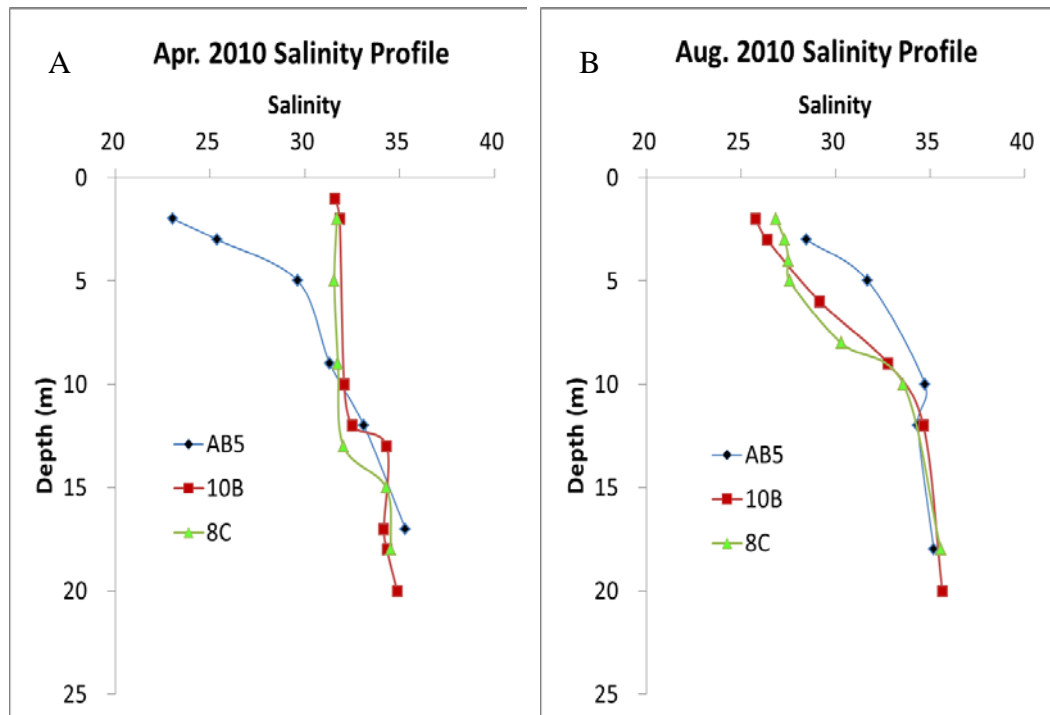


Figure 3. Seasonal changes of salinity depth-profiles at all stations. (A) April 2010 salinity profile at station AB5 (blue line and rhombuses), station 10B (red line and squares) and station 8C (green line and triangles). (B) August 2010 salinity profile at station AB5 (blue line and rhombuses), station 10B (red line and squares) and station 8C (green line and triangles).

32.84 ± 1.40, respectively, and 32.29 ± 2.96, 30.29 ± 4.14 and 31.79 ± 3.58 in August (Table 1). The mean values of salinity in surface, middle, and bottom waters in April were 29.48 ± 3.65, 32.07 ± 1.52 and 34.86 ± 0.5, respectively, and 27.27 ± 1.61, 31.79 ± 2.40 and 35.50 ± 0.57 (Table 2). All three depths showed significant differences ($p < 0.05$, one-way ANOVA, two-tailed) in salinity; increasing salinity values were observed with water depth (Fig. 3). In April, the surface salinity at station AB5 was significantly lower than the bottom layer, which indicated the large amount of fresh water input through southwest pass of Mississippi River (Fig. 3 A). The obvious curves between bottom layers and surface layers in both April and August illustrated strong stratification, which block the surface freshwater input mix with the bottom salty water, but the stratification was weaker in April than that in August due to smaller salinity differences (Fig. 3 A, B).

The mean fluorescence data showed the highest values at Stations AB5 in April (0.52 ± 0.51 RFU), and the lowest one happened at Station 10B in August (0.10 ± 0.02 RFU) (Table 1). The variability of fluorescence at Station AB5 was significantly higher than the other two stations ($p < 0.05$, one-way ANOVA, two-tailed). The mean fluorescence values for the surface, middle, and bottom waters in April were 0.47 ± 0.53 RFU, 0.26 ± 0.12 RFU and 0.31 ± 0.16 RFU, respectively, and 0.31 ± 0.19 RFU, 0.11 ± 0.16 RFU and 0.08 ± 0.16 RFU in August (Table 2). Surface water fluorescence was significantly higher ($p < 0.05$, one-way ANOVA, two-tailed) than middle and bottom waters in both seasons.

The overall mean values of TSM for Stations AB5, 10B and 8C in April were 18.05 ± 11.75 mg L⁻¹, 7.27 ± 3.33 mg L⁻¹ and 9.72 ± 6.82 mg L⁻¹, respectively, and were

$6.25 \pm 4.08 \text{ mg L}^{-1}$, $1.54 \pm 0.94 \text{ mg L}^{-1}$ and $2.67 \pm 2.23 \text{ mg L}^{-1}$ for each station in August (Table 1). TSM at Station AB5 showed significantly higher values than the other two stations and the TSM values in April also significantly higher than those in August ($p < 0.05$, one-way ANOVA, two-tailed). Mean TSM in the surface, middle and bottom waters were $7.48 \pm 8.17 \text{ mg L}^{-1}$, $5.21 \pm 6.72 \text{ mg L}^{-1}$ and $10.20 \pm 9.22 \text{ mg L}^{-1}$, respectively; TSM at different depths showed no significant differences.

3.1.2 Organic Carbon and Nitrogen

The mean concentration of DOC was $98.3 \pm 38.3 \text{ }\mu\text{M}$, while the overall mean concentrations of TDN and DON in August were $12.5 \pm 3.7 \text{ }\mu\text{M}$ and $7.7 \pm 3.2 \text{ }\mu\text{M}$, respectively. DON data were obtained by subtracting DIN values ($\bar{x} = 4.5 \pm 5.5 \text{ }\mu\text{M}$) from TDN values.

The mean DOC concentrations showed significant differences ($p < 0.05$, one-way ANOVA, two-tailed) between the regions nearest the river mouths and elsewhere. DOC values obtained near the Mississippi/Atchafalaya River plumes in April at Stations AB5 ($\bar{x} = 103.98 \pm 31.73 \text{ }\mu\text{M}$) and 8C ($\bar{x} = 95.88 \pm 13.41 \text{ }\mu\text{M}$) were significantly ($p < 0.05$, one-way ANOVA, two-tailed) higher than that of Station 10B ($\bar{x} = 58.04 \pm 15.42 \text{ }\mu\text{M}$) (Table 1). This coincided with trends in nitrate+nitrite concentrations, and DON showed no significant difference among the three stations in August ($p > 0.05$, one-way ANOVA, two-tailed). However, the strong negative correlations between DON and nitrate+nitrite concentrations at all stations (Fig.4) indicated the coupling processes between DON and nitrate+nitrite.

The mean DOC values for surface, middle, and bottom seawaters in April were $101.37 \pm 34.32 \mu\text{M}$, $86.59 \pm 26.07 \mu\text{M}$ and $72.82 \pm 17.32 \mu\text{M}$, respectively, and were $155.79 \pm 27.80 \mu\text{M}$, $92.78 \pm 24.81 \mu\text{M}$ and $80.09 \pm 17.04 \mu\text{M}$ in August. Surface DOC values were significantly ($p < 0.05$, one-way ANOVA, two-tailed) higher than middle and bottom waters in both seasons.

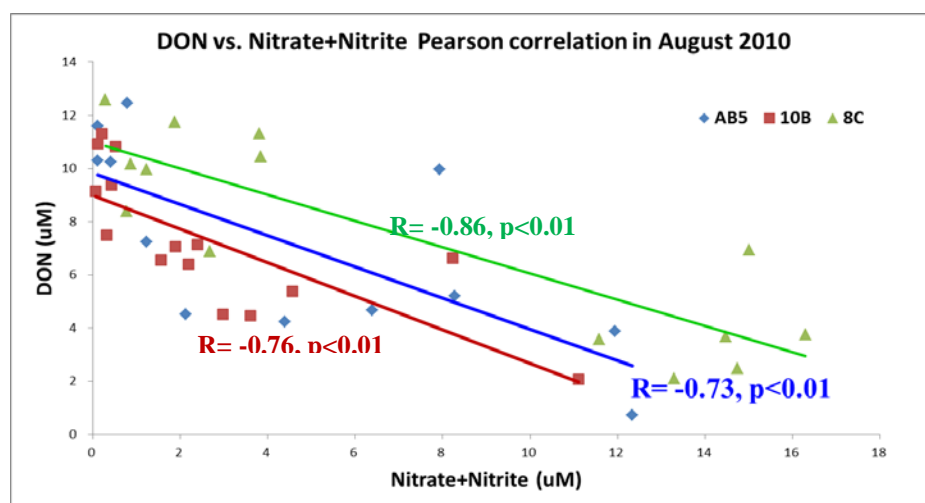


Figure 4. DON and Nitrate+Nitrite Pearson Correlation at Stations in August 2010. Station AB5 (blue, $R = -0.73$, $p < 0.01$); Station 10B (red, $R = -0.76$, $p < 0.01$); Station 8C (green, $R = -0.86$, $p < 0.01$).

The mean TDN values for surface ($11.67 \pm 1.51 \mu\text{M}$) and middle ($10.43 \pm 2.63 \mu\text{M}$) waters were significantly ($p < 0.05$, one-way ANOVA, two-tailed) lower than bottom waters ($15.14 \pm 4.13 \mu\text{M}$,) (Table 2). The DIN data showed the same trend as the TDN data, that is, significantly ($p < 0.05$, one-way ANOVA, two-tailed) higher values in bottom waters, and lower values in surface and middle waters. TDN was positively correlated with DIN concentrations ($R = 0.7$, $N = 47$, $p < 0.01$) at different water depths.

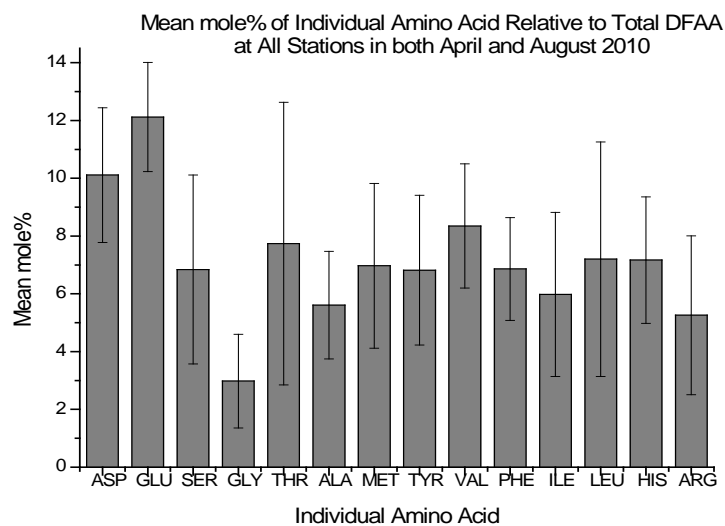
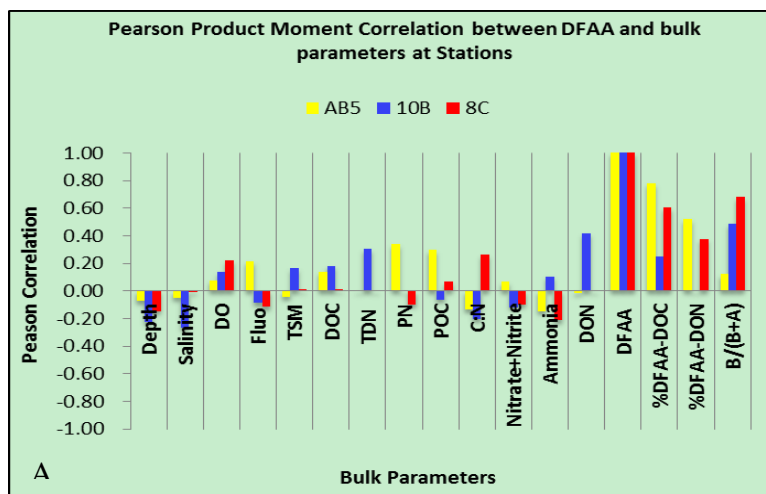
However, DON concentrations were significantly different ($p < 0.05$, one-way ANOVA, two-tailed) among surface ($10.77 \pm 1.23 \mu\text{M}$), middle ($7.07 \pm 1.92 \mu\text{M}$) and bottom ($5.11 \pm 1.87 \mu\text{M}$) waters.

