1.3.3 Ocean Acidification Studies in the Gulf of Mexico: Current Status and Future Research Needs

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1.3.3.1 Abstract

This review summarizes recent research on ocean acidification (OA) in the broad Gulf of Mexico (GOM) region. Current understanding focuses mostly on the U.S. side of open waters, continental shelves, and estuaries. There has not been a systematic examination of open Gulf acidification to date. However, recent large-scale surveys in the GOM may shed light on decadal variability of the carbonate system. Coastal OA studies mostly examined eutrophication-enhanced acidification through spatially coupled surface production and respiration at depth. In terms of estuarine acidification, hydrological condition change was used to explain gradual decrease of both total alkalinity and pH in northwestern GOM estuaries, though estuarine carbonate chemistry in other areas has not been documented. In comparison to the U.S. side of the research, there are relatively few OA studies in the southern GOM. Given the similar anthropogenic stressors in northern GOM such as eutrophication but more prominent coral reef presence in the southern GOM, it is imperative to examine how the seawater carbonate chemistry changes under both natural and impacted conditions and how these changes may affect critical habitats. International and multidisciplinary collaborations may be needed to bring the expertise in the pan-GOM countries together for future investigations and synthesis.

1.3.3.2 Background

Since the Industrial Revolution, human beings have generated an enormous amount of carbon dioxide (CO_2) through fossil fuel burning, cement production, deforestation, and land use changes (IPCC 2013). Among the estimated 600±70 Gt-C (1 Gt-C = 10^{15} g-C) in the form of CO_2 released during the period of 1750-2015, ~43% (260±5 GtC) has accumulated in the atmosphere. Both the land and the ocean take up about an equal share of the rest of the released carbon (~28% or 165±70 Gt-C and ~29% or 175±20 Gt-C) (Le Quéré et al., 2016). Because every one part per million (ppm) CO_2 concentration increase in the atmosphere is equivalent to the accumulation of 2.12 Gt-C (or 7.77 Gt CO_2) (Ballantyne et al. 2012), then the total atmospheric 260 Gt-C accumulation since the industrial revolution is translated to 123 ppm increase in CO_2 concentration, which is added to the ~280 ppm CO_2 before the industrial revolution and yields the current 400+ ppm atmospheric CO_2 level.

The ocean as a huge acid-base buffer system has absorbed ~29% human produced CO_2 so far (Sabine et al. 2004; Le Quéré et al. 2016). Oceanic uptake of CO_2 has effectively dampened CO_2 increase in the atmosphere. However, because CO_2 is a reactive gas, upon dissolution in seawater, a series of reactions occur:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + CO_3^{2-} \rightarrow 2HCO_3^-$$

The weak acid produced by CO_2 dissolution will titrate carbonate ion (CO_3^{2-}) in the seawater and reduce its concentration and at the same time, increase proton concentration (or decrease in seawater pH), a process coined as "ocean acidification" or OA (Feely et al. 2004; Doney et al. 2009). Based on thermodynamics, carbonate ion concentration decrease leads to a decrease in carbonate mineral saturation states (Ω) because calcium ion (Ca^{2+}) concentration change is small across different ocean basins:

$$\Omega = [Ca^{2+}][CO_3^{2-}]/K_{sp}$$

Here K_{sp} is the solubility constant of $CaCO_3$ mineral. The saturation level Ω exerts fundamental control on the ability of calcifying organisms in producing $CaCO_3$ skeletons (for corals and coralline algae) or hard shells (shellfish) (Waldbusser et al. 2014).

Over the past two decades or so, studies on OA have ranged from characterizing the changes in seawater carbonate chemistry (Feely et al. 2004; Bates et al. 2013; Brewer 2013; Wanninkhof et al. 2015) to investigating biological and biogeochemical consequences of such changes (Kleypas et al. 1999; Orr et al. 2005; Hoegh-Guldberg et al. 2007; Iglesias-Rodríguez et al. 2008; Millero et al. 2009; Andersson and Gledhill 2013; Waldbusser et al. 2014). Nevertheless, numerous studies have examined seawater carbonate chemistry in the open ocean, other marginal seas, and coastal areas, yet there is substantially less information on GOM in peer-reviewed literature.

