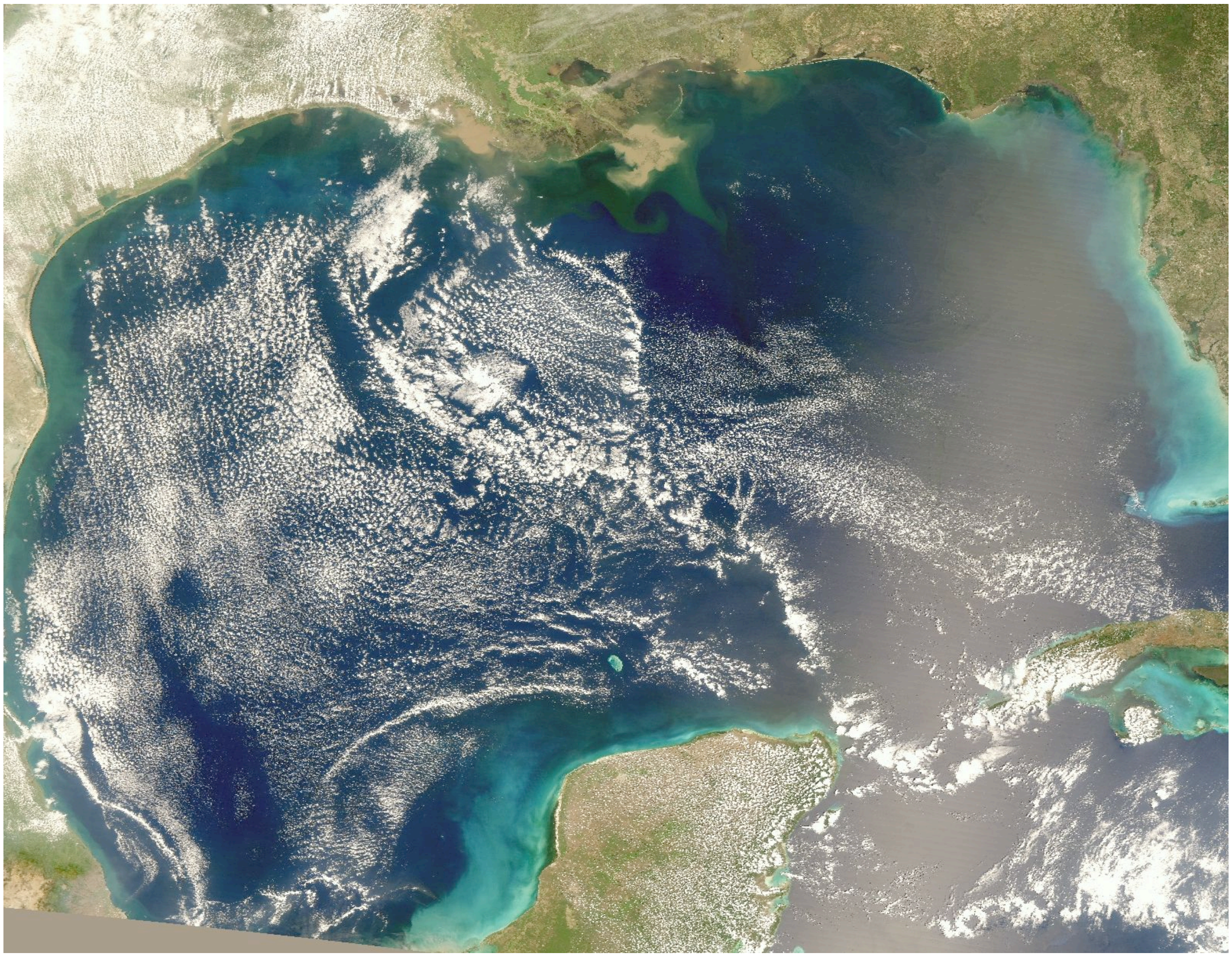
Report of the Gulf of Mexico Coastal Carbon Synthesis Workshop



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Report of the U.S. Gulf of Mexico Carbon Cycle Synthesis Workshop

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Executive Summary

Ocean margins represent a critical but poorly constrained component of the global carbon cycle. The coastal zone is a region of intense carbon and nutrient processing and transformation, but to characterize and quantify margin systems requires a level of spatiotemporal sampling that is difficult to achieve and sustain, and modeling margin systems presents significant scaling challenges. While a great deal of coastal carbon cycle research is being conducted, the associated research communities and scientific outcomes tend to be grouped by scientific discipline or flux boundary (terrestrial-river vs. river-estuary vs. estuary-open ocean), creating a need for regional synthesis exercises that cut across these boundaries to provide a comprehensive picture.

The Gulf of Mexico coastal synthesis workshop convened 38 scientists, broken down into the following flux teams: Riverine input; estuaries and submarine groundwater discharge; air-sea exchange; exchange at the ocean boundary; primary production; and respiration. The Gulf of Mexico was divided into subregions based on differing inputs, distinctive physical forcings, and ensuing biogeochemical characteristics and processes: West Florida Shelf (WFS), Louisiana Shelf (LA), Texas Shelf (TX), Mexican Shelf (MX), and Open Gulf. Like many of the marginal oceans worldwide, the Gulf of Mexico is unevenly sampled, with many regions altogether lacking in data. The main goal of this workshop was to bring together scientists studying the Gulf of Mexico and its drainage sources to develop an updated carbon budget for the region. At the workshop, flux teams met in person to discuss the updated numbers and identify key challenges and missing data. Team leaders presented their updated flux numbers, along with short-term (6-12 months) plans to improve flux estimates and long-term recommendations for future research.

River and estuarine fluxes

Riverine fluxes into the Gulf of Mexico will be discussed in an addendum to this report. Excluding the Mississippi-Atchafalaya River System (MARS), the estuarine flux team developed a preliminary organic carbon budget based on 37 Gulf estuarine systems using TOC load estimates from SPARROW (Spatially Referenced Regression on Watershed Attributes) and the same statistical modeling approach used by the east coast synthesis estuary team (Najjar et al., 2012; Herrmann et al., 2013). The preliminary synthesis suggests that Gulf estuaries receive 9.8 Tg C y^{-1} of organic carbon from rivers and export 6.8 Tg C y^{-1} off-shelf. Within the estuary, 0.21 Tg C y^{-1} is buried and the calculated net ecosystem production (NEP) is -2.7 Tg C y^{-1}. The group is planning to develop LOICZ-type phosphorus budgets for select estuaries to refine Gulf NEP estimates. In the long term, the group suggested that using a common framework to conduct comparative studies of estuaries in different North American coastal margin systems would be most effective in informing observation- and model-based estimates of carbon flux parameters. Submarine groundwater discharge (SGD) to the Gulf comprises terrestrial and recirculated marine sources. SGD team members compiled literature-based DOC and DIC flux estimates from the FL and LA shelves. DOC flux ranged from 0.001 to 7.9 g m^{-2} y^{-1}, while DIC flux ranged from 2.6 to 12.4 g m^{-2} y^{-1}. Additional studies are needed beyond the eastern Gulf of Mexico to fill in the data gaps.

Air-sea fluxes

The air-sea flux team compiled >375,000 additional $p\mathrm{CO}_2$ measurements from open and coastal waters of the Gulf, representing a 6-fold increase in the number of data points used in the new air-sea flux estimates. Fluxes were variable across the different subregions and seasons. Coastal waters represent a CO_2 sink year round. In late summer, the open waters of the Gulf are a CO_2 source, but a sink all other times of the year. The preliminary estimate of the compiled data set indicates that the Gulf is a sink with a net annual specific flux of -0.19 mol m^{-2} y^{-1}, which corresponds to an uptake for the entire Gulf of -3.57 Tg C y^{-1}. Rainwater DOC, aerosol POC, and VOCs also represent significant carbon fluxes for Gulf waters, but the measurements are sparse and unevenly distributed, leading to flux estimates that span several orders of magnitude. Future recommendations include the addition of CO_2 sensors to buoys in the Gulf and deployment of buoys in sparsely sampled regions such as the TX and MX shelves. The group also recommended the development of detailed aerosol POC and rainwater DOC protocols to facilitate routine sample collection on cruises, as well as the establishment of a comprehensive VOC-CH_4 sampling program for the Gulf.

Biological fluxes

Water column primary productivity measurements for the Gulf ranged from 84.0 g C m^{-2} y^{-1} (MX) to 474.5 g C m^{-2} y^{-1} (WFS), with the largest seasonal range occurring in the North Central Gulf. Satellite-based annual mean net primary production (NPP) estimates ranged from 149.7 g C m^{-2} y^{-1} (Open Gulf) to 445.3 g C m^{-2} y^{-1} (North Central). Annual average benthic primary productivity of Gulf phytobenthos in the upper 20 m was estimated at 280 g C m^{-2} y^{-1}. As in other regions of coastal North America, there are few existing published measurements for dark respiration rates within the Gulf of Mexico, with no data coverage in the MX and TX shelf regions. Individual regional rates contribute to a total annual respiration rate of 396 to 436 Tg C y^{-1} for the Gulf of Mexico, with the highest rates (per unit area) occurring in the LA and WFS regions. Benthic respiration data will be needed to close the Gulf carbon budget. Based on existing data (and uncertainties), better seasonal and spatial coverage are needed to assess the net metabolic state (net autotrophy vs. heterotrophy) of the Gulf and how it varies across temporal and spatial scales. This group also recommended the use of remotely sensed chlorophyll *a* distributions to examine the impact of short-term mesoscale events on NPP, R, and the carbon budget of the oligotrophic waters of the open Gulf.

Exchange at the ocean boundary

Using a Regional Ocean Modeling System (ROMS) coupled to the biogeochemical model, flux team members developed a monthly climatology of cross-shelf velocity and fluxes of DIN and POC across the 50-m isobath. Integrated cross-shelf exports of POC and DIN are estimated at ~1 x 10^{12} g C y^{-1} and ~0.1 x 10^{12} g N y^{-1}, respectively. In addition, this coupled model provides the opportunity for model-data comparison using estimates of fluxes from other groups (primary production, respiration, air-sea flux, etc.), which will result in a more internally consistent carbon budget. In the near term, this group will be working on estimating cross-shelf fluxes of DIC and DOC. In the long term, process-oriented studies on event space and time scales (10s of km, days to weeks) that combine observations and models would help improve understanding of the processes that determine fluxes and fate of carbon on Gulf of Mexico shelves.

Updated carbon budget and overarching recommendations

An updated carbon budget for the Gulf of Mexico includes better-constrained estimates of air-sea CO_2 flux and primary productivity. Synthesis of existing data yielded revised respiration, benthic primary productivity, and net ecosystem production estimates. The new budget divides the coastal zone into three regions, with separate boxes for tidal wetlands, estuaries, and coastal ocean. These inland systems (i.e. tidal wetlands, estuaries) are especially important features of the Gulf of Mexico system with regard to carbon cycling and sequestration, yet the data to constrain fluxes in these regions are lacking. Several overarching recommendations to constrain the Gulf of Mexico carbon budget came out of the meeting. All flux teams noted sparse data coverage in Mexican waters, which could be much improved by developing stronger collaborations with Mexican scientists. Additional data from tidal wetlands are also sorely needed. Other important but poorly constrained processes and flux components of the Gulf carbon budget include benthic seeps, nitrogen fixation, and sediment-water exchange, which were not addressed as part of this synthesis. Whenever possible, the group recommended model-model and model-observation comparisons to help inform observing needs and assess model performance.

1. Introduction

The contribution of coastal margins to regional and global carbon budgets is not well understood, largely due to limited information about the magnitude, spatial distribution, and temporal variability of carbon sources and sinks in coastal waters. Building on recommendations put forth during the 2005 North American Continental Margins (NACM) Synthesis and Planning Workshop (Hales et al., 2008) and progress made since then, the Ocean Carbon & Biogeochemistry (OCB) Program and the North American Carbon Program (NACP) began collaborating in 2009 on a coastal synthesis activity (http://coastalcarbon.pbworks.com/w/page/15143273/FrontPage) to synthesize individual, small-scale observational and modeling studies from different regions of the North American continental margin across broader spatial and temporal scales to improve quantitative assessments of the North American coastal carbon budget. This activity was divided geographically into five regions: East Coast, West Coast, Gulf of Mexico, Arctic, and Great Lakes. Anticipated products of the Coastal Synthesis include:

- Updated coastal carbon budgets based on literature- and model-based estimates of major carbon fluxes for each region
- Peer-reviewed papers (possibly a special journal volume) that provide preliminary coastal carbon budget estimates for the different regions and describe key processes and fluxes involved in coastal carbon cycling
- A comprehensive science plan for coastal ocean carbon and related biogeochemical research that identifies current knowledge gaps and ranks research and observing priorities to guide future agency funding initiatives

1.1. Historical context

In the late 1990s, the Carbon Cycle Interagency Working Group (CCIWG) requested that a science plan for carbon cycle research be developed. In 1999, such a plan was published (Sarmiento and Wofsy, 1999) and led to the formation of the North American Carbon Program (NACP) (http://www.nacarbon.org/nacp/) and Ocean Carbon and Biogeochemistry (OCB) Program (www.us-ocb.org), sister organizations with overlapping domains in the coastal zone of North America. Both programs recognized the importance of the coastal zone in the global carbon cycle and the relative lack of coordinated research in this area. As a result, a workshop was proposed to the CCIWG to broadly synthesize knowledge of carbon cycling in the North American Continental Margins (NACM). The workshop, funded by NASA, NOAA, and NSF, was held in 2005 and made several recommendations, including coastal data synthesis and carbon budget estimation based on a control volume concept (Hales et al., 2008).

In May 2008, OCB sponsored a scoping workshop *Terrestrial and Coastal Carbon Fluxes in the Gulf of Mexico* (Robbins et al., 2009) to bring together Gulf of Mexico researchers from multiple disciplines across the land-ocean continuum, including terrestrial, aquatic, and marine scientists, to discuss the state of knowledge of carbon fluxes, data gaps, and overarching questions in the Gulf of Mexico system. Plenary talks focused on onshore and Gulf carbon dynamics and processes that are of primary importance in controlling variability in fluxes and fates of carbon. Breakout group discussions at the workshop focused on fluxes across key interfaces (terrestrial-watershed, river-estuary, and land-ocean-atmosphere), practical considerations (issues of working across different scales of variability), and necessary resources (observational infrastructure, modeling framework for integration across the system) for quantifying these fluxes. The discussions at the workshop were intended to stimulate integrated studies of marine and terrestrial biogeochemical cycles and associated ecosystems that would help establish the role of the Gulf of Mexico in the carbon cycle and how it might evolve in the face of environmental change. This workshop and the products and collaborations that emerged essentially set the stage for a Gulf of Mexico coastal synthesis activity by identifying key players and assembling a baseline assessment of key processes involved in the Gulf of Mexico carbon cycle.

Shortly thereafter, OCB and NACP began coordinating coastal synthesis activities across their respective research communities. In December 2010, OCB and NACP convened a community workshop sponsored by NASA. The goals of this workshop were to gather active members of the coastal research community with a diverse range of expertise to:

- Identify existing datasets, publications, and ongoing and previous studies that could contribute to the development of regional coastal carbon budgets (and ultimately be archived in a community database)
- Develop consensus on the fluxes and processes that should be included in regional carbon budgets and associated models to ensure consistency and inter-comparability

During the workshop, participants broke out into small discussion groups, both by region and by flux type, to begin discussing data needs and sources, key challenges, and critical data gaps. At this workshop, participants began compiling information about regional data sets, process studies, and modeling resources that might contribute to this activity.

To follow up on the initial progress made at this larger community workshop, a series of smaller, more focused regional team meetings have been held. Participants of these small regional meetings were tasked with compiling flux numbers based on existing data and modelling resources to develop and/or refine regional carbon budgets. The East Coast regional meeting occurred in January 2012, and the workshop report, which includes an updated coastal carbon budget, is available at http://www.us-ocb.org/publications/East_coast_syn_report_FINAL.pdf. The Gulf of Mexico Coastal Carbon Workshop was held March 27-28, 2013 in St. Petersburg, FL, and the revised coastal carbon budget based on new flux estimates is available herein.

1.2. Workshop rationale and format

Ocean margins are characterized by intense geochemical and biological processing of carbon and other elements and are sites where large amounts of matter and energy are exchanged with the open ocean. The area-specific rates of productivity, biogeochemical cycling, carbon dioxide uptake and organic/inorganic matter sequestration are high in ocean margins, with as much as half of global new production occurring over continental shelves and slopes. However, the current lack of knowledge and understanding of biogeochemical processes occurring at ocean margins has left the processes largely unaccounted for in most previous global assessments of the oceanic carbon cycle. A major source of uncertainty for the North American carbon budget is the Gulf of Mexico, a large, semi-enclosed subtropical basin bordered by the United States, Mexico, and Cuba. Like many of the marginal ocean basins worldwide, the Gulf remains largely undersampled and poorly characterized with regard to carbon fluxes across key interfaces.

Here, we report on the outcomes of the Gulf of Mexico coastal carbon workshop held in March 2013 in St. Petersburg, FL. The primary objective of this 1.5-day workshop was to bring together a small group of coastal carbon cycle scientists working at different flux interfaces in the Gulf of Mexico to refine the carbon budget for this region. In Fall 2012, invitation letters were sent to scientists engaged in Gulf of Mexico carbon cycle research in an effort to establish flux teams in preparation for a regional meeting. Flux teams included river input, estuarine fluxes, submarine groundwater discharge, air-sea fluxes, primary production, respiration and NCP, and exchange at the ocean boundary. The Gulf of Mexico was subdivided into five different regions (Fig. 1.1) based on differing inputs, distinctive physical forcings and ensuing biogeochemical characteristics and processes:

- West Florida Shelf (WFS) - influenced by upwelling, river discharge, and groundwater influx
- Louisiana Shelf (LA) - river-dominated, receiving major discharge from the Mississippi-Atchafalaya River system
- Texas Shelf (TX) - dominated by upwelling and by eddies shed from the Loop Current
- Mexican Shelf (MX) - influenced by upwelling and by groundwater and river (Usumacinta-Grijalva) discharge
- Open Gulf - deep, semi-enclosed oligotrophic basin with an energetic circulation strongly connected to the Caribbean Sea and Atlantic Ocean

Large river plumes, particularly the Mississippi River, represent an important component of the Gulf carbon budget, but are difficult to constrain due to seasonal variations in the plume area. Using a salinity cutoff of 28 to define the Mississippi River plume, R. Hetland provided a model-based plume area climatology to help inform carbon flux calculations for other flux teams (See Chapter 5).

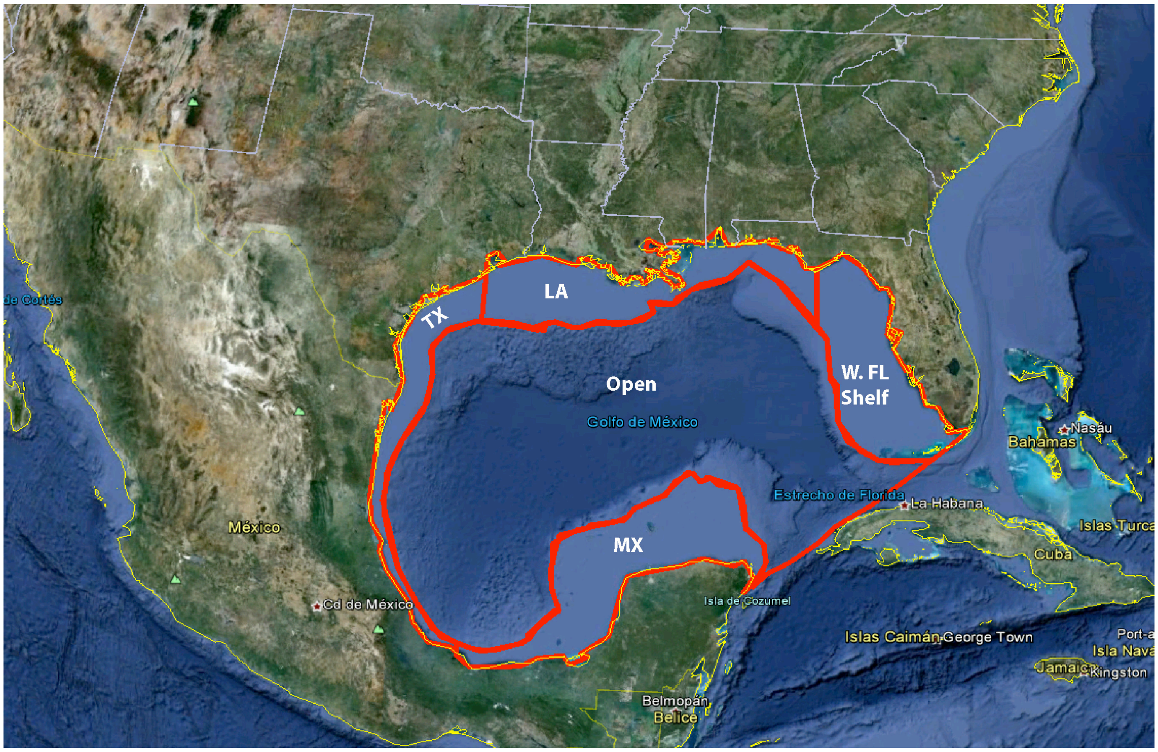


Figure 1.1. Subregions of the Gulf of Mexico established for carbon budgeting purposes

In early 2013, each team held a series of teleconferences to coordinate the compilation of flux estimates from the literature, models, etc. In addition, OCB coordinated monthly teleconferences among team leaders to stay updated on team progress and plan the workshop.

