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Modelling the Effects of Ocean Acidification in New Zealand

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EXECUTIVE SUMMARY

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The surface ocean is currently supersaturated in aragonite and calcite, the two forms of carbonate that marine calcifying organisms such as molluses, bryozoans, and habitat forming scleractinian corals use to form their structures. The depths below which dissolution of solid carbonate begins is referred to as the saturation horizon. A reduction in the carbonate saturation state has a major impact on organisms that produce carbonate structures. Ocean acidification reduces the amount of aragonite and calcite in seawater and leads to a shallower ASH and CSH. The skeletons of cold water scleractinian corals are composed of aragonite, the more soluble polymorph of carbonate, and as such this group is vulnerable to OA-induced dissolution.

Our work suggests that the ASH has already risen by 50 to 100 m over much of the New Zealand Exclusive Economic Zone (EEZ). The shoaling ASH indicates that the proportion of the region with carbonate chemistry favourable to aragonitic calcifers may have already shrunk considerably. Changes in the depth of the CSH are less clear, because the CSH occurs far deeper than ASH (2500 to 3500 m compared with 500 to 1500m) and there has been little penetration of fossil CO₂ to the depth of the CSH in our region. In addition, there are fewer historical observations at the depth of the CSH upon which to base our analysis.

This information was used to evaluate model simulations from the Coupled Model Intercomparison Project Phase 5 (CMIP5), a public repository of output from the Earth System Models (ESMs) used to predict future climate change. The subset of CMIP5 models that best capture changes in the ASH and CSH for our region suggest that the ASH and CSH will rise to a depth of about 300m on average over the NZ EEZ if the global community continues on our current emissions pathway. With further refinement, the data based estimates of historical change developed here may become an important tool for evaluating the performance of the next generation of ESMs, including CMIP6 and the New Zealand ESM currently being developed as part of the Deep South National Science Challenge. It will also inform future projections of the ASH and CSH in the southwest Pacific.

1. INTRODUCTION

Earth's oceans absorb about a quarter of all CO_2 emitted to the atmosphere from use of fossil fuels and other human activities, with the Southern Ocean accounting for more of this anthropogenic carbon uptake than any other ocean region (Sabine et al. 2004; Mikaloff Fletcher et al. 2006; Lenton et al. 2013). While this ocean carbon sink slows climate change, it has a profound impact on carbonate chemistry in the ocean. When CO_2 is absorbed by the oceans, its reactions with seawater acidify the oceans and reduce the concentration of calcite and aragonite, two crystalline forms of carbonate that calcifying organisms use to form their carbonate endo- or exo-skeletal elements structures, (e.g., see Kroecker et al. 2013). The depths below which dissolution of solid carbonate begins, is referred to as the Saturation Horizon.

Models predict that the Southern Ocean surface waters will be undersaturated with respect to aragonite by the 2060s in response to anthropogenic change. Thus, marine calcifiers such as corals, algae, molluscs, echnoids, and bryozoan will be unable to produce their structures if fossil fuel emissions continue unabated (Orr et al. 2005; Bopp et al. 2013).

The models used to simulate past and future changes in ocean acidification however, have the largest uncertainties in the Southern Ocean (e.g. Orr et al. 2005; Bopp et al. 2013). Independent, data-based estimates are needed to better understand how the aragonite and calcite saturation states have changed over the past and explore what that means for future climate change.

In order to address this gap, Bostock et al. (2013) recently developed algorithms to estimate highresolution spatial distributions of carbonate parameters in the Southern Ocean, including the waters of New Zealand's Exclusive Economic Zone (EEZ). While observations of carbonate parameters are relatively sparse in the Southern Ocean, a wealth of measurements is available for temperature, salinity, and oxygen. These authors developed algorithms to estimate dissolved inorganic carbon (DIC) and alkalinity from temperature, salinity, and oxygen where co-located measurements were available, and then used these algorithms to produce high resolution maps of these chemical components from the spatially dense temperature, salinity, and oxygen data. The aragonite and calcite saturation horizons (ASH and CSH) were then calculated from the high resolution DIC and alkalinity maps.

