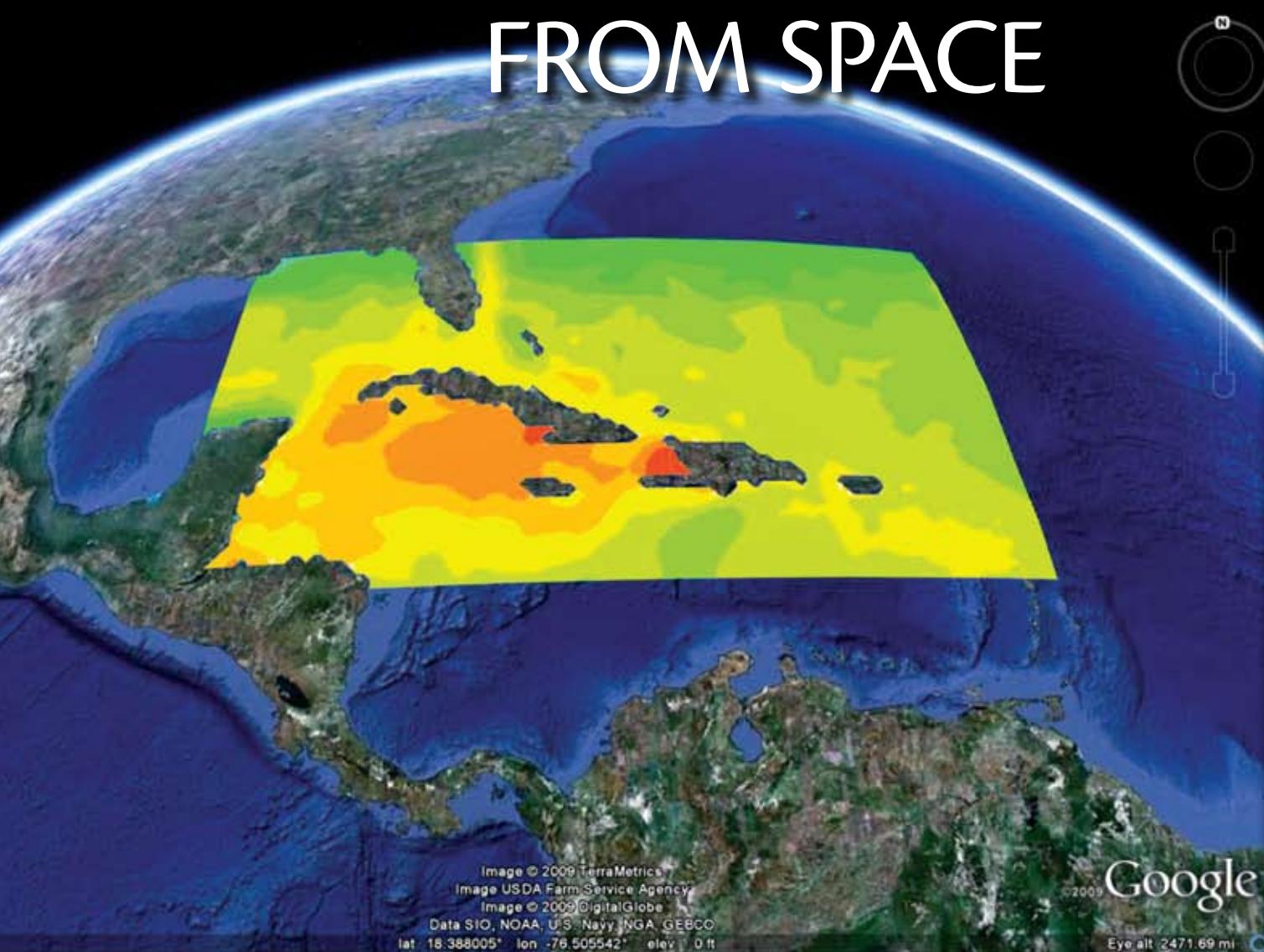


BY DWIGHT K. GLEDHILL, RIK WANNINKHOF, AND C. MARK EAKIN

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# OBSERVING OCEAN ACIDIFICATION FROM SPACE



Distribution of CO<sub>2</sub> partial pressure across the Greater Caribbean Region for October 2009, based on the Experimental Ocean Acidification Product Suite model. Generated by Google Earth

## ABSTRACT

Space-based observations provide synoptic coverage of surface ocean temperature, winds, sea surface height, and color useful to a wide range of oceanographic applications. These measurements are increasingly applied to monitor large-scale environmental and climate processes that can have an impact on important managed marine resources. From observing the development of harmful algal blooms using ocean color to tracking regions of thermal stress that can induce coral bleaching, satellites are routinely used for environmental monitoring. Here, we demonstrate an approach to monitoring changes in sea surface ocean chemistry in response to ocean acidification as applied to the Greater Caribbean Region. The method is based on regionally specific empirical algorithms derived from ongoing ship measurements applied to remotely sensed observables. This tool is important for exploring regional to basin-wide trends in ocean acidification on seasonal to interannual time scales.

## THE CHALLENGE OF OCEAN ACIDIFICATION

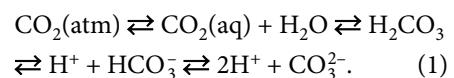
During the industrial period, rising levels of atmospheric carbon dioxide ( $\text{CO}_2$ ) have driven  $118 \pm 19$  petagrams of carbon into the global ocean, primarily in the upper 1000 m (Sabine et al., 2004). As surface water  $\text{CO}_2$  levels closely track the continued rise in atmospheric  $\text{CO}_2$  (Takahashi et al., 2009), it is anticipated that dissolved  $\text{CO}_2$  in the surface ocean will reach a level that is double pre-industrial values by the middle of this century (Orr et al., 2005). Because this  $\text{CO}_2$  is absorbed by seawater, it not only reacts, causing a slight reduction in seawater pH (or acidification), but it also has a cascading effect on the carbonic acid system, causing a decrease in carbonate ion concentration and carbonate mineral saturation states ( $\Omega_{\text{sp}}$ ). Such changes will globally affect inorganic carbonate mineral kinetics in surface waters and coastal sediments

(Morse and Arvidson, 2002; Morse et al., 2006). Moreover, numerous studies now demonstrate the effects that these changes are likely to have on marine ecosystems, especially marine biocalcification (for review, see Doney et al., 2009), which is of particular concern to coral reef ecosystems, a key source of diversity and food production in low latitudes. Reduced coral calcification rates would prove a key challenge for coral reef ecosystems because reefs need to maintain sufficient calcification and cementation to offset natural erosive processes (e.g., storms) and dissolution. Natural levels of accretion (reef growth from calcification and cementation) often only slightly exceed natural reef loss from physical and biological erosion (for review, see Glynn, 1997). Any decline in net community calcification (Langdon et al., 2000) or secondary cementation (Manzello et al., 2008), or increase in net dissolution (Andersson

et al., 2009) could compromise the long-term persistence of reef systems. Compounding the threats of overfishing, coastal pollution, high incidences of coral disease, and the climate-scale threats of rising sea surface temperatures (including increasing bleaching frequencies), ocean acidification may prove daunting to many coral reef ecosystems in coming decades (Hoegh-Guldberg et al., 2007; Veron et al., 2009).