To review the status of OA studies in the GOM region, geographical zones, including the open GOM, coastal areas, and estuaries, will be separately discussed. Because the majority of available studies relevant to OA are focused on the northern and northwestern GOM, these areas will be reviewed while implications to the southern GOM will be inferred.

1.3.3.3 Status of OA Studies in the GOM

The GOM is a marginal sea. Marginal seas are often separated from the open ocean by geological features (sills or ridges). While the upper water columns above these sills on both sides of these geological features essentially have the same origin(s), deeper water exchanges between a marginal sea and its connected open ocean are always restricted (Liu et al. 2010). Below is a list of major marginal seas in the world:

- GOM connects with the northwestern Caribbean Sea through the Yucatan Sill (2,040 m) (Rivas et al. 2005)
- The Caribbean Sea connects with the North Atlantic Ocean through the Anegada-Jungfern, or AJ passage (1,815 m) (MacCready et al. 1999) and the Windward Passage (1,700 m) (Rivas et al. 2005)
- The South China Sea connects with the West Philippine Sea to the east through the Luzon Strait (2,200 m) and the Sulu Sea to the south through the Mindoro Strait (420 m) (Chen et al. 2006).
- The East/Japan Sea connects with the North Pacific through three shallow straits (~150 m; Park et al. 2006)
- The Sea of Okhotsk connects with the North Pacific through two deep straits the Kruzenshterna (1,990 m) and the Bussol (2,300 m; Wakatsuchi and Martin 1991)
- The Mediterranean Sea connects with the North Atlantic through the Gibraltar Strait (600 m; Huertas et al. 2009)

Because of the restricted connection, OA in the marginal seas will both carry the signals of the source waters and have imprints due to disparate biogeochemical processes occurring within themselves.

1.3.3.3.1 Open GOM Acidification

GOM open water surface circulation is influenced by the Loop Current that originates from the Caribbean Sea and passes through the Yucatan Channel as well as the spinoff eddies of the Loop Current (Sturges 1993). A modeling study suggested that the strength of the Loop Current may have declined by 20–25% during the twenty-first century, leading to reduced warming in the northern GOM (Liu et al. 2012).

To date, few published studies examined open GOM carbonate chemistry and the only available studies focused on the northern and eastern GOM with the emphasis on the continental shelves (Wang et al. 2013; Wanninkhof et al. 2015). These studies are the outcomes of the two large-scale coast wide expeditions that covered both the northern GOM coast and the U.S. East Coast (GOMECC-1 and

GOMECC-2). The third GOMECC cruise took place on 18 July–21 August 2017, and the entire GOM from the shelf waters to the deep basin was examined across 10 transects, including two transects that covered both the Yucatan Channel and the Straits of Florida.

Available data suggest that the open GOM surface waters have relatively high aragonite saturation state (or Ω_{arag}). For example, in July 2007, Ω_{arag} was above 3 ($\Omega = 1$ indicates the equilibrium condition) for all three transects that ran perpendicular to the coast (Texas, Louisiana, and West Florida) in the upper 50 m of water across almost the entire northern GOM (Wang et al. 2013). Similarly, based on data collected in July 2012, Wanninkhof et al. (2015) showed that surface (<10 m) waters in the open GOM all have Ω_{arg} at the ~4 level and evaporation and precipitation control Ω_{arg} variations.

To the best of the author's knowledge, temporal variability of Ω_{arg} in the open waters of the GOM has not been broadly disseminated in the scientific literature. Although given that much of open GOM can be considered as oligotrophic because of low levels of nutrients (Biggs 1992; Xue et al. 2016), temperature probably plays an important role in regulating Ω_{arag} dynamics across the seasons. The temperature dependence of Ω_{arag} may be inferred from the similarly oligotrophic Flower Garden Banks region in the northwestern GOM near the shelf-slope break, where temperature was found to explain 70–80+% of Ω_{arag} variation (Ω_{arag} ranged 3.4–4.2) over the period of 2013–2016 (Hu et al. unpublished data; Johnston et al. 2016; Nuttall et al. 2017). Furthermore, because of the oligotrophic nature of surface water in the open GOM with small primary productivity, it is likely that Ω_{arg} will decline following the continuing increase in atmospheric CO_2, at a rate similar to those observed in the Greater Caribbean region (Gledhill et al. 2008).