The approach of Bostock et al. (2013) has provided a much more detailed picture of the present state of the ASH and CSH in waters around New Zealand, but it yields no information about how these parameters have changed over time or how they might change in the future. The algorithms were developed using relatively recent observations (post 1990s) and did not consider changes in chemistry with time due to increasing storage of anthropogenic carbon in the oceans.

A clearer picture of how the ASH and CSH have changed over time in response to industrial activities is needed to provide valuable information about how much environmental stress marine organisms in the waters around New Zealand are already under. The skeletons of stony corals are composed of aragonite, the more soluble polymorph of carbonate, which makes them vulnerable to OA-induced dissolution. Any shoaling of the ASH represents a potential threat to this group as it will become challenging to construct and maintain their skeletons in water undersaturated with respect to aragonite (Guinotte et al. 2006; Tracey et al. 2013; Bostock et al. 2015). While recent work by Bostock et al (2015) found that alkalinity was the most important predictor for the distribution of corals in the southwest Pacific, they also noted that some stony corals lie below the ASH in aragonite undersaturated waters (i.e., in a zone where conditions seem unfavourable for their growth). These authors hypothesised that previous shifts in the ASH could explain this unexpected result. The corals may have formed when the waters at that depth were supersaturated in aragonite and adapted as the ASH rose. Data based estimates of the evolution of the ASH and CSH over recent decades could

resolve this question and help shed light on the ability of certain stony corals to adapt to these changes.

In addition, better understanding of these past changes may provide insight into future changes in the ASH and CSH. The International Panel on Climate Change (IPCC) and other scientific and policy groups use simulations from the Coupled Model Intercomparison Project Phase 5 (CMIP5) suite of models to predict future changes in climate, including changing ocean acidification, temperature, nutrient distributions and other potential stressors to marine organisms. These simulations include both historical simulations and simulations of the future under different emissions scenarios. Data based estimates of changes in the ASH and CSH would provide a means to evaluate these models for the waters around New Zealand, particularly since changes over time can be a more powerful metric for accurate prediction than the mean state.

We build on our previous work by developing algorithms that account for changes in anthropogenic carbon uptake over the industrial era using a combination of data and models. We use these refined algorithms to estimate the pre-industrial ASH and CSH for oceanographic regions around New Zealand and compare these data based estimates to simulations from the CMIP5 models. The implications for future climate change are explored.

Overall Research Objective

• Determine how much the aragonite and calcite saturation horizons (ASH and CSH) have changed over the industrial era for the southwest Pacific, including New Zealand's Exclusive Economic Zone (EEZ)

Specific Research Objectives

- 1. Develop novel algorithms to estimate dissolved inorganic carbon and alkalinity that account for increased absorption of carbon by the oceans due to human activities using a combination of measurements and models. These new algorithms will be used to estimate pre-industrial ASH and CSH for several oceanographic regions in the southwest Pacific. Quantify the uncertainty of the estimates and evaluate them against independent approaches.
- 2. Compare these data-based estimates of the ASH and CSH with simulations from the Coupled Model Intercomparison Project Phase 5 (CMIP5). Explore the implications of these findings for future projections of the ASH and CSH in the southwest Pacific.

2. METHODS

Specific Objective 1

Data

The first specific objective is underpinned by high quality ship-board observations of salinity, temperature, oxygen, and also of carbonates in the southwest Pacific over the last 60 years. Carbonate data were not available as widely as the other three environmental variable data, and thus were used as a training dataset to develop our algorithms. Most of the ship-board measurements since the 1990s have been collated into publicly available databases, such as the GLODAP and CARINA/PACIFICA data that were used in previous algorithm development for modern times (Bostock et al. 2013). However, many early observations prior to the 1990s are not included in these databases.