## OCEAN ACIDIFICATION AND ITS EFFECT ON CARBONATE CHEMISTRY

The carbonic acid system describes the partitioning of multiple carbonate species within seawater as



As atmospheric carbon dioxide ( $\text{CO}_2(\text{atm})$ ) is taken up by the surface ocean ( $\text{CO}_2(\text{aq})$ ), it reacts with water to form carbonic acid ( $\text{H}_2\text{CO}_3$ ), which rapidly dissociates to  $\text{H}^+$  (thereby lowering pH—hence the term “acidification”) and bicarbonate ion ( $\text{HCO}_3^-$ ). The resulting change in pH is buffered by reaction with the carbonate ion ( $\text{CO}_3^{2-}$ ), forming bicarbonate. Thus, as  $\text{CO}_2$  dissolves in seawater, there is a net reduction of carbonate ion. This decline in carbonate ion has a corresponding effect on the degree to which seawater is saturated with respect to the carbonate mineral phases ( $\text{CaCO}_3$ , nominally aragonite) that comprise many shallow

water marine sediments and that many marine organisms use to construct their shells. The degree of saturation is the product of the calcium and carbonate ions ( $\text{Ca}^{2+} \times \text{CO}_3^{2-}$ ) to the stoichiometric solubility product ( $K_{\text{sp}}^*$ ) of the mineral phase of interest. The term  $\Omega_{\text{sp}}$  describes how far a solution is from equilibrium with respect to the mineral phase.

Tropical ocean surface seawater is generally about four times supersaturated with respect to aragonite (i.e.,  $\Omega_{\text{ar}} = 4$ ), thus favoring precipitation, a fact capitalized on by numerous marine calcifiers.

### MONITORING A SEA CHANGE

To a first-order approximation, annual changes in tropical surface ocean chemistry in response to ocean acidification can be estimated from the assumption that surface water  $\text{CO}_2$  exists in equilibrium with atmospheric concentrations (Orr et al., 2005; Bates, 2007). However, short-term and local variations in both temperature and salinity dramatically affect  $\Omega_{\text{ar}}$  on shorter temporal and spatial scales. For example, increasing temperature (or decreasing salinity) will increase the carbonate ion concentration due to

the temperature (and salinity) dependencies of the equilibrium constants governing the reactions shown in Equation 1. Perhaps counter intuitively, the apparent carbonate mineral solubility actually decreases with temperature yet increases with salinity. However, under typical salinity ranges for seawater, this enhanced apparent solubility is more than compensated for by increases in total dissolved inorganic carbon ( $\text{TCO}_2$ ), total alkalinity ( $A_T$ ), and  $\text{Ca}^{2+}$  which change conservatively with salinity thereby resulting in a net increase in  $\Omega_{\text{ar}}$ . Furthermore, other processes affecting the distribution of inorganic carbon within surface waters, such as the supply of carbon-rich waters from below the mixed layer through upwelling (e.g. Manzello et al., 2008; Feely et al., 2008) or biological modulation, particularly in coastal regions (Salisbury et al., 2008), and carbonate production (Balch et al., 2005), also affect local carbonate chemistry and therefore affect  $\Omega_{\text{ar}}$  distribution. Respiration processes can drive  $\Omega_{\text{ar}}$  values lower through the addition of  $\text{CO}_2$  (the converse is true for photosynthesis). Calcification can have a pronounced effect as well through the addition of  $\text{CO}_2$  coupled with a reduction in alkalinity (e.g., Kawahata et al., 1997; Gattuso et al., 1999).

Direct measurements of ocean chemistry through ship surveys, long-term time-series stations, and a growing number of autonomous moored and underway platforms will provide the most accurate means of tracking ocean acidification for the foreseeable future. However, these in situ measurements are inherently limited in space (time series, moored stations) and/or time (ship surveys). Although current satellite

observations do not directly measure changes in ocean carbonate chemistry, they can provide synoptic observations of a range of physical and optical parameters that allow us to model changes in the distribution of carbonate chemistry within the surface ocean where no in situ observations are available. A host of satellite-derived products are becoming available that can offer important information regarding surface ocean thermodynamics, gas exchange, biological modification, and deepwater mixing processes. Examples include not only the fundamental observations of sea surface temperature (SST) and wind speed but also more derived quantities, including surface ocean productivity and Ekman upwelling estimates (Figure 1). Through the application of a variety of techniques, ranging from simple regression analysis (e.g., Olsen et al., 2004) to the construction of self-organizing maps using neural network techniques (Telszewski et al., 2009; Friedrich and Oschlies, 2009), satellite observations are being applied to scale up and extend in situ carbonate chemistry measurements, permitting examination on spatial and temporal scales not practical through in situ observation alone.

Most efforts have applied empirical relationships between satellite-derived SST and surface water  $\text{CO}_2$  partial pressure ( $p\text{CO}_{2,\text{sw}}$ ). An early example was the application of high-resolution NOAA global area coverage (GAC) SST to ship-based seasonal  $p\text{CO}_{2,\text{sw}}$ -SST relationships in the North Pacific (Stephens et al., 1995). Lee et al. (1998) estimated interannual variability in global net air-sea  $\text{CO}_2$  flux using satellite-based SST anomalies and wind speeds. In this case,  $p\text{CO}_{2,\text{sw}}$ -SST relationships