1.3.3.3.2 GOM Coastal Waters

Compared with the changes in carbonate chemistry in relatively oligotrophic open GOM surface water, coastal waters in the GOM are much more complex because of significant terrestrial influences. The most extensively studied region around the GOM coast is the Louisiana shelf, where copious amount of anthropogenic nutrients are delivered into shelf waters via the Atchafalaya-Mississippi River system (MARS) (Turner and Rabalais 1994; Rabalais et al. 2002). In addition, due to changes in agricultural practice (e.g., application of lime in farmland to combat soil acidification) and the overall increase in continental weathering, riverine alkalinity export in this region has been increasing based on a century-long dataset (Raymond and Cole 2003; Raymond et al. 2008). Combining both increasing alkalinity export and nutrient-enhanced primary production, surface waters of the eutrophic coastal zones may have been experiencing so-called "basification" (Duarte et al. 2013; Nixon et al. 2015), instead of commonly observed acidification in the open ocean. *In situ* coastal water CO_2 partial pressure observations in the northern GOM near the coast of Mississippi also appear to support the basification notion because surface water CO_2 level shows an apparent decreasing trend over the past decade.

Contrary to the enhanced primary production-led pH increase in the surface water, subsurface and bottom waters accumulate substantial respiration-produced CO_2, and this CO_2 signal is especially strong when the water column stratification occurs in summer, as surface water becomes less saline (due to river water input) and warmer (due to surface heating). Buildup of CO_2 accompanies significant reduction of dissolved oxygen level as microbes respire the surface-produced organic matter, and when dissolved oxygen is below 2 mg L^{-1} it is termed hypoxic (Rabalais et al. 2001). As a result of aerobic respiration, bottom waters on the northern GOM continental shelf can experience substantial acidification symptoms as represented by reductions in both pH (Figure 31) and Ω_{arag}, and further acidification will occur because of continuing acidification of the open ocean water that supplies this shelf area if the eutrophication condition is not improved (Cai et al. 2011). A recent study suggested that not only water column respiration, but benthic respiration also contributes to bottom water acidification (Hu et al. 2017). In addition, the spatially-coupled pH variation as a result of enhanced nutrient cycling (i.e., pH increase in the surface (nutrient consumption) and decrease in the bottom (nutrient regeneration)) far outweighs that caused by either the river chemistry change or temperature change on decade-to-century time scales (Hu et al. 2017). Furthermore, because of lower solubility of CO_2 in the warm GOM waters compared with the cooler U.S. west coast, higher buffer capacity in the GOM to begin with, GOM waters will reach hypercapnic conditions (CO_2 partial pressure greater than 1,000 µatm) at oxygen concentration of 170 µmol kg^{-1} toward the end of this century, and the west coast will reach hypercapnia when oxygen is 260 µmol kg^{-1} (Feely et al. 2018).