The workshop agenda and participant list are provided in Appendix 1. The workshop, which convened 38 scientists, opened with an overview presentation on the history of carbon cycle and coastal synthesis activities in the U.S., followed by a presentation on the current state of the Gulf of Mexico carbon budget. Each flux team leader then presented the work they had done over the past few months to refine their flux estimates, including data synthesis from literature searches and modeling efforts. The flux teams then went into breakout sessions to discuss how they could make near-term improvements to their flux estimates, potential near-term outcomes (e.g., peer-reviewed publications), and recommendations for longer-term observational and modeling investments that would require additional funding. The flux team leaders then reported out to the entire group and the meeting closed with an open discussion about workshop outcomes, including a workshop report in the near-term and multiple peer-reviewed publications over the next 12-18 months.

2. Riverine Input

Contributors: E. Boyer (lead), H. Tian, S. Howden, M. Allison

The researchers above worked on river loading estimates for the Gulf of Mexico, and are still developing estimates for the Gulf carbon budget. This chapter will be included at a later date as an addendum to the report.

3. Estuaries

Fluxes in Estuaries

Contributors: T. Bianchi, C. Osburn, and M. Herrmann (leads), P. Montagna, J. Hererra-Silveira

The estuarine fluxes team described the variety of estuaries bordering the Gulf of Mexico and presented an overview of the challenges of constraining their carbon budgets. These systems vary considerably based on regional geology, riverine flow, and residence time. The focus of this group was the land-ocean interface: coastal wetlands, tidal freshwater wetlands, the estuary proper, and the inner shelf. The study domain excludes the Mississippi and Atchafalaya Rivers, which are being handled separately by the river flux team. However, it was noted that the lower Mississippi River, where substantial processing occurs (Dagg et al., 2005), and the complex interaction between the Atchafalaya River and its associated estuaries are generally not classified as rivers. These combined systems are collectively referred to as the Mississippi-Atchafalaya River (MAR) estuarine system. Further, the estuarine purview includes the water column and sediment-water exchanges, though the latter is covered in part by the submarine groundwater discharge flux team. The estuarine flux team also considered the inner shelf from the river/estuary mouth/pass to the 200-m isobath. Estuarine diversity and classification schemas exist and the team has adopted a watershed coupling-geochemical matrix that contrasts estuaries classified as terrigenous-clastic-based systems with those classified as carbonate-based systems. Further distinction contrasts estuaries with intensive versus minimal upstream-downstream coupling. The variability of conservative riverine fluxes, further complicated by non-conservative processes and seasonal variability, was identified as a significant challenge, particularly when trying to apply a comprehensive model across multiple estuaries.

Short-term plans

The estuarine flux team is developing an organic carbon budget for the Gulf of Mexico estuaries. The four major terms of an estuarine organic carbon budget are riverine input, burial in the sediment, net ecosystem production (NEP), and export to the ocean (Figure 3.1a). NEP is the gross primary production minus community respiration and thus describes the net metabolic status of a given system. To constrain the organic carbon budget for the estuaries in the Gulf of Mexico region we are adapting the approach that was originally developed as part of the Coastal Carbon Synthesis activity for the East Coast region (Najjar et al., 2012; Herrmann et al., 2013), in which statistical models were developed to estimate NEP as a function of riverine loading ratios of dissolved inorganic nitrogen (DIN) to total organic carbon (TOC) (Figure 3.1b) and carbon burial as a function of estuarine water residence time (τ) and total nitrogen (TN) input from upland sources (Figure 3.1c); the upland organic carbon input was taken from a data-constrained United States Geological Survey statistical water quality model SPARROW (Spatially Referenced Regression on Watershed Attributes) (Smith et al., 1997; Shih et al., 2010) and export of organic carbon to the ocean was computed by difference, assuming steady state.

For the preliminary budget calculations, we focused on 37 estuarine systems in the U.S. portion of the Gulf of Mexico, characterized in NOAA's national estuarine eutrophication assessment (NEEA) survey (Bricker et al., 2007). The preliminary organic carbon budget results are summarized in Table 3.1. We used TOC load estimates from SPARROW to estimate organic carbon input. To estimate DIN:TOC loading ratios required for modeling NEP, we used the SPARROW TN load estimates and an assumed DIN:TN ratio of 0.42 that was estimated for the East Coast region (Herrmann et al., 2013). Residence time, required for modeling burial, was calculated as the ratio of the estuarine volume to the outflow flux, estimated from constructing salt and water mass balances for each estuary: $\tau = \frac{V}{Q}\left(1-\frac{S_{EST}}{S_{OCN}}\right)$$\tau = \frac{V}{Q}\left(1-\frac{S_{EST}}{S_{OCN}}\right)$, where *V* is the volume of the estuary, *Q* is the net freshwater input to the estuary (streamflow plus direct precipitation minus evaporation), S_{EST} is the average salinity of the estuary, and S_{OCN} is the average salinity on the adjacent shelf (*Dyer*, 1997). We used SPARROW model output for the average river flow estimates and the NEEA database (Bricker et al. 2007) for all other parameters. The estimates given in Table 3.1 will be refined after we update the empirical models developed for the East Coast estuaries (Figs. 3.1b and c) with published data from the Gulf of Mexico and the uncertainty will be estimated using bootstrap resampling procedures. Gulf estuaries are generally more shallow, wind-driven, and have shorter hydraulic residence times than the East Coast estuaries – these are just a few of the distinctions between these systems that will be reflected in our revised Gulf of Mexico estuarine budget calculations. For the United States region of the Gulf of Mexico, DIN:TOC ratio estimates will be derived using the SPARROW water quality model. For Mexican estuaries, other sources of information will be needed, as the SPARROW model covers only the conterminous U.S. For the U.S. estuarine systems, the NEEA survey (Bricker et al., 2007] was identified as one of the primary sources for geospatial delineation of the systems and various auxiliary data, e.g., estuarine area, depth, climate, and other characteristics. The LOICZ (Land-Ocean Interactions in the Coastal Zone) study is a major potential source of information for the Mexican estuaries (Smith et al. 1999). Another key data source is Bianchi et al. (1999), which provides an overview of estuarine fluxes and contains information on marsh and wetland environments. These can be resolved against existing LOICZ NEP flux estimates. The team has identified data uncertainties in coastal marshes along the Florida panhandle

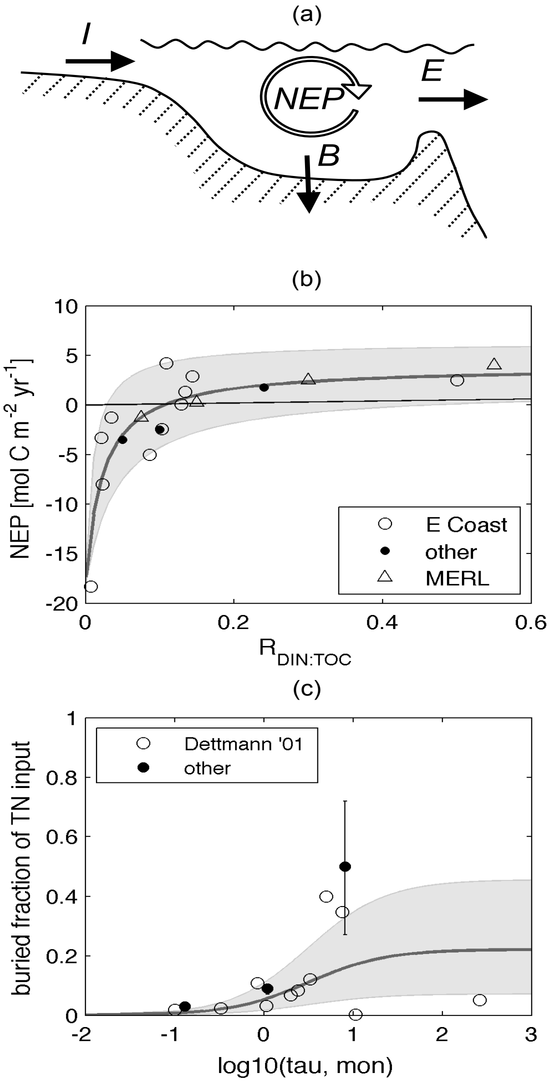


Figure 3.1. (a) A schematic diagram of organic carbon balance in an estuary. *I* is the input to the estuary (flux across the land/river-estuary interface), *E* is the export from the estuary to the ocean (flux across the estuary-shelf interface), *B* is the burial in the sediment (flux across the sediment-water interface), and *NEP* is the net ecosystem production in the estuary (the internal source term). (b) The East Coast (Herrmann et al., 2013) statistical model of net ecosystem production (NEP) as a function of riverine loading ratios of dissolved inorganic nitrogen to total organic carbon ($R_{DIN:TOC}$). The model is a hyperbolic fit of the form:

$$NEP = Y_{\max} R_{DIN:TOC} \left(K_R + R_{DIN:TOC} \right)^{-1} + Y_{\min},$$

where Y_{max} = 22.21, K_R = 0.0226, Y_{min} = -18.3. and the NEP units are mol C m^{-2} v^{-1}.

to Alabama, as well as tidal marshes fringing estuaries in general. Wetlands are another source of uncertainty. Within estuaries, uncertainty exists in benthic fluxes. Subsidence is an important uncertainty in the Louisiana estuaries.

Table 3.1. Preliminary estimates of organic carbon fluxes for the estuarine systems in the U.S. portion of the Gulf of Mexico (total estuarine area is 30.6×10^3 km^2)

	Input	**NEP**	**Burial**	**Export**
Area-integrated flux, Tg C y^{-1}	9.8	-2.7	0.21	6.8
Area-normalized flux, mol C m^{-2} y^{-1}	27	-7.5	0.57	19

The estuaries flux team is also planning to construct LOICZ-type phosphorus budgets for selected estuaries, from which NEP can be estimated (Smith et al., 1999). We will start with the estuary proper and with systems away from the MAR. The criteria chosen for selection of estuaries were systems that: 1) were well-studied; 2) had, to some extent, existing models; 3) represented the physiographic provinces around the Gulf of Mexico; and 4) were most analogous to East Coast passive margin. The estuaries chosen also represented systems the team thought would be most important for the inner shelf. The systems chosen were: Galveston Bay, which is typical of a coastal plain estuary (e.g., not lagoonal) and has two river inputs; Barataria Bay, which is an open marsh system weakly fed by rivers; Mobile Bay, which has two large rivers feeding into it; Tampa Bay, which represents the transition from the carbonate to siliciclastic province and is less river dominated than Mobile Bay; Celestun Bay, which is a karstic, groundwater influenced estuary; and Laguna de Terminos, which is river influenced but also in a carbonate region.

Long-term recommendations

While the estuaries flux team continues to gather C flux numbers, we have advocated for harmonizing our approach with that taken by the East Coast estuarine flux team in order to make an overall ecosystem comparison approach to understand these dynamic systems. In the long run, the ability to use a common approach to calculate estuarine fluxes will allow for broad integration across systems. Because individual estuaries vary with respect to forcings and responses (e.g., residence time, nutrient inputs, the amount and quality of organic matter exported from the adjacent watersheds, and subsidence), it is difficult to develop predictive frameworks at the regional level. Much of the focus to date has been the large MARS, with compartmentalized studies focused on regional estuaries (e.g., the Texas estuaries). These systems vary widely with respect to residence time and thus a comparative ecosystem approach should be taken. However, recent work has shown that small catchments can be important C fluxes to the inner shelf (Spencer et al. 2013). Thus, the MAR system may not be representative of C fluxes out of smaller estuaries and coastal wetland environments. Future efforts should be focused on: (1) synthesizing NEP for coastal marshes and wetlands in addition to estuarine waters, (2) continued measurement and modeling of the air-water CO_2 fluxes in marshes, wetlands, and estuaries, (3) investigations of the lability and photoreactivity of POM and DOM derived from wetland and watershed sources, (4) investigations into benthic fluxes in marshes, wetlands, and estuaries, (5) carbon cycling dynamics in the lower rivers below USGS gauging stations, and (6) improving lateral flux estimates and/or tidal exchange of DIC, DOC, and POC from estuaries to the coastal ocean.

The estuarine fluxes team recommends coupling estuarine and coastal circulation models that account for the complex physical, chemical, and biological transformations that affect carbon fluxes and dynamics in estuarine and coastal waters. Such models will be critical for understanding the impacts of changing climate, land use (e.g., coastal development, subsidence), and land cover. These impacts likely will influence internal C cycling in estuaries, and ultimately, the export of C to the coastal ocean.

Submarine Groundwater Discharge

Contributors: C. G. Smith, J. Cherrier

Submarine groundwater is defined as any and all fluid discharged from benthic sediments into coastal water bodies (Burnett et al., 2003) and consists primarily of marine (recirculated) and terrestrial fluid sources. Submarine groundwater has long been recognized as a potential vector for ecologically important and harmful constituents to the coastal ocean (Johannes, 1980). However, only in the last decade have reliable SGD measurement techniques become available to help quantify material fluxes and examine potential associated ecological impacts. Of the two components, the terrestrial fraction represents the allochthonous contribution to coastal systems and provides the most provocative source to consider for understanding interactions between the ecology and hydrology. Human activities onshore, including on-site waste-disposal and agriculture, can contribute nutrients to the coastal and marine waters. Global estimates of terrestrial groundwater discharge to the ocean vary substantially based on the technique used; however, Burnett et al. (2003) suggested the general range was between 5-10% of riverine input. The marine fraction (i.e., marine SGD, recirculated SGD, or RSGD) consists of seawater infiltrated into pore space in offshore shallow and deep marine geologic units and then flushed back to the overlying water. Marine SGD is influenced by processes that flush pore fluids, including thermohaline circulation, tidal and wave pumping, and biological activity. While the bulk of the fluid may merely be viewed as recycled seawater, the dissolved constituents entrained in these processes are typically far removed from the active pelagic systems above (i.e., dissolution of carbonate, remineralization of variable-age organic matter, etc). As such, marine SGD can act as both an autochthonous and an allochthonous material vector.

Not surprisingly, the interest to identify SGD as a vector of carbon to the entire Gulf of Mexico requires specific guidelines as to what fraction of SGD is of interest. Based on the formal definition presented by Burnett et al. (2003), submarine groundwater discharge (SGD) is any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition and/or driving force. Based on this definition, there are two dominant components of SGD:

1) Terrestrial groundwater driven by gravity and pressure
2) Marine surface water circulated into and out of the seabed

For large-scale budgets like the Gulf of Mexico, it is apparent from the work of Moore et al. (2008) that recirculated marine groundwater discharge is the dominant fraction. However, many local-scale studies (i.e. within the 10-m isobath or in estuaries and bays) indicate that the dominant component is often site-specific. For example, along Kings Bay, FL, fresh groundwater is the dominant fraction; yet, tidal recirculation is also important. However, despite the source, the overall importance of SGD (total) is important in driving material flux.

Some of the obvious needs to develop a regional SGD-based carbon flux are to have regionally distributed fluid fluxes (i.e., analogous to the river discharge) and end-member concentrations (i.e., analogous to the mean average carbon concentration for a river). Unfortunately, monitoring of SGD flow or fluid fluxes to the coastal zone are not obtainable due to complicating issues associated with aquifer heterogeneity and geologic variability. Transmissivity of coastal aquifers varies considerably (5-6 orders of magnitude) across the Gulf of Mexico basin but also at small regional scales due to varying geologic processes contributing to the framework stratigraphy of the region. Geologic variability not only influences the aquifers' physical characteristics but also the biogeochemical and/or redox framework. Carbonate shelves, organic-rich muds, organic-poor sands, and silts make up surficial sediments throughout the Gulf, which provides a general basis for dividing the gulf into physiographic regions similar to those defined by Coble et al. (2010). Each sediment type influences the chemistry (salinity, redox, pH) of groundwater prior to discharge and hence the cycling of carbon, nutrients, metals, and other redox-sensitive dissolved constituents (Charette et al. 2005; Roy et al. 2010; Roy et al. 2012; Dorsett et al. 2012).

Smith and Cherrier (this meeting) reviewed the current literature and found approximately 20+ articles with unique or independent estimates of submarine groundwater discharge to the Gulf of Mexico (namely the U.S.). Estimates vary considerably from < 1 L m^{-2} d^{-1} along the Louisiana shelf (Krest and Moore, 1999; McCoy et al. 2007) to > 100 L m^{-2} d^{-1} along parts of the Florida shelf (Cable et al. 1996; Santos et al. 2010; Smith et al. 2012). Regionally, the Florida and Louisiana shelves have by the far the most SGD studies (2 to 5 studies each), while no estimates exist from the Mississippi-Alabama shelf region. Additional studies along the Florida (Cherrier et al., unpublished) and Texas coastline (Swarzenski and Dellapenna, unpublished) and Yucatan (Charette, Price, Stalker, unpublished) may help address additional data gaps in these regions.

Of the 20+ studies reviewed, four directly reported carbon flux (organic, inorganic, or total), while six studies (published and unpublished) provided data that were collectively sufficient to compute fluxes for 5 additional sites. Unfortunately, all the computed fluxes were restricted to the coastal region of eastern Gulf of Mexico (i.e., Florida shelf) and only two provided a breakdown in terrestrial versus marine SGD (Santos et al. 2008; Smith and Swarzenski, 2012). Flux estimates for the various studies are presented in Table 3.2. A complete breakdown of the data provided can be found in Appendix 2. The range in DOC flux was between 0.04 and 260 mmol m^{-2} d^{-1} (0.001 to 7.9 g m^{-2} y^{-1}) while DIC flux was 84 to 409 mmol m^{-2} d^{-1} (2.6 to 12.4 g m^{-2} y^{-1}). Extrapolating these fluxes to regional load is difficult given the different geologic setting from which they originate. For example, all DIC estimates were obtained from carbonate-dominated Florida Bay, while the remainder of the DOC flux data was from siliciclastic-dominated settings. Additional studies are needed beyond the eastern Gulf of Mexico to fill in the data gaps.

Low-resolution terrestrial SGD and carbon flux (namely DIC) may be obtainable using the approach implemented by Cole et al. (2007). The first step would be to develop comprehensive water budgets for all coastal aquifers along the Gulf of Mexico to provide a first-order estimate of terrestrial SGD. Then, the fluid fluxes would be combined with total dissolved carbon data from various databases such as the USGS National Water Information System (NWIS) or EPA to obtain carbon fluxes. While this approach addresses terrestrial inputs, it would neglect a potentially large source of carbon from deep, recirculated marine SGD. Currently, abilities to estimate deep recirculation are dependent on large-scale water column budgets of radionuclides (e.g. radium-226 and radium-228), which are not well established in the Gulf of Mexico. Secondly, the terrestrial-only approach would not address potential transformation of carbon species at mixing zones, often referred to as subterranean estuaries (Moore 1996), which can result in nonlinear source/sink behavior with respect to dissolved inorganic carbon (Dorsett et al. 2011). Unfortunately, only discrete observation-based studies can fully address the effects of mixing within subterranean estuaries.

Acknowledgment

The manuscript benefited from discussions with Christopher Reich, Peter Swarzenski, and Kevin Kroeger and suggestions made by John Lisle, all of the USGS. Any use of trade, product or firm names is for descriptive purposes only and does not imply endorsement by the U.S. government.

Table 3.2. Available SGD-derived carbon fluxes for several locations in the Gulf of Mexico. A comprehensive data set providing available SGD flux rates (cm/d) and carbon concentrations are provided in Appendix 2.