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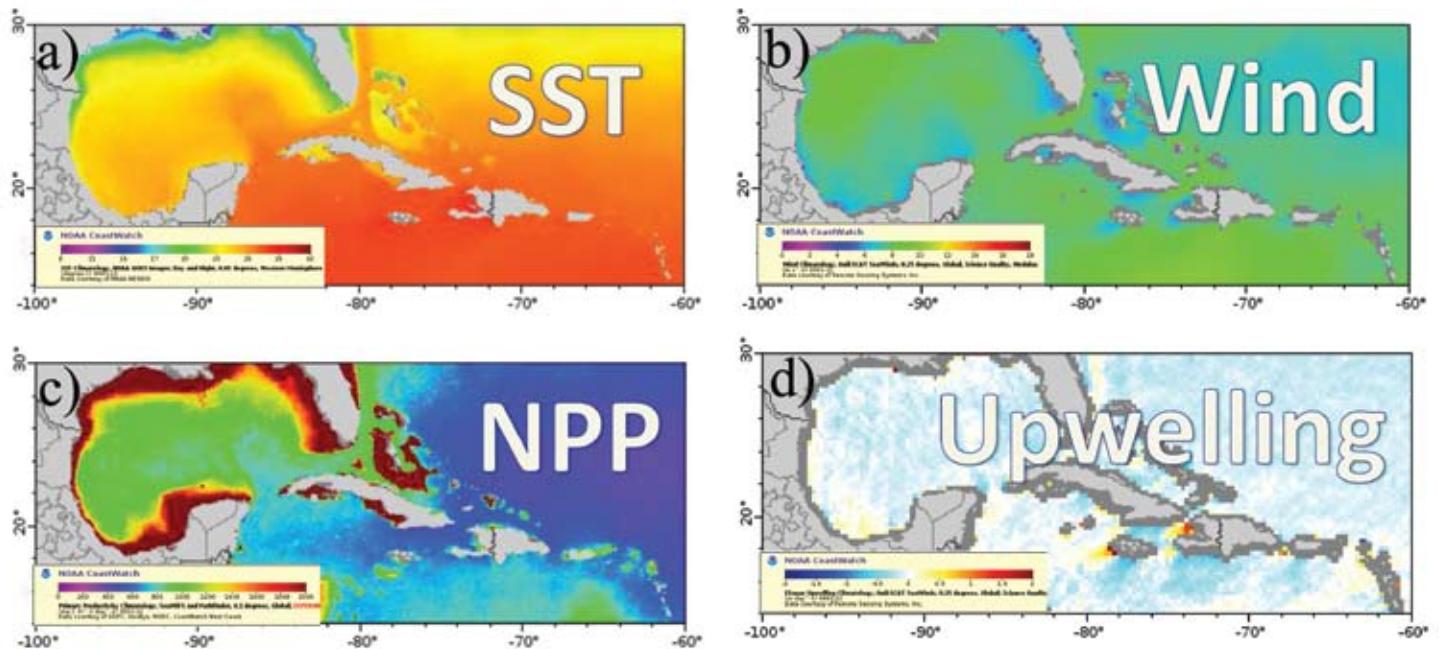


Figure 1. Examples of satellite products that can offer important information regarding surface ocean carbon dynamics: (a) SST (NOAA GOES SST), (b) sea surface wind speed (NASA JPL QuikSCAT winds), (c) surface ocean productivity estimates (obtained using SeaWiFS/Pathfinder ocean color according to Behrenfeld & Falkowski [1997]), and (d) Ekman upwelling estimates from QuikSCAT winds by the NOAA CoastWatch Program. Productivity data provided courtesy of NASA Goddard Space Flight Center, Ocean Biology Products Group

were derived using the Takahashi et al. (1997)  $\Delta p\text{CO}_2$  climatology ( $\Delta p\text{CO}_2$  is the difference between  $p\text{CO}_{2,\text{sw}}$  and the partial pressure of  $\text{CO}_2$  in air). Unique regressions were performed on each grid cell ( $4^\circ \times 5^\circ$  resolution) and for each season. Nelson et al. (2001) produced spatial fields of  $p\text{CO}_{2,\text{sw}}$  for the Sargasso Sea using NOAA Advanced Very High-resolution Radiometer (AVHRR) SST and  $p\text{CO}_{2,\text{sw}}$ -SST relationships derived at the US Joint Global Ocean Flux Study (JGOFS) Bermuda Atlantic Time-series Study (BATS) station. Lefèvre et al. (2002) were able to extrapolate  $p\text{CO}_{2,\text{sw}}$  fields in the Chilean upwelling system using an algorithm based on AVHRR satellite SST and synthetic salinity fields derived from SST-salinity relationships. Empirical relationships between SST and  $p\text{CO}_{2,\text{sw}}$  applied to satellite-derived SST

fields (Moderate Resolution Imaging Spectroradiometer [MODIS], AVHRR, and the Tropical Rainfall Measuring Mission Microwave Imager [TRIMM]) have also been used together with QuikSCAT scatterometer-derived wind speeds to estimate air-sea  $\text{CO}_2$  fluxes within the Greater Caribbean Region (e.g., Olsen et al., 2004; Wanninkhof et al., 2007). Ono et al. (2004) produced monthly basin-scale estimates of  $p\text{CO}_{2,\text{sw}}$  based on remotely sensed chlorophyll and SST from the Ocean Color Temperature Sensor (OCTS).

In contrast to standard regression analysis, more sophisticated techniques such as the development of Kohonen Feature Maps using a neural network approach (Friedrich and Oschlies, 2009; Telszewski et al., 2009) have been applied. These techniques associate various

remotely derived parameters to  $p\text{CO}_{2,\text{sw}}$  distributions. Lohrenz and Cai (2006) applied principle component analysis (PCA) to MODIS imagery to map out the distributions of  $p\text{CO}_{2,\text{sw}}$  in the river-influenced margins of the northern Gulf of Mexico. The PCA methods employed by Lohrenz and Cai (2006) entail deriving an empirical  $p\text{CO}_{2,\text{sw}}$  relationship (based on multiple linear regression) between the dominant orthogonal component scores obtained using salinity, temperature, and chlorophyll.

Although more complex analysis methods may be necessary in some areas, the predominantly oligotrophic oceanic waters of the Greater Caribbean Region lack prominent upwelling and significant biological modifications. These attributes permit application of robust empirical relationships among

surface ocean carbonate chemistry, satellite SST, and model-derived sea-surface salinities (SSS) to map out and track the evolution of ocean acidification across this region (Gledhill et al., 2008).

### THE NOAA CORAL REEF WATCH EXPERIMENTAL OCEAN ACIDIFICATION PRODUCT

In 2008, NOAA Coral Reef Watch (CRW), together with the NOAA Atlantic Oceanographic and Meteorological Laboratory (AOML), developed and released an Experimental Ocean Acidification Product Suite (OAPS), updated monthly at <http://coralreefwatch.noaa.gov> (Figure 2a). The product offers a monthly,  $0.25^\circ \times 0.25^\circ$  synthesis of satellite and modeled environmental data sets to provide a synoptic estimate of sea surface carbonate chemistry ( $\Omega_{\text{ar}}$ ,  $p\text{CO}_{2,\text{sw}}$ ,  $A_T$ , carbonate ion, and bicarbonate ion) within the oceanic waters of the Greater Caribbean Region (Gledhill et al., 2008). The OAPS system derives estimates of daily sea surface

