Highly variable nutrient concentrations in the northern Gulf of Mexico

Yuley Cardona^{1,5}, Annalisa Bracco^{1*}, Tracy A. Villareal², Ajit Subramaniam³, Sarah C. Weber⁴,
Joseph P. Montoya⁴

¹ School of Earth and Atmospheric Science, Georgia Institute of Technology, Atlanta, GA 30332,
USA

² Marine Science Institute, The University of Texas at Austin, Port Aransas, Texas 78373, USA

³ Lamont Doherty Earth Observatory at Columbia University, Palisades, NY 10964, USA

⁴ School of Biology, Georgia Institute of Technology, Atlanta, GA 30332, USA

⁵ Departamento de Geociencias y Medio Ambiente, Universidad Nacional de Colombia, Sede Medellín,
Colombia

Corresponding Author*: Annalisa Bracco: abracco@gatech.edu Tel: (1) 404-894-1749. Fax: (1)
404-894-5638. 311 Ferst Drive Atlanta, GA 30332-0340.

19
20 **Abstract**
21

22 The distribution of surface nutrients along the salinity gradient in the Mississippi-Atchafalaya River
23 outflow region was examined during four cruises, including two simultaneous cruises, conducted in the
24 northern Gulf during the summer of 2010 and 2011, and in late spring of 2012. The new, extensive data
25 set covers the salinity gradient from 11 to 37 psu (practical salinity unit) in a year of extraordinarily high
26 river discharge (2011), with few samples from a year of average (2010) and below average (2012) river
27 outflow. The overall surface concentrations of nitrate + nitrite, orthophosphate and silicate are compared
28 to those recorded in cruises spanning the 1985 – 2009 interval. Using Monte Carlo simulations to test the
29 statistical significance, we found that surface orthophosphate and nitrate+nitrite concentrations are
30 approximately three and two fold smaller, respectively, in the 2010-2012 period compared to the previous
31 years. Changes in silicate concentrations were, in most cases, not significant, and their assessment
32 complicated by different measurement techniques and potential preservation artifacts. The weighted river
33 loading of these nutrients was, on the other hand, very high in the latest period when samples mostly
34 covered 2011 during which the discharge was particularly high. The well-known negative correlation
35 between nutrient concentrations and salinity at the ocean surface is confirmed in the most recent data. The
36 area surrounding the Mississippi River mouth is characterized by inorganic N:P ratios greater than 30:1
37 that decrease to values typically less than 10:1 at about 100 km from of the mouth. Overall our analysis
38 suggests that surface nutrient concentrations in the northern Gulf of Mexico cannot be described with any
39 good accuracy by a linear model based on river discharge alone.

1. Introduction

The northern Gulf of Mexico (nGOM) is a multifaceted ecosystem whose spatial and temporal variability is driven by the interaction of large (scale of 100km) and small (scale of 1km) circulation processes (Cardona and Bracco, 2014) with the quantity and composition of river discharge. The Loop Current (LC) enters the Gulf between Cuba and the Yucatan peninsula and contributes waters of Atlantic origin with relatively low salinity and nutrients. At irregular intervals of several months, the LC sheds large anticyclonic eddies (~200 km in diameter) that in turn are often surrounded by smaller vortices, both cyclonic and anticyclonic, and intense vorticity filaments. The juxtaposition of mesoscale eddies and filaments in waters with very different densities contributes to frontal and baroclinic instabilities and to the formation of submesoscale (100 m – 10 km) convergence zones where nutrients can further accumulate (Toner et al., 2003; Zhong et al., 2012; Zhong and Bracco, 2013). In late spring and summer the generation of those submesoscale fronts is amplified by the freshwater river input that fuels the density gradients in turn required for frontogenesis to take place, despite the shallow mixed layer (Luo et al., 2016). Numerical simulations have shown that if the river discharge is small or null, the formation of submesoscale fronts is inhibited.

The river discharge to the nGOM is dominated by the Mississippi-Atchafalaya River system. This river complex represents 80% of the annual freshwater input, 90% of the total nitrogen load (mainly of agricultural origin) and 87% of the total phosphorous load to the basin (Dunn, 1996). Nitrogen fixation also provides an input of N (Mulholland et al., 2006, 2014; Lenex et al., 2010; Dorado et al., 2012). The nutrient load supports high biological activity and, when in excess, contributes to eutrophication and hypoxia (Rabalais et al., 1996; Bianchi et al., 2010). The seasonal cycle of the river system is generally characterized by greatest discharge in spring and lowest in fall. However there is a very high interannual variability in the volume and timing of the maximal discharge (Jochens, et al. 2002).

The distribution of nutrients in the Gulf is the result of a dynamic system where nutrients are continuously added by the rivers and removed by biological interactions (Dagg and Breed, 2003). The relationships between irradiance, chlorophyll, nutrients, and salinity in the vicinity of the Mississippi mouth have been evaluated in a series of papers over the last two decades (Hitchcock et al., 1997; Lohrenz et al., 1990, 1997, 1999; Wysocki et al., 2006) using measurements collected from 1988 to 1993 and in 2000. The highest rates of primary production occur at intermediate salinities, and nutrient concentrations decrease non-conservatively along the salinity gradient of the river plume. In these studies, primary production was limited by low irradiance in the most turbid region of the plume and by low nutrient availability outside the plume in waters with salinity around or higher than 30 psu. The influence of the fresh water input on surface chlorophyll-a (chl-a) and nutrient concentrations was confirmed in the northeastern Gulf of Mexico by Qian et al. (2003) and in the Louisiana-Texas (LATEX) shelf by Chen et al. (2000), where elevated nutrient concentrations were noted along the inner shelf due to low salinity flow along the coast. The Mississippi River System nutrient loading has undergone long-term changes. Turner and Rabalais (1991) noted that from the 1950s to the 1980s dissolved inorganic nutrients and total phosphorus increased 3 and 2 fold respectively, while Si concentration decreased by ~ 50%. Nitrogen rather than phosphorus limits phytoplankton growth in this system and nitrate in particular is the main contributor to the augmented nitrogen loading (Turner et al., 2006). Such increase has been linked to increased fertilizer use (Turner and Rabalais, 1991), increased streamflow following changes in annual precipitation (Donner and Scavia, 2007; Raymond et al., 2008), and variability in groundwater concentrations (Kolker et al., 2013). Most of the recorded changes occurred in the 1970s to the early 1980s (Goolsby and Battaglin, 2001) with a stabilization or even small decrease of phosphorus and silicate levels after 1983, following the national effort to reduce P eutrophication. Despite a reduction in total Kjeldahl nitrogen in domestic and industrial wastewater (Turner et al., 2007), the flow-normalized rate of nitrate leaving the Mississippi River may have increased in recent years by approximately 9% (Sprague et al., 2011) due to increasing groundwater concentrations. The northern Gulf marine ecosystem is also likely to vary on interannual to decadal time scales. For example, Parsons et al. (2002) analyzed

the abundant diatom *Pseudo-nitzschia* using cores and live counts and noted evidence of an eutrophication-linked increase in this harmful algal taxon. To further complicate our understanding of the mechanisms controlling nutrient distribution and primary production in the northern Gulf, the *Deepwater Horizon* spill in 2010 injected unprecedented amounts of hydrocarbons in the deep waters (Camilli et al. 2010; Diercks et al. 2010; Joye et al., 2011), modifying the microbial community structure of the region (Kessler et al., 2011; Valentine et al., 2010, 2012; Crespo-Medina et al., 2014).

[Figure 1 here]

Figure 1. MODIS ocean chlorophyll maps (left) and AVISO surface heights (right). The AVISO data was computed with respect to a twenty-year mean. (a-b) 2010, (c-d) 2011 and (e-f) 2012 cruise periods averages. Stations are marked as black dots.

