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Impacts of Ocean Acidification in the Coastal and Marine Environments of Caribbean Small Island Developing States (SIDS)

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EXECUTIVE SUMMARY

Oceans have absorbed one third of the carbon dioxide (CO₂) released to the atmosphere from human activities causing the seawater pH to decrease by 0.1 units since the Industrial Revolution.

There is certainty that ocean acidification caused by anthropogenic activities is currently in progress and will increase in accord with rising atmospheric CO_2 concentrations.

There is medium confidence that these changes with significantly impact marine ecosystems.

Throughout the Caribbean small islands, ocean acidification effects could be exacerbated due to local processes within coastal zones. Ocean surface aragonite saturation state (Ω_{arg}) has declined by around 3% in the Caribbean region relative to pre-industrial levels potentially already impacting tropical marine calcifying organisms.

In addition to the effect on living organisms, ocean acidification is likely to diminish the structural integrity of coral reefs through reduced skeletal density, loss of calcium carbonate, and dissolution of high-Mg carbonate cements which help to bind the reef. This would make coastal areas of the Caribbean small islands increasingly more vulnerable to the action of waves and storm surge. This is likely to have knock-on effects to the tourism sector, fisheries and coastal infrastructure.

More studies about the present and projected impacts of ocean acidification on Caribbean small islands are necessary in order to evaluate alternative adaptive strategies accounting for the different island's environmental, socioeconomic, and political settings.

What is Already Happening?

The rates of change in atmospheric warming and carbon dioxide (CO_2) emissions are unprecedented in modern history and both influence ocean acidification (IPCC, 2014).

Studies using CO_2 proxies on marine fossils, ancient ice and geochemical models, point to atmospheric CO_2 concentrations that remained under 280 parts per million (ppm) for the past 800,000 years preceding the Industrial Revolution of the 18th century (Tripati et al., 2009). However, since then atmospheric CO_2 concentration has increased to 400 ppm (Le Quéré et al., 2016) and presently the change of atmospheric CO_2 increase is more than 100 times faster than that observed over the past 800,000 years (IPCC, 2014). The oceans have absorbed approximately one third (~28%) of all the CO_2 released to the

atmosphere from human activities since the Industrial Revolution (Sabine et al., 2004; Frölicher et al., 2015).

Ocean Acidification is the process by which the ocean uptake of atmospheric CO_2 causes an increase the seawater concentration of CO_2 which in turn, results in a decrease on seawater pH and carbonate ($CO_3^{2^2}$) ions (see Box 1). Currently we know that the average surface ocean pH has decreased by 0.1 units since the Industrial Revolution (Feely et al., 2009; IPCC, 2014). A 0.1 unit change may seem to be small, but actually corresponds to a 26% increase in ocean acidity over the last 200 years. If atmospheric CO_2 concentration continues as predicted under either of the two intermediate CO_2 scenarios of the IPCC (RCP 4.5 and 6.0), then by the next century the average pH of oceanic waters will decrease by 0.1 - 0.2 units (40 - 62 % more acidic) below pre-industrial levels. Other higher- emission CO2 scenario (RCP 8.5) predict decreases

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National Oceanography Centre NATURAL ENVIRONMENT RESEARCH COUNCIL of 0.3 to 0.4 units which correspond to 100 -150% more acidity. As the ocean absorbs more atmospheric CO_2 , the magnitude and rate of ocean acidification will continue increasing.

Box 1: Ocean Acidification process

When CO₂ from the atmosphere dissolves into the ocean, it rapidly dissociates causing an increase in hydrogen (acid, H⁺) that lowers the pH. This chemical process is summarized as follows (Zeebe & Wolf-Gladrow, 2001):

- The CO₂ reacts with water to produce carbonic acid (H₂CO₃).
- 2. The carbonic acid rapidly dissociates and causes an increase in hydrogen ions (H⁺) and bicarbonate (HCO₃).
- 3. The HCO_3^{-1} dissociates and produces more H^+ , that in turn reacts with CO_3^{2-1} ions reducing the CO_3^{2-1} concentration.