$A_T$  and  $p\text{CO}_{2,\text{sw}}$  and applies them to compute the carbonic acid system (solve the distribution of the various species given in Equation 1), permitting us to solve for  $\Omega_{\text{ar}}$ . Both  $p\text{CO}_{2,\text{sw}}$  and  $A_T$  are computed through the application of a set of regionally specific algorithms. The sea surface  $p\text{CO}_{2,\text{sw}}$  algorithm is based on  $\text{CO}_2$  gas solubility according to

$$p\text{CO}_{2,\text{sw}} = y_0 + A \times \text{EXP}(-K_0/B) + p\text{CO}_{2,\text{air}}, \quad (2)$$

where  $A = 350.7 \times 10^3$ ,  $B = 30.3 \times 10^{-2}$ , and  $y_0 = -51.2$  are empirically determined constants constrained by ongoing ship observations. The temperature- and salinity-dependent gas solubility coefficient ( $K_0$ , moles  $\text{kg}^{-1} \text{ atm}^{-1}$ ) is calculated using  $0.25^\circ$  gridded daily SST fields (NOAA optimal interpolated [OI] remotely sensed radiometric SST data from in situ, AVHRR, and AMSR-E sensors [Reynolds et al., 2002], henceforth NOAA SST<sub>OI</sub>) and Real-Time Ocean Forecast System (Atlantic) SSS. It is implicit in Equation 2 that  $p\text{CO}_{2,\text{sw}}$  rises at the same rate as  $p\text{CO}_{2,\text{air}}$  but

is seasonally modulated primarily by changes in temperature as expressed by  $K_0$ . The relationship describes the surface waters of the region serving as a source of  $\text{CO}_2$  to the atmosphere during summer months, when gas solubility is relatively low, and as a sink in winter months, when gas solubility is high. Estimates of sea surface  $A_T$  are derived according to the algorithm offered by Lee et al. (2006) that is applicable to subtropical regions in the Atlantic:  $A_T = 2305 + 58.66(\text{SSS} - 35) + 2.32(\text{SSS} - 35)^2 + 1.41(\text{SST} - 20) + 0.040(\text{SST} - 20)^2$ . Monthly composites of daily  $A_T$  and  $p\text{CO}_{2,\text{sw}}$  fields are then used as input to solve the carbonic acid system using the CO2SYS program (Lewis and Wallace, 1998). When  $p\text{CO}_{2,\text{sw}}$  is elevated, it drives carbonate ion concentrations to lower values, thereby depressing  $\Omega_{\text{ar}}$  values. Conversely, when  $A_T$  is elevated, it promotes higher carbonate ion concentrations, thereby raising  $\Omega_{\text{ar}}$  values. Mapped fields of  $\Omega_{\text{ar}}$  are generated in this fashion each month using a

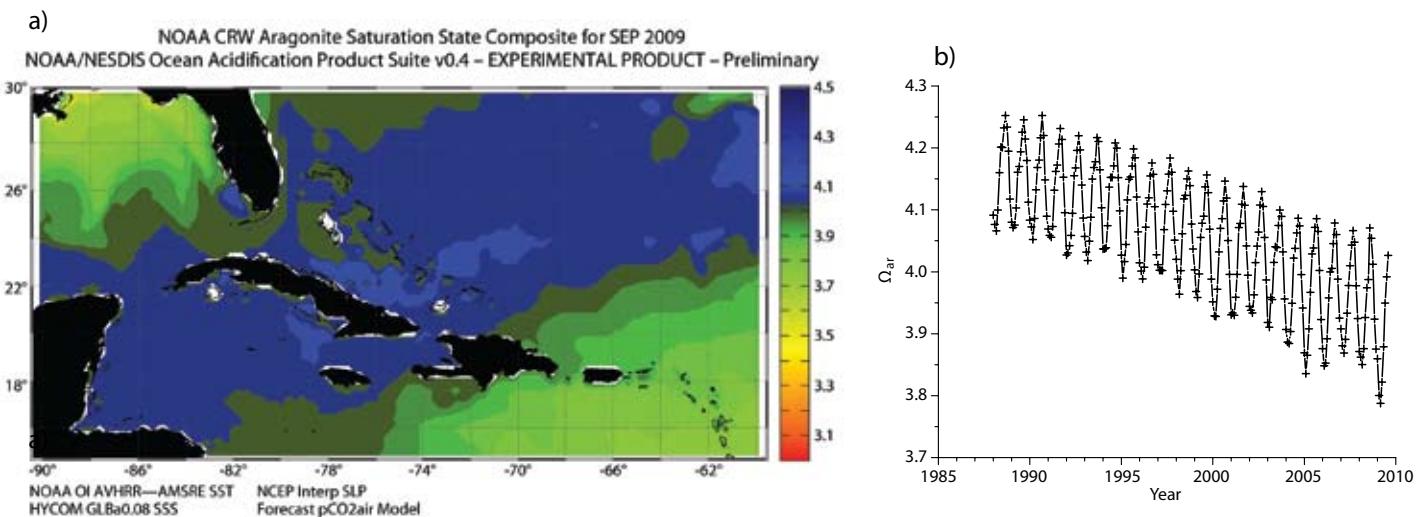


Figure 2. Example output from the Experimental Ocean Acidification Product Suite v0.3 showing (a) the distribution of aragonite saturation state ( $\Omega_{\text{ar}}$ ) across the Greater Caribbean Region for August 2009. Time series (b) of the regional mean  $\Omega_{\text{ar}}$  for the Greater Caribbean Region derived from the Experimental Ocean Acidification Product Suite v0.3.

range of satellite, in situ, and modeled data sets (Table 1). Near-real-time measurements of atmospheric CO<sub>2</sub> are not currently available but can be estimated to  $\pm 1$  ppm a year in advance based on the seasonal cycle of atmospheric CO<sub>2</sub> in the region. The near-real-time model offers preliminary estimates, which are later revised when actual quality-controlled flask sample data become available from the NOAA Global Monitoring Division (GMD) Carbon Cycle Cooperative Global Air Sampling Network (<http://www.esrl.noaa.gov/gmd/ccgg/index.html>).

The predictive performance of the model was evaluated against geochemical cruise data sets collected between 1997 and 2006. In each case, daily computed fields of  $p\text{CO}_{2,\text{sw}}$ ,  $A_T$ , and  $\Omega_{\text{ar}}$  were

compared against ship data. In large part due to the ongoing underway  $p\text{CO}_{2,\text{sw}}$  measurements performed as part of the *Explorer of the Seas* program (<http://www.aoml.noaa.gov/ocd/gcc>), considerable ship-to-model  $p\text{CO}_{2,\text{sw}}$  matchups were available ( $n = 20,141$ ). Surface measurements of  $A_T$  within the region are considerably fewer ( $n = 98$ ) as are the coupled CO<sub>2</sub> measurements necessary to compute  $\Omega_{\text{ar}}$  ( $n = 113$ ). Figure 3 shows fixed intercept (intercept = 0) linear least-squares regressions of the ship data plotted against modeled values that in all cases yield slopes very close to unity. A more comprehensive evaluation of the model's performance is offered in Gledhill et al. (2008), where the mean residuals (computed as the difference between the computed

$p\text{CO}_{2,\text{sw}}$ ,  $A_T$ , and  $\Omega_{\text{ar}}$  values, and the bin-averaged ship values) are reported as  $1.8 \pm 8.8 \mu\text{atm}$ ,  $-1.9 \pm 18 \mu\text{mol kg}^{-1}$ , and  $-0.02 \pm 0.08$ , respectively.