Here we revisit the characterization of nutrient distributions in the northern Gulf of Mexico using new data from four cruises that occurred in the summer of 2010, in the summer of 2011 (two simultaneous cruises) and in late spring of 2012. Furthermore, we assess the hypothesis that near-surface nutrient concentrations in the Gulf in those years and in particular in 2011, for which we have the largest number of measurements, differ from the previous 25 years by comparing them with a large data set compiled from cruises spanning the 1985-2009 interval.

2. Data Description

In this study we analyze *in-situ* surface nutrients collected in the northern Gulf of Mexico during the spring or summer seasons of 2010, 2011, and 2012, and we contrast them with surface data from previous field campaigns that occurred between July 1985 and November 2009. We focus mostly on 2011 data given that they represent approximately 90% of the samples.

Our cruises took place over August 22 – September 15, 2010 (R/V *Oceanus*, OC468), July 3 – July 26, 2011 (R/V *Endeavor*, EN496 and R/V *Cape Hatteras*, CH0711), and May 19 – June 19, 2012 (R/V *Endeavor*, EN509), under normal (2010), below normal (2012) and very high river discharge conditions

(2011; Table 1). The 2011-2012 campaigns focused on the waters along the Mississippi-Atchafalaya River plume salinity gradients and the associated chlorophyll field (0), as did several previous studies (see below). Samples were collected along the offshore salinity gradient associated with the river plumes, identified using maps of MODIS ocean chlorophyll. For the majority of stations, salinities were around or greater than 26 psu. In 2010, the sampling strategy was modified to accommodate collections around the *Deepwater Horizon*/Macondo site and along the direction of propagation of oxygen anomalies due to the bacterial degradation of deep hydrocarbon plumes (Camilli et al. 2010; Diercks et al. 2010; Joye et al., 2011). It is worth noting that in August 2010 the river flow was diverted to prevent oil bleaching from the spill and that northwesterlies pushed the nutrient rich freshwaters eastward and offshore (O'Connor et al., 2016) towards our sampling area. In 2011 we covered the near-surface waters above the Louisiana-Texas (LATEX) shelf, the Sigsbee escarpment, the Mississippi Shelf, Desoto Canyon, the Mississippi Fan, and the West Florida escarpment (0a) collecting 709 surface sea water samples. Additionally, 32 stations were sampled in 2010 and 43 in 2012. Nitrate + nitrite (NO_3^- and NO_2^-), orthophosphate (PO_4^{3-}), and silica (SiO_2) concentrations were measured at each site. In all cruises but CH-0711 a SBE 32 carousel water sampler containing 24 ten-liter Niskin bottles was used to collect the seawater not only near the surface but also at depths ranging from the surface to ~3200 m. During CH0711 nutrient samples were collected from the underway system of the R.V. *Cape Hatteras*; seawater was sampled through a silicone tube attached to the flowing seawater system and used to rinse the sample vials three times. Vials were capped and refrigerated until analyzed (<5 hours). Nutrient concentrations were measured at sea using a SEAL QuAAtro SFA Analyzer or a Lachat QuikChem 8000 flow injection analysis system using the manufacturer's recommended chemistries as soon as possible after samples were collected. The samples were filtered when the Chl-a values were higher than 5 μg per L based on the fluorescence measurements in the CTD trace. The choice of such a threshold closely corresponded to a step function separating low chlorophyll offshore waters from inshore samples. When samples could not be analyzed directly after sampling, they were stored at 4°C for no longer than 30 hours (Knapke, 2012). Detection limits for nitrate/nitrite, phosphate, and silicate were 0.05, 0.05, and 0.5 $\mu\text{mol L}^{-1}$, respectively. Along with the

seawater sampling, hydrographic data were acquired using a Sea-Bird Electronics, Inc. SBE 21 flow through TSG system equipped with conductivity, temperature, and fluorescence sensors and a CTD (SBE 911) equipped with conductivity, temperature, fluorescence, beam transmittance, and pressure sensors.

Surface nutrient data ($\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} , SiO_2) from past cruises covering the period July 1985 – November 2009 were downloaded from the National Oceanographic Data Center (NODC) (<http://www.nodc.noaa.gov/>). They include a total of 3,107 samples collected in the upper 5 m of the water column as part of the Nutrient Enhanced Coastal Ocean Productivity (NECOP) program (1985-1987) (<http://www.aoml.noaa.gov/ocd/necop/>), the Louisiana/Texas Physical Oceanography (LATEX) Program (1993- 1994) (Berger, 1996), the Northeastern Gulf of Mexico (NEGOM) project (1997 - 2000) (<http://seawater.tamu.edu/negom/>), the Louisiana Hypoxia Surveys (1998 – 2001), the Deepwater Program: Northern Gulf of Mexico Continental Slope Habitat and Benthic Ecology (2000-2002) (Rowe and Kennicutt, 2009), the Mechanisms Controlling Hypoxia on the Louisiana Shelf project (2004-2009) (<http://fram.tamu.edu/~stevendimarco/MCH/site/>), and the Gulf of Mexico and East Coast Carbon Cruise (GOMECC) (2007) (<http://www.aoml.noaa.gov/ocd/gcc/GOMECC1/>). We focused on campaigns sampling at least some locations where the water column was deeper than 100 m and salinity ranges comparable to ours, and measuring all nutrient concentrations of interest. After 2000, all but two of the available samples were located west of the Mississippi river mouth, and fewer than twenty were collected beyond the continental shelf (0b).

In the northern Gulf, the interannual variability of both physical and biological distributions greatly surpasses the seasonal signal (Jochens et al., 2002), as suggested by Figure 3, where the monthly river discharge is plotted in all the years for which nutrient data are used in the subsequent analysis. Cruise months are indicated by dots. This is due to an energetic and highly variable mesoscale circulation (e.g. Cardona and Bracco, 2014), to large interannual changes in the wind field despite a definite climatological seasonal cycle, and to a highly variable discharge from the river system. The river loading

is characterized, on average, by a spring peak and a fall minimum, but the intensity and timing of both minima and maxima vary greatly from year to year. The river discharge in 2011 was the strongest within the years considered and peaked late in the spring season. The aggregated streamflow and nutrient loading delivered to the Gulf of Mexico by the Mississippi-Atchafalaya River Basin are estimated by the USGS. The nutrient fluxes are derived using the Adjusted Maximum Likelihood Estimation (AMLE) method using the LOADEST program (Aulenbach et al., 2007) and are based on data collected at sampling stations near St. Francisville, LA, Tarbert Landing, MS, Melville, LA, and stream discharge from the station at Simmesport, LA. The load estimation for the nutrient fluxes associated with the Mississippi River accounts also for the flow diverted to the Atchafalaya River via the Old River Outflow Channel as measured at Knox Landing, and for data from two upstream stations, the Mississippi River at Thebes, IL, and the Ohio River at Metropolis, IL. Flux estimates on a monthly time-step can be quite inaccurate; therefore we averaged over each cruise month and over the month prior to the cruise (whenever samples were collected over two contiguous months, as in 2010 and 2012 campaigns, we considered averages over those months). Using loads only for cruise month or the average for the cruise month and one or two prior months contributes no more than 8% to the overall difference between the pre-2009 and post-2009 means. Using loads only from one or two months prior to the cruise enhances the differences in nutrient utilization between 2011 and the previous period by approximately 15%.

[Figure 2 here]

Figure 2. Top: Sampling locations during the 2010, 2011, and 2012 spring or summer cruises. Bottom: Sampling locations in the period 1985-2009.

[Figure 3 here]

Figure 3. Monthly time series of average Mississippi-Atchafalaya River Basin streamflow from USGS in m³/s during all years for which surface samples have been considered. Black dots indicate cruise timing (see Table 1).