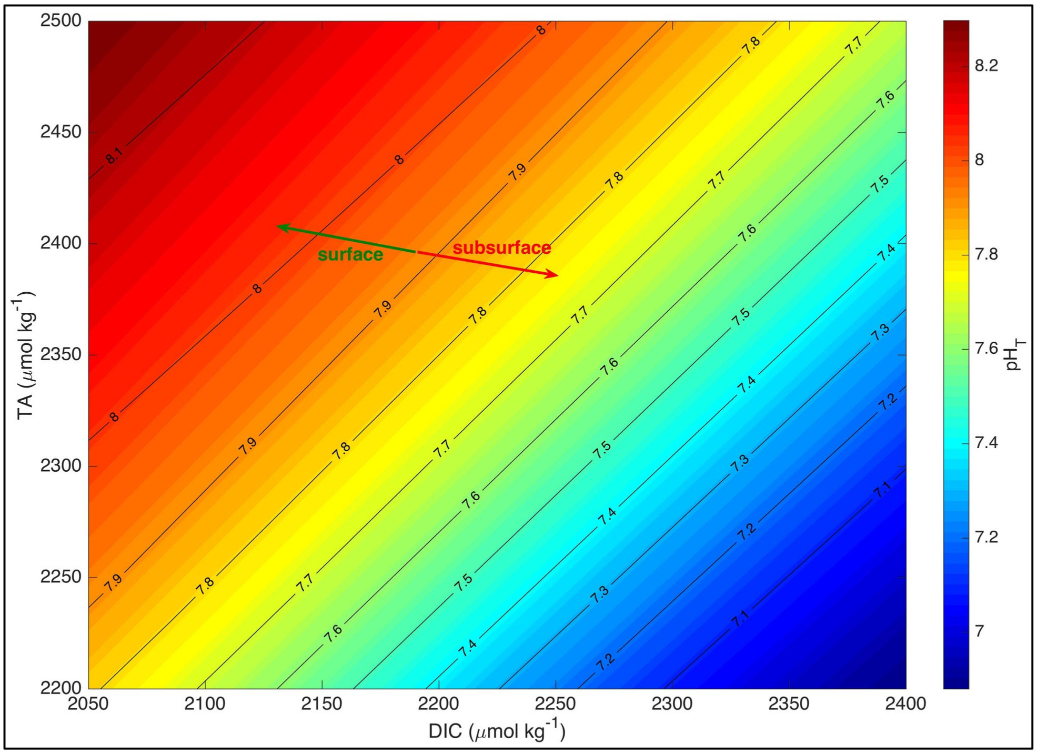

Figure 31. A simulation of seawater pH as a function of alkalinity (TA) and total dissolved CO_2 (DIC).
The green arrow indicates surface water production that follows the Redfield stoichiometry, and the red arrow represents aerobic respiration. This calculation was done using the program CO2SYS (Pierrot et al. 2006) at 20˚C and salinity 35.

The northern GOM is not the only area that experiences bottom water hypoxia in the Gulf. Smaller rivers such as the Brazos River in the northwestern GOM can have disproportionally large discharge during wet seasons that are affected by large scale climate variability (Tolan 2007). Historically, high river discharge events are not uncommon and they have been recorded in the sediment in the adjacent continental shelf (Carlin and Dellapenna 2014). Similar to that in the northern GOM, extensive hypoxia can also occur because of high river discharge in this area (DiMarco et al. 2012). Therefore, bottom water acidification along with the occurrence of hypoxia is expected in this shelf area as well (i.e., northwestern GOM).

In addition to the modern marine-produced organic matter that drives microbial respiration, additional respiration using fossil carbon (oil and natural gas) has been noted in both natural settings (Aharon et al. 1992) and after human-caused oil spills (Kessler et al. 2011; Hu et al. 2016). Respiration of these organic compounds will also lead to the production of CO_2. However, there has been no actual field study that focuses on this issue anywhere in the world other than computer-based simulations (e.g., Boudreau et al.

2015). Admittedly, CO_2 production per unit oxygen consumption from fossil carbon remineralization is lower than that from marine and even terrestrial organic carbon, due to more reduced oxidation states of carbon in hydrocarbons.

1.3.3.3.3 Acidification (or Dealkalization) of Estuaries

Because river end-members play an important role in controlling carbonate chemistry in an estuarine mixing zone (Salisbury et al. 2008; Hu and Cai 2013), rivers that have lower levels of total alkalinity result in a larger salinity range that have lower Ω_{arag} values. Therefore, estuaries that receive river waters with lower alkalinity levels potentially are subject to larger fluctuations in both pH and Ω_{arag}. The large river system in the middle of the northern GOM (MARS) has relatively high alkalinity levels (1,500–3,000 µmol kg^{-1}; Hu et al. 2017), whereas the next two largest rivers in the United States (Mobile River and Apalachicola River) have only ~900±200 µmol kg^{-1} alkalinity (USGS). However, no systematic studies have been done in the northeastern GOM estuaries from the acidification perspective.