To understand changes in historical ocean properties we downloaded observations from international databases of hydrographic measurements held at the NOAA National Centers for Environmental Information (NCEI), formally the NOAA National Oceanographic Data Centre (NODC), for a region around New Zealand. The area selected was bounded by 10°S, 60°S, 140°E and 150°W. This area

extends beyond the final study area over which results will be presented, but was selected to identify the distribution of data over time, particularly as older data will be sparse and unevenly distributed and may not lie within the New Zealand EEZ. All hydrographic data with a minimum of temperature, salinity, and dissolved oxygen were downloaded in the region of interest. Carbon and nutrient data were also downloaded for these stations where it had been collected.

These data were merged with NIWA data not yet included in the global databases. In the process of collating the data, we identified a processing error in some of the historical NIWA-held oxygen data and reprocessed these data under SSIF funded projects in order to make them available for this work as well as for other projects.

Algorithm Development

In our previous work, we treated the observed dissolved inorganic carbon (DIC) and alkalinity (Alk) as a linear combination of temperature (T), salinity with a background salinity of 35 removed (S-35), oxygen (O_2) and a constant offset (C) (Bostock et al. 2013).

 $\begin{aligned} Alk &= \alpha T + \beta(S-35) + \gamma O_2 + C \ (eq \ 1) \\ DIC &= \alpha T + \beta(S-35) + \gamma O_2 + C \ (eq \ 2) \end{aligned}$

where T has units of °C and DIC, Alk, and O_2 have units of μ mol kg⁻¹ (Bostock et al. 2013). These algorithms allowed us to produce high resolution maps of modern DIC, Alkalinity, and the ASH and CSH calculated from these chemical species, since the observational density of T, S, and O_2 is much higher than the observational density of carbonates.

The crucial limitation of this approach applied initially is that we neglected the change of DIC occurring over time due to increasing anthropogenic carbon accumulation in the ocean. Thus, we have not previously been able to evaluate how much the ASH and CSH have changed already in the waters around New Zealand, and how much change to which living organisms in our waters may have already adapted. Data-based methods have been developed to estimate the anthropogenic carbon component of DIC in seawater (e.g., Gruber et al. 1996), but these methods provide only a distinction between the anthropogenic and preindustrial components, not the time history needed to infer changes over multiple decades.

In order to address the time change of marine carbonate parameters in NZ waters, we employed ocean model simulations that have been optimised to match modern observations of anthropogenic carbon in the interior ocean (Mikaloff Fletcher et al. 2006). Since model outputs were saved every five years, these model simulations provide the time history of changes in anthropogenic carbon concentration in the ocean. However, unlike the CMIP5 models that we seek to evaluate, they have been adjusted to match modern observations using an inverse model. Thus, the anthropogenic carbon reconstructed from these inverse models (DIC_{ant}) can be used to calculate and remove the influence of anthropogenic carbon from an observation of DIC collected at a particular time, t. We then developed algorithms to fit the resulting preindustrial DIC, DIC_{preind} , and use the more abundant T, S, and O₂ data to map the preindustrial DIC, ASH, and CSH.

 $\begin{array}{l} DIC_{preind} = DIC(t) \text{-} DIC_{ant}(t) \ (eq \ 3) \\ DIC_{preind} = \alpha T + \beta (S \ \text{-} 35) + \gamma O_2 + C \ (eq \ 4) \end{array}$

We also estimated the total alkalinity following equation 1 using the expanded historical dataset. The invasion of anthropogenic CO₂ does not impact total alkalinity (Wolf-Gladrow et al. 2007), hence we did not need to apply a correction for this. Following Bostock et al. (2013), multiple linear regression was used to determine the best fits to equations 1 and 4 in two different regimes: intermediate waters and deep waters. We did not include the waters shallower than 200 m, as these surface waters display a strong physical and biological seasonal signal due to surface water mixing in the winter, biological blooms in the spring and summer and stratification in the summer. The deeper waters (>200 m) were split into intermediate and deep waters along the potential density surface of 27.5. The water masses

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were split as they have very different hydrographic properties, with intermediate waters having low salinity and high oxygen, while deep waters display higher salinity and lower oxygen. A potential density surface was chosen rather than a specific water depth as the intermediate and deep waters shoal to shallower depths at higher latitudes (approaching the Southern Ocean).

