

We thank the reviewers for the insightful comments and could not agree more. This paper lacked any significant investigation into the marine carbonate system. We ran a series of model sensitivity experiments to quantify how influential some of Hector's parameter inputs are on its outputs (in particular, pH and Ω_{Ar}). Sensitivity analyses are important to both to document model characteristics, explore model weaknesses, and to check to what degree the model behavior conforms with what we know of the ocean system. Addressing these comments has substantially improved the manuscript and taken it beyond the point of just a simple model comparison.

Interactive comment on “Projections of ocean acidification over the next three centuries using a simple global climate carbon-cycle model” by C. A. Hartin et al.

Anonymous Referee #1

Received and published: 11 January 2016

General comments

This manuscript discusses the results of a reduced-form global carbon-cycle model simulating the surface-water carbonate system between 1850 and 2300, and compares the results with medians of CMIP5 Earth System Models. Such reduced-form models are important tools as they are much cheaper and quicker to run than ESMs and thus, if properly validated, can be used to test many more emission scenarios and allow parameter sensitivity studies.

The results are interesting and, as far as I can tell, scientifically sound, although I do have some remarks on the discussion of Figure 7 (see below). However, in an earlier paper (Hartin et al., 2015) the model has been validated, and thus I expect this manuscript to go beyond the point of model comparison with CMIP5 ESMs only and additionally conduct sensitivity studies and/or explore a range of emission and/or land use change scenarios. Unfortunately, both of these last two points are lacking in the manuscript.

The aim of the manuscript is not clearly stated in the introduction and should thus, in my opinion, involve more than just “highlighting the capability... to project changes in the upper ocean carbonate system over the next three centuries”, as written in the abstract. The manuscript can generally benefit from typographical editing, as it contains some ambiguous statements and grammatical incorrect formulations. Specific points spotted by me are mentioned below.

I understand that the focus of the paper is not to discuss the setup of Hector, rather than to discuss practical applications. However, some fundamental questions came into mind when reading Sections 2 and 3, which will be discussed below. In general, the model description is somewhat difficult to understand without having read Hartin et al. (2015) and so a revision of these sections, which I would merge into one section with two sub-sections, is recommended. It is important that the reader can understand the basic concepts of the model without having to refer to Hartin et al. (2015).

In summary, I recommend major revisions for this manuscript, whereby the major point is to include additional work on sensitivity analysis and/or explore a range of emission and/or land use change scenarios.

***We thank the reviewer for these insightful comments. Addressing these comments has substantially improved the manuscript and taken it beyond the point of just a simple model comparison.*

- 1. We ran a series of model sensitivity experiments to quantify how influential some of Hector's parameter inputs are on its outputs (in particular, pH and Ω_{Ar}). Sensitivity analyses are important to both to document model characteristics, explore model weaknesses, and to check to what degree the model behavior conforms with what we know of the ocean system. We selected eight land and ocean parameters, varying each by $\pm 10\%$.*
- 2. We conducted a thorough read through of the manuscript addressing numerous typos and grammatical errors.*

3. *We have increased our discussion of Hector within the manuscript as well as adding more detail of the model to the Appendix. We hope the reader can now better understand the details and workings of Hector without having to read Hartin et al., 2015 - GMD.*

Specific comments

- p. 19270, lines 18-19: "Under a high emissions scenario: : : aragonite saturations". This sentence implies that the relations between warming and acidification / aragonite saturation, i.e. $\Delta \text{pH} / \Delta T$ and $\Delta \text{CO}_2 / \Delta T$, are linear. However, both from previous work (e.g., Riebesell et al., 2009) as from Figure 7 of this manuscript it becomes clear that this is not the case. In other words, the slopes of $\Delta \text{pH} / \Delta T$ and $\Delta \text{CO}_2 / \Delta T$ are different when there is a warming of 3_C then when there is a warming of 1_C. Please rephrase this sentence.

***We agree with the reviewer that the discussion of Figure 7 was initially unclear. After rewriting we determined that this figure did not add anything substantial to the study and we decided to remove it from the manuscript.*

- p. 19272, line 26 to p. 19273, line 2: This section describes the main advantage of using reduced-form climate models relative to ESMs, focusing mostly on the ability of running arbitrary future climate change scenarios and sensitivity studies. While reading this section, I expected both of these to show up in the manuscript. However, the model is only run with the RCP scenarios, and the discussion focuses mostly on RCP8.5. These aspects are surely missing in the manuscript and should, in my opinion, be added to it.

***The authors thank the reviewer for these insightful comments. We have substantially refocused the paper and included an experiment on the parametric sensitivities within Hector. Please see the general comments section above for a more thorough description.*

- p. 19273, lines 3-7: This section only explains why the study is timely and lacks a description of the aim of this study, except maybe for "projecting changes in the surface ocean carbonate system over the next three centuries". As such, the difference between this manuscript and Hartin et al. (2015) is not clear. One could consider the previous section of the manuscript (the advantages of reduced-form models vs. ESMs) as an aim; however, this aim is not met (see previous comment). Please describe a clear research aim and also describe the experiments carried out here or elsewhere in the introduction.

***We thank the reviewer for this comment. We have substantially changed the manuscript and included a section on quantifying the model's sensitivity to parametric inputs. For example, in the abstract, "In this study we examine the ability of Hector v1.1, a reduced-form global model, to project changes in the upper ocean carbonate system over the next three centuries, and quantify the model's sensitivity to parametric inputs." And the introduction has also been updated: "Our goal of this study is to quantify how well Hector, a reduced-form model, that explicitly treats surface ocean chemistry, emulates the marine carbonate system of both observations and the CMIP5 archive, and to explore the parametric sensitivities of Hector's ocean outputs."*

- p. 19274, line 6 (Eq. 1): why are different signs used for $\text{FO}(t)$ and $\text{FL}(t)$ as opposed to $\text{FA}(t)$ and $\text{FLC}(t)$? I understand that the latter two are by definition positive but for the other fluxes this might not necessarily be the case. From the definition of $\text{FL}(t)$ (Eq. 2) I understand why $\text{FL}(t)$ has a negative sign in

front of it (if NPP exceeds RH there is a net uptake of atmospheric CO₂), but this way of formulating is, in my opinion, not very intuitive.

***While we agree with the reviewer that this equation may not be very intuitive, we decided to leave the equation as is to be in agreement with Hartin et al., 2015 and Meinshausen et al., 2011. The total change in atmospheric carbon is from the anthropogenic emissions plus any emissions from land-use changes minus the uptake from the ocean and land systems. Within Hector uptake by both the ocean and land is positive. We agree that these signs can be easily switched but within Hector they are positive.*

- p. 19275, line 15 (Eq. 4): Please state clearly that in the current form Eq. 4 is only valid for the surface boxes, as the latter term ($F_{atm \rightarrow i}$) is only present for these boxes. More fundamentally, I was a bit confused to see that in the land part of the model NPP and RH are explicitly calculated while they are not in the ocean part of the model (which is the focus of the model). Please comment on this choice. The current implementation implies that NPP and RH in a single box are in equilibrium, i.e. do not affect $F_{atm \rightarrow i}$ and the fluxes between the various boxes. Or is this taken into account for by tuning the model such that the steady-state volume transport from the surface high latitude to the deep ocean amount to 100 Pg C?

1. ***The manuscript has been updated to reflect those changes in equation 4.*
2. *It would be great to include NPP and RH within the ocean component. However, in order to keep it simple we do not model the organic carbon cycle within the ocean. "All carbon within the ocean component is assumed to be inorganic carbon. Dissolved organic matter is less than 2% of the total inorganic carbon pool, of which a small fraction is dissolved organic carbon (Hansell and Carlson, 2006)." Being that Hector is a global model, we felt that it was more important to accurately calculate the inorganic carbon system first.*
3. *NPP and RH represent the carbon balance with the terrestrial component and they do not necessarily have to be in equilibrium with each other. NPP and RH indirectly effect the oceanic uptake of CO₂ by changes in the atmospheric CO₂ levels.*

- p. 19276, line 5: I was very surprised to see that the intermediate and deep ocean carbonate systems are not calculated by Hector. Why did the authors make this choice? Without including these waters, the reference to changes in deep waters in the introduction (p. 19272, line 16) could be removed as these changes are not further discussed.

***In order to keep Hector as computationally efficient and simple, we decided to initially develop Hector with only the carbonate system in the surface ocean in mind. We note that there may be large value in simulating the carbonate system in intermediate and deep waters and hope future releases of Hector will include these changes. We have also removed the text referring to deep water changes as we agree it is not needed.*

- p. 19276, lines 3-19: From this section, it does not become clear to me how Pg C of a box relates to the computed DIC concentration. Is all oceanic C assumed to be present as DIC or is there also a C_{org} component? If not, why not and how is this validated?

***The text of the manuscript is updated to reflect the questions above. We assume all carbon to be inorganic carbon within Hector. We acknowledge that we are missing a portion of the total carbon system, but due to small fraction of organic carbon compared to inorganic carbon we have chosen to*

simplify Hector and leave this portion out. Future versions of Hector may include calculations of the organic carbon pool. "There are four measurable parameters of the carbonate system in seawater: DIC, alkalinity (TA), $p\text{CO}_2$ and pH, and any pair can be used to describe the entire carbonate system. DIC ($\mu\text{mol kg}^{-1}$) is calculated as a function of the total carbon in the box (PgC), the mass of carbon, the density of seawater, and the volume of the box. Dissolved organic matter is less than 2% of the total inorganic carbon pool, of which a small fraction is dissolved organic carbon (Hansell et al., 2001). Therefore, for simplicity we chose not to include organic carbon within Hector."

- p. 19276, lines 16-18: I would like the authors to comment on the validity of these assumptions, thereby providing references.

***References are added and the section expanded: "We assume negligible carbonate precipitation/dissolution and assume no alkalinity runoff from the land surface to the open ocean. Most studies hold alkalinity constant with time and this is a reasonable assumption over several thousand years (Lenton, 2000; Zeebe and Wolf-Gladrow, 2001; Glotter et al., 2014; Archer et al., 2009). On glacial-interglacial time scales alkalinity and the dissolution of CaCO_3 sediments is an important factor in controlling atmospheric $[\text{CO}_2]$ (Sarmiento and Gruber, 2006). Therefore, on these scales Hector will underestimate the oceanic CO_2 uptake. For purposes of our studies we are interested in 100-300 year timeframe."*

- p. 19278, lines 10-12: This statement makes me wondering how time series were treated where more than 2 carbonate system parameters were measured. If I recall correctly, this is the case for parts of these time series. How have possible inconsistencies related to over determination of the carbonate system been dealt with?

***When DIC and TA were given we used those parameters to calculate the rest of the carbonate system to be consistent with the calculations in Hector, for example, BATS. When the entire carbonate system was available online, as in HOT, we used the values directly from the site. And for those like ESTOC, Iceland and Irminger Sea, we used those variables supplied to calculate the remaining parameters of the carbonate system.*

- p. 19278, lines 12-14: It should be mentioned here which proxy these data are based on ($_{11}\text{B}$ for pH and assuming constant TA for calculating Ar). Moreover, since Ar is also calculated in the Pelejero et al. (2005) paper, why didn't the authors also calculate other carbonate system parameters here?

***The text is updated to reflect these comments. Pelejero et al, 2005 used $_{11}\text{B}$ for the analyses of the carbonate system.*

- p. 19278, lines 14-16: In my opinion, it would be much better if historical rates of change for the various locations were compared with, and calculated on the same time interval, as the values published by Bates et al. (2014), rather than this rather arbitrarily chosen 20-year period. Such a direct comparison would make it much easier to assess the performance of the model.

***The authors agree and have since changed the comparison to more in line with Bates et al., 2014.*

- p. 19278, lines 25-26: Even though a comparison might not be statistically robust, it would still be very interesting if the authors commented on the performance of Hector relative to CMIP5 models run under prescribed emissions.

***This is an interesting and valuable suggestion and something that we may pursue in the future. It is outside of the scope of our current study, however.*

- Results and discussion: What I miss here is a discussion of the reasons behind the consistent offset of Hector and the median of the CMIP5 models, most notably in pH, Ar and DIC, where Hector consistently calculates higher DIC, pH and Ar and lower pCO₂. The bias after 2100 for pCO₂ is mentioned, but this offset is consistent throughout the whole simulation period.

***While we are not able to get to the root cause of some of these biases, we have included a table of validation metrics for both the high and low latitude ocean carbonate system comparing Hector to the CMIP5 median. The bias in DIC is most likely from our carbon pool values initialized higher than the CMIP5 median. There is bias in pCO₂ particularly in the high latitude when compared to CMIP5, but we find Hector to be in closer agreement with the observational record. The text has been updated to reflect these findings.*

- p. 19281, lines 14-19: I miss a short discussion on the impacts of seasonality in Ar (e.g. Sasse et al., 2015) and possible changes therein.

***The reviewer makes a good point about seasonality. We included some text to reflect this: "Accounting for seasonal variations in the Ω_{Ar} saturation levels may move this time of undersaturation forward by 17 ± 10 years (Sasse et al., 2015). Due to Hector's time step of 1 year, we may be overestimating the time when ocean acidification reaches a critical threshold."*

- p. 19281, line 20 to p. 19282, line 2: as said before, the sensitivities $\frac{\partial \text{pH}}{\partial T}$ and $\frac{\partial \Omega_{Ar}}{\partial T}$ are not constant with time and thus these trends are not linear. The authors must provide here which $\frac{\partial \text{pH}}{\partial T}$ is used to calculate the $\frac{\partial \text{pH}}{\partial T}$ and $\frac{\partial \Omega_{Ar}}{\partial T}$. Moreover, it would be very interesting to discuss the $\frac{\partial \text{pH}}{\partial T}$ at which $\frac{\partial \text{pH}}{\partial T}$ is maximal.

***In agreement with other reviewers after rewriting the discussion for this figure we determined that figure 7 did not add anything substantial to the study and we decided to remove it from the manuscript.*

- p. 19282, lines 3-6: this figure discussion is somewhat meagre. Discuss by how much these parameters have changed / will change and when changes will slow down and/or revert direction. Also show the high latitude projections for comparison, or, if they are very similar, discuss them. It's somewhat strange that they are mentioned everywhere except for this figure.