1. $CO_2 + H_2O = H_2CO_3$ 2. $H_2CO_3 = H^+ + HCO_3^-$ 3. $HCO_3^- = H^+ + CO_3^{-2-}$

A decrease in CO3-2 concentration in response to ocean acidification can significantly impact the degree to which seawater is saturated with respect to calcium carbonate minerals (e.g. aragonite, calcite, magnesian calcites), which are critical building blocks of most marine skeletal material. This is termed saturation state (Ω) and can be related to how difficult it is for marine calcifying organisms to build their skeletons out of calcium carbonate (CaCO₃, see Box 2). Seawater Ω can be also considered as an index that describes the tendency for a carbonate mineral to precipitate or to dissolve, and is often positively correlated with marine skeletal growth (e.g. Langdon et al., 2000; Waldbusser et al., 2015). If Ω is greater than one, conditions will be favourable to calcium carbonate precipitation, and if Ω is less than one, net dissolution of carbonate structures, shells and sediments will be favoured. A value of one is in equilibrium, with neither net precipitation nor dissolution being favoured. Surface Caribbean waters are on average about four times supersaturated with respect to the mineral aragonite (Ω = 4) while in pre-industrial periods this value likely exceeded about five times supersaturation ($\Omega = 5$).

It is certain that ocean acidification caused by anthropogenic activities is currently in progress and will increase in accord with atmospheric CO₂ emissions. Ocean acidification is measurable; however, it has been difficult and expensive to monitor with the necessary high-quality observations to understand the effects of increasing ocean acidification on marine and coastal ecosystems. Only two open ocean acidification long time series (Gruber et al., 2002; Bates et al., 2012) and few short-term records in the coastal ocean are available (Wootton et al., 2008; Provoost et al., 2010). This is mainly because of the data needed to fully constrain carbonate chemistry. To do this, two of the several possible parameters are needed, along with seawater salinity and temperature. Measurable carbonate parameters are the fugacy of CO₂, total alkalinity (TA), dissolved inorganic carbon (DIC), partial pressure of CO₂ (pCO₂) and pH. The last two are often measured by contemporary moored ocean acidification observing systems. Other carbonate parameters while important, are presently difficult to measure *in situ*.

Box 2: Saturation Index

Seawater Ω_{CaCO3} is defined as the ratio between the ion concentration product of calcium (Ca⁺²) and CO₃-² to the solubility product (a function of temperature, pressure and salinity) based on ion concentrations at saturation (K^{*}_{SP}) as given by:

 $\Omega_{CaCO3} = [Ca^{+2}][CO_3^{2-}]/K^*_{SP}$

Three common CaCO₃ mineral forms are magnesian calcite, aragonite and calcite, with calcite and aragonite representing the principal mineral components used by marine calcifying organisms to produce their internal and external skeletons (Morse et al., 2007). Magnesian calcite minerals are found in marine sediments and coral reef frameworks as important lithified or cements (Macintyre & Aronson, 2006). While they are thought to be the "first responders" to low Ω values and ocean acidification due to their tendency to dissolve, there is still large uncertainty regarding their solubility (Morse et al., 2007; Andersson et al., 2008).

Another major challenge for monitoring acidification is that seawater carbonate chemistry must be characterized precisely to distinguish between the natural CO₂ variability driven by local biogeochemical processes from human induced secular changes in atmospheric CO2. Direct long-term measurements in open ocean waters show clear relationships between increasing atmospheric CO₂ and decreasing seawater pH (Dore et al., 2009; Bates et al., 2012). However, many coastal regions already experience low surface seawater pH and Ω_{CaCO3} conditions ("localized or coastal ocean acidification") due to processes other than CO₂ uptake (Duarte et al., 2013). These processes include upwelling of low pH waters (Feely et al., 2008), deposition of atmospheric nitrogen and sulphur (Doney et al., 2007), discharge of riverine waters (Salisbury et al., 2008), as well as inputs of nutrients and organic matter that stimulate intense respiration and generation of CO₂ (Cai et al., 2011). As a result, the effect of ocean acidification on coastal zones can be several times higher and faster than typically expected for oceanic waters (Duarte et al., 2013; Venti et al., 2014).