3.1.3 Total Dissolved Amino Acids

Concentrations and compositions of DFAA are presented in Table 4. Total DFAA for all three stations and both cruises ranged from 0.18 to 0.82 μM ($\bar{x} = 0.30 \mu\text{M}$) and accounted 0.1% to 1.5% of total DOC and 1.5% to 12.4% of DON in August (no DON data were available for April).

Total DFAA concentrations for both cruise at AB5 ranged from 0.29 to 0.43 μM ($\bar{x} = 0.36 \mu\text{M}$), which were significantly higher than the concentrations at 10B ($\bar{x} = 0.26 \mu\text{M}$) and 8C ($\bar{x} = 0.27 \mu\text{M}$) ($p < 0.05$, one-way ANOVA, two-tailed). However, mole percentage of DFAA in the DOC pools ($\bar{x} = 0.3\%$) showed no significant differences among the three stations. However, percentage of DFAA in DON pool ($\bar{x} = 0.4\%$) did show significant differences ($p > 0.05$, one-way ANOVA, two-tailed) among the three stations.

There was no significant difference for total DFAA concentrations within the three depths or for the mole percentage of DFAA in DOC. However, the mole percentage of DFAA in DON in bottom waters ($\bar{x} = 5.4\%$) was significantly higher than surface waters ($\bar{x} = 2.8\%$), which coincided with the higher nutrient and DON concentrations found at the deepest depth. However, DON values showed no significant ($p > 0.05$, one-way ANOVA, two-tailed) differences with water depth.



B

Figure 5. (A) Pearson product moment correlations ($p < 0.05$) between DFAA and bulk parameters at three stations. Yellow bars are for AB5, blue bars are for 10B, and red bars are for 8C. (B) Mean %mole of individual DFAA for all stations. ASP-aspartic acid; GLU-glutamic acid; SER-serine; GLY-glycine; THR-threonine; ALA-alanine; MET-methionine; TYR-tyrosine; VAL-valine; PHE-phenylalanine; ILE-isoleucine; LEU-leucine; HIS-histidine; ARG-arginine.

3.1.4 Individual Dissolved Amino Acids

Mole percentages of individual DFAA at three stations during both spring and summer cruises on the Louisianan continental shelf are shown in Table 4. The dominant DFAA were aspartic acid ($\bar{x}=0.030 \mu\text{M}$) and glutamic acid ($\bar{x}=0.034 \mu\text{M}$), which were significantly higher than the other DFAA (Fig.5 B); they accounted for over 22% of the total DFAA. Glycine had the lowest concentration ($\bar{x}=0.009 \mu\text{M}$), which only accounted for 3% of the total DFAA. In general, glycine, arginine, alanine, and isoleucine were largely depleted in Louisiana coastal waters. Aspartic acid, glutamic acid, alanine, methionine, valine, phenylalanine, isoleucine and histidine had significantly higher ($p<0.05$, one-way ANOVA, two-tailed) concentrations at AB5 than the other two stations. However, concentrations of tyrosine were highest at Station 10B. Mean %mole values of serine, arginine and histidine accounted for higher fractions at Station 8C (8.3%, 6.4% and 8.3%, respectively) compared to from 4.5 to 6% at Stations AB5 and 10B. Tyrosine had higher concentration at 10B, and thus its mole percentage (%mole) value was higher at 10B ($\bar{x}=8\%$) than the other two stations ($\bar{x}=6\%$), and alanine showed significantly ($p<0.05$, one-way ANOVA, two-tailed) higher %mole at AB5 ($\bar{x}=8\%$) than at the other two stations ($\bar{x}=5\%$). Overall, there was no significant correlation between individual DFAA and water column depth at all stations.

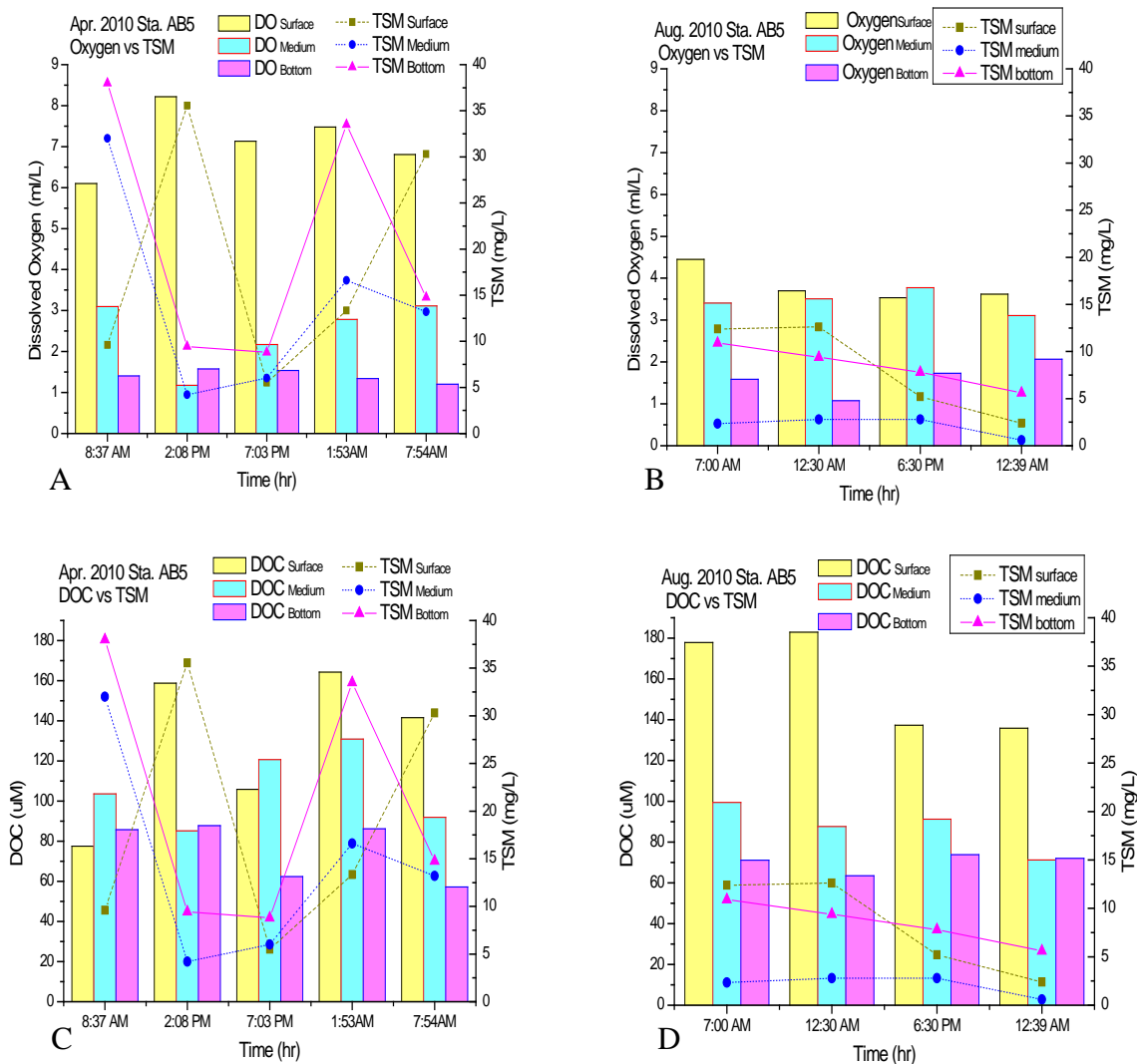


Figure 6. Bulk parameters diurnal variations at Station AB5 (1). (A) DO (column) versus TSM (symbol and line) in spring 2010; (B) DO (column) versus TSM (symbol and line) in summer 2010; (C) DOC (column) versus TSM (symbol and line) in spring 2010; (D) DOC (column) versus TSM (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom.

3.2 Seasonal and Diurnal Changes

Seasonal variations in salinity had significantly different trends among all three stations. Only AB5 surface water had lower salinity in spring ($\bar{x}=26.50$), and the salinities of middle and bottom depths did not change substantially during two seasons ($\bar{x}=30.50$ in spring; $\bar{x}=32.93$ in summer). However, both 10B and 8C had significantly higher ($p<0.05$, one-way ANOVA, two-tailed) salinity in spring ($\bar{x}=33.08$ for 10B; $\bar{x}=32.84$ for 8C) and lower salinity in summer ($\bar{x}=31.83$ for 10B; $\bar{x}=31.29$ for 8C).

3.2.1 Station AB5

For Station AB5, DO concentrations in surface waters were significantly higher than in bottom and middle waters in April, with no significant differences among all three depths in August (Fig. 6 A, B). However, low DO concentrations ($\text{DO} < 1.4 \text{ ml L}^{-1}$) were observed in bottom waters in both April and August, which indicated the continual hypoxia happened at AB5 in both seasons. DO showed a significant ($p<0.05$, one-way ANOVA, two-tailed) positive correlation with fluorescence in April, particularly in surface waters in April (Fig. 7 C, D).

TSM concentration was more constant diurnally with no significant variation observed at different depths in the August (Fig. 7 A, B). It seemed that TSM in bottom and middle waters had similar diurnal trends, but surface water TSM had the opposite trends in April – with similar trends in August. There was no significant correlation between TSM and DO. Generally, POC was significantly ($p<0.05$, one-way ANOVA, two-tailed) higher than PN and were positively correlated seasonally. Percent OC in surface waters was positively correlated with TSM in both seasons. Percent OC and PN

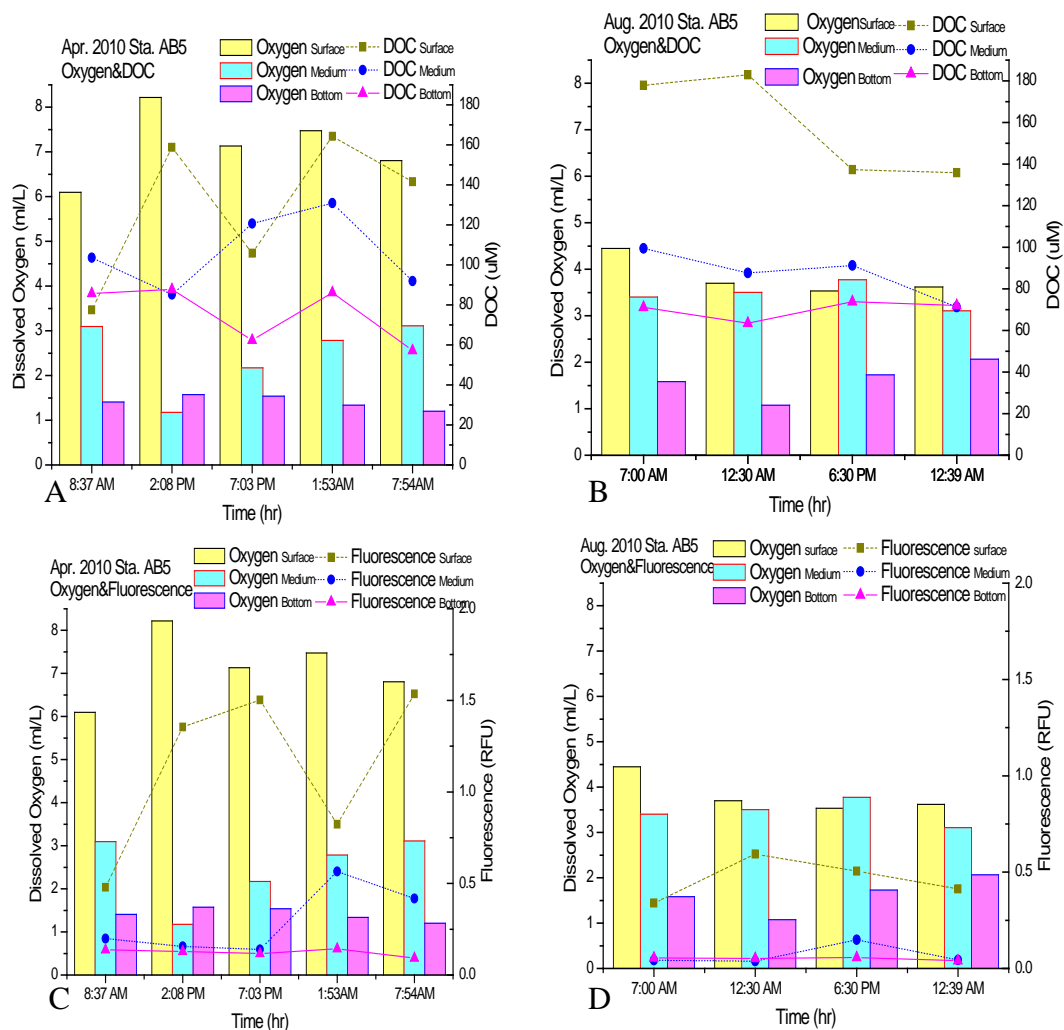


Figure 7. Bulk parameters diurnal variations at Station AB5 (2). (A) DO (column) versus DOC (symbol and line) in spring 2010; (B) DO (column) versus DOC (symbol and line) in summer 2010; (C) DO (column) versus fluorescence (symbol and line) in spring 2010; (D) DO (column) versus fluorescence (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom.