Table 1. Total Mississippi-Atchafalaya River Basin streamflow and nutrient loads delivered to the Gulf of Mexico during sampling periods (from USGS) averaged over cruise month and month prior. Also indicated the month of the river discharge peak for each year considered and the number of near surface samples with salinity above 19 psu available in areas with water column depth ≤ 200 or > 200 m. Means weighted by the number of samples in each month are also indicated for the two periods considered.

Cruise Month	Average discharge (m ³ /s)	NO ₂ +NO ₃ LOADEST AMLE load (metric tons as N)	PO ₄ LOADEST AMLE load (metric tons as P)	SiO ₂ LOADEST AMLE load (metric tons as SiO ₂)	River discharge peak	# samples ≤ 200m	# samples > 200 m
Jul-85	16,000	54,050	3,000	250,000	03	67	0
Jul-86	21,150	107,000	3,975	407,000	06	65	0
Jul-87	16,700	55,100	2,360	250,000		55	0
Jul-93	29,000	149,500	6,830	594,000	05	58	8
Aug-93	29,900	164,000	7,925	728,500	Same Cruise	42	2
Nov-93	22,050	88,100	5,140	521,000		103	12
Nov-97	9,605	20,250	1,755	161,500	03	24	30
May-98	38,950	165,000	5,575	672,500	05	31	29
Jul-98	25,850	120,500	5,435	431,500		0	3
Aug-98	21,500	97,100	5,000	372,000	Same Cruise	30	25
Nov-98	13,950	44,750	3,070	282,500		29	28
May-99	30,350	154,000	5,250	559,500	02	30	25
Aug-99	16,150	82,650	4,635	317,000		37	30
Nov-99	6,620	13,050	1,160	104,700		35	29
Apr-00	22,000	79,100	3,025	321,000	04	31	34
Jul-00	18,550	87,200	4,910	304,000		25	10
Aug-00	15,250	67,700	4,370	253,000	Same cruise	6	18
Nov-03	11,100	23,900	1,790	169,500	03	135	0
Apr-04	25,350	99,200	2,945	416,000	06	139	0
Jun-04	28,650	113,050	4,540	459,000		110	0
Jul-04	28,600	118,500	5,625	501,500	Same cruise	29	0
Aug-04	19,300	73,750	4,335	339,000		122	0
Mar-05	31,900	105,500	3,160	542,000	02	107	0

May-05	22,150	94,550	2,585	351,000		139	0
Jul-05	13,250	59,400	2,205	218,000		135	0
Aug-05	9,700	33,000	1,575	146,050		161	0
Mar-07	23,100	91,100	3,375	376,500	01-05	105	0
Jul-07	17,850	67,150	3,785	324,000		127	6
Nov-07	9,045	24,950	2,140	164,000		126	0
Apr-08	45,550	179,500	6,980	687,500	04	84	0
Jul-08	30,500	144,500	7,770	584,500		127	0
Apr-09	27,100	137,500	4,590	477,000	05	80	4
Jul-09	27,900	99,750	5,785	450,500		65	0
Weight ed MEAN	21,290	86,294	3,843	371,654		% samples 89	% samples 11
Sep-10	16,050	49,150	4,255	334,500	02	3	29
Jul-11	33,400	141,000	7,330	678,500	05	252	437
Jun-12	12,740	46,450	2,635	211,000	02	3	38
Weight ed MEAN	31,556	132,036	6,947	638,807		% samples 34	% samples 66

3. Surface nutrient distributions

As described above, our measurements cover the area extending from the Mississippi mouth towards the southeast, the LATEX shelf, and the Sigsbee escarpment. The variability of nutrient concentrations in the northern Gulf of Mexico and the relation between nutrients and river discharge have been previously analyzed in the close proximity of the Mississippi mouth by Hitchcock et al. (1997), Lohrenz et al. (1990; 1999; 2008), and Wysocki, et al. (2006), in the LATEX shelf by Chen et al. (2000), and in the broad northeastern Gulf by Qian et al. (2003). These works focus on the relationships between salinity and nutrients and describe them as nonlinear and not monotonic due to spatial variability in rates of biological activity. Overall, the pre-2009 data show an inverse relationship between salinity and nutrients for all nutrients (Figure 4, left column). Best fits obtained from the least square fit are exponential for $\text{NO}_3^- + \text{NO}_2^-$, linear for PO_4^{3-} , and logarithmic for SiO_2 but with very small coefficients of determination for the first two ($r^2 = 0.19$ and 0.11 for nitrate+nitrite and orthophosphate, respectively) and only a modest coefficient of determination for Si ($r^2=0.38$).

The corresponding fits for the samples collected in 2010-2012 are presented in the right column of Figure 4. As previously mentioned, the sample size is much greater in 2011, and the extension and magnitude of the river plume in that year allowed us to span a wider gradient of surface salinities (11 to 37 psu) than in 2010 or 2012. In all Monte Carlo simulations presented below the outcome and significance level are unchanged if only 2011 data are considered, while the significance cannot not be recovered if we consider only 2010 and 2012 data due to limited sampling size. The relationship between $\text{NO}_3^- + \text{NO}_2^-$ and salinity in our data again is best described by an exponential function, but steeper, and the goodness of the fit is higher ($r^2=0.41$). A power law describes the distribution of phosphate versus salinity best, and explains about 35% of the variance in the data set. Finally, silica concentrations are distributed according to an exponential fit ($r^2=0.66$).

3.1 Monte Carlo Simulations

The above fits are suggestive of changes between the pre- and post-2009 distributions. The mean nutrient loading associated with the river system, weighted by the number of samples in each cruise, was greater in the later period (see Weighted MEAN rows in Table 1). The fits support lesser nutrient concentrations in our samples but differences in the density of data per salinity regime and in the sampling strategies prevent us from establishing with confidence if nutrient distributions in the northern Gulf were statistically significantly different in 2011 (or 2010-2012) compared to the 1990's and 2000's. We therefore adopted a Monte Carlo framework (a general presentation of the advantages of using a Monte Carlo approach to estimate the significance of statistics can be found in Livezey and Chen, 1983 with applications to meteorological data) for evaluating the statistical probability that our data reflect changes between these two time frames.

To account for the sparseness of the samples available in both time and space, we organized the pre- and post-2009 data sets in salinity classes with 2 psu increments. We first considered all data, independent of the sampling locations and cruise time. 94% of our samples are confined to salinities between 19 and 37

psu, and we focus on this range to avoid having classes with fewer than ten samples. For each class i ($i=1,9$) we considered the number of samples available in the pre- and post- data sets, selected the smallest, n_i , and randomly extracted n_i samples from the other distribution 10,000 times to build a Monte Carlo experiment. Then, we repeated the Monte Carlo simulations by randomly extracting for each salinity class and each distribution a number of samples equal to 80%, 70%, and 60% of n_i , to build an additional 10,000 x 2 populations. By doing so, we aimed at limiting the role of possible outliers and at reducing the chances of the analysis being dominated by sampling differences in a specific subset of data.

[Figure 4 here]

Figure 4. Surface nutrient and salinity distribution for nitrite and nitrate, phosphate, and silicate (Top to bottom). Left: Period 1985-2009 and right: period 2010-2012. See 0 for color coding.

Finally, for each Monte Carlo experiment, we quantified whether the two populations ($\bar{X}_1$, $\bar{X}_2$) differed by computing Z according to equation (1), where μ_1 and μ_2 are the mean and σ_1 and σ_2 the variances of ($\bar{X}_1$, $\bar{X}_2$), and by comparing Z with the desired critical value obtained for two-sample two-tailed t-tests with significance levels $\alpha=0.005$ (99.5%) and $\alpha=0.05$ (95%).

$$Z = \frac{(\bar{X}_1 - \bar{X}_2) - (\mu_1 - \mu_2)}{\sqrt{\frac{\sigma_1^2}{n} + \frac{\sigma_2^2}{n}}} . \quad (1)$$

The two populations from which we performed random drawing are shown in Figure 5 and displayed an overall similar distribution. The results of the Monte Carlo simulations with 10,000 iterations are listed in Table 2 whenever 80% and 60% of n_i samples in each class are used.