***We agree that the discussion of old Figure 8 and new Figure 6 was lacking. We have updated the manuscript in the following way, "Lastly, Figure 6 highlights pH and Ω_{Ar} projections under all four RCPs from 1850 to 2300. Over the last 20 years both pH and Ω_{Ar} have declined sharply and will continue to rapidly decline under RCP 4.5, 6.0 and 8.5 outside of their preindustrial and present day values. These RCPs represent a range of possible future scenarios, with ocean pH varying between 8.15 and 7.46 for the high latitude and Ω_{Ar} varying between 1.94 and 0.60. High latitude Ω_{Ar} saturation levels presently are much lower than the low latitude and reach under saturation before the end of the century. Even under*

a best case scenario, RCP 2.6, low latitude pH will drop to 7.73 by 2100 and to 7.43 by 2300 and Ω_{Ar} saturations will remain outside of present day values.”

- p. 19282, lines 14-20: Move this section to the end of Section 5 (where Fig. 8 is discussed) as it fits much better there.

***These lines are now within the results section where the figure is explained. “Even under a best case scenario, RCP 2.6, low latitude pH will drop to 7.73 by 2100 and to 7.43 by 2300.” Along with most of the line within the Discussion section: “ pCO_2 and DIC are increasing rapidly as atmospheric $[CO_2]$ continues to rise under RCP 4.5, 6.0 and 8.5. pH, and Ω_{Ar} are decreasing rapidly outside of observations and are projected to continue to decrease under all scenarios (Figure 6). These changes may result in drastic changes to marine ecosystems in particular the $CaCO_3$ secreting organisms. For example, the rate of coral reef building decreases, calcification rates of planktonic coccolithophores and foraminifera decreases, changes in trophic level interactions and ecosystems, have all been proposed to be potential consequences of ocean acidification...”*

- p. 19282, lines 21-22: This information is of vital importance for the understanding of the setup of Hector and thus must be included in the method section. It partly answers my previous question (p. 19276, lines 3-19) on whether there is a Corg component in Hector, but I'd still like to see how this choice is validated.

***We agree with the reviewer that these assumptions were not properly discussed. We updated the manuscript to discuss organic carbon, TA changes and ocean circulation.*

“All carbon within the ocean component is assumed to be inorganic carbon. Dissolved organic matter is less than 2% of the total inorganic carbon pool, of which a small fraction is dissolved organic carbon (Hansell and Carlson, 2001). Therefore, for simplicity we chose not to include organic carbon within Hector.”

“We assume negligible carbonate precipitation/dissolution and assume no alkalinity runoff from the land surface to the open ocean. Most studies hold alkalinity constant with time and this is a reasonable assumption over several thousand years (Lenton, 2000; Zeebe and Wolf-Gladrow, 2001; Glotter et al., 2014; Archer et al., 2009). On glacial-interglacial time scales alkalinity and the dissolution of $CaCO_3$ sediments is an important factor in controlling atmospheric $[CO_2]$ (Sarmiento and Gruber, 2006). Therefore, on these scales Hector will underestimate the oceanic CO_2 uptake. For purposes of our studies we are interested in 100-300 year timeframe.”

“The dynamics of ocean uptake of CO_2 is strongly dependent on the rate of downward transport of CO_2 laden waters from the surface ocean to depth. We neglect any climate feedbacks on the carbon cycle resulting from changes in ocean circulation and hold ocean circulation constant in time. CMIP5 models show up to a 60% decrease in the Atlantic meridional overturning circulation (AMOC) by 2100 (Cheng et al., 2100). We use our sensitivity analyses to change the circulation thereby changing the downward transport of carbon. A 10% change in ocean circulation (T_t) results in a <4% change in air-sea fluxes and moderate effects on surface pH and Ω_{Ar} . Therefore, a 60% decline in the overturning circulation may result in roughly a 20% change in the air-sea fluxes of carbon according to this sensitivity analyses.”

- p. 19282, line 21 to p. 19283, line 5: this paragraph belongs to the Discussion, not the Conclusions section.

***This has been moved out of the conclusions section and separated into the model description section and the discussion section. Please see the comment above for details.*

- Table 2: Wouldn't it be useful to (additionally) give the values after spin-up, as they are used as historical background values, rather than the initial values?

***We agree that values after spinup are important. However, after significant reorganization of the manuscript we deleted table 2 and included more text about Hector's parameters.*

- Table 4: In its current discussion in the manuscript, the table is redundant and a reference to Taylor et al. (2012) on p. 19278 would be sufficient instead. However, I'd rather see the authors leaving the Table in the manuscript and indicating which models are used for which median and RMSE calculations. Currently, for each parameter it is only indicated how many ESMs are used for its calculation, but not which ones, while this could be important information. If they decide not to do so, they should remove Table 4.

***We agree with the reviewer that more information is needed to make this table more useful. The table is updated to reflect these comments. We added a column of carbonate parameters that were used in this manuscript.*

- Table 5: Why are _ values not calculated for 2100?

***The formatting in Table 5 was not correct. Since then, I have reformatted Table 5.*

- Figure 1: Figure 2 of Hartin et al. (2015) is much clearer than Figure 1 of this manuscript. I would advise the authors to use the former figure, or an adapted version thereof, instead of the current Fig. 1. To improve the current Fig. 1, "surface" should be added to "high latitude". Moreover, the 'earth pool' needs to be added as FA(t) and FL(t) seem now to be represented by the same arrow. Additionally, the units of the diagram are conceptually incorrect. The represented fluxes (TT, TH, EIL and EID) have units of $\text{m}^3 \text{s}^{-1}$, while the reservoirs (Ca, CHL, CLL, CIO and CDO) have units of Pg C. This should be adapted. Finally, in the caption it is stated that the initial carbon pools have units of Pg C yr⁻¹, which should obviously be Pg C.

***The authors agree that this figure was inconsistent. We have since adapted the figure from Hartin et al., 2015 – GMD.*

Technical corrections

- p. 19270, line 6: remove "the", and capitalize Earth System Models. Line 15: shouldn't 0.4 units be 0.40 units? Line 17: I know it must result from rounding but to read that $2.21 - 0.80$ equals 1.42 is a bit strange. Perhaps rephrase and leave out the 0.80. Lines 19-21: "Hector reproduces : : : compared to observations and CMIP5 models". This sentence is somewhat unclear. Add 'respectively' at the end to make the distinction between historical (trends vs. observations) and future (projections vs. models) comparisons clearer, or fully rewrite this sentence.

***We thank the reviewer for these comments. The authors have updated these comments in the manuscript.*

-19271, line 11: “there is some concern: :” Is it a bad thing per se that the oceanic sink will be less efficient? Please phrase more neutrally. Line 17: change “the preindustrial” to “preindustrial times” Line 20: change “forming H₂CO₃, dissociating: :” to “thereby forming H₂CO₃, and dissociating: :” Line 24: CO₂(aq) has not yet been defined here; additionally, H₂CO₃ has been used before and its difference with CO₂(aq) is not explained. I feel it’s better to use CO₂* as the sum of H₂CO₃ and CO₂(aq) here. Lines 25: “A doubling of CO₂”. What is meant here, atmospheric pCO₂? Please phrase clearer. Line 26: add a reference to where this percentage of ca. 10 comes from (see also previous comment).

***We thank the reviewer for these comments. The authors have updated these comments in the manuscript.*

- p. 19272, line 3: change “biogenic carbonate” to “biogenic calcium carbonate” Lines 8-9: It is a bit unnecessary to give this many references here. Please make a selection. Line 15: the IS92a scenario hasn’t been used for a while in global predictions. Please provide a reference using either of the RCP scenarios (e.g. Bopp et al., 2013). Line 21: Capitalise Earth System Models. Line 22: replace “prescribed emission pathways” by “Representative Concentration Pathways” or, in case the authors would like to keep the statement more general, define RCPs here.

***All of the above have been changed within the manuscript. The references are shorten and I updated the sentences to reflect RCPs and not IS92a scenarios.*

- p. 19273, line 16: “: :are typically parameterized”. Shouldn’t it read “: :are typically not parameterized”? Lines 21-24: the sections mentioned here do not match the sections in the manuscript. I would however advice the authors to apply the sections as described here, i.e. to merge the current sections 2 and 3 (see general comment).

***The sections have been updated. Please see the comments under general comments.*

- p. 19274, lines 19-22: Replace “consisting” by “and consists”, “deep box” by “a deep box” and “simulated” by “simulating”. Line 23: “15 % of the ocean”. Change into “15 % of the surface ocean by volume” (or at least I assume that this is meant here).

***All typos have been corrected.*

- p. 19275, lines 3-4: “in the high latitude: :” versus “for the low latitude” is inconsistent. Line 6: Shouldn’t “Fi=2” be “n=2”?

***The reviewer is correct, Fi=2 was corrected to n=2.*

- p. 19276, line 7: change “A” to “Appendix A”. Line 9: provide definitions of LL and HL here. Lines 10-11: “that when: :global ocean”. Please rephrase, this is not very clear. Line 23: “A1”. I assume Appendix A is meant here, not equation A1. Please clarify. The same applies to p. 19277, lines 2 and 8.

***All of the ‘A’s have been changed to Appendix. HL and LL are defined. And the sentence has been updated.*

-p. 19277, line 1: provide the units of this unit conversion factor. Lines 22-23: Move the definition of RCP to the introduction (see an earlier comment).

***The authors have updated the manuscript to reflect these suggestions.*

- p. 19278, lines 8-9: The references are also given in Table 3 and can thus be removed here for readability.

***The reviewer makes a good point and the references have been removed from the text.*

- p. 19280, lines 20-22: This doesn't really fit here and has already been mentioned before (Introduction / Methods). Line 23: add "compared" between "RCP8.5" and "to".

Lines 25-27: which 14-year period is meant here? Where do the numbers for CMIP5 and HOT come from? Please provide references. Also, are the CMIP5 and Hector values for the whole surface ocean or for the low latitude box? (so that it can be compared to the HOT site) Finally, these numbers are different than those presented in Table 5

, which is quite confusing. As mentioned above, I'd recommend sticking to a single comparison, i.e. the values published in Bates et al. (2014). Line 27: change "Repeat" to "Repeated"

***We compare Hector to the observational record from Bates et al., 2014 (table 6) and we also compare Hector across the CMIP record, 1850-2300 (table5). This section of the results has been cleaned up to reflect these comparisons. "Hector accurately simulates the change in Ω_{Ar} (-0.0085 yr^{-1}) compared to observations (Table 6). As with pH Hector is slightly higher than the CMIP5 median but closer to the observational record. We only highlight Ω_{Ar} , as Ω_{Ca} is similar to that of Ω_{Ar} . Repeat oceanographic surveys in the Pacific Ocean observed an average $0.34\% \text{ yr}^{-1}$ decrease in the saturation state of surface seawater with respect to aragonite and calcite over a 14-year period (1991-2005) (Feely et al., 2012); the average decrease in Hector is between 0.19% and $0.25\% \text{ yr}^{-1}$. Saturation levels of Ω_{Ar} decrease rapidly over the next 100 years in both the high and low latitude. Hector accurately captures the decline in saturations with low RMSE values for Ω_{Ar} (0.027). Under RCP8.5 Hector projects that low latitude Ω_{Ar} will decrease to 2.2 by 2100 and down to 1.4 by 2300. The high latitude oceans will be understaturated with respect to aragonite by 2100 and will drop down to 0.7 by 2300."*

- p. 19281, line 2: shouldn't the percentages of 19 and 25 % be 0.19 % and 0.25 % yr-1, as opposed to the 0.34 % per year mentioned before? Line 3: change "Of" to "of" Line 4: change "latitude" to "latitudes" Line 7: replace the second "low latitude Ca" by "a" Line 14: change "Century" to "century"

***All of these typos have been corrected.*

- Appendix: Don't start the appendix with an equation without any introduction. Add 1-2 lines before Eq. A1.

***The Appendix is now updated with a more thorough model description.*

- Table 1: Remove the first column, as these parameters do not come back anywhere else in the manuscript. Change the name of the last column to "Reference" or "Notes".

Finally, add a reference to the average wind speed (e.g. Liss and Merlivat, 1986; or Sarmiento and Gruber, 2006)

***The column name was changed to notes and references were added.*

- Table 3: The column “Ocean Carbon Measurements” needs to be renamed as not all of these parameters were actually measured.

*** “Ocean Carbon Measurements” was replaced with “Ocean Carbon Parameters”*

- Table 5: The font size is somewhat small. Moreover, the distinction between high and low latitudes is currently not very clear. I would advise the authors to use different colours instead of brackets.

***Table 5 was separated out into two tables, one for high latitude and one for low latitude.*

- Figures 2-6: units on the y-axes are lacking. For pH, add the scale. The model abbreviations at the right hand side should be replaced by proper descriptions (e.g. “High latitude” and “low latitude” within the plot area). The legend should be split into “Model” (CMIP5 and Hector) and “Observations” (the plotted time series). In most of the plots, the observations are invisible. Make sure that the observations are plotted on top of the model results, like has been done for DIC at low latitudes.

***Figure 2-6 have been updated with scales, better color schemes to see the observations, and better descriptions (“High Latitude” and “Low Latitude”). We also deleted the “Model” legend from the plot.*

- Figure 7: increase the size of the plot. Also the differently coloured dots in the upper part of the legend (“Scenario”) are rather confusing as the plot consists of both dots (Hector) and crosses (CMIP5). It would be better to use lines here instead, and save the dot and cross for the lower part of the legend (“Model”).

***We decided to remove Figure 7 from the manuscript as it did not add much to the study.*

- Figure 8: again, replace the model abbreviations on the right hand side of the plots by a proper description and add the pH scale.

***Figure 8 is updated with better descriptions, as in the other figures. Also, we include figures of both the high and low latitude under all 4 RCPs.*

References not mentioned in manuscript

Bates N. R., Astor Y. M., Church M. J., Currie K., Dore J. E., González-Dávila M., Lorenzoni L., Muller-Karger F., Olafsson J. and Santana-Casiano J. M. (2014) A timeseries view of changing ocean chemistry due to ocean uptake of anthropogenic CO₂ and ocean acidification. *Oceanography* 27, 126–141.