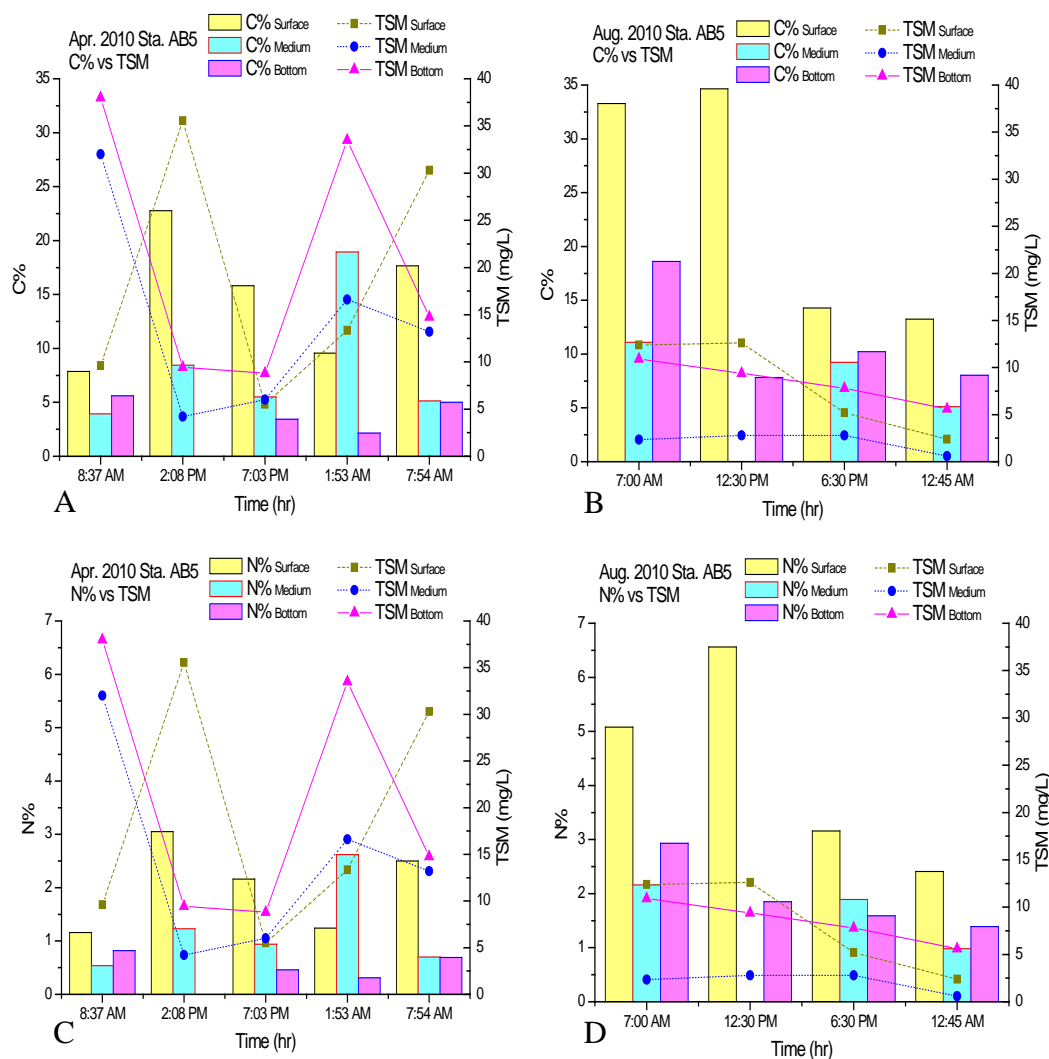


Figure 8. Bulk parameters diurnal variations at Station AB5 (3). (A) %C (column) versus TSM (symbol and line) in spring 2010; (B) %C (column) versus TSM (symbol and line) in summer 2010; (C) %N (column) versus TSM (symbol and line) in spring 2010; (D) %N (column) versus TSM (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom. %C is POC and %N is PN.

in bottom waters increased significantly in August (Fig.8). For station AB5, TSM concentrations were more constant throughout the day and no significant variation was observed at different depth in the summer. More fluctuations were observed in the spring cruise which may be caused by the changing rates of water discharge from the Mississippi river during the day.

DOC concentrations were significantly different between spring and summer at Station AB5 (Fig. 6 C, D; Fig. 7 A, B). There were significantly higher DOC concentrations in summer in surface waters when fluorescence was low.

3.2.2 Station 10B

At station 10B, DO was more well-mixed in the water column than the other two stations. However, hypoxia in bottom waters was still observed during periods of the day. DO concentrations were generally higher in spring than in summer at each depth, especially in surface waters (Fig. 9 A, B). However, fluorescence was higher in bottom waters in spring when DO was lower than the other two depths; DO also did not have any significant correlation with DOC at this station (Fig. 10). DOC was higher in summer than in spring, for the surface waters (Fig. 9 C, D). Ranges and diurnal variability of TSM at Station 10B were higher in spring, as well as the POC and PN in bottom waters. However, surface water POC and PN were both significantly ($p < 0.05$, one-way ANOVA, two-tailed) higher in summer.

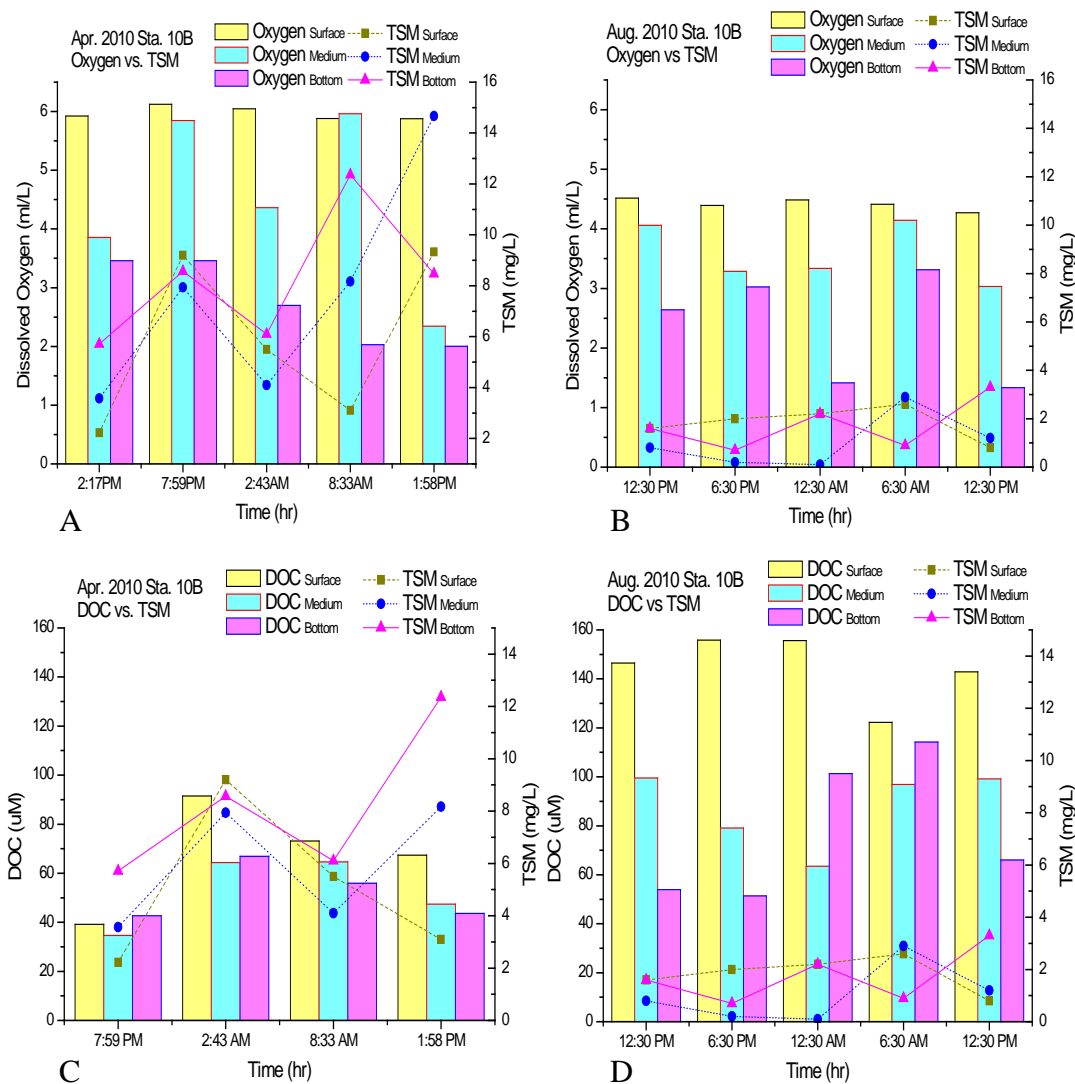


Figure 9. Bulk parameters diurnal variations at Station 10B (1). (A) DO (column) versus TSM (symbol and line) in spring 2010; (B) DO (column) versus TSM (symbol and line) in summer 2010; (C) DOC (column) versus TSM (symbol and line) in spring 2010; (D) DOC (column) versus TSM (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom.