			Flux (mmol C m^{-2} d^{-1})				
Author	**Spatial Coverage**	**Temporal Coverage**	**Low DOC**	**High DOC**	**Low DIC**	**High DIC**	**Ancillary data sources**
Santos et al. 2008, 2009	FL Panhandle	2006-2007	31.5	37.1			
Arnello et al. in prep (?)	Springs Coast, FL	in prep	29.4	205.3			SGD rates obtained from SWFWMD
Smith and Swarzenski 2012	Coastal Region off Pinellas County, FL	2009-2010	1.1	17.0			
Smith in prep	Crystal Beach Spring, FL	ongoing (2010-2012)	0.8	5.4			
Swarzenski et al. 2007	Tampa Bay, FL	2003	0.0	5.2			DOC from Swarzenski unpub. Data
Mwashote et al. 2013	North Sarasota Bay, FL	2002-2006	1.3	63.8			
	Middle and South Sarasota Bay, FL	2002-2006	11.0	259.7			
Corbett et al. 1999	Florida Bay, FL	1994-1997			84.3	408.6	DOC from Walter et al. 2007
Burdige et al. 2008, Hu and Burdige, 2008	Florida Bay, FL	2001			1	20	
Burdige et al. 2008, Hu and Burdige 2008	Bahama Banks, FL	2001				8.6	

4. Air-Sea Exchange

Contributors: *L.L. Robbins, R. Wanninkhof, L. Barbero, Xinping Hu, S. Mitra, S. Yvon-Lewis, W-J. Cai, W.-J. Huang, and T. Ryerson*

The Gulf of Mexico air-sea carbon exchange team addressed major topics of exchange of carbon species between the atmosphere and ocean, including carbon dioxide (CO_2), particulate organic carbon (POC), dissolved organic carbon (DOC) and volatile organic carbon (VOC). The previous research on air-sea exchange for each of these parameters in the Gulf of Mexico was summarized. The team's new efforts to make improved estimates for CO_2 and new calculations for VOC and DOC and POC are described below. In general, very little information was available for DOC, POC or VOC, but significant improvements of the partial pressure of carbon dioxide (pCO_2) mapping and CO_2 fluxes were made. Estimates for the carbon parameters, pCO_2, DOC, POC and VOC were provided using a modified, regional boundary map of Coble et al. (2010) (see Figure 1.1).

pCO_2

Takahashi et al. (2009) recognized the Gulf of Mexico (GOM) as the single largest area that was unknown with respect to the direction of CO_2 flux (i.e. sink vs. source) in the entire U.S. coastal margin. Based on this recognized information gap and the progress of coastal ocean CO_2 data being archived in public databases since then, our team revised early estimates for air-sea flux using new air-sea pCO_2 data. The synthesis is based on data from over 196 cruises and mooring data in the Gulf. These datasets include previously published data in repositories such as CDIAC, as well as datasets in the holdings of Principal Investigators, which are in the process of being archived.

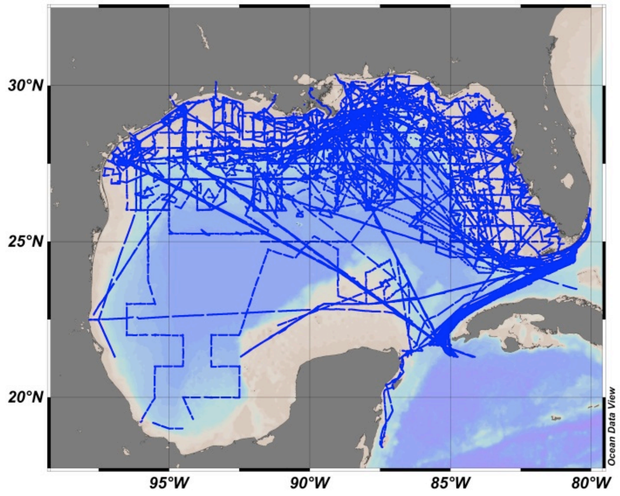
Previous calculations

With respect to pCO_2, limited previous observational data suggest that during the summer, the Gulf of Mexico is a CO_2 source to the atmosphere with a flux ranging from 0.186-3.32 mol m^{-2} y^{-1}, while during the winter it is a net sink of -0.22 to -1.18 mol m^{-2} y^{-1} (Coble et al., 2010). In the Gulf of Mexico (north of 24°N), the air-sea flux was calculated to be -11.8 Tg C y^{-1} (a net sink). Wanninkhof et al. (2009) had used 64,000 underway data points to develop an algorithm for calculation of pCO_2 fluxes and estimated that coastal waters are a very strong CO_2 sink year round and coastal waters of the NE Gulf are a moderate sink. In late summer, the open waters of the Gulf are a source of CO_2, but a sink all other times of the year.

New calculations

pCO_2 data from >375,000 measurements from years 1996-2012 were compiled. These data came from dedicated research cruises and ships of opportunity (Fig. 4.1). Over 190,000 points were compiled for the open Gulf and >185,000 points were compiled for the Gulf coastal margin areas, representing a 6-fold increase in the number of data points used in the new air-sea CO_2 flux estimates, though sampling density across regions is still highly variable. While the overall trends have remained unchanged from previous calculations, including predominantly near shore sinks and changes in direction of seasonal air-sea CO_2 fluxes, the net uptake is appreciably smaller in the new calculations relative to previous estimates.

Figure 4.1. Data compilation of *p*CO2 data from 196 cruises in the GOM.



The *p*CO_2 air-sea flux was calculated using a computed second moment of monthly wind speeds ($<U^2>$) within gridding of open ocean data into 1°x1° bins and coastal ocean data into 0.5° x 0.5° bins. Table 4.1 shows preliminary *p*CO_2 fluxes for each of the different regions and the total Gulf of Mexico. Figure 4.2 compares the net annual flux as derived from climatology presented by Takahashi et al. (2009) and the new data set. The preliminary estimate of the compiled data set indicates that the Gulf is a sink with a net annual specific flux of -0.19 mol m^{-2} y^{-1}, which corresponds to an uptake for the entire Gulf of -3.57 Tg C y^{-1}.

Table 4.1. Preliminary *p*CO_2 Flux Calculations for Regions of the Gulf of Mexico. Wind product used: CCMP monthly average, binned to 1° x 1° grid in region 1 (open ocean) and 0.5° x 0.5° grid in coastal areas (regions 2 - 5).

Region	**Flux (mol C $m^{-2}y^{-1}$)**	**Stdev**	**ΔpCO_2**	**Max ΔpCO_2**	**Min ΔpCO_2**	**# of data points**
WFS	0.37	0.11	16.90	963.80	-240.83	>35K
Northern Gulf	-0.44	0.37	-5.01	2423.51	-333.71	~95K
Western Gulf	0.18	0.05	18.83	121.04	-115.39	>10K
Mexico-	-0.09	0.05	18.30	390.18	-236.50	~8K

Yucatan						
Open Gulf	-0.48	0.07	3.22	407.82	-306.76	>150K
TOTAL	**-0.19**	**0.08**				**>300K**

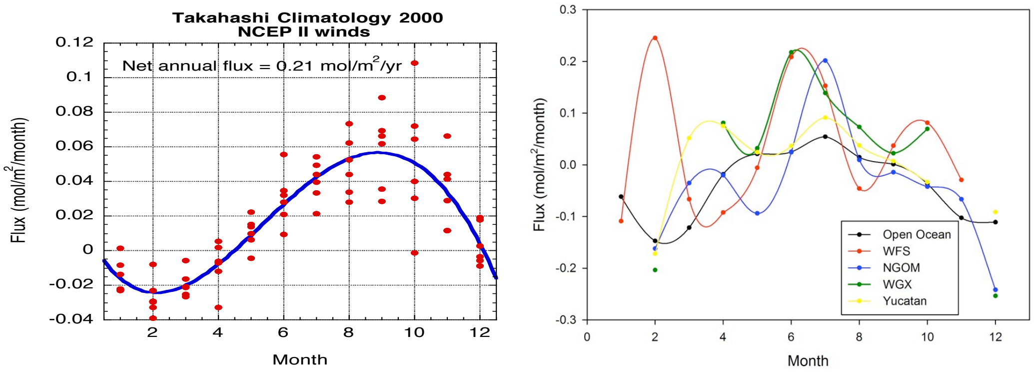
Short-term plans

The compilation of the data sets has not yet been completed; cruises are being added and those that do not meet specified accuracy and documentation criteria are being deleted. Three issues that are being addressed in the near term include:

1) the possibility of obtaining additional data in the Texas and Mexico Shelf regions;
2) discussion amongst team members of the appropriate flux coefficient(s) to be used for open vs. coastal ocean; and,
3) the use of appropriate wind fields in calculating flux data (i.e. average winds vs. in situ winds vs. second moment of the winds).

These data sets also contain estuarine $p\mathrm{CO_2}$ data. These data are not used in the flux calculations for the Gulf, but they will be extracted for the estuarine group to use for the calculations of inland carbon mass balances. A climatological study to determine monthly change in $p\mathrm{CO_2}$ maps and air-sea $\mathrm{CO_2}$ fluxes centered on the 2009 data will be initiated. (Barbero et al., in prep.)

Figure 4.2. Comparison of annual carbon flux based on **A.** Takahashi et al. (2009) climatology and **B.** new data from 5 Gulf of Mexico regions.



A.

B. Net annual flux = -0.19 mol C m^{-2} y^{-1}

Atmospheric deposition of organic carbon

Atmospheric deposition of organic carbon can occur by 1) wet deposition via precipitation scavenging of gas and aerosol phase organic compounds, 2) dry deposition of aerosol-bound organic compounds, and 3) diffusive air-sea gas exchange of organic compounds. Preliminary estimates of each of these processes for the carbon budget of the Gulf of Mexico (GOM) are made below.

DOC

Rainwater DOC can be an important source of carbon to surface waters. Changes in the composition of rainwater DOC have been identified to be regionally important (Monteith et al., 2007). For example, rainwater DOC may subsidize heterotrophic respiration in oligotrophic portions of the water column. Few datasets exist for rainwater DOC influx into the Gulf of Mexico. This paucity of rainwater data has contributed to an incomplete estimation of DOC fluxes to the Gulf of Mexico in previous budgets (Coble et al., 2010).

In this workshop, rainwater DOC influx to the Gulf of Mexico (Figure 4.3) was estimated in the following manner: First, rainwater DOC concentrations were interpolated from eight existing values from coastal and marine systems globally (range: 0.25 – 1.2 mg L^{-1}; mean 0.72 ± 0.47 mg L^{-1}). These values were coupled with the lowest and highest average annual rainfall in the Gulf of Mexico (901-1700 mm; www.emecs.or.jp, www.trmm.gsfc.nasa.gov and www.weatherchannel.com), respectively, to estimate a minimum and maximum wet deposition flux of DOC from rainwater. Estimates of wet deposition of DOC to the Gulf varied by an order of magnitude from 0.35 – 3.2 Tg C y^{-1}. Even when considering this large uncertainty, annual rainwater DOC flux values are of the same order of magnitude as the net air-sea CO_2 flux of 3.6 Tg C y^{-1} listed above.

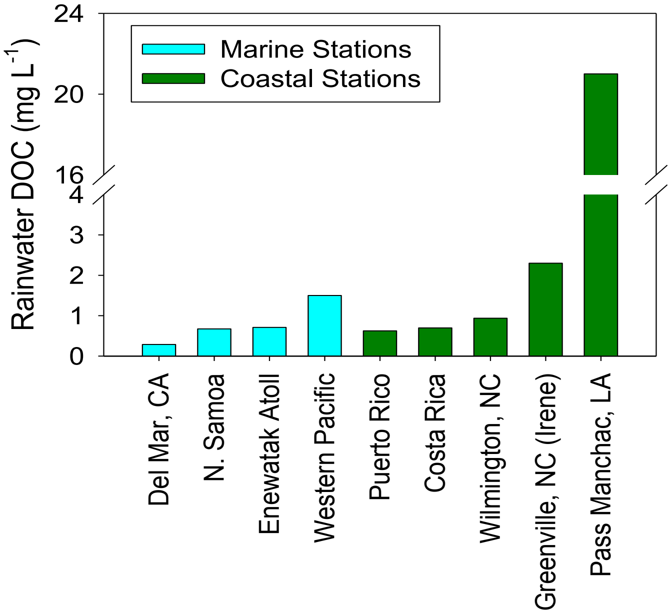


Figure 4.3. Comparison of Rainwater Dissolved Organic Carbon for Marine and Coastal Stations around the world (Willey et al., 2000; Avery et al., 2004). Data from Pass Manchac, LA, were based on rainwater DOC collected during Tropical Storm Bonnie subsequent to its crossing across Deep Water Horizon oil slick. Therefore, those carbon values were not used in the Gulf of Mexico rainwater DOC flux calculation.

Short-term plans

The team's strategy for more representative flux numbers includes a review of gray literature for possible data and continued contact with scientists who may hold datasets. The team also suggested establishment of a rainwater collection network through which seafaring scientists could collect samples while out in the Gulf of Mexico.

POC

Atmospheric deposition of aerosol carbon can be driven by dry and wet deposition. Dry and wet deposition fluxes of aerosol-bound organic carbon were calculated from the limited data available. Concentrations of POC were collected using a high volume air samples from for 4 coastal and marine sites adjacent to the Gulf of Mexico: two sites in Gulf Breeze, FL, and one site each in Dauphin Island, AL and at the Turtle Cove Galva Field Station in Louisiana (Bates et al., 2008; Yu et al., 2009; Ding et al., 2008; Scalise, 2013) and ranged from 0.32-15.2 µg m^{-3}. The large range in aerosol carbon concentration data tends to be driven by events such as biomass burning and other point source emissions. Estimates of dry and wet deposition flux of carbon were made as described below.

Dry aerosol flux was calculated using the equation

$$Fdry= [vd]*[Cp\text{-}oc]$$

in which [vd]= velocity of deposition (cm/s) and [Cp-oc] = concentration of aerosol of particulate carbon (µg/m^3).

Wet deposition flux was calculated using the equation

$$Fwet = I*[Wp]*[Cp\text{-}oc],$$

in which I = precipitation rate (m/d), Wp = washout ratio, and Cp-oc = aerosol particulate carbon. Using these equations, dry aerosol deposition of carbon into the Gulf of Mexico was calculated to be 0.0094-14.9 Tg C y^{-1} and wet aerosol deposition flux of carbon varied from 0.0898 -8.05 Tg C y^{-1}. The total (dry + wet) ranged from 0.0094- 22.95 Tg C y^{-1}. Again, these ranges are similar to the net air-sea CO_2 flux and are thus potentially important components of the total carbon flux into the GOM.

Short-term plans

Datasets from "events" such as biomass burning need to be constrained. However, accurate measurements of aerosol carbon concentrations in the Gulf of Mexico remain difficult to constrain, as there are few ambient measurements of aerosol carbon throughout the Gulf of

Mexico. As in the case of wet deposition of carbon, data mining of the "gray" literature will be pursued by the team.

VOC

Sources of VOCs to the atmosphere are plentiful in and around the Gulf of Mexico. However, most are from platforms, rigs, ships, etc. The sea-to-air fluxes of VOCs from coastal or open Gulf of Mexico waters are not well quantified. However, in certain locations and for certain VOCs, the fluxes may be significant. We are attempting to quantify these fluxes for different regions of Gulf of Mexico.

New calculations - There are few datasets in which VOC flux was measured, but the most significant data are from the methane fluxes (Brooks, 1975; Kelley and Jeffery, 2002; Kelley, 2003; Solomon et al., 2009; Yvon-Lewis et al., 2011; and Hu et al, 2012). Criteria for wide-scale extrapolation to the Gulf are now being developed. Data from these references range from -0.155 to 10,500 µmol m^{-2} d^{-1}. HYFLUX cruise data show methane fluxes ranging from -4.19 to 86.1 µmol m^{-2} d^{-1}. Measurements of VOC sea-to-air fluxes were made during the *Deepwater Horizon* oil spill event, and the results indicated that the release of methane to the atmosphere associated with the leak was about 0.27 Tg C y^{-1} (Ryerson et al, 2011)

<u>Short-term plans</u>

Measurements of VOC-CH_4 were acquired off Texas in June and August 2013, and these data will be added to the database (Yvon-Lewis, in prep).

Long-term plans for air-sea flux research

The Gulf of Mexico air-sea carbon exchange team recommends that:

1. CO_2 sensors be added to existing buoys in the Gulf of Mexico.

2. Key geographic data gaps in the Gulf of Mexico will be identified and additional buoys added with sensors.

3. Facilitation of research with Mexican and Cuban colleagues will enable us to fill in crucial data gaps in the Gulf of Mexico.

The team further notes that

4. VOC-CH_4 is undersampled and more measurements are needed in all areas. A comprehensive sampling program throughout the Gulf of Mexico is needed.

5. Aerosols (POC) and rainwater (DOC) are also undersampled in the Gulf of Mexico. The establishment of a sampling program with set protocols that could be implemented in conjunction with existing cruises is recommended.

5. Exchange at the Ocean Boundary

Contributors: Katja Fennel (lead), Ruoying He, Rob Hetland, Zuo (George) Xue

Continental shelves are generally thought of as barriers that filter terrestrial inputs before they reach the open ocean. For example, globally, shelves remove much more bioavailable nitrogen via denitrification than that which enters from rivers, estuaries and through atmospheric deposition (Seitzinger et al. 2006). This nitrogen deficit is balanced by significant onwelling of inorganic nitrogen from the open ocean (Fennel, 2010). The role that continental shelves play in carbon cycling is more complicated because inorganic carbon is actively exchanged with the atmosphere (by comparison, deposition of bioavailable nitrogen is negligible) and the complex carbonate chemistry of seawater is highly variable through space and time, and the processes that contribute to that variability are poorly characterized. Globally, shelves are thought to export inorganic and organic forms of carbon to the open ocean (Borges 2011, Gattuso et al. 1998); however, uncertainties and regional differences are large. This group addressed the question of whether the Gulf of Mexico behaves in accordance with these general expectations. More specifically, we asked: Is there cross-shelf import of inorganic nitrogen from the open Gulf to the shelf? Is there cross-shelf export of inorganic and organic carbon? Can they be quantified and, if so, how large are these fluxes?

Observational evidence suggests that cross-shelf export of organic carbon is effective when the Loop Current or Loop Current eddies interact with shelf circulation and pull filaments of carbon-rich water off the shelf (Müller-Karger et al. 1991, Toner et al. 2003, Zavala-Hidalgo et al. 2003). A recent observational study by Wang et al. (2013) also showed significant inorganic carbon export, ~ 9.1×10^9 mol C d^{-1}, from the shelf to the Loop Current, which is twice the inorganic carbon flux from the Mississippi/Atchafalaya river system. However, scaling up these local and episodic events in space and time (required for a comprehensive carbon budget) is not straightforward. The group quickly agreed to focus on biogeochemical models as a means to obtain temporally and spatially integrated flux estimates and chose to use the SABGOM model (Xue et al., submitted), which includes the entire Gulf of Mexico. The model is based on the Regional Ocean Modelling System (ROMS; http://myroms.org) coupled to the biogeochemical model of Fennel et al. (2006, 2008), the same model upon which the east coast synthesis is based.

Zuo Xue made available a monthly climatology of cross-shelf velocity and cross-shelf fluxes of dissolved inorganic nitrogen (DIN) and particulate organic carbon (POC) across the 50-m isobath, extending from Campeche Bank to the West Florida Shelf along the shelf break (Xue et al., submitted). Cross-shelf flow shows a dynamic pattern with alternating on-shore/off-shore currents along the whole section (Fig. 5.1, top panel). In some regions, the mean flow reverses its direction seasonally (e.g., the Louisiana-Texas Shelf). The on-shore/off-shore flow patterns lead to relatively large fluxes of DIN and POC near and eastward of the Mississippi delta, while fluxes are comparatively small along the rest of the section (Fig. 5.1, middle and bottom panels). Zuo Xue also provided seasonal mean circulation patterns and flux estimates for the following 4 sub-regions of the Gulf: the Bay of Campeche (BOC), the Tamaulipas-Veracruz (TAVE) shelf, the Louisiana-Texas (LATEX) shelf, and the West Florida Shelf (WFS). The BOC shelf exports POC year-round; however, the export is essentially balanced by an along-shelf import of POC fueled by upwelling north of the Yucatan Peninsula. Except for spring when there is a small onshore flux of DIN, this shelf region exports DIN to the open Gulf, driven primarily by large river inputs that were found to saturate the denitrification sink on the shelf. The TAVE shelf is narrow and characterized by export of POC, which is more than compensated for by a large along-shore import. DIN is imported into this region in along-shore and cross-shore directions, while river nutrient sources are small. The LATEX shelf is characterized by a reversal in circulation during summer when prevailing winds switch to southerly, leading to upwelling circulation on the shelf. While POC is exported from the shelf in cross-shelf direction for most of the year (most pronounced during the upwelling season in summer), the export in the along-shelf direction is much larger. DIN is also exported in cross- and along-shelf directions. This export is mainly fueled by nutrients from the Mississippi River, only two thirds of which are denitrified on the shelf. The WFS is exporting POC (primarily fueled by Mississippi River material that is imported in the along-shelf direction) and importing DIN. When integrated over the whole transect cross-shelf exports of POC and DIN are estimated at ~1 x 10^{12} g C y^{-1} and ~0.1 x 10^{12} g N y^{-1}, respectively.

In summary, on a spatial scale of ~100 km, along-shelf fluxes of DIN and POC are much larger than cross-shelf fluxes. However, when integrating over the whole Gulf, along-shelf fluxes cancel out and cross-shelf exchange becomes the dominant flux. POC and DIN are both exported in cross-shelf direction; note that the export flux amounts only to about one tenth of the POC and DIN inputs from the rivers (the Mississippi/Atchafalaya being the most important river source by far).

No estimates of cross-shelf DIC fluxes have been made yet (this is one of the short-term plans). The group would like to emphasize the fact that the coupled model provides estimates of other fluxes relevant to the synthesis activity, including primary production, respiration, and air-sea CO_2 exchange and that these flux estimates result in an internally consistent carbon budget. The value of comparing model-simulated fluxes with the observation-based estimates derived by other groups was discussed and stressed. A suggestion was made to use model estimate of river plume area to guide the scaling up of observations (e.g., primary production, respiration), which may bin naturally according to salinity. For this purpose, Rob Hetland produced areal estimates of salinity bins (Figure 5.2).