Figure 5. Number of samples per salinity class in each period considered. The 1985-2000 and 2001-2009 periods are shown summed (gray) and separately (black and green).

Table 2: Summary of Monte Carlo experiments comparing samples from waters with salinity > 19 psu

from 1985-2009 and 2010-2012. In all tables Z values indicating a confidence level higher than 99.5%

(95%) are highlighted in yellow (green) and the t-test values for significance levels corresponding to

$\alpha=0.005$ (99.5%) and $\alpha=0.05$ (95%) are indicated in the bottom two rows (see text for details). Units for

all concentrations: μM .

1985-2009 vs 2010-2012	$\sum_{i=1}^9 0.8 \times n_i = 581$			$\sum_{i=1}^9 0.6 \times n_i = 437$		
	Mean	Std	Z	Mean	Std	Z
$\text{NO}_3^- + \text{NO}_2^-$ (1985-2009)	2.44	6.20	4.10	2.42	6.15	3.56
$\text{NO}_3^- + \text{NO}_2^-$ (2010-2012)	1.12	4.64		1.12	4.59	
PO_4^{3-} (1985-2009)	0.26	0.57	5.91	0.26	0.54	5.29
PO_4^{3-} (2010-2012)	0.11	0.20		0.11	0.21	
SiO_2 (1985-2009)	5.18	7.00	-3.28	5.16	6.99	-2.82
SiO_2 (2010-2012)	6.79	9.51		6.74	9.46	
$\alpha=0.005$	t-value= ± 2.82			t-value= ± 2.82		
$\alpha=0.05$	t-value= ± 1.96			t-value= ± 1.97		

We repeated the analysis comparing our samples and the archival collected in 1985-2000 and 2001-2009 separately. Table 3 summarizes the Monte Carlo experiments comparing the older data set with our cruise samples (similar results are obtained using the 2001-2009 data instead). The differences in the populations do not depend on the period considered. A comparison of the 1985-2000 versus 2001-2009 data, on the other hand, does not reveal any statistical significant difference (not shown). Despite the large nutrient loading in 2011, our samples are characterized by lower concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and PO_4^{3-} overall.

Table 3: Same as Table 2 but for samples collected between 1985-2000 and 2010-2012. Units : μM .

1985-2000 vs 2010-2012	$\sum_{i=1}^9 0.8 \times n_i = 529$			$\sum_{i=1}^9 0.6 \times n_i = 399$		
	Mean	Std	Z	Mean	Std	Z
$\text{NO}_3^- + \text{NO}_2^-$ (1985-2000)	3.01	9.17	4.48	3.01	9.17	3.89
$\text{NO}_3^- + \text{NO}_2^-$ (2010-2012)	1.03	4.46		1.03	4.41	
PO_4^{3-} (1985-2000)	0.27	0.57	6.27	0.28	0.57	5.42
PO_4^{3-} (2010-2012)	0.11	0.20		0.11	0.21	
SiO_2 (1985-2000)	5.19	8.85	-2.02	5.18	8.83	-1.75
SiO_2 (2010-2012)	6.31	9.15		6.29	9.13	

$\alpha=0.005$	t-value= ± 2.82	t-value= ± 2.82
$\alpha=0.05$	t-value= ± 1.96	t-value= ± 1.97

We then organized the whole dataset according to the depth of the sampling location in addition to the division in salinity classes, repeating the Monte Carlo analysis for samples taken at locations on the shelf where the depth of the water column does not exceed 200 m, and on the slope and in offshore waters (depth > 200 m) as shown in Figure 6¹. This further classification reduces greatly the number of

¹ Selecting only samples taken at sites where total depth was between 20 and 100 m yields a better match between old and new locations but statistics almost identical to those in Table 4.

observations in each class, especially for the offshore samples, limiting the statistical power of the analysis. Results are summarized in Tables 4 and 5.

[Figure 6 here]

Figure 6 Sample locations for water column depth $m \leq 200$ m (left) and > 200 m (right). 1985-2009 samples in blue, and 2010-2012 samples in red.

Table 4: As in Table 2 but for samples collected at locations where the total depth of the water column is ≤ 200 m. Units: μM .

≤ 200 m	$\sum_{i=1}^9 0.8 \times n_i = 207$			$\sum_{i=1}^9 0.6 \times n_i = 157$		
	Mean	Std	Z	Mean	Std	Z
$\text{NO}_3^- + \text{NO}_2^-$ (1985-2009)	2.98	6.75	2.42	2.97	6.70	2.15
$\text{NO}_3^- + \text{NO}_2^-$ (2010-2012)	1.46	6.04		1.44	5.88	
PO_4^{3-} (1985-2009)	0.30	0.52	4.55	0.31	0.51	3.93
PO_4^{3-} (2010-2012)	0.13	0.22		0.14	0.24	
SiO_2 (1985-2009)	5.86	7.60	-1.45	5.81	7.57	-1.23
SiO_2 (2010-2012)	7.25	11.57		7.16	11.45	
$\alpha=0.005$	t-value= ± 2.84			t-value= ± 2.85		
$\alpha=0.05$	t-value= ± 1.97			t-value= ± 1.98		

Table 5: As in Table 2 but for samples collected where the total depth of the water column is > 200 m.

Units: μM .

> 200 m	$\sum_{i=1}^9 0.8 \times n_i = 162$			$\sum_{i=1}^9 0.6 \times n_i = 123$		
	Mean	Std	Z	Mean	Std	Z
$\text{NO}_3^- + \text{NO}_2^-$ (1985-2009)	0.74	3.38	0.81	0.74	3.26	0.73
$\text{NO}_3^- + \text{NO}_2^-$ (2010-2012)	0.48	2.36		0.48	2.21	
PO_4^{3-} (1985-2009)	0.08	0.23	-0.99	0.09	0.24	-0.79
PO_4^{3-} (2010-2012)	0.11	0.22		0.11	0.23	
SiO_2 (1985-2009)	2.08	2.78	-3.08	2.05	2.73	-2.74

SiO ₂ (2010-2012)	3.39	4.65		3.33	4.40	
------------------------------	------	------	--	------	------	--

$\alpha=0.005$	t-value= ± 2.85	t-value= ± 2.86
$\alpha=0.05$	t-value= ± 1.98	t-value= ± 1.98

Despite the smaller population sizes, that limit the assessments, differences in surface phosphate and nitrate+nitrite remain high and statistically significant in shallow, shelf waters. In samples taken offshore (depth > 200 m), the phosphate means are within instrument detection limits and there is no statistical difference between the two time periods. Nitrate+nitrite concentrations still appear reduced in the most recent data but the null hypothesis that the two populations are statistically identical cannot be rejected. Silica concentrations are higher in the most recent period considered in both ≤ 200 m and >200 m samples, but the difference is significant only for offshore samples.

We further isolated data collected in the same months of our cruises, June to August, from all others in the 1985-2009 period and performed the Monte Carlo analysis without differentiating by depth. Results are shown in Table 6.

Table 6: As in Table 2 but for samples collected during cruises in June, July and August only. Units: μM .