In addition to river alkalinity control in the mid- to low-alkalinity river-influenced estuaries, hydrological conditions also need to be considered in studying estuarine carbonate chemistry. Following the reasoning of ocean and coastal acidification, one may expect that both acidified ocean water (as the ocean endmember) and water column respiration may contribute to acidification of estuaries, as previous simulations have shown (Sunda and Cai 2012; Hu and Cai 2013). However, based on a 40-year data record that is maintained by the Texas Commission on Environmental Quality, a recent study found that the majority of estuaries along the coast of northwestern GOM have been experiencing a gradual loss of alkalinity and a decrease in pH values (Hu et al. 2015). The coastwide estuarine alkalinity decline is attributed to the decline in riverine alkalinity export as many rivers in this region carry high levels of alkalinity although the freshwater resources have been under increasing pressure (diversion for agricultural and industrial usage). Relatively long estuarine residence time (Montagna et al. 2013) may also contribute to further alkalinity consumption due to biogeochemical processes that are not entirely clear (author's unpublished data). On the east coast of GOM, Robbins and Lisle (2017) used a 20 plus-year dataset and found that most estuaries in Florida also have been experiencing slight acidification. The lower than open ocean pH decrease over time was attributed to local processes such as nutrient-enhanced production. Together, these studies represent two of the very few that examine long-term changes in estuarine carbonate chemistry in general.

Finally, although not located entirely within the GOM, the Florida Reef Tract has been experiencing a latitudinal gradient in net community calcification (NCC). Negative NCC indicates net carbonate dissolution, and positive NCC suggests net carbonate precipitation or calcification. For the Florida Reef Tract, NCC is negative throughout an annual cycle in reefs near the mainland in the north and increases toward the south (Muehllehner et al. 2016). The roles of acidification and direct human influence are not yet clearly understood.

1.3.3.4 Unanswered Questions

Based on the review of previous studies, the following questions are raised about the larger expanse of the GOM.

1.3.3.4.1 Open GOM

Clearly, a knowledge gap exists in the open GOM regarding the rate of acidification: What are the intra-basin differences in the rates of acidification between eastern and western GOM, and in the context of possible reduction in the Loop Current, what would be the long-term trend?

Even though the GOMECC cruises (GOMECC-1, GOMECC-2, and GOMECC-3) provide snapshots of the water column carbonate chemistry from both the coastal region to the open GOM up to 3,000 m water depth, these studies were not specifically designed to examine the open GOM because their focus is to investigate carbon exchange between the shelf and the pelagic ocean. To understand the trend and variability of carbonate chemistry changes throughout the water column, long-term efforts such as setting up time-series stations similar to those in other marginal seas, for example the CARIACO ocean time-series in the Caribbean Sea (Astor et al. 2005) and SouthEast Asian Time Series (SEATS) (Chou et al. 2007), will be needed.

As the only deep water channel that connects the GOM and the Caribbean Sea, which supplies both upper water column and the deep basin waters, the Yucatan Sill (2,040 m) should have a time series station for the examination of both inflowing surface and basin water and subsurface return flow back to the Caribbean Sea (Sturges 2005). In addition, two locations that are in the eastern and western GOM deep basins would also be useful for monitoring long-term changes (Figure 32).