Mikaloff-Fletcher et al. (2006) employed a suite of ten different ocean general circulation models (OGCMs) in order to quantify model uncertainties and the initial plan was to use the suite of all ten models to quantify uncertainties in the removal of anthropogenic carbon from the total DIC (eq 3). Our analysis however, revealed that all of the models used in this study slightly over-estimate the anthropogenic carbon correction in our region, (as discussed in more detail in the Results section of this report). Thus, the range of model results is not an accurate representation of uncertainty for this region, and the mean of these models is likely to overestimate the depth of the preindustrial ASH and CSH in our region. We chose instead to focus our analysis on results from the National Center for Atmospheric Research (NCAR) model, because it was found to be among the most skillful models for anthropogenic carbon uptake in the Southern Ocean. Additionally the NCAR model is likely to overestimate anthropogenic carbon uptake in the Southern Ocean. Additionally the NCAR model is likely to overestimate anthropogenic carbon storage in the New Zealand EEZ to a lesser degree than most of the other models applied. Goodness of fit metrics were used to estimate the uncertainty associated with this final approach.

Specific Objective 2

The preindustrial ASH estimated as part of Specific Objective 1 were compared with model simulations from the suite of CMIP5 models widely used to predict future climate change impacts. We focused our analysis on the five CMIP5 models that included the ASH in their model output (Table 1).

This work builds on independently funded research to evaluate the CMIP5 models against modern data for the New Zealand EEZ and to communicate our best understanding of future climate change impacts to stakeholders in New Zealand (Law et al., submitted). This analysis adds a unique dimension to the previously funded work (MBIE contract C01X1225). It allows us to evaluate not only the CMIP5 models' ability to capture the current mean state of the ASH but how the oceans have changed over multiple decades. This is likely to be a much more powerful metric of the models' ability to predict future changes.

Table 1. The CMIP5 models used in this analysis.

Earth System	Reference
Model	
CANESM2	Zahariev et al. 2008, Christian et al. 2010
GFDL-ESM2G	Dunne et al. 2013
GFDL-ESM2M	Dunne et al. 2013
HADGEM2-CC	Palmer & Totterdell (2001)
HADGEM2-ES	Palmer & Totterdell (2001)

3. RESULTS

3.1 Algorithm Development

We were able to fit the observed DIC between the 1950s and the near present with an R^2 of 0.96. The residual standard error (RSE) of this fit was 14 µmol kg⁻¹. The RSE in our DIC algorithm are only slightly higher than the values found using only the modern data (Table 2). The RSE and R^2 for

alkalinity are comparable to those found for the modern data. The RSE values are lower than expected, given the higher measurement uncertainty for data collected prior to 1990. Alkalinity and DIC measurements undertaken pre 1990 did not use Certified Reference Materials (CRMs) and thus the error associated with these measurements is unknown but is likely to be greater than $\pm 10 \mu$ mol kg⁻¹and more likely to be in the range of 20–30 μ mol kg⁻¹ (Dickson Pers. Comm.).

With the introduction of CRMs as part of the WOCE/GLODAP projects, the precision error improved to 1–3 μ mol kg⁻¹ for alkalinity and DIC (Dickson et al. 2007). Through quality controlling of the data and cross-checking alkalinity and DIC data from the GLODAP program and subsequent CARINA program, it is also evident that some voyages display biases in their measurements by up to 15 μ mol kg⁻¹, either positive or negative (Lamb et al. 2002; Sabine et al. 2010). However, a comparison with older datasets such as GEOSECS (1970s), suggests that the alkalinity needs to be corrected by -12 and the DIC data by -23 μ mol kg⁻¹ (Sabine et al. 2010). None of the voyages in the SW Pacific have been found to have major offsets, generally less than ±6 μ mol/kg (Lamb et al. 2002). There is a proposed correction of +6 μ mol kg⁻¹ for P15S (1990) (Sabine et al. 2010; Bostock et al. 2013). The errors associated with the hydrographic measurements are significantly smaller than for the carbonate measurements, but there are still occasional voyages where there is a bias in the salinity and oxygen measurements and a recommended adjustment made of typically +1 μ mol kg⁻¹ for oxygen (Sabine et al. 2010).