Bopp L., Resplandy L., Orr J. C., Doney S. C., Dunne J. P., Gehlen M., Halloran P., Heinze C., Ilyina T., Séférian R., Tjiputra J. and Vichi M. (2013) Multiple stressors of ocean ecosystems in the 21st century: projections with CMIP5 models. *Biogeosciences* 10, 6225–6245.

Liss P. S. and Merlivat L. (1986) Air-sea gas exchange rates: introduction and synthesis. In *The Role of Air-Sea Exchange in Geochemical Cycling* (ed. P. Buat-Ménard). NATO ASI Series, vol 185. Springer Netherlands. pp. 113–127.

Riebesell U., Körtzinger A. and Oschlies A. (2009) Sensitivities of marine carbon fluxes to ocean change. *Proc. Natl. Acad. Sci. U. S. A.* 106, 20602–9.

Sarmiento J. L. and Gruber N. (2006) Ocean Biogeochemical Dynamics., Princeton University Press, Princeton, NJ.

Sasse T. P., McNeil B. I., Matear R. J. and Lenton A. (2015) Quantifying the influence of CO₂ seasonality on future aragonite undersaturation onset. *Biogeosciences* 12, 6017–6031.

***Thank you for these references. They are now included in the manuscript.*

Interactive comment on “Projections of ocean acidification over the next three centuries using a simple global climate carbon-cycle model” by C. A. Hartin et al.

Anonymous Referee #2

Received and published: 25 January 2016

General comments:

This study presents a reduced-form model (Hector) that can be used for global-scale, long-term studies on e.g. surface ocean acidification related to CO₂ emissions and climate change. The model includes carbon exchange between the terrestrial, oceanic, and atmospheric carbon reservoirs, although with highly simplified parameterizations for many processes (e.g. constant TA, no CaCO₃ formation/dissolution and possible feedbacks over the several-century long model period, no seasonality or long-term change in oceanic productivity, etc.).

Within its limitations, the Hector model appears to be a tool that in comparison with other more complex – and much slower – models is highly useful and well suited for e.g. different future climate long-term sensitivity experiments. The model is calibrated/validated by comparing model output to both measured data and output from other models. Simulated surface water pH, pCO₂, etc., are generally in good agreement with output from the much more complex (and computationally costly) CMIP5 models – although with a considerable offset that changes over time. Finally, a sensitivity study demonstrates the model sensitivity (in terms of PH and aragonite saturation) to a couple of different RCP scenarios.

It is made clear by the authors that coastal dynamics as well as short- and long-term trends in biogeochemical processes are outside the scope of the present study. This is fine; I don't mind this type of really large-scale model set-up. However, my main issue with the paper is that we see so little discussion concerning possible problems with the approach. There are a couple of lines in the Conclusions section mentioning e.g. eutrophication and changing river loads. But first of all, these comments should be in the Discussion section, and further, they really need to be elaborated a bit. For example, what does it mean that you have no TA change, no CaCO₃ formation/dissolution, no deep water dynamics (?) and so on? I find it difficult to judge what effects these assumptions might have on the reliability of long-term model runs.

***Thank you for this comment. There were multiple assumptions within Hector that are not well described. Throughout the text we have added in the needed discussion on these assumptions.*

1. For example, “TA is calculated at the end of spinup and held constant in time, resulting in 2311.0 $\mu\text{mol kg}^{-1}$ high latitude box and 2435.0 $\mu\text{mol kg}^{-1}$ for the low latitude box. These values are within the range of open ocean observations, 2250.0 – 2450.0 $\mu\text{mol kg}^{-1}$ of solution (Key et al., 2004; Fry et al., 2015). We assume negligible carbonate precipitation/dissolution and assume no alkalinity runoff from the land surface to the open ocean. Most studies hold alkalinity constant with time and this is a reasonable assumption over several thousand years (Lenton, 2000; Zeebe and Wolf-Gladrow, 2001; Glotter et al., 2014; Archer et al., 2009). After thousands of years the dissolution of CaCO₃ will restore ocean pH, thereby increasing the uptake of more CO₂. On ~10,000 year scales Hector will underestimate the CO₂ uptake, however, we are interested in 100-300 year timeframe.”

2. “All carbon within the ocean component is assumed to be inorganic carbon. Dissolved organic matter is less than 2% of the total inorganic carbon pool, of which a small fraction is dissolved organic carbon (Hansell et al., 2001). Therefore, for simplicity we chose not to include organic carbon within Hector.”

3. *“The dynamics of ocean uptake of CO₂ is strongly dependent on the rate of downward transport of CO₂ laden waters from the surface ocean to depth. We neglect any climate feedbacks on the carbon cycle resulting from changes in ocean circulation and hold ocean circulation constant in time. CMIP5 models show up to a 60% decrease in the Atlantic meridional overturning circulation (AMOC) by 2100 (Cheng et al., 2100). We use our sensitivity analyses to change the circulation thereby changing the downward transport of carbon. A 10% change in ocean circulation (T_t) results in a <4% change in air-sea fluxes and moderate effects on surface pH and Ω_{Ar} . Therefore, a 60% decline in the overturning circulation may result in roughly a 20% change in the air-sea fluxes of carbon according to this sensitivity analyses.”*

Are the above mentioned processes (or lack of processes) the main reason for the bias between Hector and CMIP5 output, or is the bias rather related to some systematic difference between emission/concentration forced models? I understand that you don't expect a perfect match (and by the way, I don't suggest that the CMIP5 output is necessarily better than Hector output), but it would be interesting to know a bit more of why they differ.

***While we are not able to get to the root cause of some of these biases, we have included a table of validation metrics for both the high and low latitude ocean carbonate system comparing Hector to the CMIP5 median. The bias in DIC is most likely from our carbon pool values initialized higher the CMIP5 median. There is bias in pCO₂ particularly in the high latitude when compared to CMIP5, but we find Hector to be in closer agreement with the observational record. The text has been updated to reflect these findings.*

I recommend a major revision of this paper before publication – partly because of a need (in my opinion) to improve the structure and readability of the paper (see below), and further due to the reason explained above as well as numerous minor comments (see Specific comments and Technical corrections).

***The authors thank this reviewer for their very helpful comments. The manuscript has been substantially improved in both the structure and readability.*

Structure of the paper:

First of all, I think you need to describe the purpose of this study much more clearly.

As a reader you learn from the Introduction that the model is fast, powerful, robust, and timely (which I'm sure it is). I would however like to see (preferably as a final paragraph of the Introduction) a clear description of what it is that you're going to do with your model and why (without a subsequent discussion of what other models can or cannot do).

***We thank the reviewer for this comment. We agree that the abstract and introduction lacked a clear description of the purpose of this study. We have since made substantial changes. For example, this is the last paragraph of the introduction: “Our goal of this study is to quantify how well Hector, a reduced-form model, that explicitly treats surface ocean chemistry, emulates the marine carbonate system of both observations and the CMIP5 archive, and to explore the parametric sensitivities of Hector's ocean outputs. We run Hector under different emissions pathways, comparing the marine carbonate system to the observational record and CMIP5 archive. The remainder of the paper is organized as follows; section 2, a detailed description of Hector's ocean component, the data sources and simulations run, section 3, results of the model comparison and sensitivity experiments and lastly, section 4, a discussion of the results.”*

I would further prefer to see the Material and Methods section in one chapter divided into sub-sections (e.g. 2.1 Model description, 2.2 Ocean component, etc.) instead of three separate chapters – but this is of course a matter of personal preference.

***The Methods sections was combined into multiple subsections 2.0 Model Description, 2.1 The Ocean Component, 2.2 Simulation and experiments, 2.3 Data Sources. A significant portion of the model description was moved to the Appendix and expanded on.*

In order to increase readability, the Results/Discussion section could also be divided in subsections; e.g. one part that covers the model calibration/validation, and a second part focused on the model sensitivity to different RCP scenarios.

***Thank you for this comment, we have since divided the results section into 3.1 Model and Observation Comparisons and 3.2 Model Parameter Sensitivity.*

The Discussion section tends to spill over a bit into the Conclusions section. I'd like to see a Conclusions section that merely summarizes your main findings - without too much discussion (the discussion should be in the Discussions section). In my view the Conclusions section shouldn't include results/statements that have not been described earlier in the manuscript. For example, you mention for the first time in the manuscript how Atlantic meridional overturning circulation may decrease according to model studies. You "also note" that eutrophication, upwelling, etc. will affect acidification in coastal seas. However, these factors have not really been addressed in any detail earlier in the manuscript (which I think they should).

***The authors thank the reviewer for this great comment. The Discussion section stands as a discussion of the model comparison and sensitivity analysis. It is here we address some of the assumptions made within Hector. The conclusions now restate the significant findings of the paper instead of discussing these assumptions. See detailed comments above for more information on these assumptions.*

In summary I would definitely recommend quite a bit of an effort to improve the structure of the paper. Language:

I have some issues with punctuation and sentence construction here and there in the manuscript (some examples are mentioned below in "Technical corrections").

Artwork:

Figure 6 doesn't add anything that isn't already shown in Figure 5. Unless I'm mistaken, there is a more or less linear relationship between the saturation states for aragonite and calcite ($AR \cdot 1.8CA$). I suggest that you simply remove Figure 6.

***The authors agree with the reviewer and we removed Figure 6 from the manuscript.*

Figure 7: Very difficult to see anything in this figure! In its present form, Figure 7 doesn't contribute much to the manuscript.

***We agree with the reviewer and we removed this figure from the manuscript as it didn't add anything substantial to the study.*

Specific comments:

Throughout the manuscript, you use anything from 1 and up to 5 significant digits when presenting results and data. I would like to see a bit more consistency.

***The significant figures issue has been addressed and the manuscript is updated to reflect these changes.*

There are a number of acronyms in the manuscript. These should (in general) be explained the first time they appear:

p. 19270, ln. 7: Here, the CMIP5 acronym appears for the first time. Although the meaning might be evident to most people in the field, I think you should at least explain the acronym (and maybe somewhere in the Introduction even write a sentence explaining what this project is).

p. 19270, ln. 11-12: Here you should also define the RCP acronym that is used throughout the manuscript.

***The text changed to reflect these 2 comments:*

“ESMs are computationally expensive and typically run using stylized experiments or a few Representative Concentration Pathways (RCPs), greenhouse gas concentration trajectories used in the Intergovernmental Panel on Climate Change 5th Assessment Report. This generally limits the ESM-based analyses to those scenarios. The occurrence of ocean warming and acidification is consistent across the Coupled Model Intercomparison Project (CMIP5) ESMs, but their rates and magnitudes are strongly dependent upon the scenario (Bopp et al., 2013).”

p. 19272, ln. 22: You mention “earth system models” already in the abstract, so the ESM abbreviation should be defined there. Perhaps also use capital letters; “Earth System Models”?

***Corrected.*

p. 19276, ln. 3: You don’t explain that TA is short for total alkalinity.

There are numerous typos/mistakes related to descriptions of the carbonate system:

***TA is now defined within the text. “There are four measurable parameters of the carbonate system in seawater: DIC, total alkalinity (TA), pCO₂ and pH, and any pair can be used to describe the entire carbonate system.”*

p. 19271, ln. 24-25: The DIC concentration should be defined as the sum of [HCO₃⁻], [CO₃²⁻], and [CO₂*], where [CO₂*] = [CO₂ (aq)] + [H₂CO₃].

***The text has been updated: “Dissolved inorganic carbon (DIC) is the sum of [HCO₃⁻], [CO₃²⁻] and [CO₂*], where [CO₂*] = [CO₂(aq)] + [H₂CO₃].”*

p. 19272, ln. 2: Again, use CO₂* instead of CO₂ (aq). [CO₂*] is used later in the manuscript (p. 19276 and Appendix) but without an explanation of what the definition signifies.

****Corrected.** “Dissolved inorganic carbon (DIC) is the sum of $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$ and $[\text{CO}_2^*]$, where $[\text{CO}_2^*] = [\text{CO}_2(\text{aq})] + [\text{H}_2\text{CO}_3]$.”

p. 19273, ln. 19: Bicarbonate and carbonate should be written HCO_3^- and CO_3^{2-} -respectively.

****Corrected.**

p. 19276, ln. 9, 14, Here and throughout the manuscript the unit for TA should be in $\mu\text{mol kg}^{-1}$ (not mol kg^{-1}).

****Corrected.**

p. 19276, ln. 27: Surely, ΔpCO_2 is the difference in pCO_2 between atmosphere and ocean (not the difference in $[\text{CO}_2]$).

****Yes, it is the difference between the atmosphere and ocean and the manuscript has been updated.**

p. 19281, ln. 20-28: Are temperature dependent changes in pH and aragonite/calcite saturation linear? I don't think so, but maybe it's a good approximation within the current range of temperature change (?). This should be clarified.

****We agree with the reviewer that the discussion of Figure 7 was initially unclear. After rewriting we determined that this figure did not add anything substantial to the study and we decided to remove it from the manuscript.**

p. 19282, ln. 16: Calcium carbonate should be written CaCO_3 (not CaCO_3^-).

****Corrected.**

Technical corrections:

p. 19270, ln. 14-15: “low latitude ($>55^\circ$)” should be “low latitude ($<55^\circ$)”?

****Corrected.**

p. 19270, ln. 15-19: You switch between 1-3 significant digits when presenting results here.

****Significant figures have been addressed and are more consistent throughout the text.**

p. 19271, ln. 8: I would write “surface and deep water warming”. Further, “calcium carbonate saturations” sounds a bit strange to me, maybe you could write “calcite and aragonite saturation levels” instead.

****Saturations throughout the manuscript were changed to saturation levels.**

p. 19271, ln. 17: I think you should define the preindustrial pH level (8.2) here. From the abstract the reader can of course calculate the level to be 8.17 in low latitudes, and later on in table 5 find values for both low and high latitudes. In addition, on p.19271-19272 you present the DIC composition at a pH level of 8.2 without mentioning why

you choose this value. I get what you mean but it's nonetheless a bit annoying.