Caribbean Region

Although the surface ocean is alkaline (pH above 7.0) and will remain so for the foreseeable future, the process of ocean acidification (Figure 1 and 2) is readily apparent and has potentially detrimental consequences for marine life and dependant human communities, especially for the Caribbean Small Islands Developing States (SIDS).

The longest continuous record of ocean CO_2 and ocean acidification in the Caribbean region is in the North Atlantic subtropical gyre near Bermuda (Bates et al., 2012). Direct measurements at the Bermuda Atlantic Time-series Study (BATS) station shows that surface ocean acidity has increase by ~12% and surface aragonite saturation state (Ω_{arg}) has decrease by ~8% over the past 3 decades (Bates et al., 2012).

Using the Caribbean regional empirical model of Gledhill et al. (2008) from 1992 - 2015 we show a regional increase in surface ocean acidity of ~10% and a decrease on surface ocean Ω_{arg} of ~8% (Figure 2; see Box 3 for details on the domain covered).

These values agreed with those reported across the Caribbean (Gledhill et al., 2008) and Atlantic regions (Bates et al., 2012; Jiang et al., 2015) using regional and global numerical marine carbonate system models.

Box 3: Current conditions: methods

To estimate the carbonate system parameters relevant to ocean acidification we use the following data sets and models. Monthly regional mean values of ocean surface Ω_{arg} and pH were estimated using the sea surface pCO₂ values from the empirical model of Gledhill et al. (2008). The sea surface salinity (SSS) and temperature (SST) values were obtained from the Hybrid Coordinate Ocean Model (HYCOM). Atmospheric CO₂ values are from National Oceanic and Atmospheric Administration, Cooperative Global Air Sampling Network (Conway et al., 1994). The CO₂ measurements for the Caribbean region are based on weekly air samples from St. Croix, Virgin Islands, United States and Ragged Point, Barbados, The derived marine boundary layer (MBL) reference used the data extension and integration methods described by Masarie and Tans (1995). Data covered the domain defined as [30°N, 15°N, 90°W, 60°W] from 1992 to 2015. Sea surface TA values were derived as a function of SSS and SST using the empirical relationship of Lee et al. (2006) for the Caribbean region. The CO2sys software from Lewis and Wallace (1998) MatlabTM version was used to calculate Ω_{arg} and pH in seawater.



Figure 1: Time series from 1980 to 2015 shows in black monthly regional mean of dry atmospheric CO₂ mole fraction (umol/mol) in the Caribbean. In blue a time series from 1992 to 2015 of monthly regional mean of seawater pH (total scale). Data covered the domain defined as $[30^{\circ}N, 15^{\circ}N, 90^{\circ}W, 60^{\circ}W]$. The light blue line represents the seawater line. When CO₂ from the atmosphere dissolves into the ocean via the process of airsea exchange, it reacts with water and forms carbonic acid (H₂CO₃). This rapidly dissociates and causes an increase in hydrogen (acid, H+) and bicarbonate (HCO³) ions. The term "ocean acidification" refers to the process by which the pH of the ocean decreases due to the increases on seawater H+ ion concentration as a result of the uptake of CO₂ from the atmosphere.

Constraining the near-reef variability in carbonate chemistry across diel, seasonal, and annual scales is important in assigning potential biogeochemical thresholds to ocean acidification. Results by Gledhill et al. (2008) indicated that patterns in Ω_{arg} and pH change spatially and seasonally, with

higher values in spring and summer and throughout the center of the Caribbean Basin. During the fall and winter Ω_{arg} values are generally lower throughout the center and eastern Caribbean relative to the northwestern Caribbean waters. During this time, high temperatures coincide with the influx of the low-salinity Amazon and Orinoco River plumes into the eastern Caribbean (Corredor & Morell, 2001). Increase in river runoff from local and regional areas could have a significant effect on coral reefs on shorter time scales in Caribbean SIDS.



Figure 2: Time-series of surface seawater Ω_{arg} and pH shows monthly regional mean values for the Caribbean region from 1992 to 2015. Data covered the domain defined as [30°N, 15°N, 90°W, 60°W].