Using climatological salinities (World Ocean Atlas available from NOAA NODC at <http://www.nodc.noaa.gov>) and NOAA SST<sub>OP</sub>, we extended this approach to model fields back through 1988 (Figure 2b), revealing regionally averaged  $\Omega_{\text{ar}}$  values declining at a rate of about 3% per decade amid considerable seasonal variability. These values are consistent with in situ measurements obtained at the nearby BATS station (Nelson et al., 2001). We can appreciate the historical context of such changes by driving the model using the NOAA extended reconstruction SST product (NOAA\_ERSST\_V3; <http://www>.

Table 1. The Experimental Ocean Acidification Product Suite v0.3 relies on a number of satellite, modeled, and in situ data sets from a range of sources.

PARAMETER	INPUT	DATES USED	SOURCE
Sea Surface Temperature	NOAA NCDC OI AVHRR + AMSR-E OI.2	June 2006–Present	<a href="http://www.ncdc.noaa.gov">http://www.ncdc.noaa.gov</a>
	NOAA NCDC OI AVHRR OI.2	January 1988–May 2006	<a href="http://www.ncdc.noaa.gov">http://www.ncdc.noaa.gov</a>
Sea Surface Salinity	RTOFS (Atlantic)	January 2008–Present	<a href="http://polar.ncep.noaa.gov">http://polar.ncep.noaa.gov</a>
	NOAA NODC World Ocean Atlas (WOA01)	January 1988–December 2008	<a href="http://www.cdc.noaa.gov">http://www.cdc.noaa.gov</a>
Sea Level Pressure	NOAA NCEP Sea Level Pressure	January 1988–Present	<a href="http://www.ncep.noaa.gov">http://www.ncep.noaa.gov</a>
Atmospheric CO <sub>2</sub> mole fraction	NOAA Global Monitoring Division Carbon Cycle Cooperative Global Air Sampling Network	January 1988–April 2008	<a href="http://www.esrl.noaa.gov/gmd/ccgg/index.html">http://www.esrl.noaa.gov/gmd/ccgg/index.html</a>
	Statistical Forecast Model	April 2008–Present	OAPS near-real-time 'preliminary' values
Level 3 Garver-Siegel-Maritorena (GSM) model -chlorophyll $\alpha$	NASA MEaSUREs Aqua MODIS GSMchl	June 2002–February 2009	<a href="ftp://ftp.oceancolor.ucsb.edu//pub/org/oceancolor/MEaSUREs/Aqua">ftp://ftp.oceancolor.ucsb.edu//pub/org/oceancolor/MEaSUREs/Aqua</a>
	NASA MEaSUREs Seawifs GSMacdm	January 1988–May 2002	<a href="ftp://ftp.oceancolor.ucsb.edu//pub/org/oceancolor/MEaSUREs/Seawifs">ftp://ftp.oceancolor.ucsb.edu//pub/org/oceancolor/MEaSUREs/Seawifs</a>

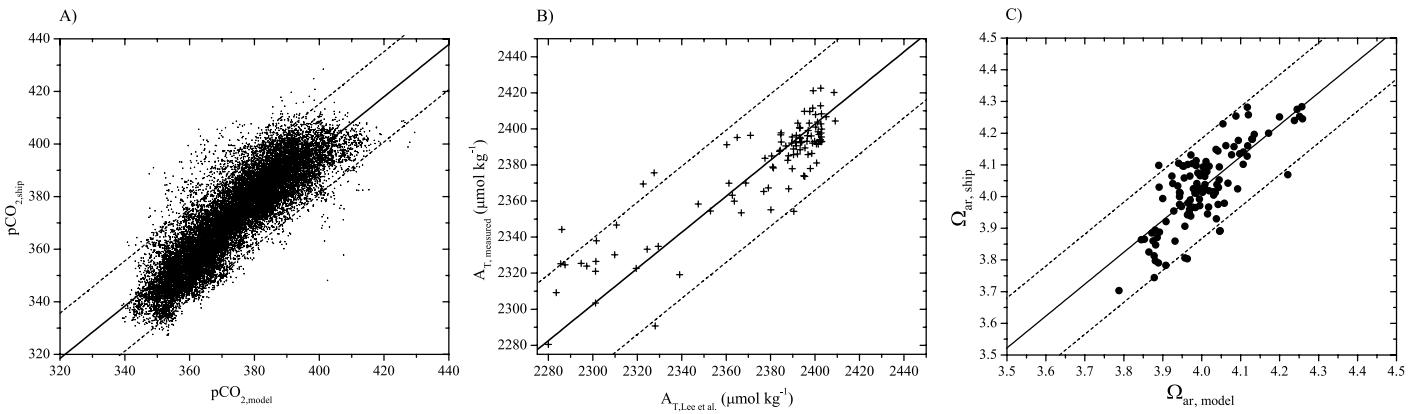


Figure 3. Predictive performance of the  $p\text{CO}_{2,\text{sw}}$  and  $A_{\text{T}}$  algorithms, and the modeled  $\Omega_{\text{ar}}$  values evaluated against geochemical survey data collected within the region between 1997 and 2006 using fixed intercept (intercept = 0) linear least-squares regressions (solid lines). In all cases, the slopes are very near unity: slope  $p\text{CO}_{2,\text{sw}} = 0.966$ , RMSE (SD) = 9  $\mu\text{atm}$ ; slope  $A_{\text{T}} = 0.998$ , RMSE (SD) = 18  $\mu\text{mol kg}^{-1}$ ; slope  $\Omega = 0.994$ , Root-MSE (SD) = 0.08. Dashed lines represent the 95% prediction bands of the fits. RMSE = root mean square error. SD = standard deviation.