***Thank you for the comment on this. We agree that this is a little confusing. We have since rewritten many of the sections where absolute values are involved and deleted the DIC composition sentence.*

p. 19272, ln. 6: I would write "saturation levels" instead of "saturations".

***All saturations were changed to saturation levels throughout the manuscript.*

p. 19272, ln. 11-12: Which model studies? I think of course that you refer to the ones in the following sentences, but just to be clear you could for example finish the "Modeling studies" sentence by a colon (:) instead of period (.).

***This sentence was deleted as it did not contribute to the manuscript.*

p. 19273, ln. 4: "capability" instead of "capabilities".

***Corrected.*

p. 19274, ln. 9-12: A couple of strange sentences here. This paragraph should be clarified.

***A more detailed model description was moved to the Appendix and was updated to reflect this comment.*

p. 19274, ln. 20-21: Strange sentence: "two surface boxes (high and low latitude), an intermediate and deep box, simulated a simple:::". Maybe you could instead write:

"two surface boxes (high and low latitude), one intermediate and one deep box, simulating a simple". The same description by the way appears on line 1-2 (same page), but without references.

***This sentence has been corrected. "It consists of four boxes; two surface boxes (high and low latitude), one intermediate, and one deep box." "Once carbon enters the high latitude surface box it is circulated between the boxes via advection and water mass exchange, simulating a simple thermohaline circulation."*

p. 19274, ln. 22: "15% of the ocean" – 15% of the ocean surface area/volume, right?

***Corrected to surface area.*

p. 19275, ln. 16: "change in change in" – remove one of the "change in".

***Corrected.*

p. 19276, ln. 20: ":::: based on salinity, temperature, and pressure" – according to ln. 7-8, same page, you have neglected the effects of pressure.

p. 19279, ln. 23 and 26: Here and throughout the manuscript you switch between preindustrial and pre-industrial. Choose one form and stick to it.

***Corrected to preindustrial.*

p. 19280, ln. 10: Change "More observations in the..." to "Moreover, observations in the"

***Corrected.*

p. 19280, ln. 14-17: Again, try to be consistent with the number of significant digits when presenting results.

***The authors correctly all significant digit issues throughout the manuscript.*

p. 19281, ln. 2: I think “19 and 25 %” should instead be “0.19 and 0.25 % yr⁻¹”, correct?

***Corrected.*

p. 19281, ln. 3: “of” instead of “Of”.

***Corrected.*

p. 19282, ln. 13: Correct the sentence here – “unprecedented in the potentially the last”.

***Corrected.*

p. 19282, ln. 16: “Organisms” instead of “organism”.

***Corrected.*

Tables:

Table 2, row 6: Change “Carbon DO” to “Deep ocean carbon”.

***After significant reorganization of the manuscript we deleted table 2 and included more text about Hector’s parameters within the manuscript.*

Table 5: Very difficult to read this table. The columns appear to have shifted one step to the right in relation to the title row.

***Table 5 was separated out into two tables, one for high latitude and one for low latitude.*

Interactive comment on “Projections of ocean acidification over the next three centuries using a simple global climate carbon-cycle model” by C. A. Hartin et al.

Anonymous Referee #3

Received and published: 19 February 2016

General comments:

The paper presents a fast and, as it seems, relatively competent model tool for future projections. This is excellent, and something I think is needed as complement to the more complex, computationally expensive earth system models. It is however a letdown that this study doesn't actually use the model for anything new, a flaw that reduces its scientific value. The manuscript would greatly improve if the models capability was used to actually investigate something.

***We could not agree more with the reviewer. This paper lacked any significant investigation. Since then, we have run a series of simplified sensitivity analyses to investigate the sensitivity of Hector's inputs on its outputs, particularly pH and aragonite saturation.*

The paper is otherwise interesting, generally well written, and presents a promising concept, but it needs more work.

Specific comments:

In the introduction the authors mention the oceans storage capacity for carbon, and its potential decline of anthropogenic CO₂ uptake. Since the model seems to calculate these fluxes anyway, why not show how they change over time? Maybe also with some different model-setting (i.e. wind speed, air-sea transfer velocities) and emission scenarios to see get an ensemble and see the sensitivity.

***We think these are all excellent ideas for future studies using Hector. We decided to run a series of model sensitivity experiments to quantify how influential some of Hector's parameter inputs are on its outputs (in particular, pH and Ω_{Ar}). Sensitivity analyses are important to both to document model characteristics, explore model weaknesses, and to check to what degree the model behavior conforms with what we know of the ocean system. We selected eight land and ocean parameters, varying each by $\pm 10\%$. Wind speed, for example was one of the parameters varied and we find that the high latitude surface pH is sensitive to changes in wind stress. We think this analysis adds significantly to the manuscript.*

How realistic is it to keep the total alkalinity constant? I think this should be stated/cited in the manuscript.

***The authors added some more text to clarify this issue. "TA is calculated at the end of spinup and held constant in time, resulting in 2311.0 $\mu\text{mol kg}^{-1}$ high latitude box and 2435.0 $\mu\text{mol kg}^{-1}$ for the low latitude box. These values are within the range of open ocean observations, 2250.0 – 2450.0 $\mu\text{mol kg}^{-1}$ of solution (Key et al., 2004; Fry et al., 2015). We assume negligible carbonate precipitation/dissolution and assume no alkalinity runoff from the land surface to the open ocean. Most studies hold alkalinity constant with time and this is a reasonable assumption over several thousand years (Lenton, 2000; Zeebe and Wolf-Gladrow, 2001; Glotter et al., 2014; Archer et al., 2009). After thousands of years the dissolution of CaCO₃ will restore ocean pH, thereby increasing the uptake of more*

CO₂. On ~10,000 year scales Hector will underestimate the CO₂ uptake, however, we are interested in 100-300 year timeframe.”

The authors should really consider creating an appendix describing the model in full, and move some of the tables with model settings (and maybe also some of the equations) there, thus focusing the main manuscript on research questions.

***We have increased our discussion of Hector within the manuscript as well as adding more detail of the model to the Appendix. We hope the reader can now better understand the details and workings of Hector without having to read Hartin et al., 2015 - GMD.*

Please specify throughout the manuscript that you with “carbon” mean dissolved inorganic carbon (DIC), as I assume you do. It is unnecessary unclear as of now.

***We have tried to clarify between carbon and DIC within the text.*

Line-by-line corrections:

Line 10: “series” is probably a typo for “serious”.

***Corrected.*

Line 20: (>55) indicate that the authors mean the high latitudes, not the low?

***Corrected.*

Line 97: Insert “latitude” after “low” to make the text clearer.

***Corrected.*

Line 101: Repeated info from line 96, please rewrite.

***A large portion of the model description was moved to the Appendix and rewritten.*

Line 112: Change to: “...simulating a simple thermohaline ...”. I’m guessing you mean thermohaline instead of thermocline?

***Yes, thank you for catching this typo. We do mean thermohaline.*

Line 155-156 I don’t understand what you mean with this; “We assume surface waters are fully equilibrated with the overlying atmosphere...” I agree that with that time step, yes, sure, it should be fully equilibrated, disregarding seasonal variations. But if it was equilibrated, shouldn’t then the flux be zero and pCO₂ in the ocean surface and air be the same? Please correct me if I get this all wrong, or rewrite the text.

***We agree with the reviewer that this sentence was not clear and inaccurate. We have since removed it from the manuscript.*

Line 168: Remove the second comma.

***Corrected.*

Line 242 and 244: The decreases are presented in different units, which makes it impossible to compare the two.

***We corrected the percentages to 0.19 yr⁻¹ and 0.25 yr⁻¹.*

Line 286: Total alkalinity should be added to this list.

***This paragraph was broken apart and added to different sections of the manuscript. Constant TA is now addressed within the model description. See general comments for more detail on this.*

Line 300-302: I agree! Please add something of this sort to this paper.

***We hope the restructuring and reorganization and add sensitivity analyses helps to highlight Hector's potential in being a critical tool to understand future changes to the marine carbonate system.*

Table 5: The table needs to be better organized/presented. Consider dividing into two.

***The table was divided into high and low latitude.*

Figure 2: Add units to the y-axis. Redo the colors so that all measurement data is clearly visible, the pink data in particular disappears into the light red fields. Have the data on top the model lines for better visibility. And remove the legend headline, all these data are not "Model".

Figure 3: Add units to the y-axis. Have the data on top the model lines for better visibility. And remove the legend headline, all these data are not "Model".

Figure 4: Redo the colors so that all measurement data is clearly visible, the pink data in particular disappears into the light red fields. Have the data on top the model lines for better visibility. And remove the legend headline, all these data are not "Model".

Figure 5: Redo the colors so that all measurement data is clearly visible, the pink data in particular disappears into the light red fields. Have the data on top the model lines for better visibility. And remove the legend headline, all these data are not "Model".

Figure 6: Redo the colors so that all measurement data is clearly visible, the pink data in particular disappears into the light red fields. Have the data on top the model lines for better visibility. And remove the legend headline, all these data are not "Model".

Figure 7: Increase size of legend and preferably also the size of the markers.

***All figures have been updated, removed legend, increased font size, more descriptive terminology, and fixed the color scheme. Also, Figure 7 was removed the manuscript as it didn't add anything substantial to the study.*

1 ~~Projections of~~ Ocean acidification over the next three centuries using a simple global climate carbon-
2 cycle model: projections and sensitivities.

3
4 C. A. Hartin*, B. Bond-Lamberty, P. Patel and Anupriya Mundra

5
6 Pacific Northwest National Laboratory, Joint Global Change Research Institute at the University of
7 Maryland-College Park, 5825 University Research Court #3500, College Park, MD 20740, USA

8
9 *Corresponding author: Corinne.hartin@pnnl.gov

10
11 **ABSTRACT**

12 Continued oceanic uptake of anthropogenic CO₂ is projected to significantly alter the chemistry of the
13 upper oceans over the next three centuries. ~~Ocean acidification is already occurring and will have, with~~
14 potentially serious consequences ~~for~~ on ~~for~~ the marine ecosystems. Relatively few models have the
15 capability to make projections of ocean acidification, limiting our ability to assess the impacts and
16 probabilities of ocean changes. ~~Rather than running the cumbersome earth system models, we can use~~
17 ~~a reduced form model to quickly emulate the CMIP5 models for projection studies under arbitrary~~
18 ~~emission pathways and for uncertainty analyses of the marine carbonate system.~~ In this study we
19 highlight ~~examine~~ the ~~cap~~ability of Hector v1.1, a reduced-form global model, to project changes in the
20 upper ocean carbonate system over the next three centuries, and quantify the model's sensitivity to
21 ~~parameteric~~parametric ~~inputs as well as investigating parametric sensitivities over the next three~~
22 centuries. Hector is run under prescribed emission pathways from the historical emissions and a high
23 emissions scenario (Representative Concentration Pathways (RCPs) 8.5), and ~~comparing~~ ed ~~its output~~
24 ~~to~~ both observations and a suite of Coupled Model Intercomparison (CMIP5) model outputs ~~that~~

25 ~~contain ocean biogeochemical cycles.~~ Current observations confirm that Changes in ocean
26 acidification ~~changes are~~ already taking place, and CMIP5 models project significant changes occurring
27 ~~over the next 2-300 years.~~ Hector is consistent with the observational record within both the high
28 (>55°) and low latitude oceans (<=55°). The model projects a low latitude surface ocean pH to decrease
29 ~~from from~~ preindustrial ~~conditions levels of 8.17 by 0.4 units~~ to 7.77 ~~at in~~ 2100, and to decrease an
30 ~~additional 0.27 units to~~ 7.50 ~~at in~~ 2300. ~~A; a~~ aragonite saturations decrease from 4.1 units by 1.85 to 2.2
31 ~~units at in~~ 2100 and down an additional 0.80 units ~~decreases to~~ 1.4 ~~units at in~~ 2300 under RCP 8.5. These
32 magnitudes and trends of ocean acidification within Hector are largely consistent with the CMIP5 model
33 outputs, although we identify small biases exists within Hector's carbonate system. Modeled changes in
34 pH are sensitive to those parameters that directly affect atmospheric CO₂ concentrations (beta and Q₁₀),
35 while changes in Ω_{Ar} saturation levels are sensitive to changes in ocean salinity and Q₁₀. We conclude
36 that although the reduced form Hector reproduces the global historical trends, and future projections
37 with equivalent rates of change over time compared to observations and CMIP5 models. Hector model
38 has limitations and some biases relative to the CMIP5 record, Hector is a robust tool well-suited for that
39 ~~can be used for quick rapid~~ ocean acidification projections, sensitivity analyses, and is and generally
40 capable of emulating emulatesing both current observations and large scale climate models under
41 multiple emission pathways.

42 1. INTRODUCTION

43 Human ~~induced~~ activities have led to increasing anthropogenic emissions of greenhouse gases
44 to the atmosphere. In the first decade of the 21st century CO₂ emissions from anthropogenic sources
45 and land use changes accounted for ~9 Pg C yr⁻¹, with future emission projections of up to 28 Pg C yr⁻¹ by
46 2100 under ~~a high emissions scenario~~ Representative Concentration Pathway 8.5 (RCP 8.5) (Riahi et al.,
47 2011). The world's oceans have played a critical role in lessening the effects of climate change by
48 absorbing 25-30% of the total anthropogenic carbon emissions since 1750 (Le Quéré et al., 2013; Sabine
49 et al., 2011).