JJA ONLY	$\sum_{i=1}^9 0.8 \times n_i = 553$			$\sum_{i=1}^9 0.6 \times n_i = 416$		
	Mean	Std	Z	Mean	Std	Z
NO ₃ ⁻ + NO ₂ ⁻ (1986-2009)	1.24	3.72	0.34	1.25	3.74	0.32
NO ₃ ⁻ + NO ₂ ⁻ (2010-2012)	1.15	4.64		1.15	4.61	
PO ₄ ³⁻ (1985-2009)	0.23	0.35	7.44	0.24	0.35	6.35
PO ₄ ³⁻ (2010-2012)	0.11	0.20		0.11	0.21	
SiO ₂ (1985-2009)	4.88	6.25	-4.86	4.87	6.25	-4.20
SiO ₂ (2010-2012)	7.30	9.92		7.28	9.91	

$\alpha=0.005$	t-value= ± 2.82	t-value= ± 2.82
$\alpha=0.05$	t-value= ± 1.96	t-value= ± 1.97

Differences in nitrate+nitrite are not significant, indicating that high values in pre-2009 data are mostly associated to winter and spring data, when consumption is likely limited due to lower phytoplankton growth rates. It is worth reminding, however, that the river input of $\text{NO}_3^- + \text{NO}_2^-$ weighted by the sample numbers was far greater in the post-2009 case. The phosphate distribution on the other hand continues to be significantly lower in the most recent dataset compared to previous decades, while silica displays the opposite behavior.

Finally, we isolated all data from the pre-2009 cruises whenever the river loading of $\text{NO}_3^- + \text{NO}_2^-$ averaged over the three months prior to the cruise time was in excess of 110,000 metric tons of N and for which the peak discharge happened two or three months before sampling. By doing so we also selected only late spring and summer data. This smaller dataset constitutes the closest possible analog to the 2011 conditions and contains mostly (> 85%) samples from the LATEX shelf that is therefore chosen as region of interest. We extracted from our 2011 measurements all those comprised between -90°W and -95°W (Fig. 7). Excluding the ten most offshore 2011 samples does not modify the outcome of the Monte Carlo analysis.

[Figure 7 here]

Figure 7. Sample locations over the LATEX shelf characterized by surface salinity greater than 19 psu in late spring or summer during years of elevated river discharge (07/1993, 08/1993, 07/2004, 08/2004, 05/2005, 07/2008, 07/2009) in blue, and in 2011 in red.

The goal of this last Monte Carlo simulation is to cluster and compare samples with nutrient loadings and water age as similar as possible, under the assumption that for a given region in the northern Gulf (the LATEX shelf in this case) the amount of river plume water is to the first order directly proportional to the discharge, and only to a second order to the wind direction and mesoscale variability. Those stringent

criteria force us to eliminate the 19-21 salinity class given that only 2 samples were collected before 2011. Only simulations considering 80% of n_i have been performed due to the paucity of data.

Table 7: Summary of Monte Carlo experiments comparing samples in waters with salinity > 21 psu collected in 2011 and in 07/1993, 08/1993, 07/2004, 08/2004, 05/2005, 07/2008, 07/2009. Units: μM .

LATEX shelf High discharge Spring and summer	$\sum_{i=1}^9 0.8 \times n_i = 172$		
	Mean	Std	Z
$\text{NO}_3^- + \text{NO}_2^-$ (1986-2009)	0.57	1.25	1.23
$\text{NO}_3^- + \text{NO}_2^-$ (2011)	0.39	1.45	
PO_4^{3-} (1993-2009)	0.18	0.26	2.95
PO_4^{3-} (2011)	0.10	0.20	
SiO_2 (1993-2009)	4.27	5.61	2.97
SiO_2 (2011)	2.80	3.27	

$\alpha=0.005$	t-value= ± 2.84
$\alpha=0.05$	t-value= ± 1.97

The decrease in the mean concentrations for surface phosphate in 2011 remain statistically significant and the null hypothesis that the two populations are equal can be rejected with a 99% confidence, while nitrate+nitrite has similar mean molarity of 0.57 ± 1.25 and $0.39 \pm 1.42 \mu\text{M}$ in past and more recent data, respectively. Differences in silica concentrations are significant but opposite in sign to those seen so far, with the 2011 samples being characterized by lower concentrations than past data. We remind the reader that the substantial decrease in the mean concentration of PO_4^{3-} seen in (at least) 2011 in all tests performed cannot be ascribed to changes in the nutrient loading from the river system. According to the USGS data, the mean loading (and concentration) of $\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} and silica weighted by the sample numbers was higher during or immediately preceding the 2010-2012 cruises than in the earlier period (Table 1).

We also verified that the pre-2009 statistics over the LATEX shelf in Table 7 were not biased towards outliers in one year by comparing the July and August 2004 samples to those collected in the same area after high discharge episodes (data from cruises in 07/1993, 08/1993, 05/2005, 07/2008, 07/2009). Notwithstanding the small sample size, no differences were found for all nutrients (Table 8).

Table 8: Summary of Monte Carlo experiments comparing samples in waters with salinity comprised between 21 and 35 psu collected in July and August 2004 against those cumulatively collected in July and August 1993, May 2005, July 2008 and July 2009. Units: μM .

LATEX shelf High discharge Spring and summer	$\sum_{i=1}^9 0.8 \times n_i = 94$		
	Mean	Std	Z
$\text{NO}_3^- + \text{NO}_2^-$ ('93, '05, '08, '09)	0.64	0.95	-0.54
$\text{NO}_3^- + \text{NO}_2^-$ (2004)	0.74	1.55	
PO_4^{3-} ('93, '05, '08, '09)	0.24	0.24	0.02
PO_4^{3-} (2004)	0.24	0.35	
SiO_2 ('93, '05, '08, '09)	4.18	5.19	-0.18
SiO_2 (2004)	4.33	6.80	
$\alpha=0.005$	t-value= ± 2.87		
$\alpha=0.05$	t-value= ± 1.98		

While all analyses discussed so far focus only on near surface samples, differences in nutrient concentrations may not be limited to the ocean upper 5 m. At a subset of our sites concentrations were measured throughout the water column both in the past and during our cruises. In deep waters the vertical spacing of the samples varies considerably and does not allow a straightforward comparison, but for sites where the depth does not exceed 200 m the spacing is sufficiently uniform throughout the database. We performed the Monte Carlo analysis considering all depths, still dividing the available measurements in salinity classes, now only between 27 and 37 psu due to data availability, for samples from sites with overall water column depth less or equal to 200 m. Using 80% of n_i in each class mean and standard

deviation for phosphate and $\text{NO}_3^- + \text{NO}_2^-$ are $0.33 \pm 0.43 \mu\text{M}$ and $4.89 \pm 5.65 \mu\text{M}$ in the pre-2010 data and $0.26 \pm 0.32 \mu\text{M}$ and $3.41 \pm 5.11 \mu\text{M}$ in our cruises. Differences were not significant at the $\alpha = 0.05$ level but the reliability of the statistics is limited by the very small number of data.

N:P ratio

Together with the distribution of single nutrients, it is useful to explore their relative abundance to assess the role of nutrient availability in potentially limiting primary producers. The stoichiometric ratio between nitrogen and phosphorus in oceanic biomass follows N:P=16:1 (Redfield, 1934). It is commonly assumed that a nutrient ratio of N:P greater than 30 indicates potential phosphorous limitation (Goldman et al., 1979), while if $\text{N} \leq 1 \mu\text{M}$ and $\text{N:P} < 10$, nitrogen limitation is likely (Dortch and Whitledge, 1992, Goldman et al., 1979, Wysocki et al., 2006). While samples collected between 1985 and 2000 and during our cruises have similar distributions despite several outliers in the older data (the similarity is confirmed by a Monte Carlo simulation performed as before, and can be extrapolated on the basis of the ratio of the mean values of nitrate + nitrite and phosphate), approximately 15% of samples from 2001-2009 display ratios higher than 50. A Monte Carlo experiment indeed confirmed that the 2001-2009 population is different from the other two. This difference can be explained by examining the spatial and temporal coverage in those years with respect to older data sets and our cruises. In the first decade of the 21st century, all samples were collected over the LATEX shelf, predominantly during late spring or summer, and targeted the hypoxic zone within the 100 m bathymetric contour. The very large values correspond to samples taken in hypoxia events where N removal through denitrification may affect the N:P ratio.