Within coastal zones where most of the affected marine organisms reside, coastal process can combine with ocean acidification to exacerbate acidification further altering the carbonate chemistry. Monitoring the effects of ocean acidification within the dynamic near-reef environment is challenging. The Atlantic Test-bed in La Parguera Marine Reserve, Puerto Rico has provided seven years of sustained high temporal observations that are used to estimate Ω_{arg} . Work in progress by Meléndez et al. (in preparation) documents a Ω_{arg} decrease of ~1.2 % over the last 7 years which is a lower rate than that suggested by Gledhill et al, 2008 (3% decade⁻¹).

These findings would suggest calcification rates have likely declined since the preindustrial period given the reduction in Ω_{arg} that has occurred (Langdon & Atkinson, 2005; Pandolfi et al., 2011). Friedrich et al. (2012) concluded that calcification rates may have already dropped by ~15% within the Caribbean with respect to their pre-industrial values. However, the decreasing carbonate production, calcification rates, hard coral cover, and biomass of major reef- building species throughout the Caribbean region are likely attributable to the interaction of multiple natural and anthropogenic stressors such as hurricanes

(Woodley et al., 1981), thermal bleaching (Aronson et al., 2000), outbreaks of disease (Mayor et al., 2006), the mass mortality of the sea urchin *Diadema antillarum* (Lessios et al., 1984) and overfishing (Rogers & Beets, 2001). Emerging evidence suggests that effects of ocean acidification on the reef structural integrity and ecosystem function are strongly related to effects on the net community dissolution (Andersson et al., 2009) and bioerosion rates (Enochs et al., 2015), decrease on calcification rates of crustose coralline algae (Johnson & Carpenter, 2012) and fertilization and recruitment success (Albright et al., 2010). Such effects could compromise reef resiliency in the face of other acute threats, such as thermal-stress, diseases, increasing storm intensity, and rising sea level.

According to Perry et al. (2013), Caribbean coral reefs in the Bahamas, Belize, Bonaire and Grand Cayman are already experiencing significant reductions in carbonate production rates with 37% of surveyed sites showing net erosion. The combination of erosion, dissolution and bioerosion processes in shallow reef habitats could accelerate the loss of calcium carbonate sediments and decrease the stability of the reef skeleton framework (Eyre et al., 2014), potentially leading to a collapse of reef structures (Hoegh-Guldberg et al., 2007). Such effects could compromise reef integrity and resiliency in the face of other acute threats such as coral bleaching, disease outbreaks, increases in storm intensity and rising sea levels (Silverman et al., 2009).

There is evidence that net dissolution is already occurring in shallow waters of reef environments (Gattuso et al., 1998; Yates & Halley, 2006; Bates et al., 2010; Muehllehner et al., 2016) due to elevated metabolic activity at night when respiration dominates community production releasing CO₂. If periods of carbonate dissolution increase in duration and magnitude and exceeded daytime calcification, it could result on a net dissolution of the carbonate minerals and cements that maintain the reef structure. Under the IPCC atmospheric CO₂ business as usual scenario (IPCC, 2014), this could happen by 2030 when the average atmospheric and seawater pCO₂ threshold values reach 560 and 650 *u*atm, respectively (Yates & Halley, 2006). Under continued periods of net dissolution, ecosystem persistence and resilient are jeopardize in the face of other climate stressors.

Seagrass beds and macroalgae could benefit as they utilize CO₂ during growth (Palacios & Zimmerman, 2007). During the period in which biomass is increasing, marine plants can sequester carbon, reducing the concentration of seawater CO₂. This could cause non-calcifying species to outcompete calcifying organisms (Fabricius et al., 2011), resulting in changes to ecosystem services. There have been studies (e.g. Florida Reef Tract) suggesting seagrass meadows may attenuate ocean acidification effects creating "refugia" for calcifying organisms and coral reefs downstream (Manzello et al., 2012). Further studies are needed on the potential ocean acidification management alternatives these ecosystems can offer to Caribbean SIDS.

What Could Happen?