50 In response to this increasing atmospheric burden of CO₂ and increasing oceanic uptake, the
51 oceans are experiencing both physical and biogeochemical changes: surface and deep water warming,
52 reduced subsurface oxygen, and a reduction in calcium carbonate saturation levels and pH (Doney,
53 2010). ~~In particular, t~~ Mean surface ocean pH has decreased by 0.1 units relative to ~~the~~ preindustrial
54 times (Caldeira et al., 2003). If current emission trends continue, ocean acidification will occur at rates
55 and extents not observed over the last few million years (Feely et al., 2004; Feely et al., 2009; Kump et
56 al., 2009; Caldeira et al., 2003). Ocean acidification occurs when atmospheric CO₂ dissolves in seawater
57 (CO₂(aq)), forming carbonic acid (H₂CO₃), dissociating into carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻),
58 and releasing protons (H⁺). The net effect of adding CO₂ to the system increases the concentrations of
59 [H₂CO₃], [HCO₃⁻], and [H⁺], while decreasing [CO₃²⁻] concentrations and lowering the pH. The sum of
60 [HCO₃⁻], [CO₃²⁻] and [CO₂^{*(aq)}], where [CO₂^{*}] = [CO₂(aq)] + [H₂CO₃] represents the total inorganic carbon
61 or dissolved inorganic (DIC) of the system ~~make up the total dissolved inorganic carbon (DIC)~~. As CO₂(aq)
62 continues to increase in the ocean it reacts with CO₃²⁻, forming HCO₃⁻, decreasing the fraction of CO₂ that
63 can be readily absorbed by the oceans. Therefore, because of the buffering capacity of the oceans, a
64 doubling of atmospheric [CO₂] will not ~~cause a~~ corresponding to a doubling of [CO₂^{*}](aq) but instead
65 will result in an increase of on the order of ~ 10% in the oceans. ~~At a pH of 8.2, 88% of the DIC is in the~~

66 ~~form of HCO_3^- ; 11% in the form of CO_3^{2-} , and 0.5% in the form of $\text{CO}_2(\text{aq})$, these percentages will change~~
67 ~~as the oceans take up more carbon.~~ Due to both these chemical and physical changes (e.g., warming
68 and stratification), the oceans may become less efficient in the uptake of anthropogenic CO_2 as the
69 climate continues to change (Sarmiento and Le Quéré, 1996; Matear and Hirst, 1999; Joos et al., 1999;
70 Le Quéré et al., 2010).

71 Numerous experiments and observations indicate that ocean acidifications ~~may~~ will have
72 significant effects on calcifying marine organisms. For example, the rate of coral reef building may
73 decrease, calcification rates of planktonic coccolithophores and foraminifera may be suppressed, and
74 significant changes in trophic level interactions and ecosystems may occur (Cooley and Doney, 2009;
75 Silverman et al., 2009; Fabry et al., 2008; Riebesell et al., 2000). ~~For example, s~~ome coral reefs are
76 believed to already be eroding for parts of the year due to changes in ocean acidification (Yates and
77 Halley, 2006; Albright et al., 2013). Global surface pH is projected to drop by up to 0.33 units (Gehlen et
78 al., 2014; Orr et al., 2005) and ~~and~~ all existing coral reefs will be surrounded by ~~ocean chemistry~~
79 conditions ~~that are~~ well outside of ~~the~~ preindustrial values and even today's saturation levels (Ricke et
80 al., 2013) under the RCP8.5 scenario.

81 ~~However, t~~hese model projections of ocean acidification come primarily from Earth System
82 Models (ESMs) that integrate the interactions of atmosphere, ocean, land, ice and biosphere to
83 estimate the present and future state of the climate. ESMs are computationally expensive and typically
84 run using stylized experiments or a few ~~prescribed emission pathways (e.g., RCPs~~ Representative
85 Concentration Pathways (RCPs), greenhouse gas concentration trajectories used in the
86 Intergovernmental Panel on Climate Change 5th Assessment Report (IPCC, 2013). This generally limits
87 ~~the~~ ESM-based analyses to those scenarios. The occurrence of ocean warming and acidification is
88 consistent across the Coupled Model Intercomparison Project (CMIP5) ESMs, ~~however but their~~ rates
89 and magnitudes are strongly dependent upon the scenario (Bopp et al., 2013).

90 ~~An alternative to ESMs are~~ Here we present Hector, a reduced-form climate carbon cycle model
91 ~~that can emulate the median climate of CMIP5.~~ Reduced-form models, relatively simple and small
92 models that can be ~~are~~ powerful tools due to their simple input requirements, computational efficiency,
93 tractability, and thus ability to run multiple simulations under arbitrary future climate change emission
94 pathways. ~~This,~~ allowing for us to conduct quantification of arbitrary climate change scenarios,
95 emulation of larger ESMs, as well as in-depth parameter sensitivity studies and uncertainty analyses
96 (Senior and Mitchell, 2000; Ricciuto et al., 2008; Irvine et al., 2012).

97 Our goal of this study is to quantify how well Hector, a reduced-form model that explicitly treats
98 surface ocean chemistry, emulates the marine carbonate system of both observations and the CMIP5
99 archive, and explore the parametric sensitivities to Hector's ocean outputs. ~~We run Hector under~~
100 ~~different emissions pathways, comparing the marine carbonate system to the observational record and~~
101 ~~CMIP5 archive. This study builds upon Hartin et al. (2015), which introduced Hector v1.0, an open-~~
102 ~~source, object-oriented simple climate model with the capabilities of projecting changes in the surface~~
103 ~~ocean carbonate system over the next three centuries. This work is timely due to the fact that the~~
104 ~~recent CMIP5 process included numerous ESMs that contain dynamic ocean biogeochemistry. Other~~
105 ~~simple models have modeled the complexity of the nonlinear carbonate system through mixed layer~~
106 ~~Impulse Response Functions (IRF) calculating air-sea fluxes (Joos et al., 1996; Joos et al., 2001;~~
107 ~~Meinshausen et al., 2011) and evaluating the parameters of the carbonate system by back-calculating~~
108 ~~from the ocean uptake of CO₂ (Tanaka et al., 2007; Harman et al., 2011). The IRF method has been~~
109 ~~widely used across the scientific community, as it is cost-effective to run, provides surface to deep~~
110 ~~mixing estimates, and can also be used to look at oceanic uptake of conservative tracers. However, the~~
111 ~~carbonate system is not directly calculated and many effects like temperature effects on CO₂ solubility~~
112 ~~are typically parameterized. The carbonate system is strongly dependent upon temperature where~~
113 ~~pCO₂ changes by about 4.2% per Kelvin (Copin Montegut, 1988; Takahashi et al., 1993). While these~~

114 models are able to reproduce changes in the global climate system, details in the carbonate system
115 (HCO_3^{2-} , CO_3 , pH, pCO_2 , and alkalinity) are not actively solved for.

116 The remainder of the paper is organized as follows: ~~S~~section 2, a detailed description of
117 Hector's ocean component, the data sources and simulations ~~run~~describes the model components
118 focusing on the ocean carbon cycle and carbonate chemistry, ~~S~~section 3, results of the model
119 comparison and sensitivity experiments ~~presents the model experiments and comparison data used and~~
120 lastly, Ssection 4, a discussion of the results ~~describes the main results and a discussion.~~

121

122 ~~2. Model Description – carbon cycle~~

123 The carbon component in Hector contains three carbon reservoirs: a single well-mixed atmosphere,
124 a land component consisting of vegetation, detritus, and soil, and an ocean component consisting of
125 four boxes (high and low surface boxes, an intermediate box, and a deep box) (Figure 1). The change in
126 atmospheric carbon is a function of the anthropogenic emissions (F_A), land-use change emissions (F_{LC}),
127 and atmosphere-ocean (F_O) and atmosphere-land (F_L) carbon fluxes. The default model time step is 1
128 year.

$$\frac{dC_{atm}(t)}{dt} = F_A(t) + F_{LC}(t) - F_O(t) - F_L(t) \quad (9)$$

129 The terrestrial cycle in Hector contains vegetation, detritus, and soil, all linked to each other and
130 the atmosphere by first-order differential equations. Vegetation net primary production is a function of
131 atmospheric CO_2 and temperature. Carbon flows from the vegetation to detritus and to soil and loses
132 fractions of carbon to heterotrophic respiration on the way. An 'earth' pool debits carbon emitted as
133 anthropogenic emissions, allowing a continual mass-balance check across the entire carbon cycle.
134 Atmosphere-land fluxes at time t are calculated by:

$$F_L(t) = \sum_{i=1}^n NPP_i(t) - RH_i(t) \quad (10)$$

135 where *NPP* is the net primary production and *RH* is the heterotrophic respiration summed over user-
 136 specified *n* groups (i.e., latitude bands, political units, or biomes) (Hartin et al 2015).

137 2.0 Model Description – Hector

138 Hector is open-source and available at <https://github.com/JGCRI/hector>. The repository
 139 includes all model code needed to compile and run the model, as well as, all input files and R scripts to
 140 process its the model output. For this study we run Hector v1.1, Git Commit # with an updated ocean
 141 temperature to better match the CMIP5 mean. Hector is a reduced form climate carbon-cycle model,
 142 which takes in emissions of CO₂, non-CO₂s and aerosols, converts emissions to concentrations where
 143 needed, calculates the global radiative forcing and then global mean temperature change. Hector
 144 contains a well-mixed global atmosphere, a land component consisting of vegetation, detritus, and soil,
 145 and an ocean component. In this study we use Hector v1.1, with an updated ocean temperature
 146 algorithm to better match the CMIP5 mean. For a detailed description of the land and atmospheric
 147 components of Hector, please refer to Appendix A and Hartin et al., 2015.

148 2.1 Ocean eComponent

149 Hector's ocean component is modeled after based on work by Lenton (2000), Knox and McElroy
 150 (1984) and Sarmiento and Toggweiler (1984). It consists consisting of four boxes; two surface boxes
 151 (high and low latitude), an one intermediate, and one deep box, simulated a simple thermocline
 152 circulation. The cold high latitude surface box makes up 15% of the ocean surface area ocean, representing the subpolar gyres (> 55°), while the warm low latitude surface box (<55°) makes up 85% of
 153 the ocean surface area. The temperatures of the surface boxes are linearly related to the global
 154 atmospheric temperature change, and are initialized at 2°C in the high latitude and 22°C for the high and
 155 low latitude boxes respectively. This temperature gradient sets up a flux of carbon into the cold high
 156

157 latitude box and a flux out of the warm low latitude box. The ocean-atmosphere flux of carbon is the
 158 sum of all the surface fluxes (F_i , $n=2$).

$$F_O(t) = \sum_{i=1}^n F_i(t) \quad (114)$$

159 Once carbon enters the high latitude surface box system it is circulated between the boxes via
 160 advection and water mass exchange, simulating a simple thermohaline circulation. In this version of
 161 Hector ~~We~~ do not explicitly model diffusion. ~~Simple~~ simple box-diffusion models and “HILDA” (e.g.,
 162 Siegenthaler and Joos, 1992) type models, are typically in good agreement with observations but are
 163 more computationally demanding than a simple box model (Lenton, 2000). The change in carbon of any
 164 ocean box i is given by the fluxes in and out, with $F_{atm \rightarrow i}$ as the atmospheric carbon flux of the two
 165 surface boxes:

$$\frac{dC_i}{dt} = \sum_{j=1}^{in} F_{j \rightarrow i} - \sum_{j=1}^{out} F_{i \rightarrow j} + F_{atm \rightarrow i} \quad (212)$$

166 The flux of ~~change in~~ carbon between the boxes is related to the transport ($T_{i \rightarrow j}$) ~~in Sverdrups~~
 167 ($Sv = 10^6 m^3 s^{-1}$) between i and j , the volume of i (V_i, m^3), and the total carbon in i (including any air-sea
 168 fluxes) ($C_i, Pg C$);

$$\frac{dC_i}{dt} = \frac{T_{i \rightarrow j} * C_i(t) * time}{V_i} * C_i \quad (3)$$

169 Volume transports are tuned to yield an approximate flow of 100 Pg_C from the surface high latitude box
 170 to the deep ocean box at steady state, simulating deep water formation. ~~The dynamics of ocean uptake~~
 171 ~~of CO₂ is strongly dependent on this downward transport rate of CO₂-laden waters from the surface~~
 172 ~~ocean to depth.~~

173 Hector includes ~~e are~~ four measurable parameters-variables of the carbonate system in
 174 seawater: DIC, total alkalinity (TA), pCO_2 and pH, ~~and~~ any pair of which can be used to describe the
 175 entire carbonate system. ~~Within Hector,~~ DIC and TA are used to solve for the surface ocean pH and

176 pCO₂ values. These detailed carbonate chemistry equations are based on numeric programs from Zeebe
177 and Wolf-Gladrow, 2001 ([Appendix BA](#)). We ~~have~~ simplified the equations by neglecting the effects of
178 pressure, since we are only concerned with the surface ocean. ~~A best-fit alkalinity (2311.0 mol kg⁻¹ for
179 HL and 2435.0 mol kg⁻¹ for LL), is solved for at the end of spinup, that when calculated with an initial DIC
180 input for each surface box results in a pre-industrial net zero flux of carbon over the global ocean.~~
181 Hector is run to equilibrium in a perturbation-free mode, prior to running the historical period, ensuring
182 that [Hector-it](#) is in steady-state (Hartin et al., 2015; Pietsch and Hasenauer, 2006). DIC (μmol kg⁻¹) in the
183 surface boxes is a function of the total carbon (Pg C) and the volume of the box. All carbon within the
184 ocean component is assumed to be inorganic carbon. Dissolved organic matter is less than 2% of the
185 total inorganic carbon pool, of which a small fraction is dissolved organic carbon (Hansell and Carlson,
186 2001). Therefore, for simplicity we chose not to include organic carbon within Hector.
187 TA is calculated at the end of model spinup (running to equilibrium in an a historical, perturbation-free
188 mode) and held constant going forward in time, resulting in ~~The alkalinity values - 2311.0 μmol kg⁻¹ for
189 the high latitude box and 2435.0 μmol kg⁻¹ for the low latitude box. These values~~ are within the range of
190 open ocean observations, 2250.0 – 2450.0 μmol kg⁻¹ (Key et al., 2004; Fry et al., 2015), ~~and are held
191 constant with time in Hector.~~ We assume negligible carbonate precipitation/dissolution ~~or alkalinity
192 runoff from the land surface over our period of interest (100–300 years) and no alkalinity runoff from the
193 land surface to the open ocean.~~ Alkalinity is typically held constant with time, a reasonable assumption
194 over several thousand years (Lenton, 2000; Zeebe and Wolf-Gladrow, 2001; Glotter et al., 2014; Archer
195 et al., 2009). On glacial-interglacial time scales alkalinity and the dissolution of CaCO₃ sediments is an
196 important factor in controlling atmospheric [CO₂] (Sarmiento and Gruber, 2006). ~~Therefore, and thus on
197 these scales Hector will underestimate the oceanic CO₂ uptake. For purposes of our studies however, we
198 are interested in 100–300 year timeframe.~~

199 ~~From this, Hector actively solves for $p\text{CO}_2$, pH (total scale), and HCO_3^- , CO_3^{2-} , and aragonite (Ω_{Ar})~~
200 ~~and calcite saturations (Ω_{Ca}) in the surface ocean boxes.~~

201 Hector solves for $p\text{CO}_2$, pH (total scale), and $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$, and aragonite (Ω_{Ar}) and calcite
202 saturations (Ω_{Ca}) in both the high and low latitude surface ocean boxes. $p\text{CO}_2$ is calculated from the
203 concentration of $[\text{CO}_2^*]$ and the solubility of CO_2 in seawater, based on salinity and, temperature, and
204 pressure. $[\text{CO}_2^*]$ is calculated from DIC and the first and second dissociation constants of carbonic acid
205 from Mehrbach et al. (1973), refit by Lueker et al. (2000) (A1Appendix B).