[Figure 8 here]

Figure 8 N:P ratio. Top panel: 1985-2000; Center panel: 2001-2009; Bottom panel: 2010-2012. Color coding indicates N:P ratio (< 10 in blue, between 10 and 30 in gray and > 30 in red). The size of the circles is proportional to the salinity value. Only data for waters with salinity > 19 psu are shown.

The spatial distribution of N:P and salinity is presented in Figure 8 for samples collected between 1985 and 2000, 2001 and 2009, and during our cruises in 2010-2012. As reported in previous works (Johnson et al., 2006; Turner et al., 2007; Turner and Rabalais, 2013), the vast majority of the Gulf is potentially nitrogen limited; indeed 79% of our stations are potentially nitrogen limited, 86% of samples collected in the late 80's and 90's display ratios lower than 10, and 73% of the data from 2001 to 2009 fall in the same category. High values of N:P, indicative of potential phosphorous limitation, are concentrated around the Mississippi and Atchafalaya mouths, in agreement with previous analyses (Smith and Hitchcock, 1994; Lohrenz et al., 1999; Qian et al., 2003; Sylvan et al., 2006; Johnson et al., 2006; Scavia and Donnelly, 2007). Finally, we note that none of the samples satisfy the conditions for silicate limitation ($\text{Si} < 2 \mu\text{M}$, $\text{Si:N} < 1$, and $\text{Si:P} < 3$; Wysocki et al., 2006).

4. Discussion and conclusions

A total of 784 sea surface locations were sampled during the summer months of 2010, 2011, and 2012 in the northern Gulf of Mexico, with most (about 90%) in 2011. They span a salinity gradient from 10 psu to 37 psu, in years of average (2010), high (2011) and below average (2012) Mississippi river discharge, and different stages of the Loop Current extension (Figure 1). The negative correlation between surface nutrient concentrations (nitrate/nitrite, phosphate, and silica) and salinity confirms that the nutrients in the northern Gulf are strongly influenced by discharge from the Mississippi River System, but the salinity and nutrient relationship is not conservative because of processes such as biological activity, mixing, and remineralization.

Using a Monte Carlo approach, we established that concentrations of $\text{NO}_3^- + \text{NO}_2^-$ and PO_4^{3-} in the northern Gulf of Mexico for the period 2010-2012 - with about 90% of samples being from 2011 - are significantly lower than those found previously and reported, for example, by Lohrenz, et al. (1990, 1999), Qian et al. (2003), Wysocki et al. (2006), and Green et al. (2008) despite the very large river discharge that preceded the 2011 cruise. This decrease is not monotonically distributed across the

northern Gulf of Mexico and in the case of nitrate/nitrite can be explained by the seasonality of its utilization by the planktonic ecosystem. The means for surface phosphate concentrations in shelf areas (water column ≤ 200 m deep), on the other hand, are significantly lower in our 2010-2012 measurements compared to prior samples, but are not statistically significantly different in offshore waters beyond the shelf (water column deeper than 200m).

Overall, silica increased in the 2010-2012 samples, though the contrast was largest where the water column was >200 m deep and a change of opposite sign characterized the LATEX shelf. The SiO_2 comparisons are complicated by a high variance. Different techniques were used to determine concentrations, including freezing at sea and thawing for samples collected before 2000, possibly resulting in increased variability and underestimates of concentration due to Si polymerization if thawing times were too short (MacDonald et al., 1986).

Our analysis suggests that a change occurred at least in surface phosphate distribution and/or utilization in the shelf of the northern Gulf of Mexico in 2011, potentially beginning in the second half of 2010 to at least 2012, compared to the previous 25 years. Considering that nitrate/nitrite concentrations are unchanged when the analysis is limited to the summer season, but that the river input was much greater due to the 2011 volume discharge, we cannot exclude an overall increase in utilization in both nitrogen and phosphorus in the high-flow year (2011).

The spatially variable distribution of the changes in nutrient distribution (significant P decreases only in shallow water, increased Si offshore) raise the possibility of changes in the cycling of N and P in those two regions that may be only indirectly linked to nutrient inputs into the northern Gulf of Mexico. Increased microbial activity following the 2010 *Deepwater Horizon* oil spill (Crespo-Medina et al., 2014) may have also contributed to the increased overall phosphate utilization, but it remains to be proven that the impact lasted at least to 2011. The sparse and spatially uneven distribution of data over the different periods makes it hard to achieve definitive conclusions but differences in circulation and/or mixing

characteristics may have played a role. The winter of 2009-2010 was characterized by an exceptionally deep mixed layer over GoM areas with total depth of 1000 m and greater, and satellite chlorophyll observations display a strong correlation to mixed-layer depth for offshore waters (Muller-Karger et al., 2014). The mixed layer depth, however, did not display any significant anomaly in summer 2010 or during 2011. August 2010, on the other hand, was characterized by an exceptionally intense phytoplankton bloom that developed to the east of the Mississippi River Delta, possibly due to the diversion of the river flow to prevent oil from the spill reaching the coast, and to northwesterly winds that pushed the nutrient rich freshwaters eastward and offshore (O'Connor et al., 2016). 2011 was, as mentioned, a year of very high river discharge and our cruises took place within two months from the discharge peak. One possible physical mechanism for explaining the differences in our data would be an enhancement of surface aggregation of nutrients in narrow frontal structures in 2011 due to increased submesoscale activity and specifically frontogenesis fueled by the extraordinary large freshwater flux (Luo et al., 2016). Such increase in frontal activity generates small filamentary regions where nutrients converge and can achieve high concentrations in combination with extensive areas from which near surface tracers are repelled (Zhong et al., 2012; Zhong and Bracco, 2013). A sampling strategy that does not target submesoscale fronts has a better chance of measuring regions of low concentrations and this sampling bias will affect non-limiting nutrients, and therefore phosphate, more than limiting ones (nitrate/nitrite).

Most importantly, the present work highlights how greatly variable in both time and space are surface nutrient concentrations in this relatively small coastal ecosystem and that they cannot be described with any good accuracy by model based on a linear dependence river discharge alone. Information on the composition of the planktonic and microbial communities as well as microbial metabolic rates throughout the year and not limited to the LATEX shelf are needed to explore the above hypotheses and to ensure the detection of trends or ecosystem changes.

Acknowledgment

457 This work was made possible by a grant (in part) from BP/the Gulf of Mexico Research Initiative to
458 support consortium research entitled “Ecosystem Impacts of Oil and Gas Inputs to the Gulf (ECOGIG)”
459 administered by the University of Mississippi. GRIID: R1.x132.134:0002, R1.x132.134:0005,
460 R1.x132.134:0047, R1.x132.134:0052, R1.x132.134:0057, R1.x132.134:0062 and R1.x132.134:0063.
461 The authors wish to acknowledge the generous support of the National Science Foundation through grants
462 OCE-0928495, OCE- OCE1048510, OCE-0926699. We thank Catherine C. Achukwu for preliminary
463 analysis of the 2010 data set, Julie A. Gonzalez, Kellie Hoppe and Kathleen M. Swanson for their
464 assistance in sample collection and analysis, and the captains and crews of the R/V *Oceanus* (OC468),
465 R/V *Endeavor* (EN496 and EN509) and R/V *Cape Hatteras* (CH0711). Two anonymous reviewers
466 greatly helped clarifying the scope of this work. ECOGIG contribution number 437.