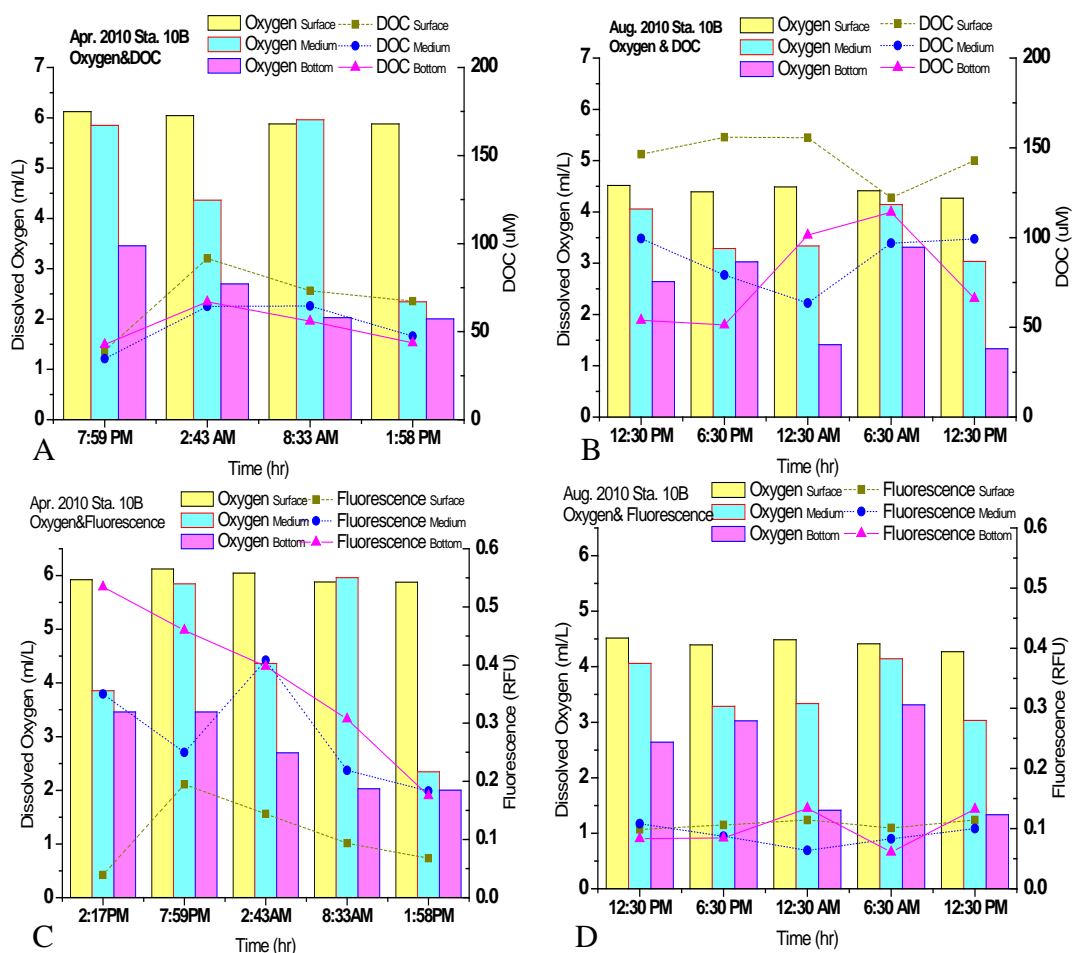


Figure 10. Bulk parameters diurnal variations at Station 10B (2). (A) DO (column) versus DOC (symbol and line) in spring 2010; (B) DO (column) versus DOC (symbol and line) in summer 2010; (C) DO (column) versus fluorescence (symbol and line) in spring 2010; (D) DO (column) versus fluorescence (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom.

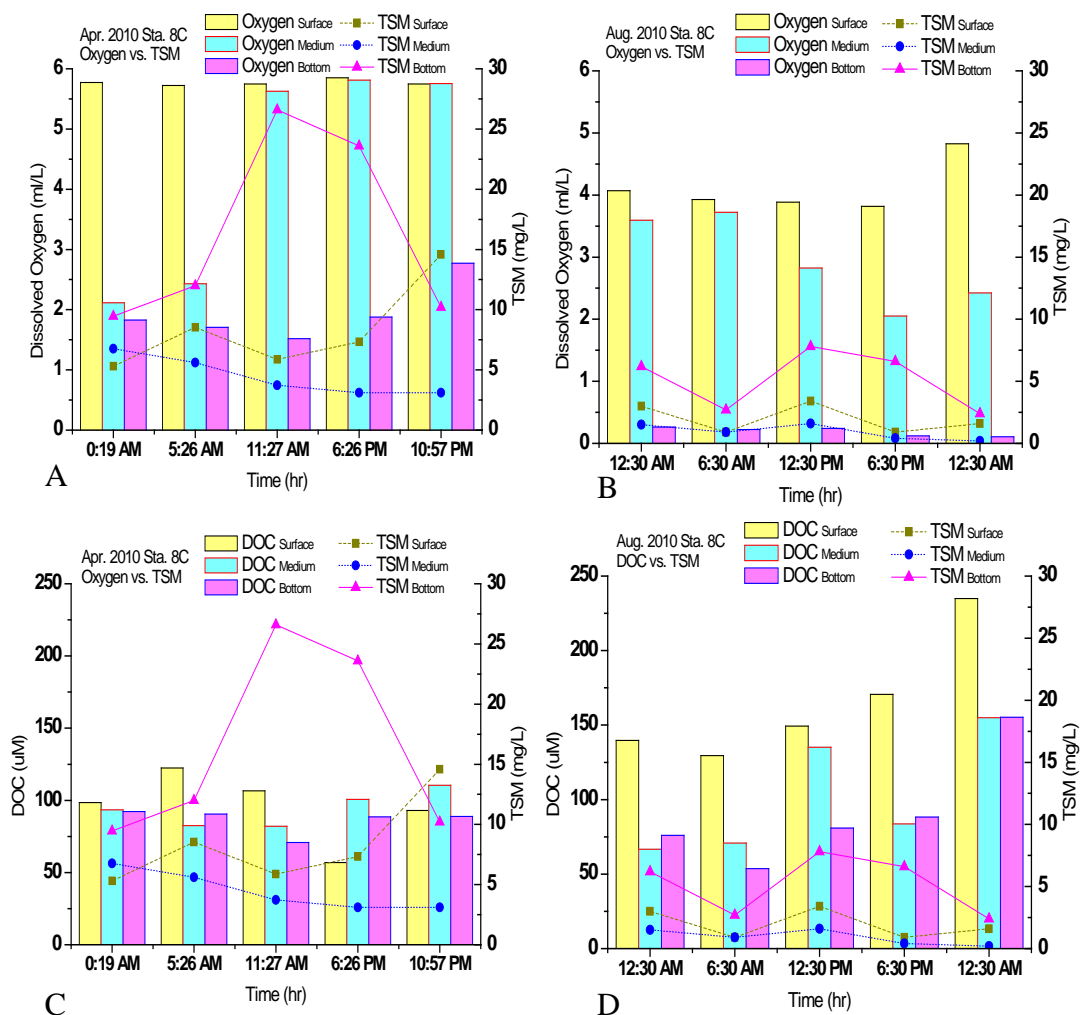


Figure 11. Bulk parameters diurnal variations at Station 8C (1). (A) DO (column) versus TSM (symbol and line) in spring 2010; (B) DO (column) versus TSM (symbol and line) in summer 2010; (C) DOC (column) versus TSM (symbol and line) in spring 2010; (D) DOC (column) versus TSM (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom.

3.2.3 Station 8C

The most intensive hypoxia occurred at 8C in both seasons, with summer DO values close to anoxic conditions ($DO < 22 \mu\text{mol L}^{-1}$). Surface water DO was significantly ($p < 0.05$, one-way ANOVA, two-tailed) higher in spring than in summer, and DO were only positively correlated with fluorescence in bottom waters (Fig. 11 C, D). However, DOC in bottom waters in summer showed the opposite trend and were negatively correlated with DO (Fig. 12, A, B). Surface water DOC at Station 8C was significantly ($p < 0.05$, one-way ANOVA, two-tailed) higher in summer than in spring, with the middle and bottom waters showing no significant seasonal variation. TSM was higher in bottom waters in spring, and POC and PN, both decreased during hypoxia events (Fig.13).

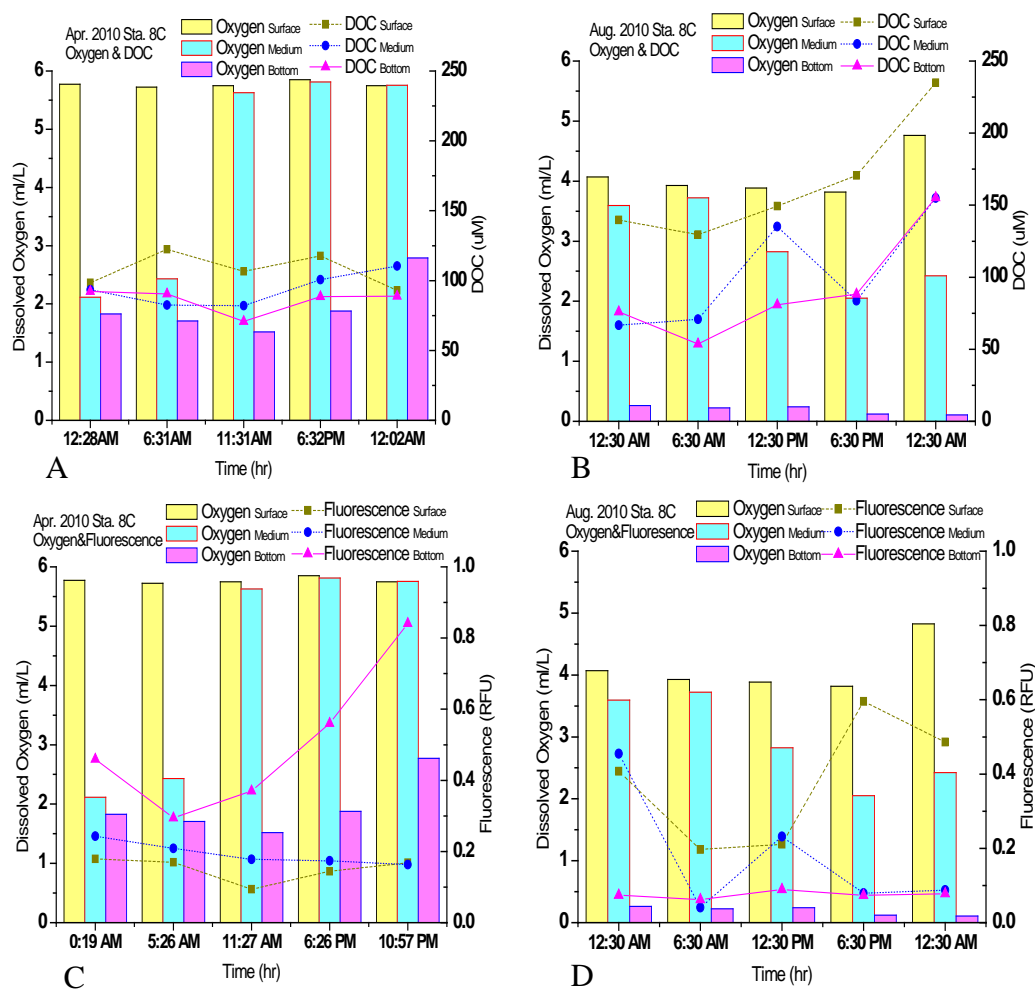


Figure 12. Bulk parameters diurnal variations at Station 8C (2). (A) DO (column) versus DOC (symbol and line) in spring 2010; (B) DO (column) versus DOC (symbol and line) in summer 2010; (C) DO (column) versus fluorescence (symbol and line) in spring 2010; (D) DO (column) versus fluorescence (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom.

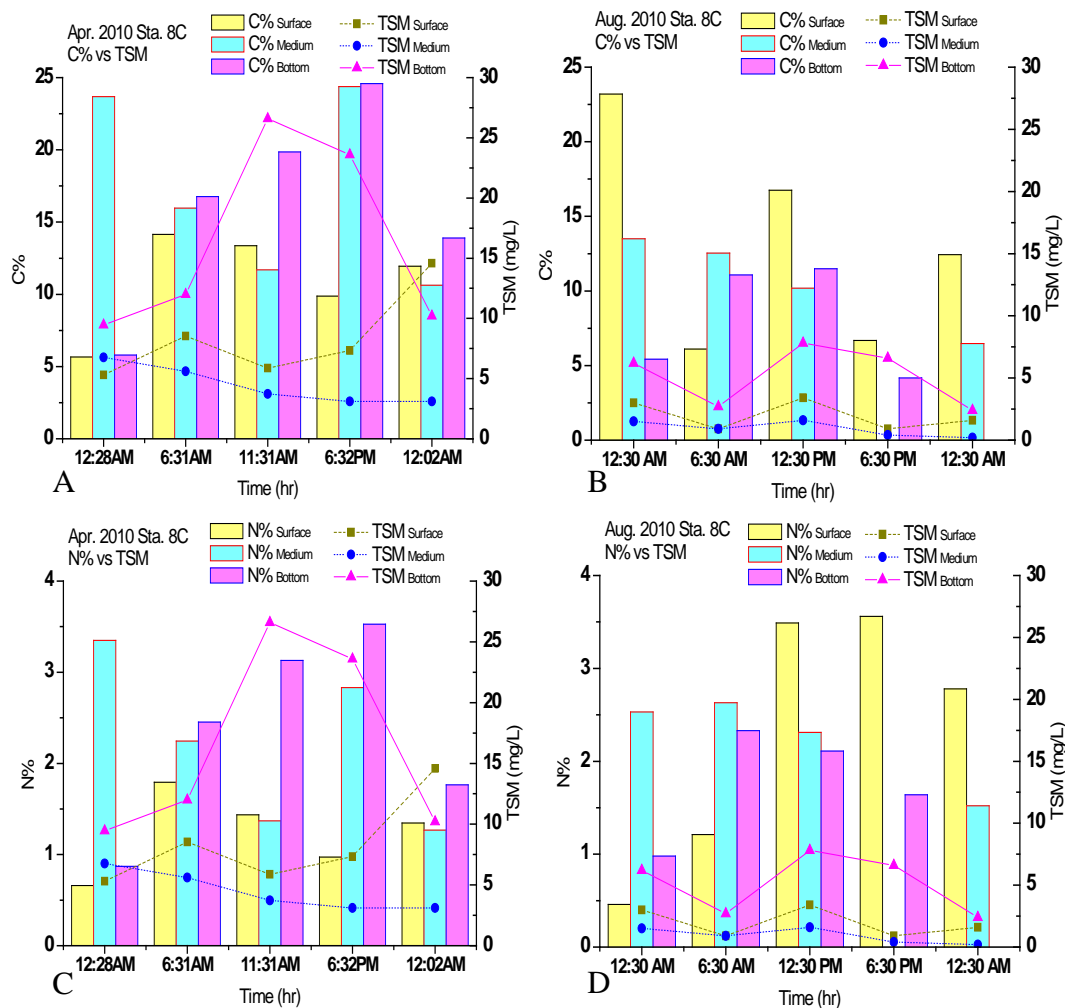


Figure 13. Bulk parameters diurnal variations at Station 8C (3). (A) %C (column) versus TSM (symbol and line) in spring 2010; (B) %C (column) versus TSM (symbol and line) in summer 2010; (C) %N (column) versus TSM (symbol and line) in spring 2010; (D) %N (column) versus TSM (symbol and line) in summer 2010. Different colors represent different depths: yellow-surface; blue-middle; magenta-bottom. %C is POC and %N is PN.