		This Study	Bos	Bostock et al. 2013				
Intermediate Waters (200m to Potential Density <27.5)								
	DIC	Alkalinity	DIC	Alkalinity				
А	-16.695	-6.597	-14.866	-7.418				
В	59.887	106.54	53.682	96.957				
γ	-0.756	0.0675	-0.569	-0.079				
Deep Waters (Potential Density >27.5)								
α	-17.095	-14.844	-23.154	-17.027				
β	28.691	106.25	13.524	100.25				
γ	-1.390	-1.127	-1.017	-0.663				
Goodness of Fit Statistics								
RSE (μ mol kg ⁻¹)	14	9.1	7.3	9.8				
\mathbb{R}^2	0.96	0.90	0.98	0.91				

Table 2. Summary of results from our algorithm and comparison with previous work.

Residuals to the fit, or differences between the observed DIC and alkalinity values and those predicted from the algorithm, are a key diagnostic to evaluate biases in the algorithm. While the residuals are generally relatively small, as demonstrated by the low RSE, both Figures 1 and 2 reveal that our algorithm consistently under-estimates preindustrial DIC in the data from the 1950s–1970s. This under-estimate is greatest in the surface waters during the 1950s suggesting that the model used in our study may over-correct for anthropogenic carbon storage during this period. This could be due in part to the fact that the model used to correct the anthropogenic carbon was run with steady state ocean dynamics and therefore does not account for decadal variability in ocean circulation or biases in the model that could not be fully corrected by the ocean interior data (Mikaloff Fletcher et al. 2006).

The fact that the algorithm under-estimates the 1950s to 1970s DIC data in deep waters, where there would have been little or no anthropogenic carbon penetration, suggests that natural variability in ocean dynamics also plays a role in the temporal coherence of the residuals. This role for natural variability is consistent with current oceanographic knowledge. Repeat ocean transects have allowed researchers to look at direct changes in the properties of the south Pacific water masses over the last 50 years. The main focus of this research has been looking at changes in the Antarctic Intermediate Waters (AAIW) as this forms in the Southern Ocean south of the Subantarctic Front, a region that is

an important sink for CO₂. There is evidence for increases in the temperature of this water mass of 0.05–0.15 °C per decade, as well as evidence for shoaling of 30–50 m in the water column and changes in density (Schneider et al. 2005; Schmidtko & Johnson 2012). Salinity trends are smaller and more variable with evidence for increasing salinity south of Australia (in the region of SR3), but freshening in the SW Pacific. The changes in temperature, salinity and nutrients in the AAIW have been found to be strongly associated with changes in the Southern Annular Mode (SAM). SAM affects the strength and position of the south westerly winds altering the wind stress curl and thus affecting the formation rates of AAIW and other mode waters such as the Subantarctic Mode Waters (SAMW; Schmidtko & Johnson 2012; Downes et al., 2011; Ayers & Strutton 2013). SAM changed to a positive mode in the 1980s, which increased the wind stress curl of the Southern Ocean and resulted in faster meridional overturning circulation (global ocean circulation). This positive mode of SAM results in a greater upwelling of older deep, carbon rich water at the polar front along with an increased equatorial transport and formation of SAMW and AAIW (Downes et al. 2011; Ayers & Sutton 2013). There is evidence for the subduction of SAMW and AAIW with higher nutrients (Ayers & Sutton 2013), which would also suggest that there would be higher carbon content in these waters during the 1990s and 2000s. Thus we should see variations in the carbon content of intermediate waters between the 1970s and the more recent period (1990's onwards).