[esrl.noaa.gov/psd/](http://esrl.noaa.gov/psd/)) and atmospheric  $\text{CO}_2$  reconstructions spanning the last century (<http://cdiac.ornl.gov/trends/co2/>). This SST is based on in situ values and thus represents an interpolation of limited values across rather coarse resolutions (monthly  $\times 2^\circ$ ), resulting in a somewhat muted seasonal amplitude relative to the satellite-based model (Figure 4). However, it does illustrate that the rate of decline during the last two decades is accelerating compared to the decline prior to 1960, corresponding to the increase in atmospheric  $\text{CO}_2$  growth rate over this time period. There remains considerable debate regarding the geochemical threshold (e.g., minimum  $\Omega_{\text{ar}}$  value) below which positive reef accretion may be compromised, but there is consensus that a saturation state well over 1 is necessary. Silverman et al. (2009) suggested that such a threshold would be crossed should atmospheric values exceed 560 ppm, at which point regionally averaged  $\Omega_{\text{ar}}$  values will decline below 3.0 across the Greater Caribbean Region (GCR). However, the considerable

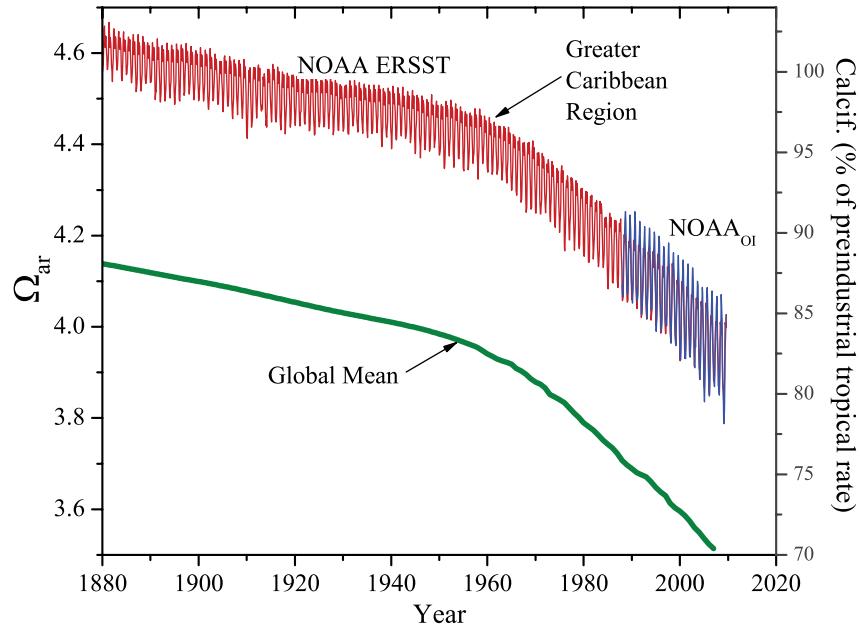


Figure 4. An extended time series of the regional mean aragonite saturation state for the Greater Caribbean Region derived using the NOAA extended reconstructed SST (ERSST V3b; red curve) with the Experimental Ocean Acidification Product Suite v0.3 values derived from satellite SST overlaid (blue curve). The global mean (green curve) is estimated from the representative SST ( $18^\circ\text{C}$ ) and  $A_{\text{T}}$  ( $2320 \mu\text{M kg}^{-1}$ ) values. The left axis depicts the aragonite saturation state while the right axis is an estimate of decline in calcification rate relative to pre-industrial calcification in the Caribbean derived according to Langdon and Atkinson (2005).

spatial and seasonal variability across the region will cause certain areas of the GCR to cross such a threshold on a seasonal basis much sooner.

The secular decline in  $\Omega_{\text{ar}}$  should have diminished regional calcification rates by nearly 20% relative to pre-industrial values, assuming the first-order empirical relationship of Langdon and Atkinson (2005), where calcification rate ( $G$ , mmol  $\text{CaCO}_3 \text{ m}^{-2} \text{ h}^{-1}$ ) =  $(8 \pm 1)(\Omega_{\text{ar}} - 1)$ . It should be noted that coral sclerochronological studies have not yet revealed a decrease in calcification rate within the GCR, although evidence of recent decline has been reported for massive corals from the Great Barrier Reef (De'ath et al., 2009), but the source of this decline is not solely attributed to ocean acidification. Ocean acidification does not occur in isolation, and there are multiple factors that could mute the response in corals, including enhanced calcification as a consequence of warming. This benefit of temperature-enhanced calcification exists only at temperatures below those that lead to physiological stress. Beyond these temperatures, thermally induced bleaching can occur, resulting in mass bleaching events such as those that occurred across the region in 2005 (Figure 5; Wilkinson and Souter, 2008). Additionally, recent work showed that acidification and rising temperatures can act in concert, potentially increasing corals' susceptibility to bleaching (Anthony et al., 2008; Crawley et al., 2009). This combination of acidification and warming is expected to continue with rising anthropogenic  $\text{CO}_2$  emissions, leading to a particularly damaging combination (Hoegh-Guldberg et al., 2007; Veron et al., 2009).

## SEASONAL AND SPATIAL VARIABILITY ACROSS THE GCR

While the model clearly describes a distinct secular decline in  $\Omega_{\text{ar}}$  across the region over the past two decades, the strong seasonality in  $\Omega_{\text{ar}}$ , primarily in response to temperature variations, is striking and often underappreciated. Furthermore, seasonality is spatially variable with much of the variability confined to the higher latitudes ( $20^{\circ}$ – $26^{\circ}\text{N}$ ) of the GCR (Figure 6). The increased  $\Omega_{\text{ar}}$  variability observed in the higher latitudes is in large part a consequence of the greater seasonal ranges in temperature. However, pronounced variations in salinity also occur in this region as a consequence of freshwater input from the northern Gulf of Mexico and along the west Florida shelf, which can impact the Florida Keys. As a result,

Florida Keys coral reefs may experience considerably greater variability in  $\Omega_{\text{ar}}$  relative to lower-latitude systems such as Puerto Rico and the US Virgin Islands. During the warmest months of the year,  $\Omega_{\text{ar}}$  values are elevated in the Florida Keys relative to the lower-latitude systems. This summertime maximum in  $\Omega_{\text{ar}}$  in August could confer about a 6% increase (based on the empirical relationship of Langdon and Atkinson [2005]) in calcification rates within the Florida Keys relative to the lower-latitude reefs. It should be noted that as a consequence of ocean acidification, the current summertime maximums in  $\Omega_{\text{ar}}$  in the higher latitudes of the GCR are less than the wintertime minimums only 20 years ago.