Short-term plans

Our short-term plans include estimation of cross-shelf fluxes of DIC and DOC. One paper on cross-shelf fluxes of DIN and POC was submitted (Zuo et al.) and two more papers are currently being planned, one focused on inorganic carbon fluxes (Zuo lead) and one focused on an integrated comparative assessment of model-simulated fluxes against observation-based estimates from the primary productivity group and the air-sea flux group (lead TBD).

Long-term recommendations

Process-oriented studies focused on events such as eddy-shelf interactions, tropical storms, hurricanes, etc. (on scales of 10s of km and days to weeks) that combine observations and modeling will help improve understanding of the processes that determine fluxes and fate of carbon on Gulf of Mexico shelves. Such studies will also guide the design of sampling strategies and will allow us to infer errors and uncertainties when scaling up direct observations. Scenario simulations will allow us to assess the effects of land-use changes, of management decisions with regard to nutrient management and agricultural practices (e.g., biofuels), and changes in weather patterns. An expanded carbon observatory based on the lessons learned in process-oriented and scenario-based studies is recommended.

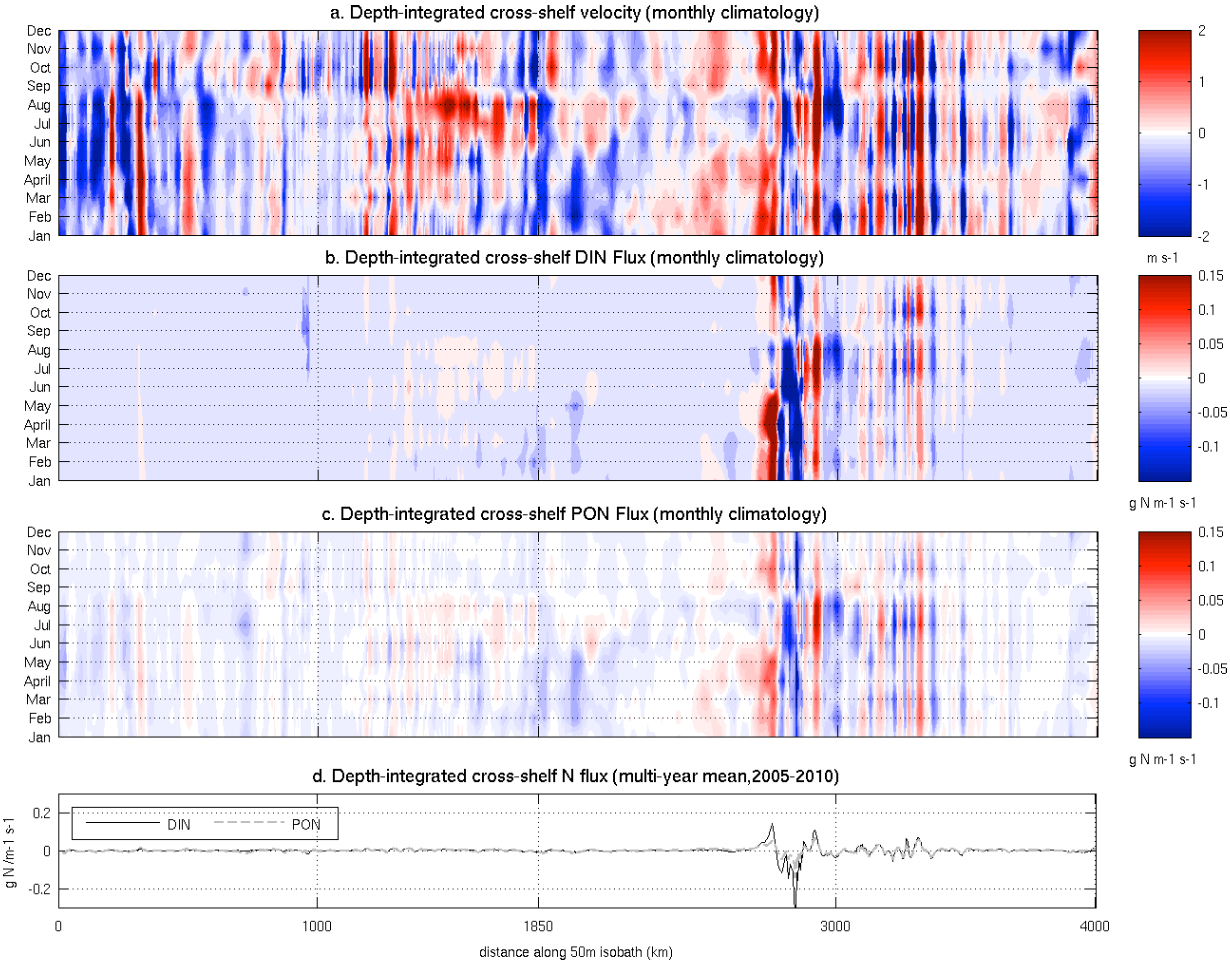


Figure 5.1: (from Zuo et al., 2013) Depth-integrated monthly mean cross-shelf (a) velocity, (b) dissolved inorganic nitrogen (DIN) flux, (c) particulate organic nitrogen (PON) flux and (d) annual mean DIN and PON flux cross the 50-m isobath. Positive/negative values represent shoreward/seaward transport.

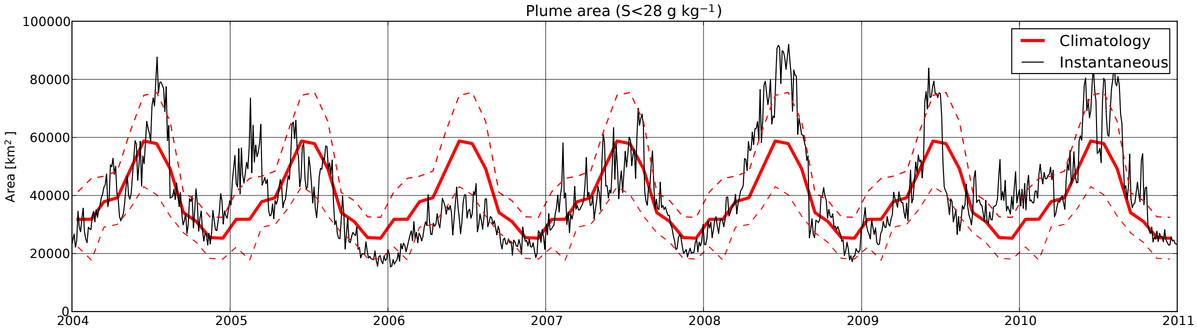


Figure 5.2: Model-derived plume area (black line) and multi-year climatology plus/minus one standard deviation (solid and dashed red lines, respectively). The plume is defined here water with as salinity <28. Based on the MCH model of Hetland and DiMarco (2012).

6. Primary Production

Contributors: S. Lohrenz, S. Chakraborty, M. Huettel, J. Herrera Silveira, K. Gundersen, D. Redalje, J. Wiggert, B. E. Denton, J. Lehrter

The Primary Production Working Group was charged with compiling relevant literature and databases related to primary production in the Gulf of Mexico in support of the development of a regional carbon budget. In addition, the working group was encouraged to collaborate (including engaging other colleagues as appropriate) in developing a synthesis of the relevant information to be presented at the regional team meeting in St. Petersburg, FL March 27-28, 2013.

Productivity measurement types considered

I. ^{14}C-based primary production estimates - bottle incubations
    a. P-E based measurements
    b. In situ
    c. Simulated *in situ* (e.g., deck incubations)
II. Oxygen-based primary production estimates
III. Satellite-derived primary production estimates
    a. Vertically Generalized Production Model, VGPM;
    b. Carbon-based Productivity Model, CbPM
IV. Numerical ecosystem models of primary production
V. Benthic primary production
    a. *In situ* Chamber
    b. Benthic chlorophyll
VI. Other groups addressing net community production and particulate and dissolved organic carbon inputs

Spatial and temporal distribution

The Gulf of Mexico was organized into different regions (Fig. 1.1) including the Northeastern Gulf of Mexico (NE), North Central (NC), Northwestern (NW), West Florida Shelf (WFS), Open Gulf of Mexico (OG), and the Southern Gulf of Mexico.

There were recommendations for modifying these regions. General ideas discussed included the following:
1) Productivity rates along North Central region are non-uniform. Consider whether the North Central Region should be further subdivided.

2) Use satellite observations to define regions
3) Should model and satellite regions be hard lines or feature/range defined?
4) Use river discharge influence to partition regions

North Central
1) Shift eastern boundary as coming off of De Soto canyon
2) Shift western boundary – Align with US/Mexico border; Seasonal Coastal eddy feature sets up here and effectively sets domain edge for Freshwater Plume

Mexican Shelf –A JGR paper in press describes a MODIS-based delineation into 3 regions:
1) Yucatan – Prominently influenced by SGD; Carbonate dominated shelf
2) Western – Associated with dry riverbeds (except under episodic precip)
3) Middle Section – North of Vera Cruz (wet region)

For the purposes on this report, we used the regions as designated in Fig. 1.1.

Synthesis of literature and data mining: Water column production

A considerable number of prior studies have provided estimates of water column primary production in the Gulf of Mexico with most measurements reported from the northwestern part of the Gulf. These data are available in a spreadsheet on the coastal carbon wiki.

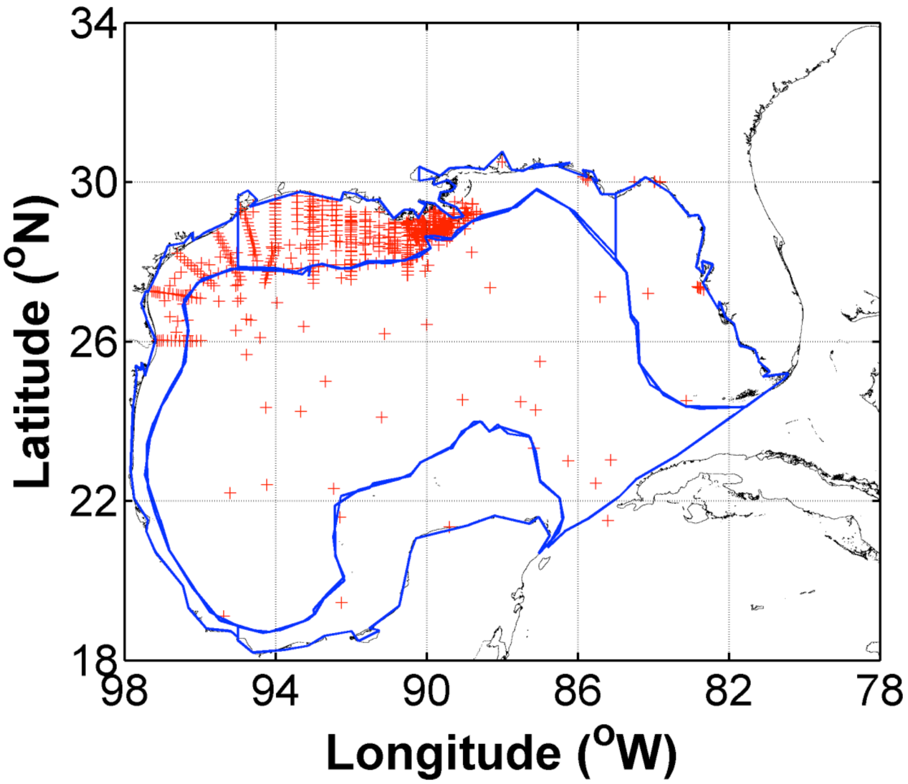


Figure 6.1. Distribution of water column primary production data in relationship to subregions of the Gulf of Mexico. See accompanying file for source information.

Highest median productivity estimates were found for the West Florida Shelf and the northern Gulf of Mexico shelf, which were comparable although the latter showed a much higher range in values including many outliers above the 25th percentile. Kendra Daly provided a summary poster from Cindy Heil for the west Florida shelf. Heil reported that the means for these data ranged 0.18 – 1.75 g C m^{-2} d^{-1} for non-bloom regions and 1.6 – 2.88 g C m^{-2} d^{-1} in bloom regions (data not included in analysis). Using similar measurement techniques (^{14}C deck incubations for 4-6 h), Lohrenz (unpublished) determined water column primary production during a *Karenia brevis* bloom in October 2001 off the West Florida shelf ranging from 1.42 – 2.27 g C m^{-2} d^{-1}, consistent with the Heil et al. results.

A summary of productivity estimates for the different regions based on these data is given in Table 6.1.

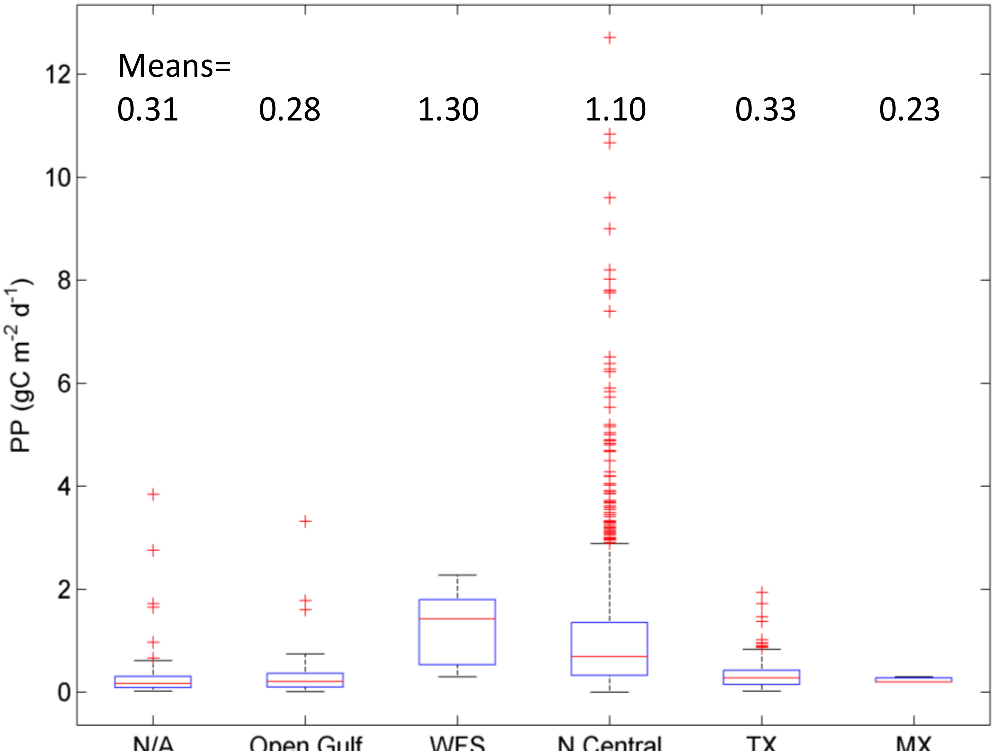


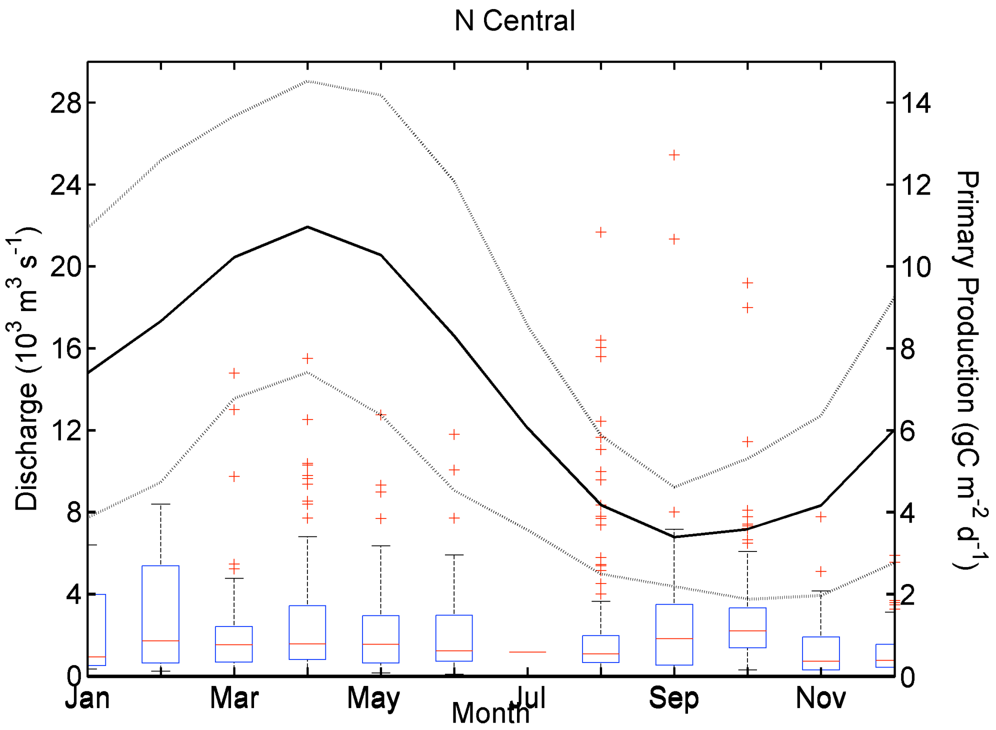
Figure 6.2. A box plot of primary production for the different Gulf of Mexico subregions. N/A corresponds to data that fell outside or between subregion boundaries. Overall means for each subregion are shown above the box. The tops and bottoms of each "box" are the 25th and 75th percentiles of the samples, respectively. The distances between the tops and bottoms are the interquartile ranges. The line in the middle of each box is the sample median. If the median is

not centered in the box, it shows sample skewness. The whiskers are lines extending above and below each box. Whiskers are drawn from the ends of the interquartile ranges to the furthest observations within the whisker length (the adjacent values). Observations beyond the whisker length are marked as outliers. By default, an outlier is a value that is more than 1.5 times the interquartile range away from the top or bottom of the box, but this value can be adjusted with additional input arguments. Outliers are displayed with a red + sign.

Table 6.1. Annual regional water column primary production based on median estimates for the different regions.

Region	**Daily PP** gC m^{-2} d^{-1}	**Annual PP** gC m^{-2} y^{-1}	**Area** km^2	**Regional PP** Gt C y^{-1}
Open	0.28	102.2	9.89E+05	0.101
TX	0.33	120.45	8.68E+04	0.010
N Central	1.1	401.5	1.47E+05	0.059
WFS	1.3	474.5	1.47E+05	0.070
MX	0.23	83.95	1.83E+05	0.015
			Total	0.256

An examination of seasonal patterns revealed peaks in primary production in spring and summer in the northern central Gulf of Mexico (Fig. 6.3). There were insufficient data in the other regions to discern any clear trend.


N Central
Discharge (10^3 m^3 s^-1)
Primary Production (gC m^-2 d^-1)
0
4
8
12
16
20
24
28
0
2
4
6
8
10
12
14
Jan
Mar
May
Jul
Sep
Nov
Month

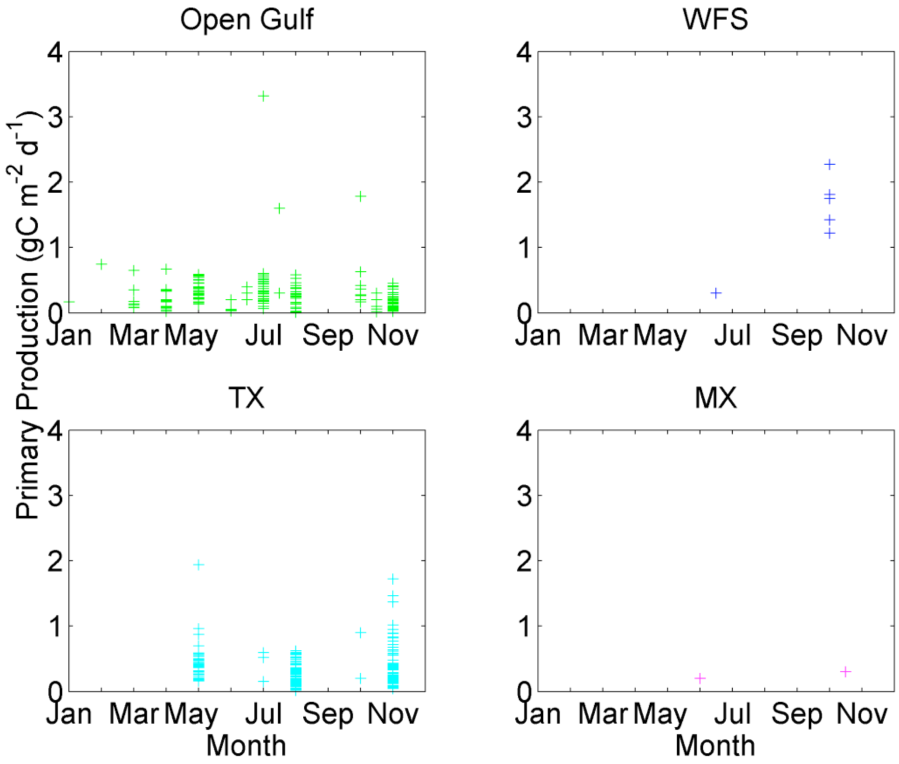

Open Gulf
WFS
TX
MX
Primary Production (gC m^-2 d^-1)
0
1
2
3
4
Jan
Mar
May
Jul
Sep
Nov
Month

Figure 6.3. Top panel is a box plot (see Fig. 6.2 for explanation) of rates of primary production for the North Central region versus month of the year. For the other regions, rates of primary production are plotted versus month of the year.