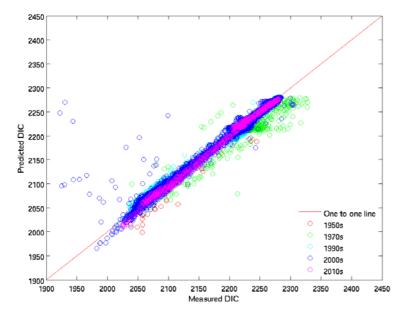


Figure 1: Comparison between the DIC predicted by our algorithm and the observed DIC (µmol kg⁻¹). The red line represents the 1:1 line, an ideal fit. Colours indicate the decade in which each observation was made: 1950s data are in red, 1970s in green, 1990s in cyan, 2000s in blue and post-2010 data in magenta.

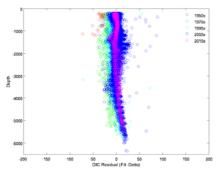


Figure 2: Residuals (DIC predicted by our algorithm minus the observed DIC) in µmol kg⁻¹ as a function of depth. Colours indicate the decade each observation was made in: 1950s data are in red, 1970s in green, 1990s in cyan, 2000s in blue and post-2010 data in magenta.

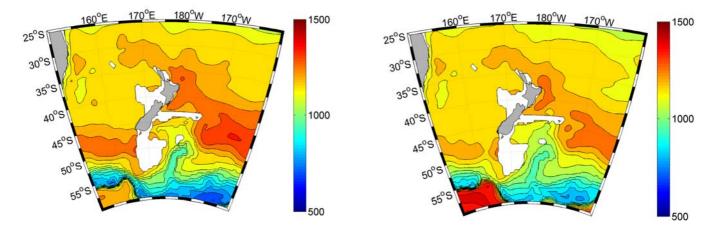


Figure 3: The depth of the ASH (m) for the NZ EEZ estimated for the preindustrial era in this study (left) and for the modern era (Bostock et al. 2015, right.) Over much of the NZ EEZ the ASH has already risen by 50 to 100 m.

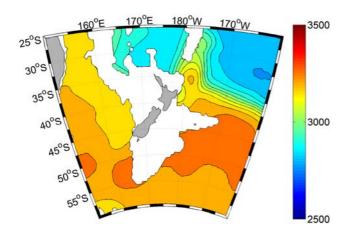


Figure 4: Depth of the CSH (m) estimated for the preindustrial era in this study.

We applied these fits to the more abundant T, S, and O_2 data to estimate DIC and alkalinity concentrations in New Zealand's EEZ at high spatial resultion, and then used these DIC and alkalinity values to map the expected ASH and CSH (Figures 3 and 4).

Our estimates suggest that the ASH may have already shoaled by on order of 50 to 100 m in some parts of the New Zealand EEZ. Bostock et al. (2015) recently found that alkalinity was the most important predictor for the distribution of scleractinian or stony corals in the southwest Pacific, but that some of these corals lie below the ASH in aragonite undersaturated waters. These authors hypothesised that shifts in the ASH could explain this unexpected result. Our results are consistent with this hypothesis. Changes to the CSH are more ambiguous due to the fact that very little anthropogenic carbon has penetrated to this depth range (2500 to 3500 m) in the Southwest Pacific.

3.2 Model Evaluation

Previous comparisons between the high resolution ASH maps for the present and the ASH estimated from the CMIP5 models suggested that three of the five CMIP5 models that included ASH output were able to match both the variance and the spatial pattern of the ASH for our region: CanESM, GFDL-ESM2G, and GFDL-ESM2M. Of these three, GFDL-ESM2G was found to be the best model due to both its ability to capture the modern ASH and its ability to capture other ocean biogeochemical properties (Law et al. submitted; Rickard et al. 2016). However, our new analysis reveals that the GFDL-ESM2G model did not accurately simulate the rise in the ASH over recent decades that has been estimated by our algorithm. This model suggests substantial decadal variability in the ASH (Figure 5) but very little change in the decadal mean between the 1960s and 2000s (Table 3).