References

- Aulenbach, B.T., Buxton, H.T., Battaglin, W.A., and Coupe, R.H., 2007. Streamflow and nutrient fluxes of the Mississippi-Atchafalaya River Basin and subbasins for the period of record through 2005. In: 2007-1080, U.S.G.S.O.-F.R. (Ed.). U.S. Geological Survey
- Berger, T.J., P. Hamilton, J. J. Singer, R. R. Leben, G. H. Born, and C. A. Fox, 1996. Louisiana-Texas shelf physical oceanography program: Eddy circulation study. Final synthesis report. In: U.S. Dept. of the Interior, M.M.S., Gulf of Mexico OCS, Region, N.O. (Eds.). OCS Study MMS-96-0051, LA, p. 294.
- Bianchi, T.S., DiMarco, S.F., Cowan Jr, J.H., Hetland, R.D., Chapman, P., Day, J.W., Allison, M.A., 2010. The science of hypoxia in the Northern Gulf of Mexico: A review. *Science of the total environment* 408 (7), 1471-1484.
- Camilli, R., Reddy, C.M., Yoerger, D.R., Van Mooy, B.A.S., Jakuba, M.V., Kinsey, J.C., McIntyre, C.P., Sylva, S.P., Maloney, J.V., 2010. Tracking hydrocarbon plume transport and biodegradation at Deepwater Horizon. *Science* 330 (6001), 201-204.
- Cardona, Y., Bracco, A., 2014. Predictability and mesoscale circulation throughout the water column in the Gulf of Mexico. *Deep Sea Research II*, <http://dx.doi.org/10.1016/j.dsr2.2014.01.008>.
- Chen, X., Lohrenz, S.E., Wiesenburg, D.A., 2000. Distribution and controlling mechanisms of primary production on the Louisiana-Texas continental shelf. *Journal of Marine Systems* 25 (2), 179-207.
- Crespo-Medina, M., Meile, C.D., Hunter, K.S., Diercks, A.R., Asper, V.L., Chanton, J.P., Orphan, V.J., Shiller, A.M., Battles, J.J., Joung, D.J., Amon, R.M.W., Bracco, A., Montoya, J.P., Villareal, T.A., Vossmeier, A., Wood, A.M., Joye, S.B., 2014. The rise and fall of methanotrophy following a deepwater oil-well blowout. *Nature Geoscience*, 7, 423-427.

488 Dagg, M.J., Breed, G.A., 2003. Biological effects of Mississippi River nitrogen on the northern Gulf of
 489 Mexico—a review and synthesis. *Journal of Marine Systems* 43 (3–4), 133-152.

490 Diercks, A.-R., Highsmith, R.C., Asper, V.L., Joung, D., Zhou, Z., Guo, L., Shiller, A.M., Joye, S.B.,
 491 Teske, A.P., Guinasso, N., Wade, T.L., Lohrenz, S.E., 2010. Characterization of subsurface polycyclic
 492 aromatic hydrocarbons at the Deepwater Horizon site. *Geophysical Research Letters* 37 (20), L20602.

493 Donner, S.D., Scavia D., 2007. How climate controls the flux of nitrogen by the Mississippi River and the
 494 development of hypoxia in the Gulf of Mexico. *Limnol. Oceanogr.* 52(2): 856-861.

495 Dorado, S., Rooker, J.R., Wissel, B., Quigg, A., 2012. Isotope baseline shifts in pelagic food webs of the
 496 Gulf of Mexico. *Marine Ecology Progress Series* 464, 37-U52.

497 Dortch, Q., Whitledge, T.E., 1992. Does nitrogen or silicon limit phytoplankton production in the
 498 Mississippi River plume and nearby regions? *Continental Shelf Research* 12 (11), 1293-1309.

499 Dunn, D.D., 1996. Trends in nutrient inflows to the Gulf of Mexico from streams draining the
 500 conterminous United States, 1972-93. U.S. Geological Survey Water-Resources Investigations Report
 501 96-4113. U.S. Environmental Protection Agency, Austin, Texas, p. 68.

502 Goldman, J.C., McCarthy, J.J., Peavey, D.G., 1979. Growth rate influence on the chemical composition
 503 of phytoplankton in oceanic waters. *Nature* 279 (5710), 210-215.

504 Goolsby, D.A., Battaglin, W. A., 2001. Long-term changes in concentrations and flux of nitrogen in the
 505 Mississippi River Basin, USA. *Hydrol. Processes* 15,1209-1226.

506 Green, R.E., Breed, G.A., Dagg, M.J., Lohrenz, S.E., 2008. Modeling the response of primary production
 507 and sedimentation to variable nitrate loading in the Mississippi River plume. *Continental Shelf Research*
 508 28 (12), 1451-1465.

509 Hitchcock, G.L., Wiseman Jr, W.J., Boicourt, W.C., Mariano, A.J., Walker, N., Nelsen, T.A., Ryan, E.,
 510 1997. Property fields in an effluent plume of the Mississippi river. *Journal of Marine Systems* 12 (1–4),
 511 109-126.

512 Jochens, A., DiMarco, S.F., Worth D. Nowlin, J., Reid, R.O., II., M.C.K., 2002. Northeastern Gulf of
 513 Mexico chemical oceanography and hydrography study: Synthesis report. OCS Study MMS 2002-055.
 514 In: U.S. Dept. of the Interior, M.M.S., Gulf of Mexico OCS Region, New Orleans, LA. (Ed.), New
 515 Orleans, LA., p. 538.

516 Johnson, M.W., Heck Jr, K.L., Fourqurean, J.W., 2006. Nutrient content of seagrasses and epiphytes in
 517 the northern Gulf of Mexico: Evidence of phosphorus and nitrogen limitation. *Aquatic Botany* 85 (2),
 518 103-111.

519 Joye, S.B., Leifer, I., MacDonald, I.R., Chanton, J.P., Meile, C.D., Teske, A.P., Kostka, J.E.,
 520 Chistoserdova, L., Coffin, R., Hollander, D., Kastner, M., Montoya, J.P., Rehder, G., Solomon, E.,
 521 Treude, T., Villareal, T.A., 2011. Comment on “A persistent oxygen anomaly reveals the fate of spilled
 522 methane in the deep Gulf of Mexico”. *Science* 332 (6033), 1033.

523 Kessler, J.D., Valentine, D.L., Redmond, M.C., Du, M., Chan, E.W., Mendes, S.D., Quiroz, E.W.,
 524 Villanueva, C.J., Shusta, S.S., Werra, L.M., Yvon-Lewis, S.A., Weber, T.C., 2011. A persistent oxygen
 525 anomaly reveals the fate of spilled methane in the deep Gulf of Mexico. *Science* 331 (6015), 312-315.

526 Kolker, A.S., Cable, J.E., Johannesson, K. H., Allison, M. A., Inniss, L. V., 2013. Pathways and processes
 527 associated with the transport of groundwater in deltaic systems. *J. Hydrology*, 498, 319-334.

528 Knapke, E.M., 2012. Influence of the Mississippi River plume on diazotroph distributions in the northern
 529 Gulf of Mexico during summer 2011, University of Texas at Austin, Austin.

530 Lenes, J. M., Heil, C.A., 2010. A historical analysis of the potential nutrient supply from the N-2 fixing
 531 marine cyanobacterium *Trichodesmium* spp. to *Karenia brevis* blooms in the eastern Gulf of Mexico. J.
 532 Plankton Res. 32(10), 1421-1431.

533 Livezey, R. E., Chen, W. Y., 1983. Statistical field significance and its determination by Monte Carlo
 534 techniques. Monthly Weather Review, 111, 46-59.

535 Lohrenz, S.E., Dagg, M.J., Whitledge, T.E., 1990. Enhanced primary production at the plume/oceanic
 536 interface of the Mississippi River. Continental Shelf Research 10 (7), 639-664.

537 Lohrenz, S.E., Fahnenstiel, G., Redalje, D., Lang, G., Chen, X., Dagg, M., 1997. Variations in primary
 538 production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the
 539 Mississippi River. Marine Ecology Progress Series 155, 45-54.