Mexican colleagues at the workshop reported that PP rate measurements were available from the Mexican PEMEX program. These data are proprietary and were not available for this analysis. Such data could be accessible but there is a need to formally request the data, make a use case argument, and collaborate with a Mexican academic partner in reporting the data. Hidalgo-Gonzalez et al. (2005) used satellite algorithms to estimate productivity in the open Gulf, Yucatan shelf and Mississippi River outflow regions. Estimates ranged 1.18 - 1.22, and 1.60 - 1.68 g C m^{-2} d^{-1} for the Yucatan and Mississippi regions, respectively. Values for deep water regions ranged 0.37-0.44 and 0.22-0.24 g C m^{-2} d^{-1} for cool and warm seasonal periods, respectively. These values are comparable to estimates determined here, although the satellite-derived values for the Yucatan are substantially above the median value for data from Mexican waters.

Photosynthesis-irradiance estimates

Photosynthesis-irradiance data are available primarily for the northern Gulf of Mexico, Texas and west Florida shelf regions (Fig. 6.4). Highest saturated rates of biomass-specific photosynthesis occurred in summer months (Fig. 6.5).

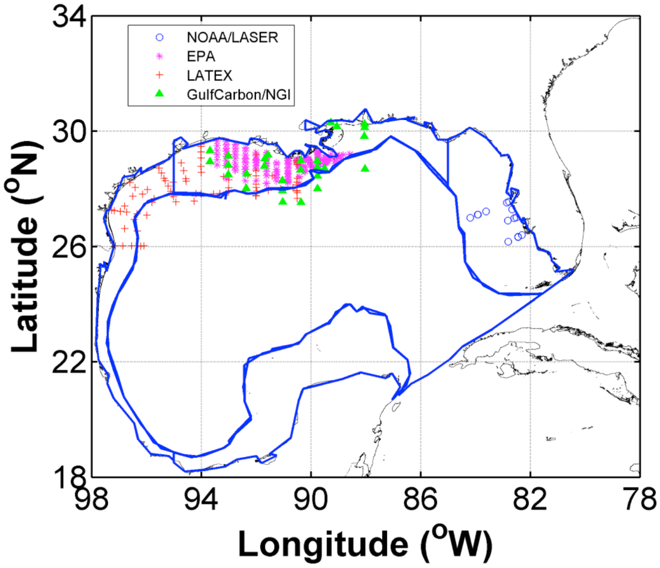


Figure 6.4. Distribution of photosynthesis-irradiance data in the Gulf of Mexico

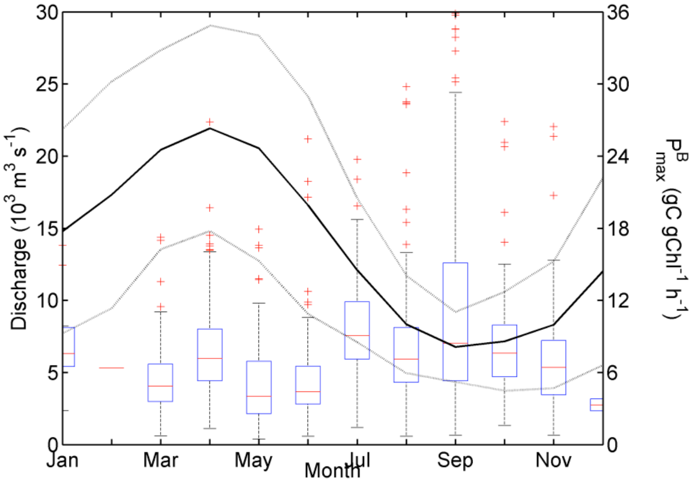


Figure 6.5. Box plot of biomass specific saturated rate of photosynthesis in relation to the average river Mississippi River discharge measured at Tarbert Landing for 1961-2012. See Fig. 6.2 for explanation of box plot.

For photosynthesis-irradiance data for which temperature measurements were also available, a relationship was evident between maximum chlorophyll-specific photosynthetic rates and temperature (Fig. 6.6). Highest rates occurred at high temperatures. Although there was considerable scatter in the data, the pattern of the relationship was generally similar to that reported by Antoine and Morel (1996).

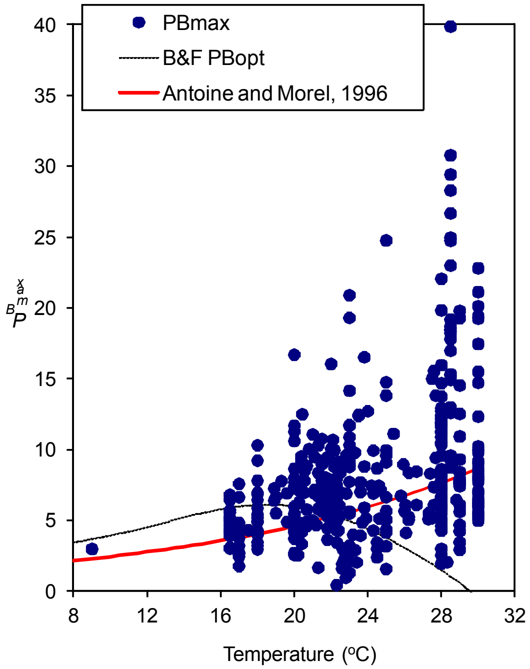


Figure 6.6. Relationship of maximum chlorophyll-specific photosynthetic rates (PBmax, g C g Chl^{-1} h^{-1}) to temperature in the Gulf of Mexico. The black dashed line corresponds to the temperature relationship given by Behrenfeld and Falkowski (1997) for the maximum chlorophyll-specific carbon fixation rate in the water colum (PBopt). The red line corresponds to the temperature relationship for PBmax given by Antoine and Morel (1996).

Satellite estimates of net primary production:

Estimates of net primary production (NPP) based on remotely sensed ocean color observations gathered by MODIS-Aqua and the Carbon-based Production Model (CbPM) developed by Behrenfeld and colleagues [*Behrenfeld, et al.*, 2005; *Westberry, et al.*, 2008] have been retrieved from the Ocean Productivity website (http://www.science.oregonstate.edu/ocean.productivity/). Using the MODIS-Aqua based values, a continuous 9-year time series (2003-2011) of ocean color observations is used to gain insight into primary production of the Gulf of Mexico and the regions prescribed in Figure 1.1.

These monthly NPP estimates provide a consistent assessment of primary production that provides context for the seasonal and interannual variability of the Gulf and its regions. To provide comparison to the in situ based production rates collected above in Table 1, the annual mean and quarterly breakdown of NPP estimate are provided in Table 6.2.

Table 6.2. Annual mean and quarterly breakdown of primary production based on CbPM production model. Units are g C m^{-2} d^{-1}.

	Annual	Feb	May	Aug	Nov
Overall	0.53	0.50	0.50	0.55	0.58
Open	0.41	0.43	0.36	0.38	0.46
WFS	0.71	0.57	0.62	0.89	0.75
N Central	1.22	1.04	1.23	1.36	1.27
TX	0.65	0.48	0.73	0.63	0.62
MX	0.75	0.58	0.68	0.87	0.89

The regional annual rates in Table 6.2 compare favorably with those for the North Central region reported in Table 6.1. For the other regions, the annual rates are 50% to 200% higher, with the Mexican shelf (MX) exhibiting the greatest deviation (0.23 gC m^{-2} d^{-1} vs. 0.75 m^{-2} d^{-1}). Hidalgo-Gonzalez et al. (2005) similarly observed higher values for satellite-derived primary production in the Yucatan shelf and open Gulf.

Seasonal variability is revealed in time series plots for the Gulf and the 5 regions in Figure 6.7. For each region, the mean seasonal cycle over the 2003-2011 time frame is shown as the dark solid line and indicates that the phasing of peak production varies considerably throughout the Gulf, with the Northern Gulf having a peak mean rate in June, the Texas Shelf mean indicating a semiannual cycle and the West Florida and Mexican Shelves having late Summer to Fall peaks, respectively. These plots also reveal the interannual variability associated with each region through the dashed lines that provide the envelope of +/- one standard deviation and the individual NPP estimates for each year represented by the blue circles.

The scatter revealed by the individual points in Figure 6.7 underscore the highly stochastic nature of the Northern Gulf region. The Texas and West Florida Shelves also exhibit elevated variance during their periods of peak production. Interestingly, the Mexican Shelf region has a rather consistent production rate during its peak season and greater variance in the spring.

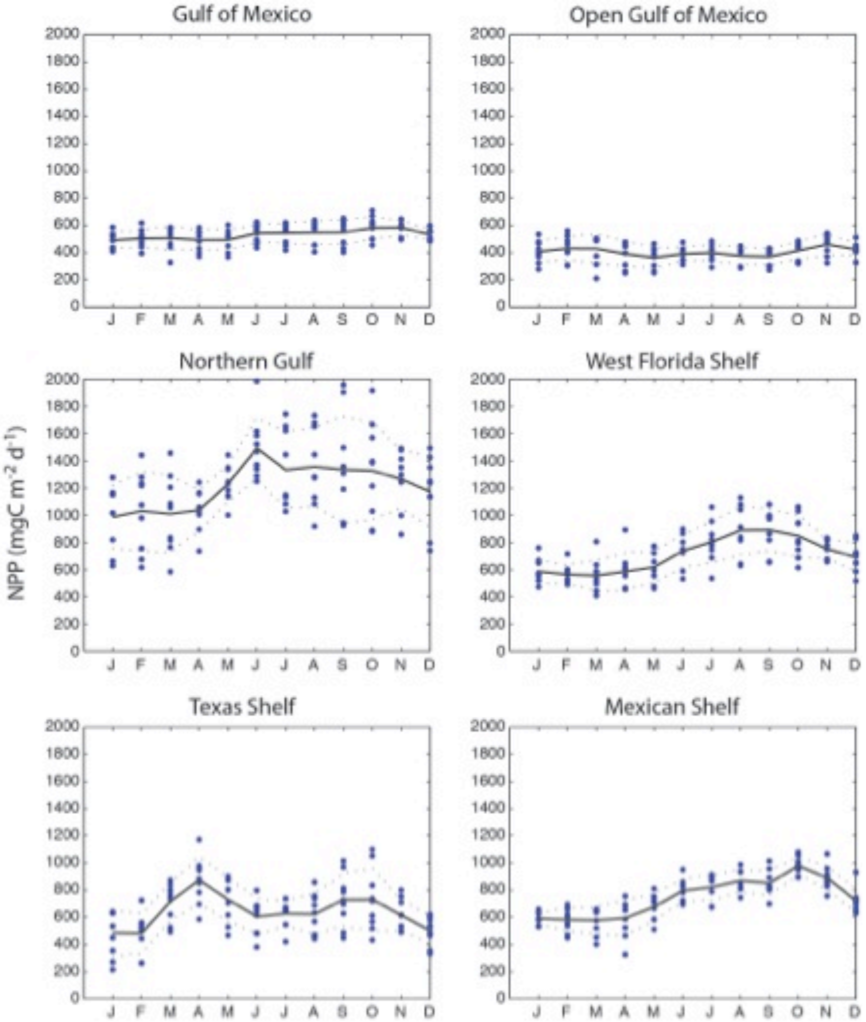


Figure 6.7. Time-series of the annual mean NPP (2003-2011) for the Gulf of Mexico and five regions as defined in Figure 6.1. The solid line represents the annual mean, while the surrounding dashed lines represent the +/- 1 standard deviation envelope. The blue symbols represent the individual monthly values obtained from the CbPM algorithm over the MODIS-Aqua (4 km) observational period (2003-2011).

Synthesis of literature and data mining: Benthic primary production

Data on benthic primary production are very limited. An analysis by Markus Huettel (unpublished and Tables 6.3 and 6.4) used Lehrter et al. (unpublished) and Jahnke et al. (2008) irradiance-production relationships to calculate the production of microphytobenthos. Photosynthetically available radiation (PAR) records published by the Apalachicola Estuarine

Research Reserve were used to estimate the annual surface light variation and it was assumed that in the Gulf of Mexico there are about 250 days in a year with clear sky.

For seagrass productivity in the Gulf, more data were available. However, seagrass cover is not very well constrained. Huettel used the area published in the seagrass atlas (Frederick T. Short) as a conservative value. No information on areal coverage of macroalgae is available, so the same area covered by seagrass was used, as the requirements are somewhat similar. Macroalgae may extend deeper than the seagrasses but this could not be confirmed from available data.

All numbers should be considered conservative, but even given this, the more recent estimates are higher than the numbers assumed in the previous workshop.

Table 6.3. Productivity estimates from prior studies

	g C m^{-2} y^{-1}	**10^{12} g C y^{-1}**	**Reference**
Benthic GMx	109.5	19 (0-20m)	Murrell et al. 2009
Benthic MAB	146	25.7 (0-20m)	Jahnke et al. 2000
Total WC		336	
Total PP		358	

Table 6.4. Estimates of Benthic Primary Production (BPP)

Benthic Primary Producer	**Total BPP** Gt C y^{-1}	**Std dev** Gt C y^{-1}	**Area** (m^{-2})	**Convert to** g C y^{-1}	**Std dev** g C y^{-1}	**Avg. BPP** g C m^{-2} y^{-1}	**Std dev** g C m^{-2} y^{-1}
Microphytobenthos (avg upper 100 m)	0.038	0.038	4.58E+11	3.79E+13	3.78E+13	83	83
Microphytobenthos (avg upper 20 m)	0.025	0.023	1.73E+11	2.45E+13	2.31E+13	142	133
Seagrass (area from seagrass atlas)	0.005	0.003	1.93E+10	4.93E+12	2.68E+12	255	139
Macroalgae (area from seagrass atlas)	0.003	0.001	1.93E+10	3.00E+12	1.00E+12	155	52
Total Gulf phytobenthos upper 100 m	0.062	0.038	4.58E+11	6.19E+13	3.78E+13	135	83

Total Gulf phytobenthos upper 20 m	0.049	0.023	1.73E+11	4.85E+13	2.31E+13	280	133

7. Respiration

Contributors: G. Hitchcock, J. Lenes, R. Benner, K. Daly, M. Murrell, B. Roberts, J. Walsh

The Respiration Working Group was charged with evaluating respiration rates from the coastal and oceanic waters of the Gulf of Mexico (GOM) in the context of developing the Preliminary Carbon Budget, as well as summarizing both short- and long-term recommendations for future research. The main goal of the Group was to consider how spatial variability might influence the existing published rates of respiration for organic carbon in the GOM. As in the coastal waters of the eastern U.S. (Cai et al., in Najjar et al., 2012), there are few existing published measurements for dark respiration rates within the GOM. The relative paucity of respiration measurements as compared to net primary production rates (NPP) is a direct result of the widespread application of the ^{14}C incubation method in preference to oxygen-based measures of productivity (Marra, 2009). In general, there exist approximately an order of magnitude more determinations of NPP in marine surface waters than rates of dark community respiration (R), net community production (NCP), and gross primary production (GPP). Thus, R datasets exist in only three of the five regions that make up the GOM Carbon Budget study area (Fig. 1.1). To our knowledge, no published values of R exist for shelf waters off the Texas and Mexico coasts, although benthic respiration rates are available for the Texas shelf.

Published rates of R from the Northern Gulf, West Florida Shelf, and Central Gulf waters were evaluated by Working Group members that had previously conducted research in each of those regions. In all three areas, respiration rates were mainly measured as changes in dissolved oxygen concentrations from dark bottle incubations. The oxygen-based measurements were converted to carbon-based rates with a respiratory quotient of 1 in order to facilitate future comparisons with rates derived from other methods, and published ^{14}C-based rates of primary production in the GOM.

Here, we 1) review the magnitude of R from the published rates in the Northern Gulf, West Florida Shelf (WFS), and open Gulf to estimate the magnitude of the total annual respiration in these regions; 2) extrapolate R for the Texas and Mexico shelves from rates in the WFS; and 3) estimate a total annual respiration for the GOM. Several recommendations are proposed to better constrain R for the Carbon Budget in the Gulf of Mexico.

Regional Respiration Rates

Northern Gulf (Louisiana-east Texas Shelf)

There have been a sufficient number of studies on the Louisiana shelf for respiration rates to be evaluated within a four-compartment box model (Fig. 7.1). The nearshore segments correspond to volumes 1 (surface) and 3 (bottom) in Figure 7.1, while offshore segments are volumes 2 (surface) and 4 (bottom). The respiration rates for this region were compiled and evaluated by M. Murrell and B. Roberts from the studies cited in Murrell and Lehrter (2011), Murrell et al. (2013), and Roberts et al. (In prep.). The surface area of the shelf was provided courtesy of Rik Wanninkhof (AOML/NOAA), with the <20-m region encompassing 34% of the total area. The bathymetry for the Northern Gulf shelf and the WFS was computed by M. Murrell utilizing a Matlab script, which provided volumes for each compartment in the box model as listed below in Table 7.1.

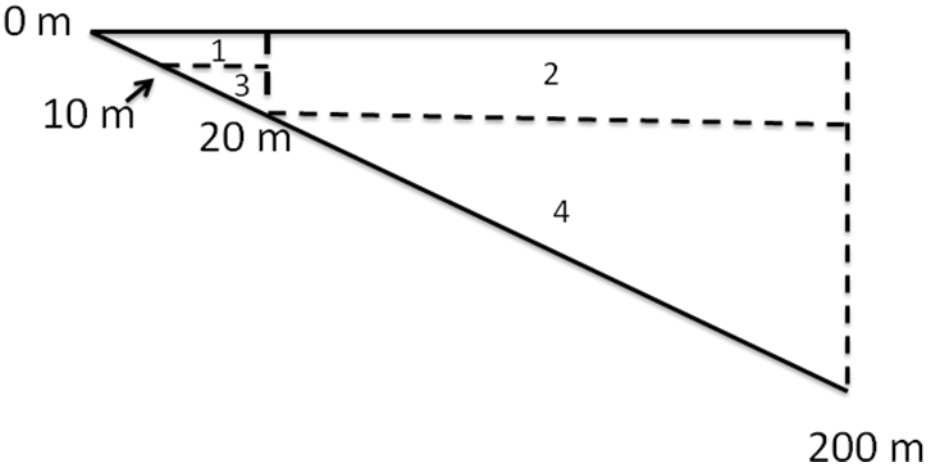


Figure 7.1. The LA shelf R-value is based on a 4-compartment box model. Nearshore segments correspond to volumes 1 (surface) and 3 (bottom), with offshore segments 2 (surface) and 4 (bottom).

Table 7.1. Volume, annual volumetric respiration rate (R_{vol}), and the annual total respiration (R) for compartments 1 to 4 (Fig. 7.1) in the Northern Gulf.

	VOLUME (m^3)	**R_{vol} ($g\ C\ m^{-3}\ y^{-1}$)**	**R ($10^{12}\ g\ C\ y^{-1}$)**
R1	3.96×10^{11}	46.6	18.5
R2	17.6×10^{11}	29.7	52.2
R3	1.44×10^{11}	31.9	4.59
R4	35.9×10^{11}	16.2	58.2

In total, the Northern Gulf has an annual respiratory demand of 133×10^{12} g C y^{-1}, largely supported by the nutrient and dissolved organic matter flux delivered to the northern Gulf from the Mississippi-Atchafalaya River system (MARS) (Rabalais et al., 2007). This annual rate exceeds R derived for the WFS, and the larger, oligotrophic surface waters of the open Gulf, as estimated below.

West Florida Shelf (WFS)

The area of the WFS is almost equivalent to that of Northern Gulf at 147 x 10^9 m^2 (Table 7.2), with 42.7 x 10^9 m^2 within the 0 to 20-m isobath. Harmful algal blooms (HABs) of the species *Karenia brevis* correspond to the annual maximum in both productivity (Vargo et al., 1987) and respiration (Hitchcock et al., 2010). We make the simplified assumption that these blooms occupy 5,000 km^2 of the inner shelf and occur for three months each year (G. Vargo, pers. comm.). A median bloom respiration rate of 76.5 mmol C m^{-3} d^{-1} from the literature corresponds to a daily rate of 0.918 g C m^{-3} d^{-1} for the 0 to 20-m area occupied by the blooms. These assumptions yield a bloom respiration of 4.13 x 10^{12} g C for those 3 months.

Table 7.2. Annual regional respiration rates based for the different GOM regions.

REGION	**DAILY R** (gC m^{-3} d^{-1})	**AREA** (10^9 m^2)	**ANNUAL R** (10^{12} gC yr^{-1})
Northern	0.044 – 0.128	147	133
WFS	0.076 – 0.918	147	55.9
Open	0.009 – 0.012	989	130-168
Texas	(0.076 – 0.152)[a]	8.68	(26.7)[b]
Mexico	(0.076)[a]	183	(52.8)[b]
		TOTAL	**396 to 436**

[a]Respiration rates are extrapolated from WFS. No direct measurements are available from the literature.