CHAPTER IV

DISCUSSION

4.1 DOM Sources and Linkages with DO

DOC and DON showed a positive correlation with fluorescence and decreased quickly with increasing depth which demonstrated that the main source of both DOC and DON was likely from *in situ* phytoplankton production. DOC and DON also reached peak values in surface waters with the highest photosynthetically active radiation (PAR) and DIN concentrations - further supporting linkages with primary production. The overall concentration of DOC at all three stations was similar that reported from earlier work by Wysocki *et al.* (2006).

The coupling between DOM and primary production was clearly affected by changes in river discharge. For example, the Mississippi-Atchafalaya system reached its highest flow period in the spring resulting in the highest inputs of DIN to the river plume. Station 10B, which received relative less DIN inputs than the two stations closer to the mouth of the Mississippi and Atchafalaya Rivers also had lower DOC values. Since the Mississippi River is a particle-rich and relatively low DOC source to Louisiana coastal waters (Bianchi *et al.*, 2004, 2008), the lower DOC values at Station 10B were likely the result of greater de-coupling from phytoplankton sources - as a result of lower DIN at this station. DIN has been shown to be quickly removed from the near-field plume regions resulting in significantly lower DIN in most far-field station like 10B (Dagg *et al.*, 2004; Bianchi *et al.*, 2010, and references therein). Increases in both DOC and DO and DIN in near-field surface waters further suggested that *in situ* phytoplankton

production was a dominant source of DOC and likely enhanced DO concentrations from photosynthetic activity.

While the relationship between DO and DOC was quite evident in surface waters, it was less clear in bottom waters - where hypoxia commonly occurs. Some of this may be related to inputs of DOC from coastal marshes that are decoupled from phytoplankton-derived DOC in surface waters. Bianchi *et al* (2009) have shown that marshes are sources of DOC to both surface and bottom waters on the inner Louisiana shelf waters, and may in part, support hypoxia in the more western regions - where surface primary productivity is considerably less in the near-field regions (Dagg *et al.*, 2004). We did see an increase in fluorescence at certain depths near the pycnocline (around middle layer), where recent work has reported a persistent sub-surface chlorophyll layer. This subsurface phytoplankton biomass is supported by greater PAR at depth in the more far-field stations where TSM is considerably lower. This sub-surface chlorophyll peak may also provide a new source of DOC at depth for bacteria (Zhao *et al.*, unpublished), which may be linked to hypoxia in bottom waters. It should be noted that we do not always see an alignment with fluorescence and the subsurface chlorophyll peak near the pycnocline. The reason for this may be due the greater inefficiency of tracking chlorophyll with fluorescence in bottom waters due to increased interference of fluorescence bands from terrestrially-derived DOC inputs and sediment fluxes porewater (Del Castillo and Miller, 2008). More work is needed to better understand the role of this sub-surface chlorophyll layer, DOC sources, and hypoxia.

DON concentrations, which were higher in surface waters, were also linked with DOC and fluorescence, further demonstrating linkages with DIN and primary productivity near the plume. Previous work has shown enrichment of DON in surface waters in the Mississippi-Atchafalaya River plume (Lopez-Veneroni and Cifuentes, 1992). Past work has also shown that DON in the plume was being incorporated by phytoplankton and rapidly recycled by bacteria (Amon and Benner, 1998). DON concentrations at all of our stations reached their highest concentrations in surface waters in the summer, which was linked with DIN inputs from riverine source, high primary production and enhanced recycling by bacteria in the plume region (Dagg *et al.*, 2004; Amon and Benner, 1998; Gardner *et al.*, 1994). Finally, at certain times of the year TDN and DIN were found to be higher in bottom waters compared to surface waters at all stations; this was likely linked with regeneration of nutrients from sediments and sinking particles in the water column. It is well known that nutrient regeneration rates are strongly influenced by phytoplankton production in the Mississippi-Atchafalaya river plume waters (Gardner *et al.*, 1994). These higher concentrations of TDN and DIN at depth may also support the sub-surface peak in chlorophyll, as discussed earlier, as one moves further to the west away from the plume regions. This further supports prior work which has suggested that the role of nutrient regeneration in sediments and bottom waters is a more important mechanism for controlling hypoxia than surface riverine nutrients in western far-field stations (Rowe and Chapman, 2002; Hetland and DiMarco, 2007; Bianchi *et al.*, 2010).

4.2 Rapid Cycling of DFAA and Hypoxia

The spatial variation of DFAA showed a similar trend as that of DOC and was likely linked to the rapid recycling of phytoplankton in surface waters. DFAA typically have very short life-time in coastal waters due to their high bioavailability to the bacterial community (Fuhrman, 1990) Bacteria preferentially utilize DFAA as their main nitrogen source (Kirchman and Hodson, 1986; Keil and Kirchman, 1991; Cherrier and Bauer, 2004). Similarly, Fuhrman (1990) and Jorgensen et al. (1993) also reported that more than 64% of the C demand and 100% of the N demand for coastal bacterial populations were supported by labile forms of DOM such as DFAA. The total concentrations of DFAA in this study are similar to those found in the lower Mississippi river (Duan and Bianchi, 2007) and Mississippi River plume (Grace and Bianchi, 2010). As expected, concentrations were higher in surface waters in spring as shown in prior studies, which further supported the previously discussed linkages with primary production, DIN, and high river discharge at this time of year. The highest DFAA values were found in surface waters at Stations AB5 and 8C which were likely more linked with plume processes. The inverse relationship between DFAA and DO in middle and bottom waters may suggest that DFAA were an important source of C and N for oxygen-consuming bacterial populations in hypoxic bottom water. Amon and Benner (1998) observed that bacterial production rates decreased in surface waters moving from the plume region to the west, but increased below the pycnocline. This was attributed to the fact that when the surface waters move westward from the plume, some of the sinking primary production will fuel bottom bacterial activity. Thus, DO is depleted and DFAA

is cycled quickly by the more active bacterial community in stratified bottom waters. The DFAA concentrations were extremely low at the three stations in our study, which may suggest that the lower primary production and sinking phytodetritus in our stations, which were further west than those studied by Amon and Benner (1998), resulted in lower ambient DFAA concentrations. So, the sources at these depths remain to be determined, since a “fresh” source would likely be needed at these depths. However, once again the role of sub-surface phytoplankton biomass found near the pycnocline may be important here. Moreover, changes in DOC and DON were not closely linked with the DFAA pool (Fig.5 A) likely because DFAA represents a relatively small and more rapidly cycling fraction of these bulk pools. For example, DFAA have been shown to typically represent only < 1% of the bulk DOC and DON pools (Billen and Fontigny, 1987; Fuhrman, 1987; Suttle *et al.*, 1991; Keil and Kirchman, 1991). Diffusion of DFAA between its sources (phytoplankton) and sinks (primarily bacterial) typically occurs within a few minutes (Fuhrman, 1990).

4.3 Distribution of Basic and Acidic Amino Acids

Aspartic and glutamic acids were the most abundant amino acids and sorption processes may have had an effect their relative abundance (Fig.5 B). The selective absorption of DFAA by particles under oceanic pH, as well as the runoff of amino acids from surface soils, has been shown to be an important process in controlling DFAA concentrations and composition (Kaiser *et al.*, 2004; Yano *et al.*, 2004). Duan and Bianchi (2007) and Grace and Bianchi (2010) showed that the dominant amino acids in the lower Mississippi River and Mississippi River plume were glycine and serine, which

are neutral amino acids. Thus, the dominance of aspartic and glutamic acids and low concentrations of glycine in our study suggest a spatial effect by sorptive partitioning across our stations. Particle-seawater interactions have been shown to play an important role in the distribution of amino acids (Maier *et al.*, 2000). In general, amino acids of opposite charge to ambient particles will be preferentially absorbed due to coulombic interactions. It is well known that seawater has a weakly basic pH (e.g., 7.5 to 8.4) whereby clay particles should be negatively charged. Therefore, positively charged amino acids would be adsorbed more than negatively charged amino acids, such as aspartic acid and glutamic acid. As a result, the bulk concentrations of these two acidic amino acids in the dissolved amino acid pool should be enhanced after selective sorption.

The relative abundance of DFAA at our station was also likely affected by biotic effects. For example, high glycine concentrations in the Mississippi River plume were linked with the high abundance of diatoms (Duan and Bianchi, 2007; Grace and Bianchi, 2010). Glycine is preferably utilized over many other amino acids by microbial communities and this may be why we do not see as much glycine in waters west of the plume - where more degradation has occurred during transport. Cherrier and Bauer (2004) observed that glycine had the highest degradation rates of all DFAA in the open ocean. In conclusion, both physical (e.g., sorptive processes) and biotic (e.g., direct release from phytoplankton and recycling by bacteria) processes likely contributed to DFAA composition and abundance at our stations.

4.4 Linkages between DIN, DOM, and Hypoxia

Although this work has focused on DOM, it is well known that observed hypoxia is generally concentrated in the near-field high-nutrient- LDE region of the Louisiana shelf. We observed a negative correlation with nitrate-nitrite concentration and DO. DIN species have been shown to play an essential role in the removal of oxygen at bottom waters (Rabalais *et al.*, 2007). In addition to the major inputs of nitrate from the Mississippi River, DIN inputs to this could come also enter in the form of ammonium through ammonification of solubilized sediments (Neubacher *et al.*, 2011). Another source of ammonium is NH_4^+ generated from dissimilatory nitrate reduction to ammonium (DNRA) (Gardner *et al.*, 1994). Aquatic NH_4^+ remains biologically available and could be oxidized to nitrate or nitrite through nitrification pathway if diffuses to areas with suitable O_2 concentration (Maier *et al.*, 2000). Both nitrate and nitrite are able to be involved in the denitrification and in the DNRA reaction in hypoxia regions where the N-oxygen is converted to H_2O oxygen to support the energy of anaerobic processes. In other words, ammonium is serving as a pump which transports oxygen in the form of nitrogen oxides and helps in the consumption of DO. The high nitrate-nitrite concentration in hypoxia regions is likely in part, related to the production of nitrification during ammonium oxidation (Maier *et al.*, 2000).

CHAPTER V

CONCLUSIONS

1. DOC and DON reached peak values with the highest light and nutrient availability. A positive correlation between DOC, DON and fluorescence demonstrated that the main source of both DOC and DON was likely to be *in situ* phytoplankton production.

Surface waters in the near-field showed this relationship more than at stations to the west where a sub-surface chlorophyll peak near the pycnocline may also provide a source of DOC and DON in bottom waters. So, there appears to be a shift from surface to bottom dominated sources of DOM when moving from east to west on the Louisiana inner shelf.