540 Lohrenz, S.E., Fahnenstiel, G.L., Redalje, D.G., Lang, G.A., Dagg, M.J., Whitledge, T.E., Dortch, Q.,
 541 1999. Nutrients, irradiance, and mixing as factors regulating primary production in coastal waters
 542 impacted by the Mississippi River plume. Continental Shelf Research 19 (9), 1113-1141.

543 Lohrenz, S.E., Redalje, D.G., Cai, W.-J., Acker, J., Dagg, M., 2008. A retrospective analysis of nutrients
 544 and phytoplankton productivity in the Mississippi River plume. Continental Shelf Research 28 (12),
 545 1466-1475.

546 Luo, H., Bracco, A., Cardona, Y., McWilliams, J.C., 2016. Submesoscale circulation in the Northern Gulf
 547 of Mexico: Surface processes and the impact of the freshwater river input. Ocean Modelling 101, 68-82.

548 MacDonald, R.W., McLaughlin, F.A., Wong, C.S., 1986. The storage of reactive Silicate samples by
 549 freezing. Limnology & Oceanography 31, 1139-1142.

550 Muller-Karger, F.E., Smith, J.P., Werner, S., Chen, R., Roffer, M., Liu, Y., Muhling, B., Lindo-Atichati,
551 D., Lamkin, J., Cerdeira-Estrada, S., Enfield, D. B., 2015. Natural variability of surface oceanographic
552 conditions in the offshore Gulf of Mexico, Progress Oceanogr., 134, 54–76

553 Mulholland, M.R., Bernhardt, P.W., Heil, C.A., Bronk, D.A., O'Neil, J.M., 2006. Nitrogen fixation and
554 release of fixed nitrogen by *Trichodesmium* spp. in the Gulf of Mexico. Limn. Oceanogr. 51, 1762-1776.

555 Mulholland, M.R., Bernhardt, P.W., Ozmon, I., Procise, L.A., GarrettB, M., O'Neil, J.M., Heil, C.A.,
556 Bronk, D.A., 2014. Contribution of diazotrophy to nitrogen inputs supporting *Karenia brevis* blooms in
557 the Gulf of Mexico. Harmful Algae 38, 20-29.

558 O'Connor, B.S., Muller-Karger, F.E., Nero, R.W., Hu, C., Peebles, E.B., 2016. The role of Mississippi
559 River discharge in offshore phytoplankton blooming in the northeastern Gulf of Mexico during August
560 2010. Remote Sensing Environ. 173, 133-144

561 Parsons, M. L., Dortch, A., Turner, R.E., 2002. Sedimentological evidence of an increase in Pseudo-
562 nitzschia (Bacillariophyceae) abundance in response to coastal eutrophication. Limnology and
563 Oceanography, 47(2), 551-558.

564 Qian, Y., Jochens, A.E., Kennicutt II, M.C., Biggs, D.C., 2003. Spatial and temporal variability of
565 phytoplankton biomass and community structure over the continental margin of the northeast Gulf of
566 Mexico based on pigment analysis. Continental Shelf Research 23 (1), 1-17.

567 Rabalais, N.N., Turner, R.E., Justic, D., Dortch, Q., Wiseman, W.J., SenGupta, B.K., 1996. Nutrient
568 changes in the Mississippi River and system responses on the adjacent continental shelf. Estuaries 19
569 (2B), 386-407.

570 Raymond, P.A., Oh, N. H., Turner, R.E., Broussard, 2008. Anthropogenically enhanced fluxes of water
571 and carbon from the Mississippi River. Nature, 451, 449-452.

572 Redfield, A.C., 1934. On the proportions of organic derivatives in sea water and their relation to the
573 composition of plankton. James Johnstone Memorial Volume . R. J. Daniel, 177.

574 Rowe, G.T., Kennicutt, M.C., 2009. Northern Gulf of Mexico continental slope habitats and benthic
575 ecology study In: Interior, U.S.D.o.t., Service, M.M., Region, G.o.M.O. (Eds.), New Orleans, LA p. 417.

576 Scavia, D., Donnelly, K.A., 2007. Reassessing hypoxia forecasts for the Gulf of Mexico. Environmental
577 Science & Technology 41 (23), 8111-8117.

578 Smith, S., Hitchcock, G., 1994. Nutrient enrichments and phytoplankton growth in the surface waters of
579 the Louisiana Bight. Estuaries 17 (4), 740-753.

580 Sprague, L.A., Hirsch, R.M., Aulenbach, B.T., 2011. Nitrate in the Mississippi River and its tributaries,
581 1980 to 2008: Are we making progress? Environmental Science & Technology, 45, 7209-7216.

582 Sylvan, J.B., Dortch, Q., Nelson, D.M., Maier Brown, A.F., Morrison, W., Ammerman, J.W., 2006.
583 Phosphorus limits phytoplankton growth on the Louisiana shelf during the period of hypoxia formation.
584 Environmental Science & Technology 40 (24), 7548-7553.

585 Toner, M., Kirwan, A.D., Poje, A.C., Kantha, L.H., Müller-Karger, F.E., Jones, C.K.R.T., 2003.
586 Chlorophyll dispersal by eddy-eddy interactions in the Gulf of Mexico. Journal of Geophysical Research:
587 Oceans 108 (C4), 3105.

588 Turner R.E., Rabalais, N.N., 1991. Changes in the Mississippi River this century: Implications for coastal
589 food webs. BioScience 41, 140–147.

590 Turner, R.E., Rabalais, N.N. Justic, D., 2006. Predicting summer hypoxia in the northern Gulf of Mexico:
591 Riverine N, P, and Si loading. Marine Pollution Bull. 52, 139-148.

592 Turner, R.E., Rabalais, N.N., Alexander, R.B., McIsaac, G., Howarth, R.W., 2007. Characterization of
 593 nutrient, organic carbon, and sediment loads and concentrations from the Mississippi River into the
 594 northern Gulf of Mexico. *Estuaries and Coasts* 30 (5), 773-790.

595 Turner, R.E., Rabalais, N.N., 2013. Nitrogen and phosphorus phytoplankton growth limitation in the
 596 northern Gulf of Mexico. *Aquatic Microbial Ecol.*, 68, 159–169.

597 Valentine, D.L., Kessler, J.D., Redmond, M.C., Mendes, S.D., Heintz, M.B., Farwell, C., Hu, L.,
 598 Kinnaman, F.S., Yvon-Lewis, S., Du, M., Chan, E.W., Tigreros, F.G., Villanueva, C.J., 2010. Propane
 599 respiration jump-starts microbial response to a Deep Oil Spill. *Science* 330 (6001), 208-211.

600 Valentine, D.L., Mezić, I., Maćešić, S., Črnjarić-Žic, N., Ivić, S., Hogan, P.J., Fonoberov, V.A., Loire, S.,
 601 2012. Dynamic autoinoculation and the microbial ecology of a deep water hydrocarbon irruption.
 602 *Proceedings of the National Academy of Sciences*.

603 Wysocki, L.A., Bianchi, T.S., Powell, R.T., Reuss, N., 2006. Spatial variability in the coupling of organic
 604 carbon, nutrients, and phytoplankton pigments in surface waters and sediments of the Mississippi River
 605 plume. *Estuarine, Coastal and Shelf Science* 69 (1-2), 47-63.

606 Zhong, Y., Bracco, A., 2013. Submesoscale impacts on horizontal and vertical transport in the Gulf of
 607 Mexico. *Journal of Geophysical Research: Oceans* 118 (10), 5651-5668.

608 Zhong, Y., Bracco, A., Villareal, T.A., 2012. Pattern formation at the ocean surface: Sargassum
 609 distribution and the role of the eddy field. *Limnology & Oceanography: Fluids & Environments* 2, 12-27.