[b]Estimates based on R from WFS.

The corresponding ‘non bloom’ environment of the inner WFS is estimated for the area of the 0 to 20-m isobath (42.7 x 10^9 m^2) with an average mixed layer depth of 10 meters. Literature-based estimates of respiration rates in these ‘non-bloom’ WFS waters are 12.7 mmol C m^{-3} d^{-1}, or 0.152 g C m^{-3} d^{-1}. The annual respiration rate for ‘non-bloom’ waters of the WFS is equal to the ‘non-bloom’ volumetric respiration rate distributed over the inner shelf volume minus that contributed by surface waters during blooms over 5,000 km^2. This is equivalent to 23.0 x 10^{12} gC y^{-1}. The total respiration on the inner WFS (0 to 20 m) was therefore calculated as the sum of 1) HAB rate over an area of 5,000 km^2 for three months, 2) the ‘non-bloom’ contribution for the 5,000 km^2 over 9 months, and 3) the remaining inner shelf area at a rate corresponding to non-bloom waters. Thus, the total R for the inner shelf is 27.1 x 10^{12} g C y^{-1}, of which 15% of the annual respiration is due to HAB blooms.

The ‘offshore’ waters of the WFS (20 m to 200 m) extend over an area of 104 x 10^9 m^2 but only one study conducted measurements of respiration, and that was located on the 25-m isobath (Hitchcock et al., 2000). A mixed layer depth of 10 m yields a volume of 1.04 x 10^{12} m^3. We make an arbitrary assumption that the respiration rates are half of that in the nearshore area during non-bloom intervals, which extrapolates to a daily rate of 0.076 g C m^{-3} d^{-1}. At that rate, the outer WFS has an annual respiration of 28.8 x 10^{12} g C y^{-1}, contributing to a total WFS respiration of 55.9 x 10^{12} g C y^{-1}, less than half that of the northern GOM waters.

Open Gulf of Mexico

Respiration rates from the open Gulf waters (bottom depth > 1000m) were generated from the only two published studies from the region (Pomeroy et al., 1995; Biddanda and Benner, 1997). Rates are generally very low, approaching the limit of detection for the bottle incubation technique, requiring a measurement of R over longer time intervals to resolve decreases in dissolved oxygen. Values for the central GOM range from 30.0 to 38.8 nmol O_2 l^{-1} h^{-1}, or 0.009 to 0.012 g C m^{-3} d^{-1}, and are comparable to rates from similar techniques utilized in the Sargasso Sea (Obernosterer et al., 2003).

The offshore waters of open Gulf of Mexico encompass an area of 989.0 x 10^9 m^2, with an average mixed layer depth of approximately 40 m, yielding a mixed layer volume of 39.6 x 10^{12} m^3. These dimensions translate to a range in annual respiration rates for the open Gulf of 130 x 10^{12} g C y^{-1} to 168 x 10^{12} g C y^{-1}. Although the daily rates in the oligotrophic surface waters are low, the large area of the open GOM contributes to a respiration rate on the order of that in the northern GOM.

Texas Shelf

Respiration rates for the Texas shelf were estimated from rates for the non-bloom periods on the WFS. This estimate includes an assumption that the influence of the MAR discharge is limited to the Northern Gulf region. Additionally, HABs occur on the Texas shelf (Mangaña et al., 2003), though there are insufficient data to estimate their influence on respiration. Thus, R calculated for the Texas shelf is an underestimate. The area of the inner Texas shelf (0 to 20-m isobath) was extrapolated from data provided by R. Wanninkhof (9.51 x 10^9 m^2), with an assumed R of 0.152 g C m^{-3} d^{-1} to yield an annual R of 5.29 x 10^{12} g C y^{-1}. The remaining area on the outer shelf (77.3 x 10^9 m^2) was assumed to have R equivalent to that on the outer WFS (0.076 gC m^{-3} d^{-1}), distributed over a 10-m mixed layer, to yield an annual R of 21.4 x 10^{12} g C y^{-1}. The total annual R for the Texas shelf is therefore estimated at 26.7 x 10^{12} g C y^{-1}, although it is recognized that this value is an underestimate.

East Mexico Shelf

As with R values for the Texas shelf, the estimate for the Mexican shelf is based on a value extrapolated with rates from the WFS during non-bloom periods. Harmful algal blooms do occur in the coastal waters of the east Mexican shelf (Cortes-Altamirano et al., 1995), but there are no rates published for productivity or respiration during these periods of high plankton biomass. There is no data available for the inner shelf area (0 to 20 m), so the simplified estimate was calculated by extrapolating the outer WFS rate of 0.076 g C m^{-3} d^{-1} over the east Mexico shelf area of 183 x 10^3 m^2. With a 10-m mixed layer, an estimated annual R is equivalent to 52.8 x 10^{12} g C y^{-1}, a value comparable to that for the WFS.

Annual Respiration Rate

Individual regional rates contribute to an annual respiration rate of 396 to 436 x 10^{12} g C y^{-1} for the GOM. The rate of annual primary production for the water column in the GOM is estimated by Lohrenz et al. (this volume) at 256 x 10^{12} g C y^{-1} with benthic NPP contributing to a total NPP on the order of 358 x 10^{12} g C y^{-1}. While a higher value for R than NPP can, in part, be attributed to respiration of allochthonous organic matter introduced into the GOM, this carbon source would be unlikely to account for the total discrepancy. The annual input of organic matter from the MARS, for example, is approximately 5 Tg (R. Benner, pers. comm.), a minor quantity in the GOM carbon budget. This value is small compared to autotrophic production. As stated in the introduction, a debate now exists on factors that could contribute to higher values of R, as compared to NPP, that are typically reported for oligotrophic waters. The following recommendations are posed to refine the estimated R in the GOM, and thereby contribute to a realistic regional carbon budget.

Recommendations

a. Direct measures of pelagic R in the Central oligotrophic GOM, as well as the Texas and Mexican continental shelves, are essential to evaluate representative rates for the GOM carbon budget. Presently a debate exists regarding the application of oxygen- (or carbon-) based measurements from incubations to estimate R in oligotrophic waters (Ducklow and Doney, 2013; Duarte et al. 2013; Williams et al. 2013) such as the open GOM. Respiration rates from short-term (day) bottle incubations regularly suggest that the oligotrophic ocean is net heterotrophic with R > GPP (Duarte et al., 2013). Measures of the metabolic state of the oligotrophic ocean derived from biogeochemical indices, in contrast, suggest that when R and GPP are integrated over longer intervals than a day, the surface waters are net autotrophic with R < GPP (Williams et al., 2013). The uncertainty in the magnitude of these rates, especially R, and the sensitivity of the measures to the fine 'balance' between the production and degradation of organic matter in oligotrophic waters imply that present rates have a degree of uncertainty that requires further evaluation. Future rates for R from the central GOM should include observations at seasonal to annual scales, and the measurements should be compared with those from biogeochemical indices.

b. Benthic respiration rates should be measured throughout the GOM, which at present has relatively few benthic rates. Rates of benthic R have been measured in the northern GOM shelf (Rowe et al., 2002; Roberts and Murrell, pers. comm.), but there are far fewer observations than for pelagic R. Benthic respiration rates are a crucial parameter to improve the present estimates for R in the GOM ecosystem.

c. Coupled biophysical models should consider a range of R and NPP within each spatial region of the Gulf. These models could vary factors that are not considered within this evaluation. For example, N_2 fixation is prevalent throughout the GOM and could contribute a significant amount of organic matter to the carbon budget. In addition, the depth of the mixed layer varies seasonally, although the estimates in this report have used values of 10 m and 20m. Representative rates of R should be considered in deep waters coupled to any seasonal variability in the flux of sinking particulate organic matter. Collectively the models could provide a range of R, and provide guidance for design of future field studies.

d. Remotely-sensed chlorophyll *a* distributions in oligotrophic surface waters provide an opportunity to evaluate a potential role of short-term, mesoscale features that increase photoautotrophic biomass. These ‘blooms’ could potentially result in an episodic increase in organic matter and R in the Open GOM. Intense atmospheric cyclones, for example, could enhance nutrient inputs to oligotrophic surface waters and result in elevated plankton biomass (e.g., Babin et al., 2004). Examination of archived ocean color imagery for the GOM should be undertaken to estimate the potential input to NPP from ‘episodic’ events, and the potential contribution of resultant photosynthetic carbon to NPP and R, particularly in the open Gulf. The validity of this approach will require a thorough evaluation of the relationships between NPP and R with color imagery.

8. Revised Carbon Budget and Overarching Recommendations

A revised carbon budget for the Gulf of Mexico

Although there remain numerous unknown quantities in the latest version of the carbon budget show in Figure 8.1, there has also been much progress. One major change is the division of the water column into three regions with the addition of separate boxes for tidal wetlands and estuaries. There is a scarcity of published data for these two regions, and even areal estimates are lacking at this time, but the boxes are nevertheless retained to provide conformity with the East Coast Budget (Najjar et al., 2012) and to accentuate areas where additional research is required.

A major advance over the budget as it existed prior to this workshop is the compilation of more than 375,000 direct observations of $p\text{CO}_2$ collected in the Gulf of Mexico since 1996. The overall result is a net uptake for the entire Gulf of -3.57 TgCy^{-1} versus -11.8 TgCy^{-1} in the previous budget. Primary productivity estimates were also based on additional data and resulted in a slight decrease from 336 to 256 TgCy^{-1}. This was due in part to better approximation of the areal extent and seasonal variability in the Mississippi River plume. Preliminary estimates of benthic primary productivity are also included. Lastly, we have included preliminary estimates of estuarine net ecosystem production (NEP) and respiration rates for the entire Gulf of Mexico. Note that the estimate of methane flux is solely from data collected during the *Deepwater Horizon* oil spill incident.

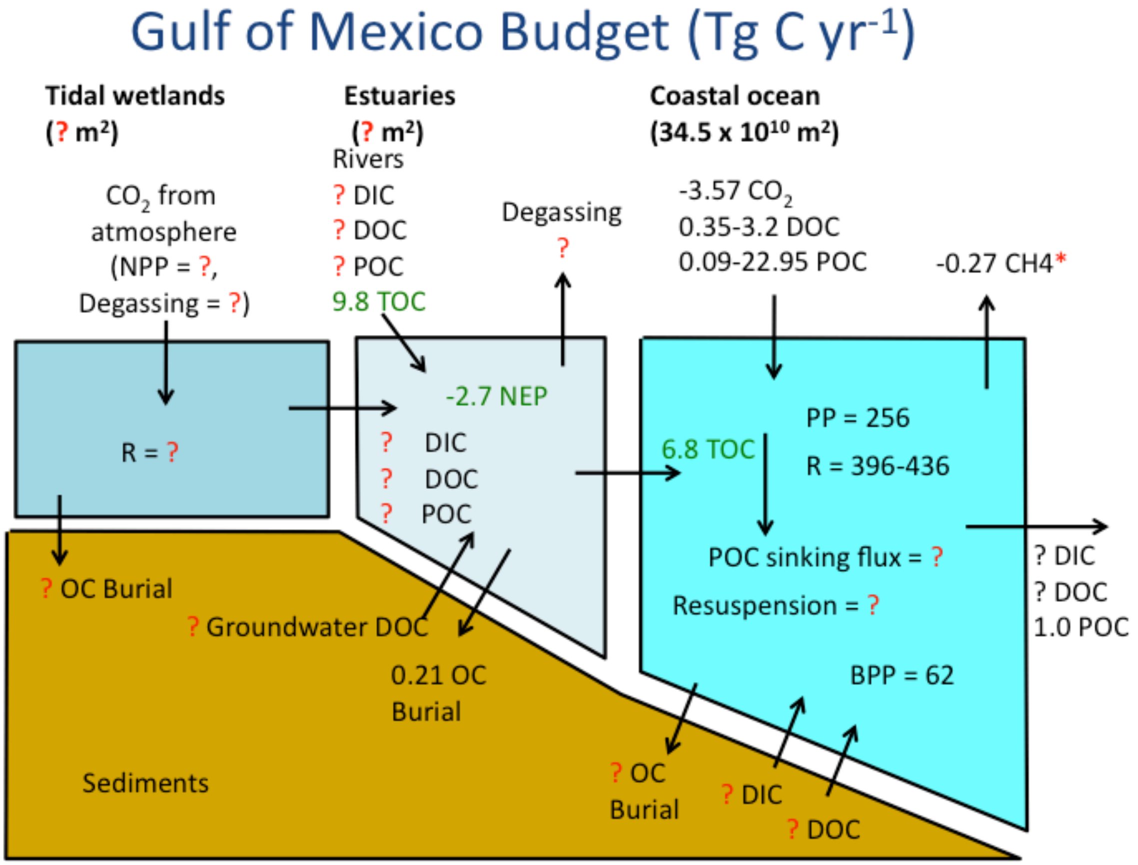


Figure 8.1. Updated carbon budget for the Gulf of Mexico based on synthesis activities conducted in preparation for the workshop and shortly thereafter. R = respiration, OC = organic carbon, POC = particulate organic carbon, DOC = dissolved organic carbon, DIC = dissolved inorganic carbon, PP = primary production, BPP = benthic primary production, NEP = net ecosystem production.

Future research and observational priorities

In addition to the detailed recommendations made by each flux team, there were a few overarching recommendations that emerged from the workshop:

- Comparative studies of estuaries in different North American coastal margin systems could be very useful in informing observation- and model-based estimates of carbon flux parameters - e.g., the east coast net ecosystem production (NEP) approach based on the LOICZ (Land-Ocean Interaction in the Coastal Zone) method, see Kemp et al. (2012)

- The interface between rivers and estuaries is highly dynamic with regard to physical circulation and carbon cycling. Participants determined that in addition to observations, quantifying carbon fluxes at this critical interface requires coupling estuarine and coastal circulation models that account for the complex physics and biogeochemical processing that occurs here.

- All flux teams noted sparse data coverage in one or more of the Gulf of Mexico subregions, particularly Mexican waters. Overall, the data coverage is better in the northern Gulf, open Gulf, and WFS regions, and data are particularly lacking in Mexican waters. Participants stressed a need to build and reinforce collaborations with Mexican colleagues.

- Nitrogen fixation is an important carbon and nitrogen supply mechanism for the coastal (e.g., MARS) and open waters of the Gulf of Mexico, but robust data sets are lacking and models do not currently resolve this process. A recent NSF-funded study (2009-2012) by Montoya et al. (http://osprey.bco-dmo.org/project.cfm?flag=view&id=158) will be instrumental in helping to constrain regional and Gulf-wide nitrogen fixation rates and associated diazotroph distributions. Nutrient data should also be added to the models.

- Model-observation and model-model comparisons are needed
    - Regional vs. entire Gulf estimates (compare different modeling approaches and outputs)
    - Global NEWS estimates from US and MX waters (cross-compare US estimates of SPARROW vs. Global NEWS, use Global NEWS estimates for MX)
    - The value of comparing model-simulated fluxes with the observation-based estimates derived by other groups was discussed and stressed

- A synthesis effort like this really requires a central repository for all compiled data (primary productivity, $p\mathrm{CO}_2$, etc.), including well documented metadata

- This group did not address sediment-water carbon fluxes. This is an important interface, but it spans rivers, estuaries, and the coastal-open ocean boundary, so participants determined that it should be its own group, of which submarine groundwater discharge would be a subcomponent. This group would be subdivided into depth zones spanning from the terrestrial boundary all the way out to the shelf edge. The group needs to assemble a flux team with the necessary expertise to constrain this piece of the Gulf carbon budget.

- Closing the Gulf carbon budget will require additional data from tidal wetlands (e.g., mangroves, salt marshes, etc.), including air-sea CO_2 fluxes

- More data on natural benthic seeps are needed to quantify their contribution to the Gulf carbon budget. L. Mayer et al. have been using a deep water multibeam echosounder (MBES) to map gas seeps in the Gulf (http://oceanexplorer.noaa.gov/okeanos/explorations/ex1202/background/seeps/welcome.html), which could help constrain initial estimates.

References

Antoine, D., and Morel, A. (1996). Oceanic primary production: I. Adaptation of a spectral light-photosynthesis model in view of application to satellite chlorophyll observations. *Global Biogeochem. Cycles*, **10**: 43-55.

Bates, T.S., Quinn, P.K., Coffman, D.J., Schulz, K., Covert, D.S., Johnson, J.E., Williams, E.J., Lerner, B.M., Angevine, W.M., Tucker, S.C., Brewer, W.A., and Stohl, A. (2008). Boundary layer aerosol chemistry during TexAQS/GoMACCS 2006: Insights into aerosol sources and transformation processes. *J. Geophys. Res*.: Atmospheres, **113**: D00F01, doi:10.1029/2008JD010023.

Babin, S.M., Carton, J.A., Dickey, T.D., and Wiggert, J.D (2004). Satellite evidence of hurricane-induced phytoplankton blooms in an oceanic desert. *J. Geophys. Res*., **109**: doi:10.1029/2003JC001938.

Behrenfeld, M.J., and Falkowski, P.G. (1997a). Photosynthetic rates derived from satellite-based chlorophyll concentration. *Limnol. Oceanogr*., **42**: 1-20.

Behrenfeld, M.J., Boss, E., Siegel, D.A., and Shea, D.M. (2005). Carbon-based ocean productivity and phytoplankton physiology from space. *Global Biogeochem. Cycles*, **19**, doi:10.1029/2004GB002299.

Bianchi, T.S., Pennock, J., and Twilley, R., editors (1999). Biogeochemistry of Gulf of Mexico Estuaries. John Wiley & Sons, 428 pp.

Biddanda, B., and Benner, R. (1997). Major contribution from mesopelagic zooplankton to heterotrophic metabolism in the upper ocean. *Deep-Sea Res. I*, **44**: 2067-2085.

Biggs, D.C. (1992). Nutrients, plankton and productivity in a warm-core ring in the western Gulf of Mexico. *J. Geophys. Res*., **97**: 2143-2154.

Biggs, D.C., Zimmerman*,* R.A., Gasca*, R.,* Suárez-Morales*, E.,* Castellanos*, I.,* and Leben, R.R. (1997). Note on plankton and cold-core rings in the Gulf of Mexico. *Fishery Bulletin*, **95(2)**: 369-375.

Bittaker, H.F. (1975). A comparative study of the phytoplankton and benthic macrophyte primary productivity in a polluted versus an unpolluted coastal area. M.S. thesis, Florida State University, Tallahassee, FL, 174 pp.

Bogdanov, D.V., Sokolov*, V.A., and* Khromov*, N.S.* (1968). Regions of high biological and commercial productivity in the Gulf of Mexico and Caribbean Sea. *Oceanology*, **8**: 371-381.

Borges, A.V. (2011). Present Day Carbon Dioxide Fluxes in the Coastal Ocean and Possible Feedbacks under Global Change, In: P. Duarte and J.M. Santana-Casiano (eds.), Oceans and the Atmospheric Carbon Content, DOI 10.1007/978-90-481-9821-4_3, Springer Science+Business Media B.V.

Bricker, S.B., Longstaff, B., Dennison, W., Jones, A., Boicourt, K., Wicks, C., and Woerner, J. (2007). Effects of Nutrient Enrichment in the Nation's Estuaries: A Decade of Change, NOAA Coastal Ocean Program Decision Analysis Series No. 26, National Centers for Coastal Ocean Science, Silver Spring, MD.

Brooks, J.M., Reid, D.F., and Bernard, B.B. (1981). Methane in the Upper Water Column of the Northwestern Gulf of Mexico. *J. Geophys. Res.*, **86**: 11029-11040.

Burdige, D.J., Zimmerman, R.C., and Hu, X.P. (2008). Rates of carbonate dissolution in permeable sediments estimated from pore-water profiles: The role of sea grasses. *Limnology and Oceanography*, **53**: 549-565.

Burnett, W.C., Bokuniewicz, H., Huettel, M., Moore, W.S., and Taniguchi, M. (2003). Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*, **66**: 3-33.

Cai, W.-J. (2003). Riverine inorganic carbon flux and rate of biological uptake in the Mississippi River plume. *Geophysical Research Letters*, **30**(2): 1-4, doi:10.1029/2002GL016312.

Cai, W.-J. (2011). Estuarine and Coastal Ocean Carbon Paradox: CO2 Sinks or Sites of Terrestrial Carbon Incineration? *Annual Review of Marine Science*, **3**: 123-145, DOI: 10.1146/annurev-marine-120709-142723.

Cai, W.-J., Friedrichs, M., Najjar, R., Vlahos, P., and Xue, J. (2012). Respiration and net community production. In: R.G. Najjar, M.A.M. Friedrichs, and W.-J. Cai (editors). Report of the East Coast Carbon Cycle Synthesis Workshop. January 19-20, 2012, Ocean Carbon and Biogeochemistry Program and North American Carbon Program. 34 pp.

Cardenas-Valencia, A.M., Adornato, L.R., Bell, R.J., Byrne, R.H., and Short, R.T. (2012). Evaluation of reagentless pH modification for in situ ocean analysis: determination of dissolved inorganic carbon using mass spectrometry. *Rapid Communications in Mass Spectrometry*, **5**: 635-642.