2. DFAA always had relatively low concentrations at all water depths, which further supports prior work which has shown rapid cycling and high consumption rates of DFAA by heterotrophic bacteria.

3. In addition to biotic controls, selective adsorption of DFAA likely contributed to the dominance of aspartic and glutamic acids at our stations.

4. Hypoxia was generally observed in bottom waters in both spring and summer 2010.

Dissolved oxygen generally revealed a negative correlation with nitrate-nitrite concentrations. Based on other work, one possible reason for such linkages may be from NH_4^+ released from DNRA which could involve further O_2 consumption through the nitrification pathway. Another possible reason may be the high degradation of labile DOM (such as DFAA) as shown by high respiration in bottom waters in prior work by Amon and Benner (1998).

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APPENDIX A

Table A3 Hydrography, DOC, TDN, DON and TSM (ND=no data) data in April and August 2010.

Station	Lat./Long.	GMT Time	Local Time	Depth (M)	Salinity	DO (ml/L)	Fluo (RFU)	TSM (mg/L)	DOC (µM)	TDN (µM)	Nitrate+ Nitrite (µM)	DON (µM)	POC %N	POC %C	POC C:N		
Spring AB5	29°04.892'N/ 89°56.306'W	13:37	7:37 AM	S 5	30.68	6.10	0.48	9.60	73.35 81.68	ND ND	0.82	ND	1.16	7.87	7.94		
				M 12	31.91	3.10	0.20	32.00	100.82 106.40	ND ND	2.48	ND	0.54	3.94	8.57		
				B 17	35.13	1.41	0.14	38.00	88.09 83.42	ND ND	18.02	ND	0.82	5.61	7.99		
		19:08	1:08 PM	S 3	25.38	8.21	1.35	35.56	174.09 143.54	ND ND	5.52	ND	3.05	22.77	8.72		
				M 12	34.31	1.18	0.16	4.20	77.18 93.17	ND ND	16.74	ND	1.23	8.44	7.99		
				B 17	35.39	1.58	0.13	9.44	104.24 71.19	ND ND	16.12	ND	ND	ND	ND		
		0:03	18:03 PM	S 2	23.59	7.13	1.50	5.50	108.65 102.99	ND ND	5.52	ND	2.16	15.81	8.53		
				M 9	31.32	2.17	0.14	6.00	130.38 111.07	ND ND	9.18	ND	0.94	5.51	6.88		
				B17	35.41	1.54	0.12	8.80	57.11 67.69	ND ND	16.70	ND	0.46	3.44	8.70		
		6:53	12:53 AM	S 2	24.64	7.48	0.82	13.34	180.42 148.20	ND ND	8.08	ND	1.24	9.56	8.96		
				M 5	29.63	2.79	0.57	16.60	142.54 119.22	ND ND	5.18	ND	2.62	18.93	8.43		
				B 17	35.37	1.34	0.14	33.50	104.74 67.52	ND ND	17.45	ND	0.31	2.16	8.03		
		12:54	6:54 AM	S 2	20.89	6.81	1.54	30.30	126.05 157.19	ND ND	16.77	ND	2.50	17.66	8.25		
				M 5	28.57	3.11	0.42	13.20	92.50 91.42	ND ND	4.28	ND	0.70	5.13	8.58		
				B 17	35.22	1.20	0.09	14.75	59.70 54.78	ND ND	17.44	ND	0.69	5.01	8.47		
		Spring 10B	28°37.447'N/ 90°33.1336'W	19:17	1:17 PM	S 1	31.59	5.92	0.04	2.22	63.11 ND	ND ND	0.28	ND	0.59	4.39	8.72
						M 17	32.81	3.86	0.35	3.57	ND ND	ND ND	0.63	ND	1.45	12.09	9.75
						B 20	34.41	3.46	0.53	5.71	ND ND	ND ND	0.21	ND	2.05	18.49	10.54
0:59	6:59 AM			S 1	31.59	6.12	0.20	9.20	39.13 ND	ND ND	0.49	ND	2.48	22.97	10.81		
				M 10	31.85	5.85	0.25	7.94	32.39 36.88	ND ND	0.22	ND	1.37	11.70	9.97		

			B 18	34.32	3.46	0.46	8.57	31.14	ND	0.12	ND	2.62	20.06	8.97	
								54.28	ND						
	7:43	1:43 AM	S 2	31.62	6.05	0.14	5.50	70.94	ND	1.12	ND	1.45	10.84	8.75	
								112.15	ND						
			M 12	32.49	4.36	0.41	4.10	64.36	ND	0.97	ND	2.37	17.80	8.76	
								ND	ND						
			B17	34.75	2.70	0.40	6.10	70.77	ND	5.45	ND	2.62	19.33	8.62	
								63.11	ND						
	13:33	7:33 AM	S 2	31.90	5.88	0.09	3.10	70.27	ND	1.07	ND	1.03	7.02	7.98	
								76.10	ND						
			M 10	32.27	5.96	0.22	8.17	75.85	ND	0.07	ND	1.87	12.80	8.00	
								53.37	ND						
			B 17	34.92	2.03	0.31	12.36	55.95	ND	5.40	ND	2.09	16.07	8.98	
								ND	ND						
	18:58	1:58 PM	S 2	31.98	5.88	0.07	9.33	52.54	ND	0.27	ND	1.87	14.16	8.85	
								82.18	ND						
			M 13	34.31	2.35	0.18	14.67	47.37	ND	5.07	ND	1.19	8.16	8.01	
								ND	ND						
			B 20	35.32	2.00	0.18	8.47	43.63	ND	7.24	ND	1.89	13.50	8.32	
								ND	ND						
Spring 8C	28°57.9814'N/ 91°55.808'W	5:28	11:28 PM	S 2	31.68	5.77	0.18	5.31	102.91	ND	0.20	ND	0.66	5.66	10.01
								94.08	ND						
			M 15	34.28	2.11	0.24	6.76	86.50	ND	0.31	ND	3.35	23.69	8.25	
								100.24	ND						
			B 18	34.94	1.83	0.46	9.46	60.61	ND	1.33	ND	0.87	5.79	7.77	
								123.80	ND						
	11:31	5:31 AM	S 5	31.55	5.72	0.17	8.53	118.31	ND	0.40	ND	1.79	14.15	9.21	
								126.55	ND						
			M 13	32.03	2.43	0.21	5.60	102.99	ND	0.74	ND	2.25	15.96	8.29	
								61.86	ND						
			B 18	34.94	1.71	0.29	12.00	99.49	ND	2.10	ND	2.45	16.76	7.97	
								81.59	ND						
	16:31	10:31 AM	S 2	31.56	5.75	0.09	5.87	108.07	ND	0.38	ND	1.44	13.37	10.85	
								105.07	ND						
			M 9	31.71	5.63	0.18	3.73	86.26	ND	0.51	ND	1.37	11.70	9.97	
								77.93	ND						
			B18	34.93	1.52	0.37	26.60	75.68	ND	0.94	ND	3.13	19.85	7.40	
								65.86	ND						
	23:32	5:32 PM	S 2	31.77	5.85	0.14	7.33	117.73	ND	0.48	ND	0.97	9.87	11.83	
								ND	ND						
			M 9	31.80	5.81	0.17	3.10	118.06	ND	0.26	ND	2.83	24.38	10.05	
								83.34	ND						
			B 18	34.39	1.88	0.56	23.60	85.76	ND	0.54	ND	3.53	24.58	8.13	
								91.42	ND						
	5:02	11:02 PM	S 2	31.72	5.75	0.17	14.58	119.06	ND	0.21	ND	1.35	11.94	10.35	
								66.86	ND						
			M 9	31.73	5.75	0.16	3.10	118.56	ND	0.18	ND	1.27	10.63	9.77	
								102.24	ND						
			B 18	33.52	2.79	0.48	10.20	94.91	ND	0.24	ND	1.76	13.89	9.18	

		17:30	12:30 PM	S 3	27.59	4.26	0.11	0.80	152.77	12.71	0.76	10.84	2.64	15.01	6.64		
									132.87	10.50							
				M 6	32.52	3.03	0.10	1.20	100.24	9.85	2.62	7.12	2.72	14.68	6.31		
									98.16	9.64							
				B 20	35.60	1.33	0.13	3.30	63.44	15.64	8.39	6.63	1.67	10.68	7.48		
									68.68	14.42							
Summer 8C	28°59.252'N/ 91°58.213'W	5:30	12:30 AM	S 4	26.77	4.07	0.40	3.00	144.03	11.99	1.52	9.97	2.53	13.49	6.23		
										135.29	11.00						
				M 8	27.08	3.59	0.45	1.50	66.85	14.92	11.91	3.58	0.46	23.20	59.18		
											66.43	16.06					
						B 18	35.41	0.26	0.07	6.20	78.42	20.63	16.63	3.76	0.98	5.42	6.44
											73.68	20.13					
		11:30	6:30 AM	S 2	26.85	3.92	0.19	0.90	129.54	10.28	2.50	8.39	2.63	12.53	5.56		
												129.54	11.49				
				M 8	32.87	3.72	0.04	0.90	72.76	6.85	9.79	-2.79	1.22	6.10	5.86		
											68.85	7.13					
						B 18	35.55	0.22	0.06	2.70	55.78	18.27	13.48	2.09	2.33	11.07	5.55
											51.45	12.85					
		17:30	12:30 PM	S 4	28.28	3.88	0.21	3.40	158.85	13.63	1.52	10.16	2.31	10.19	5.14		
												139.70	9.71				
				M 8	28.79	2.82	0.23	1.60	140.87	11.85	5.51	6.87	3.56	6.68	2.19		
											129.46	12.92					
						B 18	35.55	0.24	0.09	7.80	84.50	16.49	14.78	3.68	2.11	11.49	6.36
											77.17	20.41					
11:30	6:30 PM	S 5	27.57	3.81	0.59	0.90	156.52	14.35	4.46	11.32	ND	ND	ND				
										184.74	17.20						
		M 10	33.59	2.05	0.07	0.40	83.92	15.92	2.08	11.73	3.56	6.68	2.19				
									83.50	11.70							
				B 18	35.59	0.12	0.07	6.60	84.92	19.84	15.60	6.93	1.64	4.17	2.97		
									91.49	25.20							
5:30	12:30 AM	S 3	27.31	4.76	0.54	1.60	237.94	11.99	0.30	12.59	1.52	6.47	4.96				
										231.95	13.77						
		M 8	32.46	2.42	0.08	0.20	168.84	17.27	4.40	10.45	2.78	12.44	5.23				
									141.12	12.42							
				B 18	35.58	0.10	0.08	2.40	124.46	18.63	15.47	2.48	ND	ND	ND		
									185.99	17.27							

APPENDIX B

Table A4 Concentrations of individual DFAA and total DFAA in all stations in April and August 2010.