By contrast, the CanESM and GFDL-ESM2M models are able to accurately capture both the recent past and the change in the ASH over recent decades. We recommend that these become the flagship models in future analysis. If we continue on our current emissions pathway, CanESM and GFDL-ESM2M predict that the ASH in the New Zealand EEZ will rise to an average depth of 237 to 333 m (Table 3, Figure 6).

	Change in the ASH(m) ¹	Predicted ASH in 2100 (m)	Model Evaluation based present ²	Model evaluation based on observed change
CanESM	39	237	Fair	Fair
GFDL-ESM2G	-2.4	322	Best	Poor
GFDL-ESM2M	113	333	Fair	Best
HadGEM2-CC	49	803	Poor	Fair
HadGEM2-ES	5	808	Poor	Poor

Table 3. Summary of CMIP5 model performance in the NZ EEZ.

1. Difference between 1960–1970 average and the 1995–2005 average over the NZEEZ.

2. Law et al., submitted.

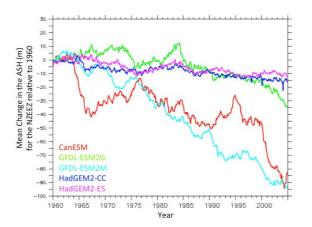


Figure 5: Mean change in the ASH (m) for the NZ EEZ relative to 1960 for the CMIP5 models analysed in this study.

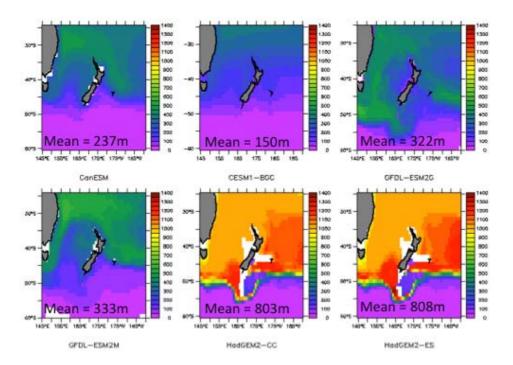


Figure 6: CMIP5 simulations of the ASH in m (2090–2100 mean) under the business as usual emissions scenario.

4. DISCUSSION

The algorithms presented here suggest that the ASH may already have risen by 50 to 100 m in much of the New Zealand EEZ due to the effects of ocean acidification, although changes in the deeper CSH are not yet clear. This is consistent with repeat hydrography data from a cruise track, which showed that the ASH shoaled by $1-2 \text{ m yr}^{-1}$ between 1990 and 2000 in the southwest Pacific (Feely et al. 2012). Our work suggests that the shoaling of the ASH observed across this line extends through most of the NZ EEZ.

Bostock et al. (2015) recently found a significant population of deepwater stony corals living in conditions that are unexpected due to ocean chemistry within the New Zealand EEZ. Our work suggests that these corals may have become established when the ASH was much deeper.

Our findings have been applied to evaluate the CMIP5 models. Those models that exhibit the most rapid change in the ASH over the historical period best match our data based estimates of change in the ASH. The CMIP5 models that best match the present and past ASH for our region project that the ASH is likely to rise to 237–333 m on average over the New Zealand EEZ by the end of this century if we continue on our current emissions pathway.

5. CONCLUSIONS

This research has helped to identify risks that are likely to arise for marine calcifiers as a consequence of climate change effects in New Zealand waters. While the algorithms we have developed generally match the observations well, temporal biases in the anthropogenic carbon correction remain a concern. Implementing more recent anthropogenic carbon estimates that better represent decadal variability may significantly improve our results.

International Earth System Modelling (ESMs) centres are currently running the next generation of CMIP simulations, CMIP6. In tandem, New Zealand is developing its own earth system model under the Deep South National Science Challenge. With further development and refinement, these maps of the changing ASH could be an important tool for evaluating the next generation of models and so help inform ecosystem impacts for the region.

6. ACKNOWLEDGMENTS

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