Charette, M.A., and Sholkovitz, E.R. (2006). Trace element cycling in a subterranean estuary: Part 2. Geochemistry of the pore water. *Geochim. Cosmochim. Acta*, **70**: 811-826.

Chavez, F., Takahashi, T., Cai, W.-J., Friederich, G.E., Hales, B.E., Wanninkhof, R., and Feely, R.A. (2007). Chapter 15, The Coastal Ocean. In: The First State of the Carbon Cycle Report (SOCCR): The North American Carbon Budget and Implications for the Global Carbon Cycle. Report by the U.S. Climate Change Science Program and the Subcommittee on Global Change Research, edited by: King, A.W., Dilling, L., Zimmerman, G.P., Fairman, D.M., Houghton, R.A., Marland, G., Rose, A.Z., and Wilbanks, T.J., National Oceanic and Atmospheric Administration, National Climatic Data Center, Asheville, NC, USA, pp. 157-166.

Chen, C., Wiesenburg, D.A., and Xie, L. (1997). Influence of river discharge on biological production in the inner shelf: A coupled biological and physical model of the Louisiana-Texas Shelf. *Journal of Marine Research*, **55**: 293-320.

Chen, X. (2000). Phytoplankton primary production in the Northwestern Gulf of Mexico. University of Southern Mississippi, Hattiesburg, MS, 207 pp.

Chen, X., Lohrenz, S.E., and 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.

Coble, P.G., Robbins, L., Daly, K.L., Cai, W.-J., Fennel, K., and Lohrenz, S.E. (2010). A preliminary carbon budget for the Gulf of Mexico. *Ocean Carbon and Biogeochemistry News*, **3**: 1-4.

Cole, J., Prairie, Y., Caraco, N., McDowell, W., Tranvik, L., Striegl, R., Duarte, C., Kortelainen, P., Downing, J., Middelburg, J., and Melack, J. (2007). Plumbing the global carbon cycle: Integrating inland waters into the terrestrial carbon budget. *Ecosystems,* **10**: 172-185.

Corbett, D.R., Chanton, J., Burnett, W., Dillon, K., Rutkowski, C., and Fourqurean, J.W. (1999). Patterns of groundwater discharge into Florida bay. *Limnology and Oceanography*, **44**, 1045-1055.

Cortes-Altamirano, R., Hernandez-Becerril, D.U., and Luna-Soria, R. (1995). Mareas rojas en Mexico, una revision. (in Spanish). *Rev. Lat.-Am. Microbial.*, **37**: 343-352.

Curl, H.C., Jr. (1956). The hydrography and phytoplankton ecology of the inshore, northeastern Gulf of Mexico. Ph.D. dissertation, Florida State University, Tallahassee, FL, 285 pages.

Dagg, M., Grimes, C., Lohrenz, S., McKee, B., Twilley, R., and Wiseman, W., Jr. (1991). Continental shelf food chains of the northern Gulf of Mexico. In: Food Chains, Yields, Models, and Management of Large Marine Ecosystems. K. Sherman, L.M. Alexander, and B.D. Gold (editors), Westview Press, Boulder, CO, pp. 67-106.

Dagg, M.J., Bianchi, T.S., Breed, G.A., Cai, W.-J., Duan, S., Liu, H., McKee, B.A., Powell, R.T., and Stewart, C.M. (2005). Biogeochemical characteristics of the lower Mississippi River, USA, during June 2003. *Estuaries*, **28**: 664-674.

Dai, M., Yin, Z., Meng, F., Liu, Q., and Cai, W.-J. (2012). Spatial distribution of riverine DOC inputs to the ocean: an updated global synthesis. *Current Opinion in Environmental Sustainability*, **4**(2): 170-178.

Dawes, C.J. (1998). Biomass and photosynthetic responses to irradiance by a shallow and a deep water population of *Thalassia testudinum* on the west coast of Florida. *Bulletin of Marine Science*, **62**: 89-96.

Day, J.W., Jr., Hopkinson, C.S., and Conner, W.H. (1982). An analysis of environmental factors regulating community metabolism and fisheries production in a Louisiana estuary. In: Estuarine Comparisons. V.S. Kennedy (editor), Academic Press, New York, pp. 121-136.

Deegan, L.A., Johnson, W.B., Gosselink, J.G., Day, J.W., Jr., Yanez-Arancibia, A., Woodsum, G., and Duever, M. (1983). Estuarine primary production in the Gulf of Mexico - a complex response to physiographic climatic and marine processes. *Estuaries,* **6**(3): 284-285.

Dettmann, E.H. (2001). Effect of water residence time on annual export and denitrification of nitrogen in estuaries: A model analysis. *Estuaries*, **24**(4): 481-490: doi:10.2307/1353250.

Dorsett, A., Cherrier, J., Martin, J.B., and Cable, J.E. (2011). Assessing hydrologic and biogeochemical controls on pore-water dissolved inorganic carbon cycling in a subterranean estuary: A 14C and 13C mass balance approach. *Marine Chemistry*, **127**: 76-89.

Duarte, C.M., Regaudie-de-Gioux, A., Arrieta, J.M., Delgado-Huertas, A., and Agustí, S. (2013). The oligotrophic ocean is heterotrophic. *Ann. Rev. Mar. Sci.*, **5**: 551-569.

Ducklow, H.W., and Doney S.C. (2013). What is the metabolic state of the oligotrophic ocean? A debate. *Ann. Rev. Mar. Sci*., **5**: 525-533.

Dyer, K.R. (1997). Estuaries: A Physical Introduction. Wiley, Chichester, England.

Eadie, B.J., McKee, B.A., Lansing, M.B., Robbins, J.A., Metz, S., and Trefry, J.H. (1994). Records of nutrient enhanced coastal ocean productivity in sediments from the Louisiana continental shelf. *Estuaries*, **17**(4): 754-765.

El-Sayed, S.Z. (1972). Primary productivity and standing crop of phytoplankton. Chemistry, primary productivity, and benthic algae of the Gulf of Mexico. In: Serial Atlas of the Marine Environment. V.C. Bushnell, W.M. Sackett, and L.M. Jeffrey (editors), American Geographical Society, New York, Folio 22, 29 pp.

El-Sayed, S.Z., and Turner, J.T. (1977). Productivity of the Antarctic and tropical/subtropical regions: a comparative study. In: Polar Oceans. M.J. Dunbar (editor). Arctic Institute of North America, McGill University Montreal, pp. 463-503.

Fahnenstiel, G.L., McCormick, M.J., Lang, G.A., Redalje, D.G., Lohrenz, S.E., Markowitz, M., Wagoner, B., Carrick, H.J. (1992). Taxon-specific production and growth rates of dominant phytoplankton from the northern Gulf of Mexico. *Journal of Phycology*, **28**(SUPPL S3): 3-15.

Fennel, K. (2010). The role of continental shelves in nitrogen and carbon cycling: Northwestern North Atlantic case study. *Ocean Science*, **6**: 539-548, doi:10.5194/os-6-539-2010.

Fennel, K., Wilkin, J., Levin, J., Moisan, J., O'Reilly, J., and Haidvogel, D.B. (2006). Nitrogen cycling in the Middle Atlantic Bight: Results from a three-dimensional model and implications for the North Atlantic nitrogen budget. *Global Biogeochemical Cycles*, **20**: GB3007, doi:10.1029/2005GB002456.

Fennel, K., Wilkin, J., Previdi, M., and Najjar, R. (2008). Denitrification effects on air-sea CO2 flux in the coastal ocean: Simulations for the Northwest North Atlantic, *Geophysical Research Letters*, **35**: L24608, doi:10.1029/2008GL036147.

Franceschini, G.A., and El-Sayed, S.Z. (1968). Effect of Hurricane Inez (1966) on the hydrography and productivity of the western Gulf of Mexico. *Deutsche Hydrographische Zeitschrift*, **21**: 193-202.

Fucik, K.W., and El-Sayed, S.Z. (1979). Effect of oil production and drilling operations on the ecology of phytoplankton in the OEI study area. *Rice University Studies*, **65**: 325-354.

Gao, Z., Chen, L., Sun, H., Chen, B., and Cai, W.-J. (2012). Distributions and air-sea fluxes of carbon dioxide in the Western Artic Ocean. *Deep-Sea Research II*, **81-84**: 46-52.

Gattuso, J.P., Frankignoulle, M., and Wollast, R. (1998). Carbon and Carbonate Metabolism in Coastal Aquatic Ecosystems. *Annual Review of Ecology and Systematics*, **29**: 405-434.

Green, R.E., Breed, G.A., Dagg, M.J., and Lohrenz, S.E. (2008). Modeling the response of primary production and sedimentation to variable nitrate loading in the Mississippi River plume. *Continental Shelf Research*, **28**(10-11): 1451-1465.

Guo, X., Lohrenz, S.E., Huang, W.-J., Wang, Y., Chen, F., Murrell, M.C., and Culp, R. (2012). Carbon dynamics and community production in the Mississippi River plume. *Limnolog. Oceanography*, **57**: 1-17.

Hales, B., Cai, W.-J., Mitchell, B.G., Sabine, C.L., and Schofield, O., editors (2008). North American Continental Margins: a synthesis and planning workshop. Report of the North American Continental Margins Working Group for the U.S. Carbon Cycle Scientific Group and Interagency Working Group, U.S. Carbon Cycles Science Program, Washington, DC.

Herrmann, M., Najjar, R.G., Kemp, W.M., McCallister, S.L., Alexander, R.B., Cai, W.-J., Griffith, P., and Smith, R.A. (submitted). Net ecosystem production and organic carbon balance of U.S. East Coast estuaries: A synthesis approach. *Global Biogeochem. Cycles*.

Hetland, R., and DiMarco, S. (2012). Skill assessment of a hydrodynamic model of the circulation over the Texas-Louisiana continental shelf. *Ocean Model.*, **43/44**, 64-76.

Hidalgo-González, R.M., Alvarez-Borrego, S., Fuentes-Yaco, C., and Platt, T. (2005). Satellite-derived total and new phytoplankton production in the Gulf of Mexico. *Indian Journal of Marine Sciences*, **34**: 408-417.

Hitchcock, G.L., Vargo, G.A., and Dickson, M.L. (2000). Plankton community composition, production, and respiration in relation to dissolved inorganic carbon on the West Florida Shelf, April 1996. *Journal of Geophysical Research. C. Oceans*, **105**(C3): 6579-6589.

Hitchcock, G.L., Kirkpatrick, G., Minnett, P., and Plubok, V. (2010). Net community production and dark community respiration in a *Karenia brevis* bloom in west Florida coastal waters, USA. *Harmful Algae*, **9**: 351-358.

Hu, X., Cai, W.-J., Wang, Y., and Guo, X. (2011). Geochemical environments of continental shelf-upper slope sediments in the northern Gulf of Mexico. *Palaeogeography, Palaeoclimatology, Palaeoecology,* **312**(3-4): 265-277.

Hu, X.P., and Burdige, D.J. (2008). Shallow marine carbonate dissolution and early diagenesis-implications from an incubation study. *Journal of Marine Research*, **66**: 489-527.

Iverson, R.L., and Hopkins, T.L. (1981). A summary of knowledge of plankton production in the Gulf of Mexico: recent phytoplankton and zooplankton research. Proceedings of a Symposium on Environmental Research Needs in the Gulf of Mexico (GOMEX). NOAA/ADML, Miami, pp. 147-211. (Invited Paper).

Jahnke, R.A., Nelson, J.R., Richards, M.E., Robertson, C.Y., Rao, A.M.F., and Jahnke, D.B. (2008). Benthic primary productivity on the Georgia midcontinental shelf: Benthic flux measurements and high-resolution, continuous in situ PAR records. *J. Geophys. Res.*, **113**: C08022, doi:10.1029/2008JC004745.

Johannes, R.E. (1980). The ecological significance of the submarine discharge of groundwater. *Marine Ecology Progress Series*, **3**: 363-373.

Justic, D., Rabalais, N.N., Turner, R.E., and Wiseman, W.J. Jr. (1993). Seasonal coupling between riverborne nutrients, net productivity and hypoxia. *Marine Pollution Bulletin*, **26**(4): 184-189.

Kaldy, J.E., and Dunton, K.H. (2000). Above- and below-ground production, biomass and reproductive ecology of *Thalassia testudinum* (turtle grass) in a subtropical coastal lagoon. *Marine Ecology Progress Series,* **193**: 271-283.

Kemp, M., McCallister, L., Anderson, I., Brush, M., Canuel, E., Hall, E., Herrmann, M., Kroeger, K., Najjar, R., Tzortziou, M., and Zimmerman, R. (2012). Fluxes in estuaries. In: Najjar, R.G., Friedrichs, M.A.M., and Cai, W.-J. (editors), Report of The U.S. East Coast Carbon Cycle Synthesis Workshop. January 19-20, 2012, Ocean Carbon and Biogeochemistry Program and North American Carbon Program, pp. 7-8.

Keul, N., Morse, J., Wanninkhof, R., Gledhill, D.K., and Bianchi, T.S. (2010). Carbonate Chemistry Dynamics of Surface Waters in the Northern Gulf of Mexico. *Aquatic Geochemistry*, **16**(3): 337-351.

Koblentz-Mishke, O.I., Volkovinsky, V.V., and Kabanova, J.G. (1970). Plankton primary production of the world ocean. In: Scientific Exploration of the South Pacific, proceedings of a symposium held during the Ninth General Meeting of the Scientific Committee on Oceanic Research. W.W. Wooster (editor), National Academy Press, Washington, D.C., pp. 183-193

Kowalski, J.L., Deyoe, H.R., and Allison, T.C. (2009). Seasonal Production and Biomass of the Seagrass, *Halodule wrightii* Aschers. (Shoal Grass), in a Subtropical Texas Lagoon. *Estuaries and Coasts*, **32**: 467-482.

Krest, J.M., Moore, W.S., and Rama (1999). Ra-226 and Ra-228 in the mixing zones of the Mississippi and Atchafalaya rivers: Indicators of groundwater input. *Marine Chemistry*, **64**: 129-152.

Lehrter, J.C., Murrell, M.C., and Kurtz, J.C. (2009). Interactions between freshwater input, light, and phytoplankton dynamics on the Louisiana continental shelf. *Continental Shelf Research*, **29**(15): 1861-1872.

Lohrenz, S.E. (1995). Relationship of primary production to physical oceanography in the Northeastern Gulf of Mexico. Northeastern Gulf of Mexico Physical Oceanography Workshop; proceedings of a workshop held in Tallahassee, Florida, April 5-7, 1994. A. J. Clarke. New Orleans, LA, U.S. Department of the Interior, Minerals Management Service, Gulf of Mexico OCS Region, pp. 43-49.

Lohrenz, S.E., Fahnenstiel, G.L., Redalje, D.G., and Lang, G.A. (1992). Regulation and distribution of primary production in the northern Gulf of Mexico. Nutrient Enhanced Coastal Ocean Productivity, NECOP Workshop Proceedings, October 1991. N. C. O. Program. College Station, TX, Texas Sea Grant Publications, pp. 95-104.

Lohrenz, S.E., Fahnenstiel, G.L., and Redalje, D.G. (1994). Spatial and temporal variations of photosynthetic parameters in relation to environmental-conditions in coastal waters of the northern Gulf of Mexico. *Estuaries*, **17**(4): 779-795.

Lohrenz, S.E., Redalje, D.G., Fahnenstiel, G.L., McCormick, M.J., Lang, G.A., Prasad, K., Chen, X., Atwood, D.A., and Chen, B. (1995). Phytoplankton rate processes in coastal waters of the northern Gulf of Mexico and relationships to environmental conditions. Nutrient-Enhanced Coastal Ocean Productivity. N. C. O. P. Office, Baton Rouge, LA, Sea Grant Publications: 56-66.

Lohrenz, S.E., Fahnenstiel, G.L., Redalje, D.G., Lang, G.A., Chen, X, and Dagg, M.J. (1997). Variations in primary production of northern Gulf of Mexico continental shelf waters linked to nutrient inputs from the Mississippi River. *Marine Ecology Progress Series*, **155**: 45-54.

Lohrenz, S.E., Wiesenburg, E., Arnone, D.A., and Che, R.A.(1999). What controls primary production in the Gulf of Mexico? The Gulf of Mexico Large Marine Ecosystem: Assessment, Sustainability and Management. K. Sherman, H. Kumpf and K. Steidinger, editors, Malden, MA, Blackwell Science, Inc., pp. 151-170.

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

Lohrenz, S., Cai, W.-J., Chen, F., Chen, X., and Tuel, M. (2010). Seasonal variability in air-sea fluxes of CO2 in a river-influenced coastal margin. *Journal of Geophysical Research*, **115** (C10): DOI: 10.1029/2009JC005608.

MacIntyre, H.L., and Cullen, J.J. (1996). Primary production by suspended and benthic microalgae in a turbid estuary: time-scales of variability in San Antonio Bay, Texas. *Marine Ecology Progress Series*, **145**: 245-268.

Madden, C.F. (1992). Control of phytoplankton production in a shallow, turbid estuary. Ph.D. dissertation, Louisiana State University, Baton Rouge.

Magaña, H.A., Contreras, C., and Villareal, T.A. (2003). A historical assessment of *Karenia brevis* in the western Gulf of Mexico. *Harmful Algae*, **2**: 163-171.

Marra, J. (2009). Net and gross productivity: weighing in with 14C. *Aquat. Microbial Ecol.*, doi: 10.3354/ame01306.

McCoy, C.A., Corbett, D.R., McKee, B.A., and Top, Z. (2007). An evaluation of submarine groundwater discharge along the continental shelf of Louisiana using a multiple tracer approach. *Journal of Geophysical Research*, **112** (C3): DOI: 10.1029/2006JC003505.

Medina-Gomez, I., and Herrera-Silveira, J.A. (2006). Primary production dynamics in a pristine groundwater influenced coastal lagoon of the Yucatan Peninsula. *Continental Shelf Research*, **26**(8): 971-986.

Moncreiff, C.A., Sullivan, M.J., and Daehnick, A.E. (1992). Primary production dynamics in seagrass beds of Mississippi Sound - the contributions of seagrass, epiphytic algae, sand microflora, and phytoplankton. *Marine Ecology Progress Series*, **87**: 161-171.

Moore, W.S. (1999). The subterranean estuary: A reaction zone of ground water and sea water. *Marine Chemistry*, **65**: 111-125.

Moore, W.S., Sarmiento, J.L., and Key, R.M. (2008). Submarine groundwater discharge revealed by Ra-228 distribution in the upper Atlantic Ocean. *Nature Geosciences*, **1**: 309-311.

Müller-Karger, F.E., Walsh, J.J., Evans, R.H., and Meyers, M.B. (1991). On the seasonal phytoplankton concentration and sea-surface temperature cycles of the Gulf of Mexico as determined by satellites. *J. Geophys. Res.-Oceans*, **96**: 12645-12665.

Murrell, M.C., Hagy, J.D., Lores, E.M., and Greene, R.M. (2007). Phytoplankton production and nutrient distributions in a subtropical estuary: Importance of freshwater flow. *Estuaries and Coasts*, **30**(3): 390-402.

Murrell, M.C., Stanley, R.S., Lehrter, J.C., Hagy, J.D., III (2013). Plankton community respiration, net ecosystem metabolism, and oxygen dynamics on the Louisiana continental shelf: Implications for hypoxia. *Continental Shelf Research*, **52**(0): 27-38.

Murrell, M.C., and Lehrter, J.C. (2011). Sediment and lower water column oxygen consumption in the seasonally hypoxic region of the Louisiana Continental Shelf. *Estuaries and Coasts*, **34**: 912-924.

Murrell, M.C., Stanley, R.S., Lehrter, J.C. and Hagy, J.D., III (2013). Plankton community respiration, net ecosystem metabolism, and oxygen dynamics on the Louisiana continental shelf: Implications for hypoxia. *Continental Shelf Research*, **52**: 27-38.

Mwashote, B.M., Murray M., Burnett, W.C., Chanton, J., Kruse, S., and Forde, A. (2013). Submarine groundwater discharge in the Sarasota Bay system: Its assessment and implications for the nearshore coastal environment. *Continental Shelf Research*, **53**: 63-76.

Myers, V.B., and Iverson, R.L. (1981). Phosphorus and nitrogen limited phytoplankton productivity in northeastern Gulf of Mexico coastal waters. In: Estuaries and Nutrients. B.J. Neilson and L.E. Cronin (editors), Humana Press, Clifton, N. J., pp. 569-582.

Najjar, R., Butman, D.E., Cai, W.-J., Friedrichs, M.A., Kroeger, K.D., Mannino, A., Vlahos, P. (2010). Carbon budget for the continental shelf of the eastern United States: a preliminary synthesis. *Ocean Carbon and Biogeochemistry News*, **3**(1): 1-4.

Najjar, R.G., Friedrichs, M.A.M., Cai, W.-J., editors (2012). Report of the U.S. East Coast Carbon Cycle Synthesis Workshop, January 19-20, 2012, Ocean Carbon and Biogeochemistry Program and North American Carbon Program, 34 pp.