206 ~~$p\text{CO}_2$ is needed to calculate a~~ Carbon fluxes between the atmosphere and ocean are calculated
207 (Takahashi et al., 2009):

$$F = k \alpha * \Delta p\text{CO}_2 = \text{Tr} * \Delta p\text{CO}_2 \quad (4)$$

208 where k is the CO_2 gas-transfer velocity, α is the solubility of CO_2 in seawater (K_0 , Appendix B), and the
209 $\Delta p\text{CO}_2$ is the difference in ~~$p\{\text{CO}_2\}$~~ between the atmosphere and ocean. The product of k and α results in
210 Tr , the sea-air gas transfer coefficient, where $\text{Tr} (\text{g C m}^{-2} \text{ month}^{-1} \mu\text{atm}^{-1}) = 0.585 * \alpha * \text{Sc}^{-1/2} * U_{10}^2$, 0.585
211 is a unit conversion ~~factor~~ factor (from mol liter⁻¹ atm⁻¹ to g-C m⁻³ μatm^{-1} and from cm h⁻¹ to m month⁻¹)
212 and Sc is the Schmidt number. The Schmidt number (Appendix BA1) is calculated from Wanninkhof
213 (1992) based on the temperature of each surface box. The average wind speed (U_{10}) of 6.7 m s⁻¹ is the
214 same over both surface boxes (Table 1). ~~We assume surface waters are fully equilibrated with the~~
215 ~~overlying atmosphere given our time step of 1 year; the average time for surface waters to come into~~
216 ~~equilibrium (Broecker and Peng, 1982).~~ pH (total scale), $[\text{HCO}_3^-]$, and $[\text{CO}_3^{2-}]$ are calculated using the
217 $[\text{H}^+]$ ion and solved for in a higher order polynomial (Appendix BA1).

218 Aragonite and calcite are the two primary carbonate minerals within seawater. The degree of
219 saturation in seawater with respect to aragonite (Ω_{Ar}) and calcite (Ω_{Ca}) is calculated from the product of
220 the concentrations of calcium $[\text{Ca}^{2+}]$ and carbonate ions $[\text{CO}_3^{2-}]$, divided by the solubility (K_{sp}). The
221 ~~calcium concentration~~ $[\text{Ca}^{2+}]$ is based on equations from Riley and Tongudai (1967) at a constant salinity

222 of 34.5. If $\Omega = 1$, the solution is at equilibrium, and if $\Omega > 1$ ($\Omega < 1$) the solution is supersaturated
223 (undersaturated) with respect to the mineral.

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \quad (5)$$

224

225 ~~32.2. Model experiments and data sources~~ Simulation and experiments

226 Hector is run under prescribed emissions from 1850-2300 for all four Representative
227 Concentration Pathways (RCP 2.6, RCP 4.5, RCP 6, RCP 8.5) (Moss et al., 2010; van Vuuren et al., 2007).

228 We compare how well Hector can emulate the carbonate system of the CMIP5 median. Our results
229 section will mainly focus on RCP8.5, to exploreing the response of the carbonate system under a high
230 emissions scenario.

231 We also ran a series of model sensitivity experiments to quantify how influential some of
232 Hector's parameter inputs are on its outputs (in particular, ~~X~~pH and ~~Y~~ Ω_{Ar}). Such sensitivity analyses are
233 important to document model characteristics, explore model weaknesses, and determine to what
234 degree the model behavior conforms to our existing understanding of the ocean system. Present climate
235 biases and future climate changes may be sensitive to changes in model parameter values. Therefore, a
236 series of sensitivity experiments are run varying key parameters within Hector. We do not sample
237 Hector's entire parameter space, a computationally demanding exercise, but instead choose a list of the
238 parameters that we expect, a priori, to be important in calculating the marine carbonate system. We
239 selected eight land and ocean parameters, varying each by $\pm 10\%$ relative to the RCP8.5 control. We, and
240 compare the percentage change from the reference and the perturbation cases in 2005, 2100, and 2300.

241 2.3 Data Sources

242 The Hector code is open-source and available at <https://github.com/JGCRI/hector>. The
243 repository includes all model code needed to compile, as well as, all input files and R scripts to process
244 the model output. For this study we run Hector v1.1, Git Commit #, with updated ocean temperature to

245 ~~better match the CMIP5 mean. Hector is run under prescribed emissions from 1850–2300 for all four~~
246 ~~Representative Concentration Pathways (RCP 2.6, RCP 4.5, RCP 6, RCP 8.5). All RCP input emissions data~~
247 ~~is-are~~ available at <http://tntcat.iiasa.ac.at/RcpDb/>.
248 Comparison data are obtained from a suite of CMIP5 Earth System Models (Table 2) (Taylor et al., 2012).
249 The CMIP5 output is available from the Program for Climate Model Diagnostics and Intercomparison
250 (<http://pcmdi3.llnl.gov/esgcet/home.htm>). We took the 0-100m (depth) mean for all available CMIP5
251 data for six output variables, computing the monthly mean for all years in the historical (1850-2005) and
252 RCP 8.5 (2006-2300) experiments. All outputs were regridded to a standard 1-degree grid using bilinear
253 interpolation in CDO version 1.7.1rc1, and then high latitude (-90 to -55 and 55 to 90 degrees), low
254 latitude (-55 to 55), and global area-weighted means computed using R 3.2.4. All CMIP5 comparisons
255 used in this study are from model runs with prescribed atmospheric CO₂ concentrations. We
256 acknowledge that this is not a perfect comparison, as Hector is emissions-forced-between-emissions
257 forced-Hector-and-being compared to the concentration-forced CMIP5 models-, but vVery few CMIP5
258 models-of the latter were run under prescribed emissions. We use a combination of root mean square
259 error (RMSE), rates of change (Δ) and bias (degree of systematic over or underestimation) as-our-metrics
260 to characterize how-well Hector's performance relative-compares to the CMIP5 median.
261 We also compare Hector to Comparison data-is-obtained-from a series of observational surface
262 ocean data ~~and a suite of CMIP5 models~~. Surface ocean observations of DIC, pCO₂, pH, Ω_{Ar} , and Ω_{Ca} are
263 from ~~ocean~~ time-series stations in both the high and latitude oceans; Hawaii Ocean Time Series (HOT),
264 Bermuda Atlantic Time Series (BATS), the European Station for Time Series in the Ocean at the Canary
265 Islands (ESTOC), the Irminger Sea, and the Iceland Sea (Table 3) . The time-series data are annually
266 averaged over the upper 100m of the water column. The carbonate parameters not found in Table 3- are
267 computed from temperature, salinity, and carbonate parameter pairs using the CO2SYS software (Lewis
268 and Wallace, 1998). Lastly, a longer record (1708 – 1988) of pH and Ω_{Ar} from Flinder's Reef in the

269 western Coral Sea, ~~calculated from boron isotope measurements, is~~ used in the comparison (Pelejero
270 et al., 2005). We use rates of change (Δ) from 1988-2014 ~~similar to BATS and HOT~~ time series, ~~to~~
271 quantify how well Hector ~~does at~~ ~~simulating~~ the observed changes in the ocean carbonate parameters
272 (Table 6).

~~We also compare Hector to a suite of 15 CMIP5 Earth System Models (Table 4) (Taylor et al.,
273 2012). The CMIP5 output is available from the Program for Climate Model Diagnostics and
274 Intercomparison (<http://pcmdi3.llnl.gov/esgcat/home.htm>). The CMIP5 data are converted to annual
275 global, high latitude and low latitude averages over the upper 100m of water depth, with one standard
276 deviation of the annual averages and CMIP5 model range calculated using the RCMIP5 package
277 (<https://github.com/JGCRI/RCMIP5>). All CMIP5 comparisons used in this study are from model runs
278 with prescribed atmospheric concentrations. We acknowledge that this is not a perfect comparison
279 between emissions forced Hector and concentration forced CMIP5. However, very few CMIP5 models
280 were run under prescribed emissions. We use a combination of root mean square error (RMSE) and
281 rates of change (Δ) as our metrics to characterize how well Hector compares to the CMIP5 median.
282~~

283

284 **34. Results**

285 **3.1 Model and Observation Comparisons**

286 **~~and Discussion~~**

287 Hartin et al. (2015) conducted a thorough analysis of Hector v1.0 demonstrating ~~how that~~ it can
288 reproduce the historical trends and future projections of atmospheric [CO₂], radiative forcing, and global
289 temperature ~~change~~ under the ~~four~~ RCPs. ~~For this discussion~~ In this study we focus on the upper ocean
290 high and low latitude inorganic carbon chemistry under RCP 8.5, ~~comparing to a suite of earth system~~
291 ~~models~~ ~~ESM included in the CMIP5 archive and~~ ~~ocean observations~~. ~~Hector's primary carbonate~~

parameter outputs are summarized in Table 5. Figures 2–6 compare Hector to observations and CMIP5 median, one standard deviation and model spread.

DIC and $p\text{CO}_2$, functions of the inorganic carbon species in seawater, are directly related to rising temperatures and atmospheric $[\text{CO}_2]$. Hector captures the trend in DIC concentrations for both the high and low latitude surface ocean with a global n-average RMSE average of $47.0 \mu\text{mol kg}^{-1}$ when compared to CMIP5 models over the historical period (Table 4; Figure 2). We note that there is a systematic bias in both the high and low latitude surface boxes when compared to CMIP5. First, Low latitude DIC is slightly higher than the CMIP5 range, but rates of change are similar between 1850 and 2100, 1.27 yr^{-1} for Hector and 1.24 yr^{-1} for CMIP5 (Table 5). To obtain a steady state, the carbon pools of the surface boxes are Hector is initialized with carbon values slightly higher than the median CMIP5 values. Second, we note that after 2100 the CMIP5 median begins to decline, while Hector rises and stabilizes. Only 3 CMIP5 models ran out to 2300, with one model driving the decline. Regardless, this offset only results in a $<3\%$ global difference between CMIP5 and Hector.

Hector accurately tracks the $p\text{CO}_2$ in both the high and low latitude surface ocean with similar rates of change from 1850–2300 (Figure 3). There is a low bias in Hector compared to CMIP5 models after 2100, due to the low bias in projected atmospheric $[\text{CO}_2]$ within Hector over the same time period (Hartin et al., 2015). We do find Hector to be in closer agreement with the observation record.

Figure 4 shows the high and low latitude surface pH of Hector The oceanic uptake of CO_2 since the preindustrial has caused the marine carbonate system to shift to lower pH and lower $[\text{CO}_3^{2-}]$. Hector accurately captures the decline in pH compared to CMIP5 and observations from BATS, HOT, ESTOC, Irminger Sea, Iceland Sea, and Flinders Reef (Figure 4). While the high latitude surface pH is slightly higher than the CMIP5 models, Hector is more similar to high latitude observations. Since the pre-industrial, observations of surface ocean pH decreased by 0.08 units, corresponding to a 24% increase in $[\text{H}^+]$ concentrations and an 8% decrease in $[\text{CO}_3^{2-}]$. This is in close agreement with similar to numerous

316 studies (Feely et al., 2004; Sabine et al., 2004; Caldeira et al., 2003; Orr et al., 2005) that estimate an
317 average global decrease in pH of 0.1 or a 30% increase in $[H^+]$.

318 The Flinder's Reef pH record provides a natural baseline to compare future trends in ocean
319 acidification. While we ~~don't~~ did not expect the model to match exactly, as this reef site is heavily
320 influenced by coastal dynamics and, internal variability, ~~and upwelling~~, rates of change from the
321 preindustrial (1750) to 1988 are the same (0.0002 yr^{-1}) for both Hector and Flinder's Reef (~~Table 5~~).
322 Over the limited observational record from both the Pacific and Atlantic Oceans (~~1992-2006~~), Hector
323 accurately simulates the decline ~~change~~ in pH (~~-0.0017-0.0015~~ yr^{-1}) compared to ~~BATS (-0.0018 yr^{-1}), HOT~~
324 ~~(-0.0014 yr^{-1}), ESTOC (-0.0017 yr^{-1}) and CMIP5 (-0.0017 yr^{-1}).~~ observations (Table 6). ~~More observations~~
325 ~~in the North Pacific show surface changes of pH of up to 0.06 units between 1991 and 2006 with an~~
326 ~~average rate of -0.0017 yr^{-1} (Byrne et al., 2010). Rates of change in high latitude pH over the same time~~
327 ~~period are -0.0018 yr^{-1} for Hector and CMIP5.~~ Other observations in the North Pacific show surface
328 changes of pH up to 0.06 units between 1991 and 2006 with an average rate of -0.0017 yr^{-1} (Byrne et al.,
329 2010). Recent work, suggests that the North Atlantic absorbed 50% more anthropogenic CO_2 in the last
330 decade compared to the previous decade, decreasing surface pH by 0.0021 (Woosley et al., 2016).