Seasonal changes in carbonate chemistry, rather than other environmental

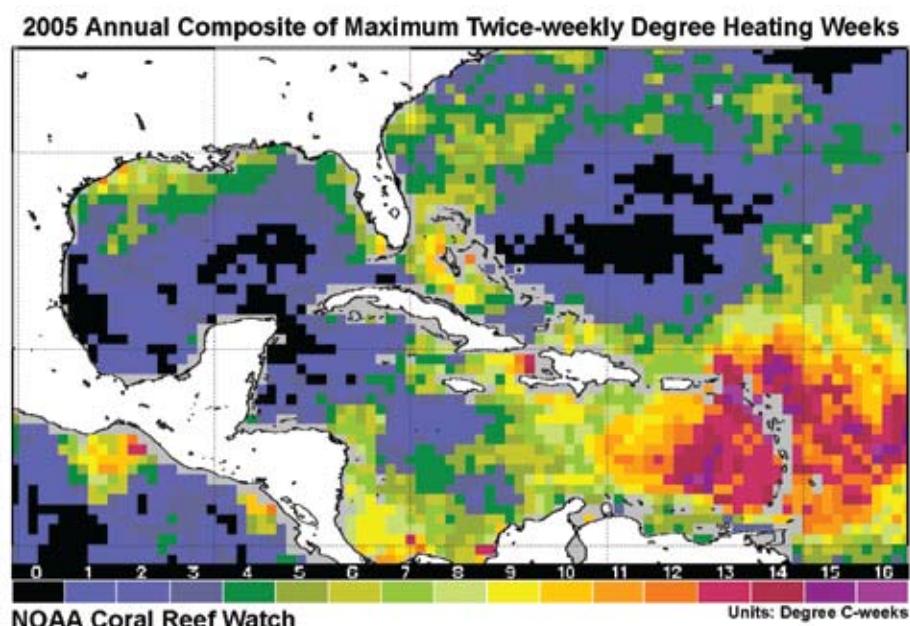


Figure 5. Ocean acidification does not occur in isolation. The Greater Caribbean Region experienced a significant thermal stress event in 2005, resulting in mass coral bleaching and high incidences of mortality, especially for the US Virgin Islands. The figure shows the 2005 annual composite of satellite-derived thermal stress as measured in Degree Heating Weeks (Eakin et al., 2009). Data from NOAA Coral Reef Watch (<http://coralreefwatch.noaa.gov>)

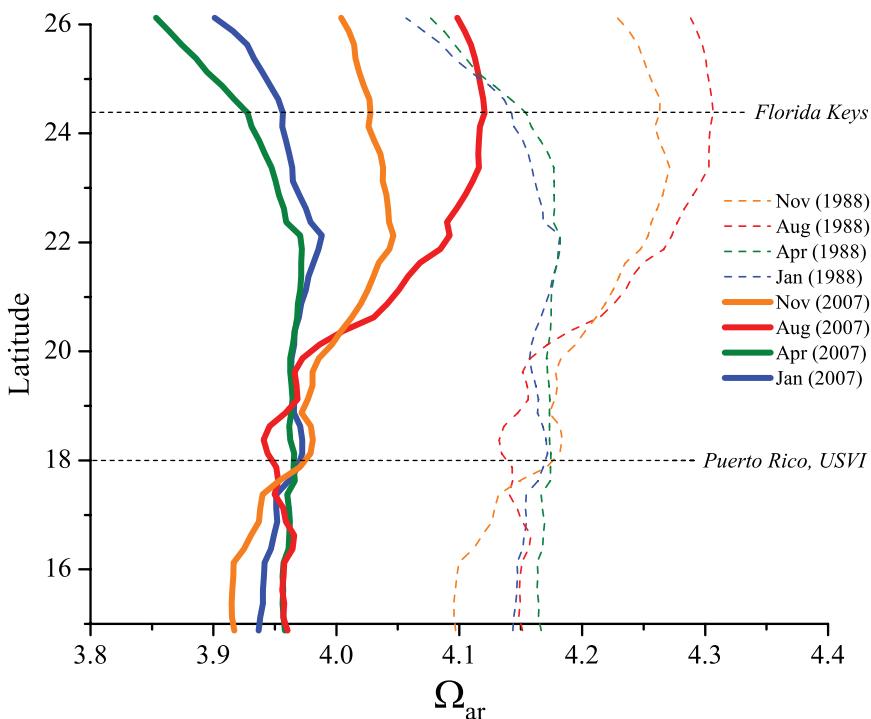


Figure 6. Longitudinal averages (60–90°W) of the Experimental Ocean Acidification Product Suite v0.3-derived  $\Omega_{\text{ar}}$  values for the Greater Caribbean Region for the years 1988 (dashed) and 2007 (solid) for January (blue), April (green), August (red), and November (orange). Note that there is considerably greater seasonal variability at latitudes greater than about 20° with a summertime maximum occurring in the vicinity of the Florida Keys beginning around August.

factors such as light and temperature, have been identified recently as an important factor for high-latitude Bermuda corals, where a strong correlation was found between the in situ rates of calcification for the major framework-building coral species *Diploria labyrinthiformis* and the seasonal variability of  $\Omega_{\text{ar}}$  (Bates et al., in press). So, whether the seasonal variability in carbonate chemistry observed between 20° and 26°N within the GCR is beneficial to these reef systems is not known, but should be an area for future research. It is also important to consider that these modeled fields of  $\Omega_{\text{ar}}$  represent open-ocean values, while metabolic processes that occur at the reef itself

can significantly control the ambient carbonate chemistry on diel time scales. The metabolic influence of the reef community on local carbonate chemistry is largely a function of reef topography (Suzuki and Kawahata, 2004). In some reefs, there may be periods when respiration and calcification processes act collectively to drive up  $p\text{CO}_{2,\text{sw}}$ , thereby depressing  $\Omega_{\text{ar}}$  well below that of the oceanic waters. Yates and Halley (2006) reported net dissolution occurring on a reef flat in Molokai, Hawaii, during the evening as carbonate ion concentrations declined more than 100  $\mu\text{mol kg}^{-1}$  below daytime values. Also, despite supersaturation of surface oceanic waters, dissolution is an ongoing process in sediments

and microenvironments due to localized production of  $\text{CO}_2$  through microbial metabolic activity and actively boring endoliths (organisms that bore inside coral rock). Ocean acidification could exacerbate these processes (Andersson et al., 2009).

## CHALLENGES, CAVEATS, AND FUTURE DIRECTIONS

While the Experimental Ocean Acidification Product Suite offers an important first step toward satellite-based monitoring of ocean acidification, it is important to recognize that the algorithms that govern the model are geographically restricted to the oceanic surface waters of the Greater Caribbean Region. GCR oceanic waters represent a relatively simple system that is largely oligotrophic, and they exhibit limited upwelling compared to higher-latitude systems and the equatorial Pacific.

