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Highly variable nutrient concentrations in the Northern Gulf of Mexico

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ABSTRACT

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

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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 Kjehldahl 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-nitzchia* 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).

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 (Fig. 1), 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 (Fig. 2a) 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 h). 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 h (Knapke, 2012). Detection limits for nitrate/nitrite, phosphate, and silicate were 0.05, 0.05, and 0.5 μmol 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 ($NO_3^-+NO_2^-$, 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 3107 samples collected in the upper 5 m of the water column as part of the Nutrient Enhanced Coastal Ocean Productivity (NECOP) program

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