331 Under RCP 8.5, Hector projects a decrease ~~of in low latitude pH of 8.17 in 1850 to 7.77 in 2100~~ over 0.40
332 units to 7.77 from 1850 to 2100 and ~~by over 0.6 units down~~ to 7.5 by 2300 in low latitude ocean pH,
333 similar to CMIP5 (Table 55) ~~and findings from intermediate complexity models (Montenegro et al.,~~
334 ~~2007).~~ At approximately 2050, atmospheric $[\text{CO}_2]$ is double the pre-industrial concentrations,
335 corresponding to ~~a 0.20 pHa~~ decrease in pH of 7.96. Shortly after this doubling, pH values are well
336 outside the ~~lowest observed~~ natural variability found in Flinder's Reef.

337 Figure 5, illustrates the high and low latitude surface Ω_{Ar} . We only highlight Ω_{Ar} , as Ω_{Ca} is similar
338 to that of Ω_{Ar} . ~~Aragonite and calcite are forms of biogenic calcium carbonate. Foraminifera and~~
339 ~~coccolithophorids are composed of calcite the less soluble form of biogenic calcium carbonate, while~~

340 corals and pteropods are composed of aragonite. Hector accurately simulates the decline in saturations
341 (Ω_{Ar} and Ω_{Ca}) from 1850-2300 under RCP8.5 to CMIP5 and observations (Figure 5). Since the
342 preindustrial, surface low (high) latitude Ω_{Ar} decreased by 0.4 (0.3) units, with similar rates for CMIP5.
343 Rates of change over a 14 year period for Hector (-0.007 yr^{-1}) agree well with CMIP5 (-0.006 yr^{-1}) and
344 HOT (-0.010 yr^{-1}). As with pH, Hector is slightly higher than the CMIP5 Ω_{Ar} median but closer to the
345 observational record. Hector accurately simulates the change in Ω_{Ar} (-0.0090 yr^{-1}) compared to
346 observations (Table 6). Repeated oceanographic surveys in the Pacific Ocean have observed an average
347 $0.34\% \text{ yr}^{-1}$ decrease in the saturation state of surface seawater with respect to aragonite and calcite over
348 a 14-year period (1991-2005) (Feely et al., 2012); the average decrease in Hector is between $0.19\% \text{ yr}^{-1}$
349 and $0.25\% \text{ yr}^{-1}$. Saturation levels of Ω_{Ar} decrease rapidly over the next 100 years in both the high and
350 low latitude. Hector accurately captures the decline in saturations with low RMSE values for Ω_{Ar} . Under
351 RCP8.5 Hector projects that low latitude Ω_{Ar} will decrease to 2.2 by 2100 and down to 1.4 by 2300. The
352 high latitude oceans will be understaturated with respect to aragonite by 2100 and will drop down to
353 0.7 by 2300.

354
355 Saturations of both Ar and Ca decrease rapidly over the next 100 years in both the high and low
356 latitude. Hector accurately captures the decline in saturations with low RMSE values for both Ω_{Ar} (0.027)
357 and Ω_{Ca} (0.012). Under RCP8.5 Hector projects that low latitude Ω_{Ar} will decrease by 1.85 units to 2.21 by
358 2100 and by 2.6 units to 1.42 by 2300. For low latitude Ω_{Ca} , Hector projects low latitude Ω_{Ca} decrease by
359 2.88 units to 3.34 by 2100 and by over 4.09 units to 2.31 by 2300. A lowering of Ω_{Ar} from approximately
360 4 to 3 is predicated to lead to significant reductions in calcification rates in tropical reefs. In agreement
361 with Roy et al., (2015) and Ricke et al., (2013) by the end of the 21st century (2072 under RCP8.5) Hector
362 projects that the low latitude oceans Ω_{Ar} will drop below 3, well outside of the preindustrial values of Ω_{Ar}
363 >3.5 and the Ω_{Ca} high latitude will drop below 2. While at the end of the 21st Century, the oceans are

364 not undersaturated ($\Omega < 1$), the threshold for biogenic carbonate precipitation is species dependent and
365 can be significantly higher than 1 when combined with other factors. For example, some coral reef
366 communities need to develop in waters that have $\Omega_{Ar} > 3.3$ (Pelejero et al., 2010; Hoegh-Guldberg et al.,
367 2007; Kleypas et al 1999). The lowest observed Ω_{Ar} found in individual coral reef ecosystems was $\Omega_{Ar} =$
368 2.85 (Shamberger et al., 2011).

369 **Figure 7** highlights the relationship between surface temperature change and surface carbonate
370 chemistry changes across the 4 RCPs. Under RCP 8.5, for every one degree of surface warming surface
371 in Hector (CMIP5), pH declines by 0.107 (0.122) units (change relative to 1990-1999 plotted over 2006-
372 2100). This is similar to Bopp et al., who calculated a global change of 0.125 units/ $^{\circ}$ C across the CMIP5
373 models. Under RCP 8.5, for every one degree of surface warming surface in Hector (CMIP5), aragonite
374 saturation declines by 0.438 (0.432) units. For calcite saturations (not shown), for every one degree of
375 surface warming in Hector (CMIP5), calcite saturations decrease by 0.681 (0.673) units. Our high latitude
376 ocean box warms faster than the rest of the world's oceans, therefore, we chose to combine both the
377 high and low latitude oceans into one global value, also making it easier to compare to Bopp et al.
378 (2013). This is an area of future research to better emulate the high latitude surface ocean temperature.

379 Lastly, Figure 68 highlights pH and Ω_{Ar} projections under all four RCPs from 1850 to 2300. Over
380 the last 20 years, both pH and Ω_{Ar} have declined sharply and will continue to decline under RCP 4.5, 6.0
381 and 8.5, outside of their preindustrial and present day values. These RCPs represent a range of possible
382 future scenarios, with ocean pH varying between 8.15 and 7.46 for the high latitude and Ω_{Ar} varying
383 between 1.94 and 0.60. High latitude Ω_{Ar} saturation levels presently are much lower than the low
384 latitude and reach under saturation before the end of the century. Even under a best case best-case
385 scenario, RCP 2.6, low latitude pH will drop to 7.73 by 2100 and to 7.43 by 2300 and, with Ω_{Ar}
386 saturations will remaining well outside of present day values.

387 **3.2 Model Parameter Sensitivity**

388
389 Parametric sensitivities vary across are different between pH and Ω_{Ar} , and between the high and
390 low latitude surface ocean boxes. ~~We compare the percentage change from the reference and the~~
391 ~~perturbation cases in 2005, 2100, and 2300.~~ The reference, RCP8.5, refers to the tuned set of
392 parameters found in Hector v1.1, resulting in Figures 2-6. Global pH is fairly insensitive to the values of
393 the input parameters used, while Ω_{Ar} is slightly more sensitive (Table 7). For example, a 10% change in
394 input parameters results in range from 0.0 - 0.21% in pH and 0.0 - 7.18% in Ω_{Ar} . In comparison a 10%
395 parameter change results in a range from 0.0 - 10.3% in global atmospheric temperature change. In the
396 near term (from 2005-2100) the calculation of pH is sensitive to salinity and beta (terrestrial CO₂
397 fertilization), while on longer time scales (to 2300), pH is the most sensitive to changes in Q_{10} (terrestrial
398 respiration temperature response). Global Ω_{Ar} is most sensitive to changes in salinity in both the near
399 and long term. Similar to pH, Ω_{Ar} becomes more sensitive to changes in Q_{10} in the long term.

400 Interestingly, the high and low latitude surface boxes respond differently to the same change in
401 input parameters. pH in the high latitude surface ocean is most sensitive to changes in wind stress in
402 the near term. ~~pH~~ In contrast, in the low latitude surface ocean pH is most sensitive to changes in
403 salinity and beta in the near term. Ω_{Ar} in the both the high and low latitude surface ocean is most
404 sensitive to changes in salinity and temperature in both the near and long term. However, Ω_{Ar} in the low
405 latitude surface ocean becomes more sensitive to Q_{10} after 2100.

408 **54. Discussion**

409 The marine carbonate system is projected to undergo significant changes under the RCPs. pCO_2
410 and DIC are increasing rapidly as atmospheric [CO₂] continues to rise under RCP 4.5, 6.0 and 8.5. pH, and
411 Ω_{Ar} are decreasing rapidly outside of observations and are projected to continue to decrease under all

412 scenarios (Figure 6). Only under RCP 2.6 do pH and Ω_{Ar} values begin to increase back towards present
413 values. A lowering of Ω_{Ar} from approximately 4.0 to 3.0 is predicted to lead to significant reductions in
414 calcification rates in tropical reefs (Kleypas et al., 1999; Silverman et al., 2009). In agreement with Roy et
415 al., (2015) and Ricke et al., (2013) by the end of the 21st century (2072 under RCP8.5) Hector projects
416 that the low latitude oceans Ω_{Ar} will drop below 3.0, well outside of the preindustrial values of $\Omega_{Ar} > 3.5$.
417 At the end of the 21st Century, the high latitude oceans are close to undersaturation ($\Omega < 1$) (Figure 6).
418 However, the threshold for biogenic carbonate precipitation is species dependent and may be
419 significantly higher than 1.0 when combined with other factors. For example, some coral reef
420 communities need to develop in waters with $\Omega_{Ar} > 3.3$ (Pelejero et al., 2010; Hoegh-Guldberg et al.,
421 2007; Kleypas et al 1999). Accounting for seasonal variations in the Ω_{Ar} saturation levels may move this
422 time of under saturation forward by 17 ± 10 years (Sasse et al., 2015). Due to Hector's time step of 1
423 year, we may be overestimating the time when ocean acidification reaches a critical threshold. We also
424 note that other factors such as eutrophication, river discharge, and upwelling will likely increase the
425 probability that coastal regions will experience the effects of ocean acidification sooner than the
426 projected open ocean values in Hector (Ekstrom et al., 2015).

427 In this study we find that pH is fairly insensitive to most parametric changes, but in both the
428 near and long term, pH is sensitive to those parameters that indirectly affecting atmospheric $[CO_2]$ (Q_{10}
429 and beta). Changes in both beta and Q_{10} , (the terrestrial CO_2 fertilization effect and the respiration
430 temperature response, respectively) are responsible for the uptake and release of carbon within the
431 land. Uncertainties in the land carbon cycle have been attributed to uncertainties in future CO_2
432 projections within the CMIP5 models (Friedlingstein et al., 2014). Therefore, uncertainties in the land
433 carbon cycle will also have implications for the marine carbonate system.

434 Beta is the terrestrial CO_2 fertilization effect and Q_{10} is the respiration temperature response in
435 the land carbon cycle. Global Ω_{Ar} saturation levels are most sensitive to changes in salinity. Within

436 Hector, salinity is directly involved in the calculation of $[Ca^{2+}]$; is used to determine Ω_{Ar} . Typically the
437 carbonate system is normalized to changes in salinity to understand the chemical changes within the
438 system, instead we show that Ω_{Ar} may be sensitive not only to future changes in atmospheric $[CO_2]$ but
439 also sensitive to changes in precipitation and evaporation. This may be important, as studies suggest
440 significant changes in precipitation patterns under a changing climate (Held and Soden, 2006; Liu and
441 Allan, 2013).

442 The dynamics of ocean uptake of CO_2 are strongly dependent on the rate of downward
443 transport of CO_2 laden waters from the surface ocean to depth. Climate feedbacks on the carbonate
444 system resulting from changes in ocean circulation are neglected in Hector, as the model ~~and~~ holds
445 ocean circulation constant in time. CMIP5 models project a weakening in the Atlantic meridional
446 overturning circulation by an average of 36% under RCP8.5 by 2100 (Cheng et al., 2013). We investigate
447 the sensitivity of the carbonate system to a change in ocean circulation by varying the thermohaline
448 circulation parameter (T_t in Figure 1). This parameter represents a portion of the high latitude surface to
449 the deep ocean circulation. A 10% change in ocean circulation (T_t) results in a <4% change in air-sea
450 fluxes and moderate effects on surface pH and Ω_{Ar} . If we scale up from a 10% change in T_t to a 36%
451 change, which is projected from the CMIP5 models, it may result in a roughly 14% change in the air-sea
452 fluxes of carbon to the surface ocean and a 0.3% and 5.0% change in pH and Ω_{Ar} , respectively.

453

454 **6. Conclusions**

455 We developed a simple, open-source, object oriented carbon cycle climate model, Hector, that
456 reliably reproduces the median of the CMIP5 climate variables (Hartin et al., 2015). The ocean
457 component presented in this study, ~~directly~~ calculates the upper ocean carbonate system (pCO_2 , DIC,
458 pH, Ω_{Ar} , Ω_{Ca}). Under all four RCPs, pH and Ω_{Ar} ~~and Ω_{Ca}~~ decrease significantly outside of their
459 preindustrial values matching both observations and CMIP5. In the near future the open ocean and

460 coral reef communities are likely to experience pH and carbonate saturation levels unprecedented in the
461 ~~potentially the~~ last 2 million years (Hönisch et al., 2009).

462 ~~Even at a best case scenario, RCP 2.6 (Figure 8), pH will drop to 7.73 by 2100 and to 7.43~~
463 ~~by 2300. This may result in drastic changes to marine ecosystems in particular the CaCO₃-secreting~~
464 ~~organism. For example, the rate of coral reef building decreases, calcification rates of planktonic~~
465 ~~coccolithophores and foraminifera decreases, changes in trophic level interactions and ecosystems, have~~
466 ~~all been proposed to be potential consequences of ocean acidification (Cooley and Doney, 2009;~~
467 ~~Silverman et al., 2009; Fabry et al., 2008; Riebesell et al., 2000).~~

468 ~~Organic carbon, CaCO₃ sediment interactions, and changes in ocean circulation are not currently~~
469 ~~simulated within Hector. We assume negligible CaCO₃ interactions on hundred year time scales;~~
470 ~~however, this is a necessary component under interglacial and glacial cycles. We neglect any climate~~
471 ~~feedbacks on the carbon cycle resulting from changes in ocean circulation. CMIP5 models show up to a~~
472 ~~60% decrease in the Atlantic meridional overturning circulation by 2100 (Cheng et al., 2013). While this~~
473 ~~may have a significant impact on the uptake and transport of carbon, in Hector v1.1, we hold ocean~~
474 ~~circulation constant with time and accurately simulate global variables out to 2100 with a slight bias~~
475 ~~after 2100. We also note that other factors such as eutrophication, river discharge, and upwelling will~~
476 ~~likely increase the probability that coastal regions will experience the effects of ocean acidification~~
477 ~~sooner than the projected open ocean values in Hector (Ekstrom et al., 2015).~~

478 This study is timely because the CMIP5 archive, includes a large suite of ESMs that contained
479 dynamic biogeochemistry, allowing us to study future projections of the marine carbon cycle. Rather
480 than running the ~~earth system models~~ESMs, we can use Hector to quickly emulate the CMIP5 median
481 for projection studies under different emission pathways and sensitivity analyses of the marine
482 carbonate system. Overall, we find that parameters directly involved changes in atmospheric [CO₂] have
483 the most impact on future changes in ocean acidification. Due to Hector's simplistic nature and fast

484 execution times, Hector has the potential to be a critical tool to the decision-making, scientific, and
485 integrated assessment communities, allowing for further understanding of future changes to the marine
486 carbonate system.