Station	Time GMT	Local Time	Depth (M)	ASP (uM)	GLU (uM)	HIS (uM)	SER (uM)	ARG (uM)	GLY (uM)	THR (uM)	ALA (uM)	TYR (uM)	MET (uM)	VAL (uM)	PHE (uM)	ILE (uM)	LEU (uM)	Sum (uM)	
Spring AB5	13:37	7:37 AM	S 5	0.039	0.031	0.017	0.014	0.013	0.008	0.037	0.013	0.021	0.028	0.035	0.031	0.019	0.014	0.014	0.325
				0.036	0.030	0.016	0.015	0.015	0.008	0.039	0.012	0.018	0.026	0.034	0.033	0.017	0.015	0.015	0.320
			M 12	0.032	0.032	0.017	0.028	0.012	0.007	0.016	0.014	0.016	0.019	0.026	0.025	0.012	0.016	0.016	0.279
				0.030	0.031	0.017	0.031	0.011	0.007	0.015	0.015	0.016	0.018	0.027	0.027	0.012	0.017	0.017	0.280
			B 17	0.026	0.032	0.015	0.023	0.013	0.006	0.013	0.017	0.027	0.025	0.034	0.020	0.012	0.024	0.024	0.294
				0.027	0.029	0.016	0.021	0.012	0.007	0.012	0.018	0.029	0.027	0.035	0.022	0.014	0.023	0.023	0.300
	19:08	1:08 PM	S 3	0.104	0.080	0.050	0.031	0.027	0.010	0.012	0.047	0.013	0.075	0.051	0.064	0.067	0.058	0.058	0.6946
				0.011	0.074	0.060	0.029	0.026	0.010	0.014	0.052	0.013	0.089	0.049	0.073	0.058	0.050	0.613	
			M 12	0.095	0.073	0.053	0.037	0.018	0.010	0.013	0.050	0.012	0.073	0.047	0.055	0.064	0.055	0.662	
				0.089	0.068	0.058	0.033	0.020	0.011	0.012	0.054	0.013	0.082	0.045	0.063	0.066	0.052	0.672	
			B 17	0.116	0.065	0.068	0.040	0.025	0.011	0.011	0.049	0.014	0.069	0.050	0.056	0.065	0.057	0.703	
				0.104	0.083	0.052	0.037	0.026	0.012	0.014	0.053	0.016	0.073	0.058	0.063	0.077	0.060	0.734	
	0:03	6:03 PM	S 2	0.038	0.044	0.031	0.043	0.026	0.019	0.026	0.063	0.030	0.053	0.061	0.064	0.082	0.028	0.613	
				0.031	0.037	0.025	0.038	0.022	0.017	0.024	0.070	0.023	0.051	0.055	0.052	0.079	0.026	0.557	
			M 9	0.029	0.039	0.020	0.023	0.016	0.014	0.016	0.022	0.021	0.018	0.027	0.024	0.021	0.024	0.321	
				0.031	0.041	0.026	0.031	0.024	0.018	0.018	0.028	0.022	0.019	0.024	0.020	0.018	0.0244	0.352	
			B17	0.032	0.040	0.023	0.019	0.020	0.015	0.021	0.028	0.023	0.019	0.025	0.024	0.023	0.016	0.334	
				0.034	0.039	0.022	0.030	0.018	0.022	0.017	0.025	0.028	0.017	0.025	0.019	0.017	0.018	0.337	
	6:53	12:53 AM	S 2	0.024	0.030	0.014	0.010	0.013	0.005	0.048	0.019	0.012	0.012	0.022	0.011	0.009	0.011	0.246	
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
			M 5	0.021	0.027	0.013	0.005	0.011	0.004	0.037	0.010	0.013	0.011	0.019	0.009	0.008	0.011	0.206	
				0.020	0.028	0.014	0.006	0.009	0.003	0.043	0.011	0.014	0.008	0.019	0.011	0.008	0.009	0.210	
			B 17	0.022	0.029	0.015	0.008	0.010	0.002	0.065	0.008	0.029	0.025	0.041	0.014	0.011	0.013	0.299	
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
12:54	6:54 AM	S 2	0.022	0.029	0.017	0.010	0.009	0.005	0.025	0.009	0.029	0.025	0.022	0.013	0.015	0.020	0.255		
			0.024	0.029	0.015	0.015	0.010	0.007	0.042	0.010	0.012	0.010	0.026	0.015	0.012	0.010	0.243		

Spring 10B	19:17	1:17 PM	M 5	0.023	0.031	0.016	0.022	0.009	0.005	0.019	0.011	0.016	0.013	0.017	0.014	0.009	0.018	0.230
				0.030	0.029	0.015	0.031	0.009	0.008	0.042	0.014	0.013	0.010	0.019	0.018	0.011	0.015	0.271
			B 17	0.031	0.032	0.017	0.022	0.011	0.0063	0.014	0.024	0.022	0.018	0.017	0.012	0.009	0.021	0.261
				0.035	0.030	0.013	0.017	0.011	0.005	0.044	0.008	0.030	0.026	0.024	0.016	0.011	0.011	0.288
			S 1	0.025	0.032	0.018	0.024	0.010	0.003	0.021	0.009	0.032	0.028	0.0212	0.015	0.013	0.021	0.276
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	M 17	0.026	0.030	0.019	0.016	0.009	0.003	0.026	0.012	0.039	0.035	0.037	0.018	0.013	0.020	0.309		
		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
	B 20	0.025	0.031	0.016	0.012	0.009	0.005	0.008	0.010	0.013	0.010	0.016	0.019	0.012	0.017	0.208		
		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
	0:59	6:59 AM	S 1	0.026	0.043	0.029	0.024	0.011	0.005	0.022	0.020	0.034	0.030	0.017	0.013	0.010	0.016	0.307
			0.024	0.030	0.014	0.013	0.014	0.006	0.017	0.011	0.014	0.012	0.021	0.016	0.008	0.012	0.218	
	M 10		0.023	0.029	0.015	0.017	0.0091	0.006	0.051	0.012	0.015	0.012	0.016	0.016	0.009	0.018	0.255	
			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	B 18		0.027	0.030	0.013	0.013	0.009	0.006	0.037	0.008	0.016	0.013	0.016	0.012	0.010	0.010	0.225	
			0.022	0.029	0.014	0.009	0.009	0.005	0.025	0.009	0.017	0.014	0.019	0.011	0.011	0.012	0.210	
	7:43	1:43 AM	S 2	0.022	0.030	0.015	0.010	0.011	0.005	0.010	0.011	0.014	0.010	0.018	0.015	0.009	0.013	0.199
			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
M 12	0.024		0.031	0.020	0.016	0.009	0.005	0.012	0.009	0.033	0.029	0.018	0.026	0.012	0.026	0.274		
	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
B17	0.024		0.031	0.015	0.014	0.009	0.005	0.026	0.010	0.022	0.019	0.015	0.013	0.014	0.011	0.232		
	ND		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	
13:33	7:33 AM	S 2	0.028	0.036	0.021	0.045	0.013	0.009	0.026	0.023	0.021	0.0188	0.017	0.015	0.013	0.023	0.315	
		0.024	0.032	0.016	0.025	0.011	0.005	0.009	0.008	0.016	0.022	0.021	0.017	0.011	0.015	0.239		
M 10		0.030	0.035	0.012	0.022	0.018	0.010	0.018	0.025	0.040	0.016	0.015	0.018	0.013	0.012	0.289		
		0.024	0.030	0.016	0.017	0.014	0.009	0.020	0.019	0.032	0.018	0.014	0.014	0.011	0.010	0.255		
B 17		0.026	0.030	0.022	0.011	0.011	0.004	0.031	0.015	0.021	0.0186	0.032	0.015	0.011	0.011	0.266		
		0.023	0.037	0.022	0.009	0.012	0.004	0.010	0.008	0.023	0.019	0.028	0.015	0.009	0.011	0.237		
18:58	1:58 PM	S 2	0.024	0.035	0.019	0.010	0.011	0.003	0.060	0.008	0.030	0.027	0.038	0.016	0.011	0.013	0.310	
		0.023	0.029	0.014	0.009	0.010	0.004	0.047	0.010	0.028	0.018	0.031	0.014	0.014	0.010	0.269		
M 13		0.023	0.029	0.015	0.008	0.012	0.005	0.007	0.013	0.015	0.011	0.021	0.014	0.010	0.012	0.201		

				0.027	0.040	0.029	0.009	0.016	0.048	0.011	0.0331	0.011	0.0721	0.014	0.042	0.058	0.039	0.453
			B 20	0.022	0.048	0.022	0.010	0.022	0.008	0.007	0.021	0.031	0.0284	0.016	0.016	0.013	0.011	0.280
				0.022	0.031	0.015	0.009	0.019	0.007	0.008	0.019	0.028	0.031	0.013	0.015	0.014	0.010	0.247
Spring 8C	5:28	11:28 PM	S 2	0.023	0.032	0.014	0.010	0.011	0.003	0.007	0.009	0.014	0.011	0.015	0.016	0.011	0.022	0.204
				0.024	0.031	0.019	0.026	0.024	0.005	0.010	0.016	0.012	0.021	0.018	0.013	0.012	0.010	0.245
			M 15	0.022	0.032	0.019	0.029	0.019	0.004	0.007	0.012	0.018	0.015	0.013	0.025	0.027	0.011	0.260
				0.020	0.043	0.018	0.026	0.020	0.008	0.011	0.015	0.017	0.014	0.017	0.017	0.034	0.013	0.277
			B 18	0.029	0.034	0.024	0.021	0.010	0.007	0.018	0.008	0.022	0.014	0.024	0.013	0.011	0.010	0.251
				0.024	0.032	0.051	0.030	0.017	0.008	0.016	0.008	0.016	0.035	0.025	0.018	0.013	0.014	0.314
	11:31	5:31 AM	S 5	0.025	0.030	0.026	0.031	0.008	0.009	0.022	0.012	0.022	0.019	0.016	0.015	0.012	0.020	0.272
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			M 13	0.024	0.036	0.021	0.009	0.014	0.007	0.013	0.013	0.019	0.017	0.023	0.017	0.012	0.012	0.243
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			B 18	0.026	0.033	0.046	0.017	0.012	0.005	0.028	0.009	0.041	0.008	0.016	0.016	0.011	0.011	0.285
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	16:31	10:31 AM	S 2	0.030	0.033	0.0441	0.024	0.012	0.011	0.035	0.019	0.010	0.037	0.016	0.021	0.021	0.012	0.330
				0.028	0.030	0.017	0.028	0.011	0.005	0.038	0.020	0.029	0.034	0.025	0.019	0.010	0.018	0.317
			M 9	0.027	0.039	0.027	0.024	0.013	0.016	0.075	0.012	0.022	0.039	0.018	0.013	0.010	0.026	0.366
				0.030	0.034	0.038	0.062	0.015	0.014	0.081	0.011	0.013	0.037	0.018	0.015	0.014	0.018	0.406
			B18	0.028	0.032	0.064	0.034	0.012	0.005	0.023	0.010	0.024	0.020	0.016	0.019	0.011	0.024	0.327
				0.025	0.030	0.027	0.014	0.009	0.006	0.013	0.009	0.019	0.016	0.018	0.014	0.013	0.023	0.240
	23:32	5:32 PM	S 2	0.025	0.032	0.016	0.015	0.009	0.003	0.025	0.009	0.011	0.008	0.019	0.018	0.009	0.025	0.230
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			M 9	0.023	0.029	0.025	0.010	0.013	0.004	0.039	0.008	0.020	0.022	0.031	0.019	0.011	0.017	0.277
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			B 18	0.027	0.029	0.016	0.029	0.010	0.005	0.018	0.008	0.012	0.007	0.018	0.014	0.008	0.011	0.219
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	5:02	11:02 PM	S 2	0.069	0.033	0.035	0.176	0.010	0.036	0.073	0.024	0.012	0.047	0.014	0.013	0.031	0.023	0.604
				0.026	0.029	0.032	0.019	0.019	0.006	0.014	0.017	0.0102	0.022	0.015	0.014	0.013	0.011	0.253
			M 9	0.024	0.029	0.013	0.016	0.010	0.004	0.054	0.011	0.012	0.009	0.020	0.018	0.010	0.020	0.257
				0.025	0.030	0.028	0.025	0.011	0.007	0.008	0.019	0.011	0.034	0.019	0.025	0.021	0.015	0.286