Nixon, S.W., Ammerman, J.W., Atkinson, L.P., Berounsky, V.M., Billen, G., Boicourt, W.C., Boynton, W.R., Church, T.M., Ditoro, D.M., Elmgren, R. (1996). The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. *Biogeochemistry*, **35**: 141-180.

Obernosterer, I., Kawasaki, N., and Benner, R. (2003). P-limitation of respiration in the Sargasso Sea and uncoupling of bacteria from P-regeneration in size-fractionation experiments. *Aquat. Microb. Ecol.*, **32**: 229-237.

Okey, T.A., Vargo, G.A., Mackinson, S., Vasconcellos, M., Mahmoudi, B., and Meyer, C.A. (2004). Simulating community effects of sea floor shading by plankton blooms over the West Florida Shelf. *Ecological Modelling*, **172**: 339-359.

Ortner, P.B., and Dagg, M.J. (1995). Nutrient-enhanced coastal ocean productivity explored in the Gulf of Mexico. *Eos, Transactions, American Geophysical Union*, **76**: 97-109.

Ortner, P.B., Ferguson, R.L., Piotrowicz, S.L., Chesal, L., Berberian, G., and Palumbo, A.V. (1984). Biological consequences of hydrographic and atmospheric advection within the Gulf Loop intrusion. *Deep-Sea Research Part A. Oceanographic Research Papers*, **31**: 1101-1120.

Park, G.-H., Wanninkhof, R., Doney, S.C., Takahashi, T., Kitack, L., Feely, R.A., Lima, I.D. (2010). Variability of global net sea-air CO2 fluxes over the last three decades using empirical relationships. *Tellus*, **62**(5): 352-368, DOI: 10.1111/j.1600-0889.2010.00498.x.

Pennock, J.R., Sharp, J.H., and Schroeder, W.W. (1994). What controls the expression of estuarine eutrophication? Case studies of nutrient enrichment and phytoplankton production from the Delaware Bay and Mobile Bay estuaries, USA. In: Changes in Fluxes in Estuaries: Implications from Science to Management. K. Dyer and C. D'Elia (editors), Olsen and Olsen, pp. 139-146.

Pennock, J.R., Boyer, J.N., Herrera-Silveira, J.A., Iverson, R.L., Whitledge, T.E., Mortazavi, B., and Comin, F.A. (1999). Nutrient behavior and phytoplankton production in Gulf of Mexico estuaries. Biogeochemistry of Gulf of Mexico Estuaries, T.S. Bianchi, J.R. Pennock, and R.R. Twilley (editors), John Wiley & Sons, Inc., New York, pp. 109-162.

Pierrot, D., Neill, C., Sullivan, K., Castle, R., Wanninkhof, R., Luger, H., and Cosca, C.E. (2009). Recommendations for autonomous underway pCO2 measuring systems and data-reduction routines. *Deep-Sea Research II*, **56**(8-10): 512-522.

Pomeroy, L.R., Sheldon, J.E., Sheldon, W.M. Jr., and Peters, F. (1995). Limits to growth and respiration of bacterioplankton in the Gulf of Mexico. *Mar. Ecol. Prog. Ser.*, **117**: 259-268.

Prasad, K.S., Lohrenz, S.E., Redalje, D.G., and Fahnenstiel, G.L. (1994). Primary production in the Gulf of Mexico coastal waters using remotely-sensed trophic category approach. Journal of Mississippi Academy of Sciences, **39**: 62.

Prasad, K.S., Lohrenz, S.E., Redalje, D.G., and Fahnenstiel, G.L. (1995). Primary production in the Gulf of Mexico coastal waters using remotely-sensed trophic category approach. *Continental Shelf Research*, **15**(11-12): 1355-1368.

Quigg, A., Sylvan, J.B., Gustafson, A.B., Fisher, T.R., Oliver, R.L., Tozzi, S., and Ammerman, J.W. (2011). Going West: Nutrient Limitation of Primary Production in the Northern Gulf of Mexico and the Importance of the Atchafalaya River. *Aquatic Geochemistry*, **17**(4-5): 519-544.

Quiñones-Rivera, Z.J., Wissel, B., and Justić, D. (2009). Development of Productivity Models for the Northern Gulf of Mexico Based on Oxygen Concentrations and Stable Isotopes. *Estuaries and Coasts*, **32**(3): 436-446.

Rabalais, N.N., Lohrenz, S.E., Redalje, D.G., Dortch, Q., Justić, D., Turner, R.E., Qureshi, N.A., Dagg, M.J., Eadie, B.J., and Fahnenstiel, G.L. (1999). Nutrient-enhanced coastal productivity and ecosystem responses. In: Nutrient Enhanced Coastal Ocean Productivity in the Northern Gulf of Mexico - Understanding the Effects of Nutrients on a Coastal Ecosystem. W. J. Wiseman, Jr., M.J. Dagg, N.N. Rabalais, and T.E. Whitledge, (editors). Silver Spring, MD, NOAA Coastal Ocean Program, pp. 51-78.

Rabalais, N.N., Turner, R.E., Gupta, B.K.S., Platon, E., and Parsons, M.L. (2007). Sediments tell the history of eutrophication and hypoxia in the northern Gulf of Mexico. *Ecological Applications, Special Issue, Nutrient Enrichment of Estuarine and Coastal Marine Environments*, **17**(5): S129-S143.

Rabouille, C., Conley, D.J., Dai, M.H., Cai, W.-J., Chen, C.T.A., Lansard, B., Green, R., Yin, K., Harrison, P.J., Dagg, M., McKee, B., (2008). Comparison of hypoxia among four river-dominated ocean margins: The Changjiang (Yangtze), Mississippi, Pearl, and Rhone rivers. *Continental Shelf Research*, **28**(12): 1527-1537.

Randall, J.M., and Day, J.W. Jr. (1987). Effects of river discharge and vertical circulation on aquatic primary production in a turbid Louisiana estuary. *Netherlands Journal of Sea Research*, **21**: 231-242.

Redalje, D.G., Lohrenz, S.E., and Fahnenstiel, G.L. (1992). The relationship between primary production and the export of POM from the photic zone in the Mississippi River plume and inner Gulf of Mexico shelf regions. Nutrient Enhanced Coastal Ocean Productivity, NECOP Workshop Proceedings, October 1991. N. C. O. Program. College Station, Texas, Texas Sea Grant Publications: 105-110.

Redalje, D.G., Lohrenz, S.E., and Fahnenstiel, G.L. (1994). The relationship between primary production and the vertical export of particulate organic matter in a river impacted coastal ecosystem. *Estuaries*, **17**: 829-838.

Robbins, L.L., Coble, P.G., Clayton, T. and Cai, W.-J. (2009). Terrestrial and Coastal Carbon Fluxes in the Gulf of Mexico Workshop, 6-8 May, 2008, St. Petersburg, FL, USA, USGS Open File Report 2009-1070, 80 pp.

Rowe, G.T., Cruz-Kaegi, M.E., Morse, J., Boland, G., and Escobar Briones, E.G. (2002). Sediment community metabolism associated with continental shelf hypoxia, northern Gulf of Mexico. *Estuaries*, **25**: 1097-1106.

Roy, M., Martin, J.B., Smith, C.G., and Cable, J.E. (2011). Reactive-transport modeling of iron diagenesis and associated organic carbon remineralization in a Florida (USA) subterranean estuary. *Earth and Planetary Science Letters*, **304**: 191-201.

Roy, M., Martin, J.B., Cherrier, J., Cable, J.E., and Smith, C.G. (2010). Influence of sea level rise on iron diagenesis in an east Florida subterranean estuary. *Geochim. Cosmochim. Acta*, **74**: 5560-5573.

Ryerson, T. B., et al. (2011), Atmospheric emissions from the Deepwater Horizon spill constrain air-water partitioning, hydrocarbon fate, and leak rate, Geophys. Res. Lett., 38, L07803, doi:10.1029/2011GL046726.

Sanchez, L. (1992). Primary productivity of the northwest Gulf of Mexico: shipboard measurement in July 1990, October 1990, and March 1991. M.S. thesis, Texas A&M University, College Station, TX, 120 pp.

Santos, I.R., Burnett, W.C., Chanton, J., Mwashote, B., Suryaputra, I.G.N.A., and Dittma, T. (2008). Nutrient biogeochemistry in a Gulf of Mexico subterranean estuary and groundwater-derived fluxes to the coastal ocean. *Limnology and Oceanography*, **53**: 705-718.

Santos, I.R., Burnett, W.C., Dittmar, T., Suryaputra, I.G.N.A., and Chanton, J. (2009). Tidal pumping drives nutrient and dissolved organic matter dynamics in a Gulf of Mexico subterranean estuary. *Geochim. Cosmochim. Acta*, **73**: 1325-1339.

Scalise, K. 2013. Atmospheric Distributions of Polycyclic Aromatic Hydrocarbons (PAHs) in Coastal Northern Gulf of Mexico, USA, Associated with the Deepwater Horizon Oil Spill. MS Thesis. East Carolina University. 116 pp.

Seitzinger, S., Harrison, J., Bohlke, J., Bouwman, A., Lowrance, R., Peterson, B., Tobias, C., and Drecht, G. (2006). Denitrification across landscapes and waterscapes: a synthesis. *Ecol. Appl*., **16**: 2064-2090.

Sherman, K., Alexander, L.M., and Gold, B.D., editors (1991). Food Chains, Yields, Models, and Management of Large Marine Ecosystems. Westview Press, Inc., Boulder, CO, 320 pp.

Shih, J.S., Alexander, R.B., Smith, R.A., Boyer, E.W., Schwarz, G.E., Chung, S. (2010). An Initial SPARROW Model of Land Use and In-Stream Controls on Total Organic Carbon in Streams of the Conterminous United States, U.S. Geological Survey Open-File Report 2010–1276, 22 pp., available at http://pubs.usgs.gov/of/2010/1276.

Sklar, F.H.,s and Turner, R.E. (1981). Characteristics of phytoplankton production off Barataria Bay in an area influenced by the Mississippi River. *Contributions in Marine Science*, **24**: 93-106.

Smith, C.G., and Robbins, L.L. (2012). Surface-water radon-222 distribution along the west-central Florida shelf. U.S. Geological Survey Open File Report 2012-1212, U.S. Department of the Interior, Reston, Virginia, 22 pp.

Smith, C.G., and Swarzenski, P.W. (2012). An investigation of submarine groundwater-borne nutrient fluxes to the west Florida shelf and recurrent harmful algal blooms. *Limnology and Oceanography*, **57**: 471-485.

Smith, R.A., Schwarz, G.E., and Alexander, R.B. (1997). Regional interpretation of water-quality monitoring data. *Water Resources Research*, **33**: 2781-2798.

Smith, S.V., Marshall Crossland, J.I., and Crossland, C.J. (1999). Mexican and Central American Coastal Lagoon Systems: Carbon, Nitrogen and Phosphorus Fluxes (Regional Workshop II), LOICZ Reports & Studies No. 13, LOICZ IPO, Texel, The Netherlands, ii + 115 pp.

Spencer, R.G., Aiken, G.R., Dornblaser, M.M., Butler, K.D., Max Holmes, R., Fiske, G., Mann, P.J., and Stubbins, A. (2013). Chromophoric dissolved organic matter export from US rivers. *Geophysical Research Letters*, **40**(8) 1575-1579. DOI: 10.1002/grl.50357.

Steele, J.H. (1964). A study of production in the Gulf of Mexico. *Journal of Marine Research*, **22**(3): 211-222.

Swarzenski, P.W., Reich, C., Kroeger, K.D., and Baskaran, M. (2007). Ra and Rn isotopes as natural tracers of submarine groundwater discharge in Tampa Bay, Florida. *Marine Chemistry*, **104**: 69-84.

Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D.C.E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J., Arnarson, T.S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C.S., Delille, B., Bates, N.R., and de Baar, H.J.W. (2009). Climatological mean and decadal change in surface ocean pCO2 and net sea-air CO2 flux over the global oceans. *Deep-Sea Research II*, **56**(8-10): 554-577.

Thomas, W.H., and Simmons, E.G. (1960). Phytoplankton production in the Mississippi Delta. In: Recent Sediments, Northwest Gulf of Mexico. F.P. Shepard, F.B Phleger, and T.H. van Andel (editors), American Association of Petrologists, Tulsa, pp. 103-116.

Thompson, C., Smith, L., and Maji, R. (2007). Hydrogeological modeling of submarine groundwater discharge on the continental shelf of Louisiana. *Journal of Geophysical Research*, **112**: C03014, doi:10.1029/2006JC003557.

Toner, M., Kirwan, A.D., Poje, A.C., Kantha, L.H., Müller-Karger, F.E., and Jones, C.K.R.T. (2003) Chlorophyll dispersal by eddy-eddy interactions in the Gulf of Mexico. *J Geophys. Res.-Oceans*, **108**: C4, DOI: 10.1029/2002JC001499.

Tsung-Hung, P., and Wanninkhof, R. (2010). Increase in anthropogenic CO2 in the Atlantic Ocean in the last two decades. *Deep-Sea Research I*, **57**(6): 755-770.

Vargo, G.A., Crader, K.L., Gregg, W., Shanley, E., and Heil., C. (1987). The potential contribution of primary production by red tides to the west Florida shelf ecosystem. *Limnol. Oceanogr*., **32**: 762-767

Wang, Z.A., Cai, W.-J., Wang, Y., and Ji, H. (2005). The southeastern continental shelf of the United States as an atmospheric CO2 source and an exporter of inorganic carbon to the ocean. *Continental Shelf Research*, **25**(16): 1917-1941.

Wang, Z.A., Liu, X., Byrne, R.H., Wanninkhof, R., Bernstein, R.E., Kaltenbacher, E.A., and Patten, J. (2007). Simultaneous spectrophotometric flow-through measurements of pH, carbon dioxide fugacity, and total inorganic carbon in seawater. *Analytica Chimica Acta*, **596**(1): 23-36.

Wang, Z.A., Wanninkhof, R., Cai, W.-J., Byrne, R.C., Hu, X., Peng, T.-H., and Huang, W.-J. (2013). The marine inorganic carbon system along the Gulf of Mexico and Atlantic coasts of the United States: Insights from a transregional coastal carbon study. *Limnol. Oceanogr*., 58(1): 325-342, doi10.4319/lo.2013.58.1.0325.

Wanninkhof, R., Park, G.-H., Takahashi, T., Feely, R.A., Bullister, J.L., and Doney, S.C. (2013). Changes in deep-water CO2 concentrations over the last several decades determined from discrete pCO2 measurements. *Deep-Sea Research I*, **74**: 48-63.

Wawrik, B., and Paul, J.H. (2004). Phytoplankton community structure and productivity along the axis of the Mississippi River plume in oligotrophic Gulf of Mexico waters. *Aquatic Microbial Ecology*, **35**(2): 185-196.

Westberry, T., Behrenfeld, M.J., Siegel, D.A., and Boss, E. (2008). Carbon-based primary productivity modeling with vertically resolved photoacclimation. *Global Biogeochem. Cycles*, **22**: doi: 10.1029/2007gb003078.

Williams, P.J. LeB., Quay, P.D., Westberry, T.K., and Behrenfeld, M.J. (2013). The oligotrophic ocean is autotrophic. *Annu. Rev. Mar. Sci*., **5**: 535-549.

Xue, Z., He, R., Fennel, K., Cai, W.-J., and Lohrenz, S. (2013). Modeling Ocean Circulation and Biogeochemical Variability in the Gulf of Mexico. *Biogeosciences* **10**, 7219-7234, doi:10.5194/bg-10-7219-2013.

Zavala-Hidalgo, J., Morey, S.L., and O'Brien, J.J. (2003). Seasonal circulation on the western shelf of the Gulf of Mexico using a high-resolution numerical model. *Journal of Geophysical Research*, **108**(C12): 3389, doi:10.1029/2003JC001879.

Appendix 1.

North
American
Carbon
Program

Ocean Carbon
& Biogeochemistry

Gulf of Mexico Coastal Carbon Synthesis Workshop

March 27-28, 2013
U.S. Geological Survey, St. Petersburg, FL

Wednesday - March 27, 2013

08:00 Breakfast (catered at USGS)

08:30 **Welcome and opening remarks** (P. Coble)

08:35 **History and overview of the Coastal Carbon Synthesis activities** (H. Benway)

08:50 **Gulf of Mexico Carbon Budget: Existing budget and progress to date** (P. Coble) - Discussion of choices for GMx regional boundaries

09:20 **Group presentations** (15 min presentations followed by 15 min discussion)
- 09:20-09:50 **Riverine input** (E. Boyer)
- 09:50-10:20 **Air-sea fluxes** (L. Robbins)

10:20 Break

10:30 **Group presentations (cont'd)**
- 10:30-11:00 **Primary production** (S. Lohrenz)
- 11:00-11:30 **Respiration and NCP** (G. Hitchcock)
- 11:30-12:00 **Exchange at the ocean boundary** (K. Fennel)

12:00 Lunch (catered at USGS)

13:00 **Group presentations (cont'd)**
- 13:00-13:30 **Fluxes in estuaries, sediment-water exchange** (C. Osburn, M. Herrmann)
- 13:30-14:00 **Submarine groundwater discharge** (C. Smith)

14:00 **Breakout groups** (each group will have an assigned space, see signage)

Breakout discussion guidelines

- **Identify key uncertainties in the revised flux estimates, including regions of GMx with sparse data coverage**
- **Develop short-term (6-12 months) strategy to improve flux estimates**
- **Make long-term research recommendations**

15:15 Break

15:45 **Breakout groups (cont'd)**

17:30 Adjourn

18:30 Group dinner (Columbia Restaurant, directions in your folders and on wiki)

Thursday - March 28, 2013

08:00 Breakfast (catered at USGS)

08:30 **Breakout Reports** (15 minutes each)
Riverine input
Fluxes in estuaries, sediment-water exchange
Submarine groundwater discharge
Air-sea fluxes
Primary production
Respiration and NCP
Exchange at the ocean boundary

10:15 Break

10:30 **Group discussion – revisit the GMx carbon budget with new flux estimates from workshop** (P. Coble moderate)

11:30 **Group discussion - final recommendations** (P. Coble and H. Benway moderate)

- ***What data sets are sorely needed to improve GMx budget?***
- ***New NASA ROSES '13 funding opportunities***

12:30 Lunch (catered at USGS, box lunches to take)

Adjourn

1:30-4:00 **Team leaders meet to outline report**

Gulf of Mexico Coastal Carbon Synthesis Workshop
U.S.G.S. Normile Conference Center
St. Petersburg, Florida
March 27-28, 2013

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Appendix 2.

Data table showing data extracted from published journal articles that contain SGD information and dissolved carbon measurements for the Gulf of Mexico.

			Specific Discharge (cm/d)		Concentration (µM)						Flux (mmol/m^2/d)				If C flux not in original Pub, reference to C concentrations
Author	**Spatial Coverage**	**Temporal Coverage**	**Low SGD**	**High SGD**	**Low DOC**	**High DOC**	**Low DIC**	**High DIC**	**Low TC**	**High TC**	**Low DOC**	**High DOC**	**Low DIC**	**High DIC**	
Carbon Parameters Provided															
Santos et al. 2008, 2009	FL Panhandle	2006-2007	10.3	12.4	329.0	405.0					31.5	37.1			
Arnello et al. in prep (?)	Springs Coast**	in prep	88	154	33	133					29.4	205.3			
Smith and Swarzenski 2012	Coastal Region off Pinellas County, FL	2009-2010	0.9	10.8	119.7	157.7					1.1	17.0			
Smith in prep	Crystal Beach Spring	on-going (2010-2012)	0.9	2.1	87.8	258					0.8	5.4			
Swarzenski et al. 2007	Tampa Bay	2003	0.04	1.7	107.5	305.1					0.0	5.2			Swarzenski unpub. Data
Mwashote et al. 2013	North Sarasota Bay, Florida	2002-2006	0.7	5.9	186	1082					1.3	63.8			
	Middle and South Sarasota Bay, Florida	2002-2006	5.9	24	186	1082					11.0	259.7			
Corbett et al. 1999	Florida Bay	1994-1997	2.6	6.7			3.24	6.10					84.3	408.6	Walter et al. 2007
Burdige et al. 2008, Hu and Burdige 2008	Florida Bay	2001											1	20	
Burdige et al. 2008, Hu and Burdige 2008	Bahama Banks*	2001												8.6	
SGD															
McCoy et al. 2007	LA Shelf	2003-2004	0.01	0.14											
Thompson et al. 2007	LA Shelf	2003-2004	0	0.1											
Krest et al. 1999	LA Shelf*	1993-1994		0.03											
Corbett and Iverson	Apalachicola Bay, FL	1997-1999	4.4	16.8											
Cable et al. 1996, 1997	FL Panhandle	1992-1994	2.0	16.0											
Su et al. 2012	Little Lagoon, FL	2010-2011	0.57	1.45											
Smith and Robbins, 2012	Entire West Florida Shelf (Collier County to Levy County 5 to 120 km offshore)	2009	0.09	8.1											

*Denotes that only one value and no error was reported

**Specific discharge based on the an area of 2.42 km^2