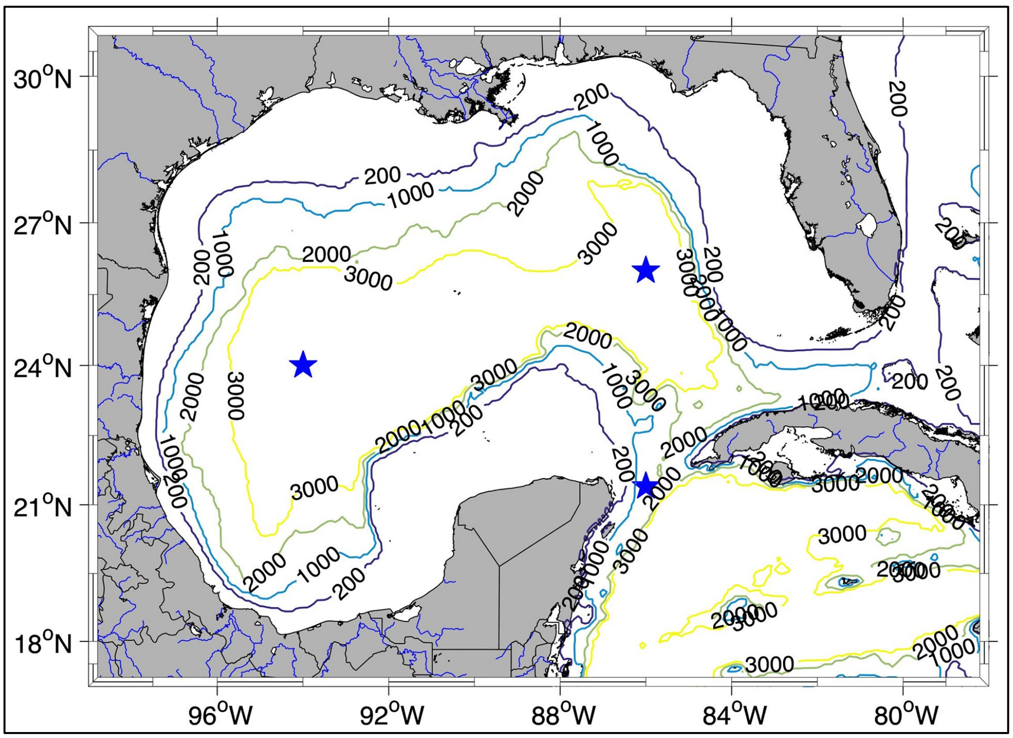

Figure 32. Bathymetry of the GOM.
Blue stars indicate the approximate locations of the proposed time-series stations.

These stations can offer answers to questions not only regarding acidification in GOM, from source water (Caribbean) to the deep basin, but biogeochemical cycle questions associated with climate variability in this important marginal sea. For example, How might the possible future changes in the strength of the Loop Current alter biogeochemical cycles? What are the roles of episodic events (e.g., hurricanes, warm rings originated from the Loop Current) on the biogeochemical processes in the upper water column?

A research topic relevant to OA is the study of anthropogenic CO_2 accumulation in the water column of various ocean basins (Peng et al. 1998; McNeil et al. 2003; Sabine et al. 2004; Sabine and Tanhua 2010; Wanninkhof et al. 2010). Compared to the open ocean, understanding of anthropogenic CO_2 storage in marginal seas is still relatively lacking (Park et al. 2006; Park et al. 2008; Watanabe et al. 2013; Ingrosso et al. 2017). However, the benefit of studying changes in the marginal seas, especially the semi-isolated deep basin, is that the shallow sills around the basin rim can largely “filter” out short-term variabilities in the incoming waters (Joyce et al. 1999) that are often encountered in the open ocean. Therefore, long-term study of deep basins such as the GOM deep waters is beneficial from both the oceanographic and climatic perspectives.

1.3.3.4.2 Acidification in the Southern GOM: Nutrient and Petroleum Impact?

Although perhaps not as serious as in the northern GOM, coastal eutrophication due to nutrients delivered by Mexican rivers has been noted in the literature (Ulloa et al. 2017). As a result, harmful algal blooms have been observed along the Mexican coast of the GOM Large Marine Ecosystem, and the main nutrient sources are Coatzacoalcos River in the southwestern Bay of Campeche and the Grijalva-Usumacinta Rivers in the southwestern Bay of Campeche (Ulloa et al. 2017). It is currently unclear whether coastal eutrophication is associated with any type of acidification effect in this region. Therefore, a question arises: Does eutrophication induce hypoxia in the southwestern GOM shelf, which subsequently leads to coastal bottom water acidification?

The significance of studying coastal OA-related issues is that the southwestern GOM coast hosts a "reef corridor" (Ortiz-Lozano et al. 2013), where reef systems are already severely threatened by anthropogenic activities, including nutrient pollution and sediment loading. Even though the shallow and warm GOM waters are supposed to have relatively high pH and Ω_{arag}, hence acidification alone may not lead to unfavorable conditions. However, in combination with other stressors (low oxygen, high nutrients, and high turbidity), these multistressor effects could be amplified and cause detrimental effects to the calcifiers (DeCarlo et al. 2015).