			B 18	0.026	0.029	0.017	0.009	0.012	0.008	0.012	0.013	0.021	0.013	0.023	0.016	0.008	0.012	0.227
				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Summer AB5	12:00	7:00 AM	S 3	0.036	0.027	0.016	0.012	0.010	0.006	0.035	0.011	0.019	0.026	0.032	0.025	0.017	0.016	0.294
				0.029	0.029	0.015	0.014	0.012	0.008	0.038	0.012	0.016	0.023	0.030	0.030	0.015	0.012	0.290
			M 12	0.021	0.030	0.015	0.024	0.009	0.006	0.015	0.013	0.015	0.016	0.023	0.022	0.010	0.015	0.242
				0.024	0.027	0.016	0.027	0.009	0.007	0.013	0.014	0.014	0.014	0.025	0.027	0.011	0.013	0.249
			B 18	0.021	0.028	0.014	0.019	0.012	0.006	0.012	0.016	0.025	0.024	0.029	0.018	0.012	0.020	0.262
				0.019	0.030	0.013	0.017	0.011	0.005	0.011	0.018	0.028	0.028	0.033	0.021	0.013	0.021	0.275
	17:30	12:30 PM	S 3	0.094	0.070	0.040	0.021	0.017	0.008	0.011	0.037	0.010	0.060	0.041	0.054	0.057	0.048	0.574
				0.089	0.064	0.050	0.019	0.016	0.007	0.013	0.042	0.011	0.082	0.039	0.063	0.048	0.040	0.589
			M 10	0.085	0.063	0.0436	0.027	0.014	0.009	0.012	0.040	0.011	0.070	0.037	0.045	0.054	0.045	0.562
				0.076	0.058	0.048	0.023	0.015	0.008	0.011	0.044	0.012	0.080	0.035	0.053	0.056	0.042	0.568
			B 18	0.107	0.055	0.058	0.030	0.015	0.010	0.010	0.039	0.012	0.061	0.040	0.046	0.055	0.047	0.591
				0.101	0.073	0.042	0.027	0.017	0.010	0.014	0.043	0.014	0.071	0.048	0.053	0.067	0.0509	0.635
23:30	6:30 PM	S 3	0.034	0.034	0.021	0.036	0.018	0.009	0.016	0.053	0.020	0.043	0.051	0.054	0.072	0.0256	0.4926	
			0.021	0.027	0.011	0.021	0.012	0.007	0.014	0.410	0.013	0.041	0.045	0.042	0.069	0.0160	0.755	
		M 5	0.019	0.029	0.010	0.013	0.009	0.004	0.006	0.012	0.011	0.008	0.017	0.014	0.011	0.0148	0.183	
			0.026	0.031	0.016	0.021	0.015	0.008	0.012	0.022	0.012	0.009	0.014	0.010	0.008	0.0144	0.224	
		B18	0.022	0.030	0.013	0.009	0.010	0.005	0.011	0.018	0.013	0.009	0.015	0.014	0.013	0.0066	0.194	
			0.024	0.029	0.012	0.017	0.008	0.012	0.007	0.015	0.020	0.007	0.015	0.009	0.007	0.008	0.196	
5:45	12:45 AM	S 3	0.021	0.029	0.017	0.026	0.009	0.016	0.009	0.015	0.012	0.012	0.021	0.009	0.007	0.022	0.232	
			0.025	0.026	0.013	0.031	0.008	0.012	0.009	0.016	0.013	0.011	0.020	0.013	0.012	0.008	0.2244	
		M 12	0.021	0.027	0.013	0.025	0.008	0.011	0.012	0.012	0.013	0.010	0.019	0.009	0.007	0.011	0.205	
			0.020	0.026	0.014	0.024	0.010	0.010	0.011	0.013	0.015	0.006	0.019	0.012	0.010	0.006	0.202	
		B 18	0.024	0.029	0.014	0.018	0.010	0.005	0.009	0.013	0.020	0.005	0.023	0.009	0.007	0.017	0.209	
			0.020	0.028	0.013	0.012	0.009	0.004	0.009	0.018	0.011	0.009	0.017	0.009	0.007	0.019	0.190	
Summer 10B	17:30	12:30 PM	S 2	0.021	0.028	0.014	0.011	0.013	0.005	0.007	0.010	0.011	0.011	0.018	0.009	0.018	0.021	0.203
				0.021	0.033	0.017	0.013	0.012	0.019	0.009	0.032	0.012	0.009	0.016	0.013	0.006	0.008	0.225
			M 6	0.034	0.033	0.017	0.009	0.010	0.005	0.009	0.027	0.015	0.012	0.019	0.009	0.007	0.019	0.231
				0.020	0.028	0.010	0.010	0.009	0.003	0.009	0.011	0.015	0.007	0.025	0.009	0.007	0.021	0.191
			B 20	0.026	0.026	0.013	0.025	0.008	0.013	0.015	0.013	0.020	0.016	0.026	0.010	0.008	0.020	0.2463
				0.020	0.028	0.013	0.012	0.009	0.004	0.009	0.018	0.011	0.009	0.017	0.009	0.007	0.019	0.190

			0.021	0.027	0.010	0.010	0.009	0.005	0.017	0.012	0.015	0.008	0.020	0.009	0.007	0.020	0.196	
	23:30	6:30 PM	S 3	0.019	0.027	0.011	0.009	0.009	0.003	0.042	0.024	0.016	0.010	0.019	0.010	0.007	0.021	0.232
				0.018	0.032	0.010	0.010	0.008	0.005	0.005	0.009	0.011	0.064	0.013	0.009	0.007	0.018	0.226
			M 9	0.020	0.027	0.010	0.009	0.010	0.005	0.016	0.008	0.019	0.006	0.021	0.009	0.006	0.018	0.189
				0.019	0.026	0.010	0.011	0.011	0.005	0.069	0.010	0.014	0.011	0.020	0.015	0.014	0.012	0.254
			B 20	0.018	0.027	0.011	0.012	0.009	0.003	0.010	0.015	0.013	0.007	0.016	0.010	0.007	0.0155	0.181
				0.020	0.029	0.012	0.018	0.010	0.007	0.017	0.028	0.013	0.012	0.019	0.010	0.007	0.0147	0.220
	5:30	12:30 AM	S 3	0.023	0.027	0.011	0.019	0.013	0.011	0.012	0.008	0.006	0.004	0.018	0.033	0.041	0.0221	0.252
				0.038	0.046	0.033	0.058	0.017	0.012	0.060	0.011	0.014	0.008	0.017	0.025	0.034	0.016	0.395
			M 12	0.020	0.027	0.013	0.012	0.011	0.006	0.006	0.008	0.013	0.010	0.016	0.022	0.023	0.0114	0.205
				0.018	0.027	0.011	0.009	0.016	0.003	0.010	0.012	0.012	0.009	0.024	0.018	0.018	0.016	0.208
			B 20	0.023	0.027	0.012	0.013	0.010	0.004	0.013	0.008	0.015	0.011	0.017	0.009	0.007	0.0189	0.192
				0.018	0.029	0.013	0.011	0.030	0.002	0.050	0.013	0.012	0.009	0.017	0.018	0.018	0.011	0.258
	11:30	6:30 AM	S 2	0.018	0.027	0.011	0.011	0.008	0.003	0.005	0.009	0.016	0.006	0.016	0.017	0.036	0.024	0.214
				0.019	0.030	0.025	0.022	0.009	0.004	0.005	0.011	0.012	0.004	0.015	0.021	0.015	0.010	0.209
			M 6	0.019	0.027	0.011	0.010	0.015	0.004	0.070	0.009	0.012	0.009	0.020	0.017	0.017	0.016	0.262
				0.018	0.029	0.012	0.008	0.011	0.006	0.017	0.008	0.016	0.006	0.032	0.027	0.010	0.039	0.245
			B 20	0.025	0.030	0.014	0.010	0.012	0.0071	0.020	0.008	0.014	0.006	0.015	0.019	0.038	0.025	0.249
				0.024	0.027	0.011	0.012	0.008	0.006	0.017	0.009	0.032	0.019	0.026	0.022	0.072	0.035	0.324
	17:30	12:30 PM	S 3	0.018	0.027	0.033	0.019	0.022	0.026	0.062	0.012	0.014	0.014	0.015	0.036	0.039	0.020	0.363
				0.018	0.030	0.035	0.023	0.031	0.028	0.051	0.012	0.022	0.012	0.023	0.037	0.041	0.029	0.397
			M 6	0.034	0.028	0.011	0.011	0.011	0.0061	0.013	0.023	0.033	0.024	0.031	0.025	0.017	0.032	0.305
				0.058	0.038	0.029	0.025	0.009	0.005	0.021	0.011	0.033	0.010	0.016	0.026	0.024	0.027	0.339
			B 20	0.020	0.029	0.013	0.006	0.015	0.005	0.010	0.011	0.016	0.017	0.013	0.017	0.017	0.030	0.223
				0.021	0.032	0.016	0.006	0.011	0.005	0.007	0.009	0.020	0.021	0.017	0.023	0.017	0.034	0.245
Summer 8C	5:30	12:30 AM	S 4	0.019	0.030	0.013	0.006	0.011	0.010	0.006	0.008	0.011	0.017	0.015	0.027	0.029	0.029	0.237
				0.018	0.039	0.024	0.006	0.013	0.027	0.011	0.009	0.019	0.024	0.014	0.028	0.023	0.035	0.297
			M 8	0.019	0.031	0.016	0.010	0.016	0.032	0.014	0.015	0.010	0.013	0.013	0.024	0.015	0.269	0.500
				0.021	0.031	0.015	0.011	0.013	0.034	0.013	0.014	0.008	0.015	0.014	0.021	0.011	0.030	0.257
			B 18	0.018	0.030	0.024	0.026	0.014	0.016	0.011	0.012	0.012	0.017	0.014	0.020	0.017	0.030	0.267
				0.019	0.0301	0.034	0.029	0.012	0.014	0.009	0.015	0.010	0.018	0.016	0.013	0.012	0.022	0.259

11:30	6:30 AM	S 2	0.026	0.027	0.019	0.025	0.018	0.006	0.007	0.017	0.015	0.012	0.016	0.014	0.014	0.011	0.234
			0.019	0.030	0.013	0.011	0.013	0.007	0.007	0.011	0.013	0.010	0.021	0.012	0.022	0.013	0.211
		M 8	0.043	0.028	0.015	0.021	0.017	0.008	0.008	0.015	0.017	0.014	0.017	0.013	0.014	0.013	0.2473
			0.023	0.028	0.014	0.012	0.015	0.009	0.008	0.013	0.011	0.009	0.015	0.012	0.017	0.013	0.204
		B 18	0.020	0.029	0.026	0.017	0.011	0.005	0.007	0.012	0.011	0.008	0.017	0.013	0.016	0.012	0.210
			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
17:30	12:30 PM	S 4	0.019	0.027	0.012	0.012	0.012	0.003	0.025	0.009	0.016	0.011	0.022	0.015	0.008	0.013	0.210
			0.019	0.026	0.011	0.009	0.010	0.003	0.032	0.011	0.013	0.010	0.024	0.015	0.007	0.015	0.210
		M 8	0.021	0.027	0.012	0.012	0.012	0.004	0.018	0.012	0.010	0.009	0.017	0.013	0.006	0.017	0.197
			ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		B 18	0.018	0.028	0.013	0.013	0.013	0.006	0.011	0.010	0.011	0.014	0.014	0.013	0.007	0.012	0.189
			0.023	0.027	0.012	0.012	0.012	0.003	0.013	0.010	0.013	0.013	0.025	0.015	0.008	0.014	0.203
11:30	6:30 PM	S 5	0.018	0.028	0.013	0.008	0.010	0.003	0.006	0.009	0.014	0.015	0.019	0.014	0.007	0.010	0.181
			0.018	0.027	0.012	0.006	0.008	0.003	0.008	0.006	0.009	0.022	0.014	0.015	0.006	0.010	0.171
		M 10	0.032	0.029	0.012	0.026	0.012	0.006	0.005	0.012	0.023	0.025	0.038	0.015	0.015	0.008	0.264
			0.025	0.027	0.011	0.019	0.024	0.004	0.006	0.016	0.012	0.016	0.033	0.012	0.012	0.008	0.231
		B 18	0.024	0.028	0.012	0.010	0.011	0.003	0.008	0.010	0.012	0.019	0.031	0.013	0.016	0.008	0.210
			0.020	0.030	0.012	0.013	0.013	0.003	0.015	0.011	0.015	0.012	0.018	0.013	0.017	0.011	0.209
5:30	12:30 AM	S 3	0.055	0.035	0.023	0.010	0.016	0.005	0.017	0.012	0.011	0.007	0.017	0.022	0.017	0.020	0.271
			0.041	0.038	0.028	0.025	0.018	0.004	0.015	0.012	0.011	0.007	0.013	0.012	0.017	0.016	0.263
		M 8	0.034	0.034	0.013	0.116	0.089	0.017	0.041	0.013	0.013	0.021	0.018	0.017	0.014	0.022	0.468
			0.031	0.033	0.018	0.114	0.098	0.019	0.032	0.013	0.013	0.023	0.022	0.014	0.016	0.024	0.475
		B 18	0.030	0.034	0.015	0.009	0.085	0.023	0.024	0.011	0.012	0.021	0.033	0.014	0.014	0.018	0.350
			0.022	0.031	0.013	0.010	0.053	0.018	0.021	0.021	0.017	0.012	0.020	0.012	0.010	0.017	0.283

VITA

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