While significant changes in surface chemistry have been observed over the previous decades, clear evidence of widespread degradation of reef environments that can be directly attributed to ocean acidification is remains matter of debate (Carricart-Ganivet et al., 2012). However, like most tropical oceans, the Caribbean is subject to accelerating changes in water chemistry that could subject ecosystems sub-optimal conditions by the century's end (Perry et al., 2013). Future acidification pressures will not act independently from other environmental phenomena such as changes in ocean warming, relatively frequency and intensity of storm events, sea level rise, human pollution and fishing pressure that can act synergistically or antagonistically to either assuage or increase the harm done to Caribbean ecosystems.

Results show the 2015 averaged annual pH (Figures 3A) and Ω_{arg} (Figures 4A) as well as the percent change in acidity (Figures 3B and C) and Ω_{arg} (Figures 4B and C) that takes place between the years 2015 to 2050 and 2015 to 2100 (see Box 4 for method details). The results are notable with the Caribbean becoming more acidic by 20% and 58% in 2050 and 2100, respectively. Sea surface Ω_{arg} , also declines (16% and 32%) to an average of 3.3 in 2050 and 2.6 in 2100. Most modern coral reef systems currently reside well above a value of 3.0 which has been suggested as a potential threshold to maintain net reef accretion (Guinotte et al., 2003). Model projections of Ω_{arg} are concerning as prior to 2100 values drop below this threshold.

Box 4: Future conditions: methods

To examine future changes in surface seawater pH and Ω_{arg} in the Caribbean region (defined previously) we use a combination of the aforementioned modelled and observed SST, SSS and atmospheric pCO_2 measurements. Recent trends in the data were taken from the Puerto Rico Climate Change report (PRCCC, 2013) and propagated into the future to determine values for 2050 and 2100. A linear increase of 0.026°C SST per year and a linear decrease of -0.0024 units SSS per year were used (for temporal range and analysis details refer to the PRCCC, 2013). The trend on atmospheric pCO_2 was solved using a first-degree polynomial, which when projected to 2050 and 2100, agrees with the intermediate IPCC (2104) emission scenarios. The future seawater pCO_2 , SSS and SST changes were applied within the context of the Gledhill et al. 2008 model to predict sea surface pH and Ω_{arg} values for 2050 and 2100 with respect to 2015 average values.

We note that our predictions are based on coarse oceanic models and do not account for effects attributable to changes in productivity, wind stress, remote river forcing (e.g. Amazon River discharge) or coastal processes. For example, coastal oceans adjacent to large populations may also experience exacerbated acidic conditions caused by anthropogenic nutrient fluxes. In addition to the potential for increase acidity, nutrients can stimulate preferential growth of macrophytes that may stunt coral growth (Smith et al., 2006), or contribute to light-attenuating sedimentation processes that also inhibit healthy reef production. Ocean current patterns may change, delivering more, or less, fresh water originating from the South American continent. In addition, predominant wind patterns may change, affecting ocean mixing or stratification. While the effects of future acidification pressures on ecosystems are not clear, even less is known about how such effects will propagate into the economy of the Caribbean SIDS.



Figure 3: A) Modeled pH for 2015. B) Percent change in pH from 2015 to 2050. C) Percent change in pH (-log10(pH)) from 2015 to 2100. See text for model details. Note the scale change on B and C color bars.



Figure 4: A) Modeled Ω arg for 2015. B) Percent change in Ω arg from 2015 to 2050. C) Percent change in Ω arg from 2015 to 2100. See text for model details. Note the scale change on B and C color bars.

Confidence Assessment

What is already happening



observations / models) modelled)

What could happen in the future



The carbon dioxide system of seawater is well understood and established. As such, the basic equilibria governing the process of ocean acidification dates backs to at least 1960 (Bolin, 1960) and represents a foundational understanding of modern chemical oceanography. The ecological consequences of anthropogenically-induced changes to the system (i.e. ocean acidification) is, however, a considerably new field. Both of these themes were assessed in light of recent findings and based on adequate observed local data (e.g. atmospheric pCO₂ values are based on measurements of weekly air samples from St. Croix, Virgin Islands, United States and Ragged Point, Barbados) complemented with empirical models. Projected changes in climate for the Caribbean islands were based on the future projections of fossil fuel emissions driven by reasonable models from the IPCC (2104). Further understanding on the expected ocean acidification effects of the species and habitats in the Caribbean is based on evidence tested elsewhere, so there is a lack of empirical specie's response data in these areas.