Finally, given the large oil and gas reserves in the southern GOM shelf region (Tampico-Misantla and Saline-Comacalco basins and the Villahermosa Uplift etc.; Paull et al. 2005), the impact of natural oil and gas release on the water column carbonate chemistry remains an open question. Studying fossil carbon remineralization induced acidification is important given that the rising ocean temperature could both destabilize the uppermost gas hydrate (Lapham et al. 2010; Phrampus and Hornbach 2012) and enhance the rate of microbial respiration (Burdige 2011).

1.3.3.4.3 Estuarine Acidification

Estuaries along the southern GOM coast have a wide range of hydrological conditions, from semiarid Laguna Madre (Mexico side) in the north that is a *de facto* negative estuary, to intermediate systems such as Laguna Tamiahua and Laguna La Mancha, and then to river-influenced systems including Laguna de Términos. Even though not strictly river-fed estuaries (Moore 1999), along the coast of Yucatan Peninsula, distinct karst systems are present and produce significant coastal subterranean groundwater discharge (SGD; Yáñez-Arancibia et al. 2013). It is probably safe to say that the narrower longitudinal band of the Mexican GOM coast encompasses the same variety of estuarine and coastal systems as exist from Texas to Florida on the U.S. side.

To date, understanding of the Mexican coastal ecosystem and its biogeochemistry is still constrained by the lack of data in general (Camacho-Ibar and Rivera-Monroy 2014), at least in the public domain. Therefore, initiation of environmental monitoring and making available data accessible are essential for the community to begin understanding the "baseline" conditions of these disparate systems. Meanwhile, characterization of carbonate chemistry in the major rivers that feed the various river-dominated estuaries as well as understanding of the metabolic processes (cf. Figure 31) in these riverine estuaries will prove useful for understanding the temporal and spatial variability of carbonate system parameters along the salinity gradient. Information gathered through such research efforts can be utilized by natural resource managers and policy makers in regulating and reducing the human impacts on these environments.

Tidally-driven SGD is known to affect carbonate chemistry in coral-reef-dominated environments because groundwater typically has much higher CO_2 partial pressure and lower pH than the receiving coastal water due to the accumulation of respirational products (Santos et al. 2011; Cyronak et al. 2014; Wang et al. 2014). This type of acidification remains poorly quantified globally. Given the fact that the total SGD could be on par with the total river flux (Moore et al. 2008) and climate variability also controls the SGD dynamics (Gonneea et al. 2013), evaluation of the acidification effect of SGD in the ecologically sensitive coral reef regions is needed. Studies that integrate net community production and net community calcification will be useful to assess the overall health of the corals reefs along the coastline (Andersson and Gledhill 2013).

1.3.3.5 Summary

Compared with that in the open ocean and temperate/subpolar North American coastal regions, OA study in the GOM is still in its early stages with geographical locations currently limited to the northern GOM shelf waters and coastal estuaries in northwestern GOM. There is a knowledge gap in our understanding of how the open GOM responds to atmospheric CO_2 increase, the state of coastal and estuarine carbonate chemistry in the southern GOM, and the acidification effect of SGD along the Yucatan Peninsula.

Understanding these various environments is useful for assessing variability in and limits on living conditions for the numerous calcifying organisms that are both ecologically and economically important. It must be acknowledged that acidification is not isolated from other anthropogenic stressors such as eutrophication/hypoxia and climate-induced changes in nature, including enhanced respiration of marine and seabed-released fossil carbon. Therefore, an integration of expertise from multiple disciplines is needed to investigate OA in the broader expanse of the GOM. International collaborations which focus on the open GOM and assess the ecological impact of OA on coastal and estuarine organisms will help to push the research forward in this important marginal sea, so that it can better serve the countries around it in a sustainable fashion.

1.3.3.6 Acknowledgments

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1.3.3.7 References

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