Upwelling-affected regions will demand increasingly complex algorithms that combine multiple satellite data streams to infer processes beyond the simple thermodynamic forcing that dominates GCR variability. Even within the GCR/Gulf of Mexico region, we found areas where the current model's performance is compromised. As part of a NASA-funded effort to evaluate and improve the model, we established a rigorous carbonate chemistry sampling campaign throughout the GCR region with particular emphasis on areas that are either historically data poor (e.g., the Caribbean Sea itself) or exhibit considerable variability (e.g., northern Gulf of Mexico). Figure 7a illustrates the spatial distribution of model bias (model-ship) between discrete samples collected during 2008 as part of this project where

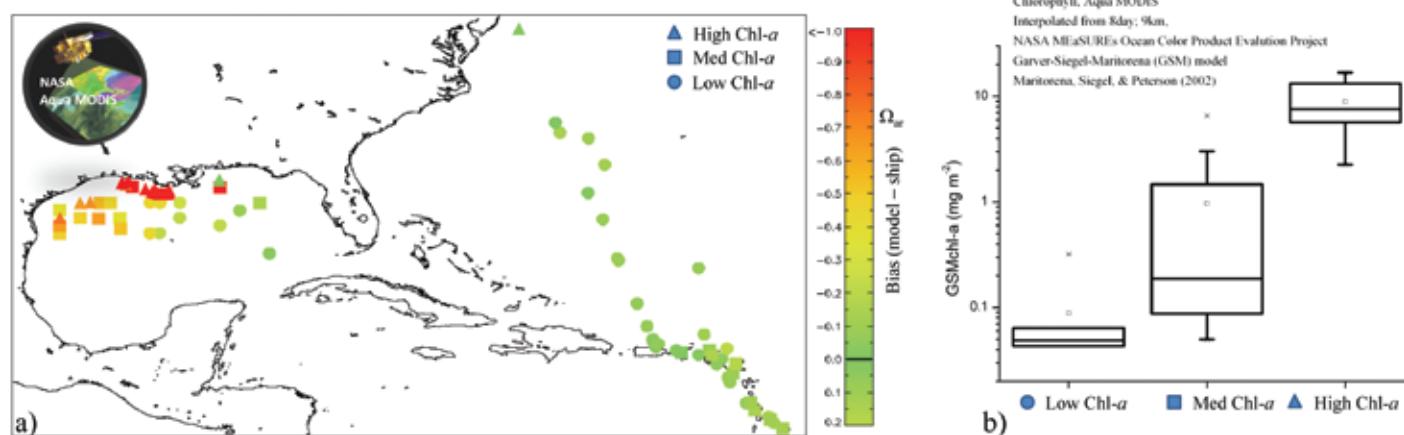
at least two aqueous inorganic carbon parameters were measured contemporaneously (nominally  $A_T$  and  $pCO_{2,sw}$ ). In waters where satellite-derived chlorophyll estimates are low (e.g., Case I waters; circles in Figure 7), the model performs well, particularly throughout the western tropical Atlantic and Lesser Antilles region. However, in the northern Gulf of Mexico, in the presence of elevated concentrations of chlorophyll (squares in Figure 7), the model tends to underestimate  $\Omega_{ar}$  values. In particular, the model significantly underestimates  $\Omega_{ar}$  for waters very near the Mississippi River outlet where satellite estimates of chlorophyll concentration are very high (triangles in Figure 7).

The underestimation of  $\Omega_{ar}$  throughout much of the northern Gulf of Mexico is largely attributed to the model's dependence on the Lee et al. (2006) subtropical algorithm for alkalinity. Of the total survey data applied in the derivation by Lee et al. (2006) of the

(sub)tropical  $A_T$  algorithm, only a minor fraction of the samples was collected within the marginal basin and coastal regions that constitute the GCR. Where surface alkalinity data are available within the Caribbean region's oceanic oligotrophic waters, OAPS data generally show good agreement with Lee et al. (2006) (Gledhill et al., 2008). In contrast, waters in the northern Gulf of Mexico region are more complex and exhibit a strong riverine influence (particularly that of the Mississippi River) that can export considerable alkalinity to the northern Gulf of Mexico and thus export carbonate to the shelf off Louisiana and Texas. Total alkalinity values for the Mississippi River sometimes exceed those of seawater, which can serve to increase local  $\Omega_{ar}$  values.

The complexity we observe in the northern Gulf of Mexico is not unique and illustrates the limitations of the regression analysis approach applied here. It can be expected that no single

stringent algebraic relationship between sea surface carbonate chemistry and remotely sensed parameters is likely to prevail that would prove applicable globally. A rapidly emerging approach being applied to model oceanographic processes using satellite imagery is the self-organizing maps (SOM) method (for review, see Richardson et al., 2003; Kalteh et al., 2008). Telszewski et al. (2009) used a neural network SOM approach to estimate monthly  $1^\circ \times 1^\circ pCO_{2,sw}$  fields in the North Atlantic based on in situ  $pCO_{2,sw}$  data, modeled mixed-layer depth, and satellite observations of SST and chlorophyll *a* for 2004–2006, while Friedrich and Oschlies (2009) simulated the application of SOM using a high-resolution model for the North Atlantic. Adoption of these advanced techniques may provide improved predictive abilities, especially in more complex environments such as in the northern Gulf of Mexico.



**Figure 7.** Comparison of Experimental Ocean Acidification Product Suite v0.3 derived  $\Omega_{ar}$  with those calculated from in situ  $A_T$  and  $pCO_{2,sw}$  data. The Experimental Ocean Acidification Product Suite v0.3 performs well in waters where NASA MODIS-derived chlorophyll *a* estimates are low (circles). However, the model substantially underestimates  $\Omega_{ar}$  in the northern Gulf of Mexico, particularly near the Mississippi River discharge where chlorophyll *a* estimates are high (triangles, as classified according to the box-diagram shown on right). The cruises represent a series of 2008 NASA-sponsored carbonate chemistry surveys throughout the region, including a compilation of *Explorer of the Seas* cruises in the western tropical Atlantic (spring and fall 2008) and NOAA *Gordon Gunter* and Texas A&M *Pelican* cruises throughout much of the northern Gulf of Mexico (summer 2008).

## SUMMARY

As efforts advance to evaluate the potential consequences of ocean acidification on marine ecosystems, there is a need to improve characterization of short-term and seasonal variability in carbonate chemistry onto which ocean acidification is transposed. Satellite observations can provide synoptic observations of a host of physical and optical parameters that reflect processes that control the distribution of carbonate chemistry within the surface ocean, helping us to model such changes in areas where no in situ observations are available. A satellite-based ocean acidification product is now routinely delivering monthly synoptic estimates of surface-ocean carbonate chemistry across the GCR. Despite current limitations, particularly where riverine and coastal processes dominate, the model allows us to explore regional to basinwide trends in ocean acidification on seasonal to interannual time scales within the largely oligotrophic surface waters of the GCR. The model reveals prominent seasonal variations in carbonate chemistry that are largely confined to the upper latitudes of the GCR ( $20\text{--}26^{\circ}\text{N}$ ), which could confer some benefit in the form of a summer-time “bump” in  $\Omega_{\text{ar}}$  relative to the lower-latitude systems. Seasonal variability in carbonate chemistry should be a focus of future research as we work to better understand the potential consequences of ocean acidification. Ongoing efforts are extending this approach to increasingly complex systems. These systems will demand synthesis of additional satellite-derived physical and optical parameters to better constrain biogeochemical and mixing processes that can

overwhelm the simple thermodynamic drivers that govern the carbonate chemistry distributions within the GCR.

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