Knowledge Gaps

Species and Ecosystem Vulnerability, Resilience, and Adaptive Capacity: Economic and social costs of ocean acidification impacts and the resulting adaptation options are scarcely known but are of the utmost importance. Ocean acidification will likely affect the tourism sector, fisheries and coastal infrastructure. Studies that can identify specific and collective island vulnerability are needed since ocean acidification effects depend on the unique biophysical nature of the island and its social,

economic, and political setting. Estimating the value of alternative adaptive strategies to mitigate ocean acidification will depend on individual community priorities, vulnerabilities and resilience.

Ecosystem and Organism Response: The value of the loss of ecosystem services to ocean acidification is unknown. Such losses are attributable to degradation of ecosystems that support important economic marine species such as coral, conch, oysters, fish larvae, urchins and pelagic fish on Caribbean SIDS. There is strong evidence for decreasing carbonate production, calcification rates, coral cover, and biomass of major reefbuilding species throughout the Caribbean region. However, there is still not enough evidence to conclude that these decreased ecosystem processes are due to ocean acidification. There are only a few studies on ecosystem and organismal responses to climate stressors (e.g. ocean warming) that consider ocean acidification in Caribbean SIDS. For instance, low pH values could affect nursery areas of commercially important species such as tuna, presenting a source of vulnerability for the economy, but studies are scarce. Ocean acidification could also affect the food web dynamics at lower trophic levels and have physiological effects at larval stages that would likely cascade upwards-impacting coral and fish recruitment.

Chemical and Physical Baseline Information: Baseline studies that can address the current ecosystem conditions in terms of ocean acidification are lacking in the Caribbean region. Baseline assessments that can address the spatial and temporal variability are required to better understand the present ocean acidification conditions and rates of change. For instance, there is evidence that the carbonate saturation state has decreased about 3% per decade and that the values change spatially and temporally throughout the Caribbean region. However, it is unknown how remote processes, such as the Amazon/Orinoco river discharge, circulation patterns or aeolian deposits could alter the effects of ocean acidification. Processes controlling localized coastal acidification, including anthropogenic nutrient fluxes and local discharge are poorly constrained. In addition, it is predicted that coastal reef zones are going to surpass the predicted open ocean chemical thresholds where dissolution exceeds precipitation, but the timing and rate of change are currently unknown.

Socio-economic Impacts

The effects of ocean acidification on coral reefs, shellfish, fish, and marine mammals will likely cause an economic impact on fisheries, coastal protection and tourism in Caribbean SIDS. Ocean acidification will exacerbate the current global warming effects on coral reefs and it will likely continue deteriorating reef conditions and cause ecological regime shifts from coral to algal reefs (Hoegh-Guldberg et al., 2007; Anthony et al., 2011). The primary impact to reef communities will probably be through a reduction in their capacity to recover from acute events such as thermal bleaching.

Corals reefs in Caribbean SIDS are of particular importance due to their role in supplying sand to island shores, reducing the

potential for shore erosion, providing habitat for commerciallyimportant marine species as well as underpinning beach and reef-based tourism and economic activity (Perch-Nielsen, 2010). The projected loss of benefits from fisheries, dive tourism and shore protection is between US\$350 million to US\$870 million by 2050 (Burke & Maidens, 2004). For instance, decreasing rates of reef accretion and increasing erosional processes due to ocean acidification will impact reef-protected coastlines from wave and storm surges. The coastline, and other back-reef and inshore environments, such as seagrass meadows, salt marshes and mangroves, will become vulnerable to wave action and storm surge. These reef barriers also protect beaches and critical infrastructure such as power plants, hospitals, airports, seaports, roads and other major structures from erosion and severe coastal storm damage through dissipation of wave energy. The estimated value of shoreline protection services provided by Caribbean reefs is between US\$700 million and US\$2.2 billion per year. Within the next 50 years, coral degradation and death could lead to losses totalling US\$140 million to US\$420 million annually (Burke & Maidens, 2004).

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