487 **Appendix A: Model Description – carbon cycle**

488 The carbon component in Hector contains three carbon reservoirs: a single well-mixed atmosphere,
489 a land component and an ocean component. The change in atmospheric carbon is a function of the
490 anthropogenic emissions (F_A), land-use change emissions (F_{LC}), and atmosphere-ocean (F_O) and
491 atmosphere-land (F_L) carbon fluxes. The default model time step is 1 year.

$$\frac{dC_{atm}(t)}{dt} = F_A(t) + F_{LC}(t) - F_O(t) - F_L(t) \quad (1)$$

492 The terrestrial cycle in Hector contains vegetation, detritus, and soil, all linked to each other and
493 the atmosphere by first-order differential equations. Vegetation net primary production is a function of
494 atmospheric CO₂ and temperature. Carbon flows from the vegetation to detritus to soil and loses
495 fractions of carbon to heterotrophic respiration on the way. An ‘earth’ pool debits carbon emitted as
496 anthropogenic emissions, allowing a continual mass-balance check across the entire carbon cycle.

497 Atmosphere-land fluxes at time t are calculated by:

$$F_L(t) = \sum_{i=1}^n NPP_i(t) - RH_i(t) \quad (2)$$

498 where NPP is the net primary production and RH is the heterotrophic respiration summed over user-
499 specified n groups (i.e., latitude bands, political units, or biomes) (Hartin et al 2015).

500

501 **Appendix B: Ocean Carbonate Chemistry**

502 The ocean’s inorganic carbon system is solved via a series of equations

503 Modified from Zeebe and Wolf-Gladrow (2001). TA and DIC are used to calculate the other variables
504 of the carbonate system:

$$DIC * \left(\frac{K_1}{[H^+]} + 2 \frac{K_1 K_2}{[H^+]^2} \right) = \left(TA - \frac{K_B B_T}{K_B + [H^+]} - \frac{K_W}{[H^+]} + [H^+] \right) * \left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2} \right) \quad (1)$$

505 This equation results in a higher order polynomial equation for H^+ , in which the roots (1 positive, 4
 506 negative) are solved for. Once H^+ is solved for, pH, pCO_2 , HCO_3^- , and CO_3^{2-} can be determined. We
 507 ignore the nonideality of CO_2 in air and therefore use the partial pressure of CO_2 instead of the fugacity
 508 of CO_2 . Fugacity is slightly lower by ~0.3% compared to pCO_2 (Riebesell et al., 2009; Sarmiento and
 509 Gruber, 2006).

$$[CO_2^*] = \frac{DIC}{\left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right)} \quad (2)$$

$$pCO_2 = \frac{[CO_2^*]}{K_H} \quad (3)$$

$$[HCO_3^-] = \frac{DIC}{\left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right)} \quad (4)$$

$$[CO_3^{2-}] = \frac{DIC}{\left(1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1 K_2}\right)} \quad (5)$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[CO_2]} \quad (6)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (7)$$

510 K_1 and K_2 are the first and second acidity constants of carbonic acid from Mehrbach et al. (1973) and
 511 refit by Lueker et al. (2000).

$$K_B = \frac{[H^+][B(OH)_4^-]}{[B(OH)_3]} \quad (8)$$

512 K_B is the dissociation constant of boric acid from DOE (1994).

$$K_W = \frac{[H^+]}{[OH^-]} \quad (9)$$

513 K_W is the dissociation constant of water from Millero (1995).

$$K_{sp} = [Ca^{2+}] * [CO_3^{2-}] \quad (10)$$

514 K_{sp} of aragonite and calcite is calculated from Mucci, (1983).

515

516 For those equations with multiple coefficients:

517

518 ~~For those equations with multiple coefficients please see the references listed below.~~

519 1) K_H and K_0 are similar equations calculating Henry's constant or the solubility of CO_2 , ~~however~~ but

520 they return different units ($mol\ kg^{-1}\ atm^{-1}$ and $mol\ L^{-1}\ atm^{-1}$) (see Weiss, 1974 for equations and

521 coefficients). K_H is used to solve pCO_2 while K_0 is used to solve air-sea fluxes of CO_2 .

522 2) The Schmidt number is taken from Wanninkhof (1992) for coefficients of CO_2 in seawater.

523 ~~3)~~ $[Ca^{2+}]$ ($mol\ kg^{-1}$) is calculated from Riley and Rongudai (1967).

524 3)

525

526

527 **Acknowledgements**

528 This research is based on work supported by the US Department of Energy. The Pacific Northwest

529 National Laboratory is operated for DOE by Battelle Memorial Institute under contract DE-AC05-

530 76RL01830.

531

532 **Author Contributions**

533 C.Hartin designed and carried out the experiments. C. Hartin, B.Bond-Lamberty, and P.Patel
534 developed the model code. A.Mundra process data, design and prepare figures. C.Hartin prepared
535 the manuscript with contributions from all co-authors.

536 **Table 1:** Description and values of ocean parameters ~~constant~~ in Hector.

Description	Value	Value Notes
Area of ocean	3.6e14 m ²	Knox and McElroy, 1984
Fractional area of HL	0.15	Sarmiento and Toggweiler, 1984
Fractional area of LL	0.85	Sarmiento and Toggweiler, 1984
Thickness of surface ocean	100 m	Knox and McElroy, 1984
Thickness of intermediate ocean	900 m	
Thickness of deep ocean	2677 m	Total <u>ocean</u> depth 3777m
Volume of HL	5.4e15 m ³	
Volume of LL	3.06e16 m ³	
Volume of IO	3.24e17 m ³	
Volume of DO	9.64e17 m ³	
Surface Area of HL	5.4e13 m ²	
Surface Area of LL	3.06e14 m ²	
Salinity HL and LL	34.5	
Thermohaline circulation (T _T)	7.2e7 m ³ s ⁻¹	Tuned to give ~100 Pg C flux from surface to deep
High latitude circulation (T _H)	4.9e7 m ³ s ⁻¹	Tuned to give ~100 Pg C flux from surface to deep
Water mass exchange (intermediate to deep - E _{ID})	1.25e7 m ³ s ⁻¹	Lenton (2000); Knox and McElroy (1984)
Water mass exchange (low latitude to intermediate - E _{IL})	2.08e7 m ³ s ⁻¹	Lenton (2000); Knox and McElroy (1984)
Wind speed HL and LL	6.7 m s ⁻¹	Takahashi et al., 2009; Liss and Merlivat, 1986

537

538
539

Table 2: CMIP5 ESM models used in this study containing ocean carbonate parameters. Ω_{Ar} , Ω_{Ca} were calculated from the model sea surface temperature, sea surface salinity, and CO_3 concentrations.

Model	Model Name	Parameters (RCP 8.5)
BCC-cm1-1	Beijing Climate Center Climate System Model	pCO_2^* , temperature
BNU-ESM	Beijing Normal University Earth System Model	pCO_2
CanESM2	Second Generation Canadian Earth System Model	DIC, pH, salinity
CESM1-BGC	Community Earth System Model version 1, Biogeochemistry	CO_3 , DIC, pH, salinity
CMCC-CESM	Centro Euro-Mediterraneo sui Cambiamenti Climatici - Carbon Earth System Model	pCO_2 , temperature, CO_3 , DIC, pH, salinity
CNRM-CM5	National Center for Meteorological Research Climate Model version 5	CO_3 , DIC
GFDL-ESM2G	Geophysical Fluid Dynamic Laboratory Earth System Model with GOLD ocean component	pCO_2 , temperature, pH, salinity
GFDL-ESM2M	Geophysical Fluid Dynamic Laboratory Earth System Model with MOM ocean component	pCO_2 , temperature, CO_3 , pH, DIC, salinity
GISS-E2-H-CC	Goddard Institute for Space Studies – HYCOM ocean model with interactive carbon cycle	pCO_2 , temperature, DIC, salinity
GISS-E2-R-CC	Goddard Institute for Space Studies – Russell ocean model with interactive carbon cycle	pCO_2 , temperature, DIC, salinity
HadGEM2-CC	Hadley Centre Global Environmental Model, version 2 (Carbon Cycle)	pCO_2 , temperature, CO_3 , DIC, pH, salinity
HadGEM2-ES	Hadley Centre Global Environmental Model, version 2 (Earth System)	pCO_2 , temperature, CO_3^* , DIC*, pH, salinity
IPSL-CM5A-LR	L’Institut Pierre-Simon Laplace Coupled Model, version 5A, low resolution	Temperature*, CO_3^* , DIC*, pH*, salinity*
IPSL-CM5A-MR	L’Institut Pierre-Simon Laplace Coupled Model, version 5A, medium resolution	Temperature, CO_3 , DIC, pH, salinity
IPSL-CM5B-LR	L’Institut Pierre-Simon Laplace Coupled Model, version 5A, new atmospherical physic at low resolution	Temperature, CO_3 , DIC, pH, salinity
MIROC-ESM	Model for Interdisciplinary Research on Climate, Earth System Model	pCO_2 , temperature, salinity
MIROC-ESM-CHEM	Model for Interdisciplinary Research on Climate, Earth System Model, with atmospheric chemistry model	pCO_2 , temperature, salinity

MPI-ESM-LR	Max Planck Institute Earth System Model, low resolution	pCO ₂ *, temperature*, CO ₃ *, DIC*, pH*, salinity*
MPI-ESM-MR	Max Planck Institute Earth System Model, medium resolution	pCO ₂ , temperature, CO ₃ , DIC, pH, salinity
MRI-ESM1	Meteorological Research Institute of Japan – Earth System Model	pCO ₂ , temperature
NorESM1-ME	Norwegian Earth System Model, version 1, intermediate resolution	pCO ₂ , temperature, CO ₃ , DIC, pH, salinity

540 * Variable output to 2300.

541 ~~† solved for after spinup and then remains constant~~
 542 ~~* represents those parameters found within the input file~~ **Table 3:** Observational time-series
 543 information and carbonate parameters from each location.
 544

Time-Series Site	Location	Time-Series Length	Reference	Ocean Carbon Measurements Parameters	Data Access
BATS	Sargasso Sea	1988-2011	Bates, 2007	TA, DIC	http://www.bios.edu/research/projects/bats
HOT	North Pacific	1988-2011	Dore et al., 2007	TA, DIC, pH, pCO ₂ , Ω _{Ar} , Ω _{Ca}	http://hahana.soest.hawaii.edu/hot/hot_jgofs.html
ESTOC	Canary Islands	1995-2009	Gonzalez-Davila, 2009	TA, pH, pCO ₂	http://www.eurosites.info/estoc.php
Iceland Sea	Iceland Sea	1985-2013	Olafsson, 2007a	DIC, pCO ₂	http://cdiac.ornl.gov/oceans/Moorings/Iceland_Sea.html
Irminger Sea	Irminger Sea	1983-2013	Olafsson, 2007b	DIC, pCO ₂	http://cdiac.ornl.gov/oceans/Moorings/Irminger_Sea.html
Flinders Reef	Coral Sea	1708-1988	Pelejero et al., 2005	pH, Ω _{Ar}	ftp://ftp.ncdc.noaa.gov/pub/data/paleo/coral/west_pacific/great_barrier/flinders2005.txt

545

546 **Table 4:** Model validation metrics for the a) high latitude and b) low latitude ocean carbonate variables
 547 comparing Hector to CMIP5 from 1850-2004.

548

a)	RMSE	R2	Bias
DIC	10.00	0.26	47.10
pCO ₂	2.65	0.98	-31.78
pH	0.004	0.975	0.061
Ω _{Ar}	0.01	0.98	0.37
Ω _{Ca}	0.02	0.98	0.58

b)	RMSE	R2	Bias
DIC	6.50	0.76	101.28
pCO ₂	3.43	0.98	-4.62
pH	0.004	0.966	0.025
Ω _{Ar}	0.02	0.97	0.36
Ω _{Ca}	0.03	0.97	0.53

549

550

551

552 **Table 5:** Absolute values and rates of change per year (Δ) for the a) high and b) low latitude surface
 553 ocean between 1850, 2100 and 2300 under RCP 8.5 for DIC (μmol kg⁻¹), pCO₂ (μatm), total pH (unitless),
 554 Ω_{Ar} (unitless) and Ω_{Ca} (unitless).

a)	DIC			pCO ₂			pH			Ω _{Ar}			Ω _{Ca}		
	1850	2100	2300	1850	2100	2300	1850	2100	2300	1850	2100	2300	1850	2100	2300
Hector	2107.5	2258.1	2335.5	244.7	816.6	1732.1	8.23	7.76	7.46	2.2	1.0	0.6	3.5	1.5	0.9
Δ		0.602	0.387		2.29	4.58		-	-		-	-0.002		-0.008	-0.003
								0.0019	0.0015		0.0048				
CMIP5	2104.50	2175.79	2243.41	271.62	871.00	1903.82	8.17	7.70	7.38	1.82	0.75	0.44	2.90	1.20	0.70
Δ		0.285	0.34		2.40	5.16		-	-		-	-		-	-
								0.0019	0.0016		0.0012	0.0016		0.0068	0.0025

555

b)	DIC			pCO ₂			pH			Ω _{Ar}			Ω _{Ca}		
	1850	2100	2300	1850	2100	2300	1850	2100	2300	1850	2100	2300	1850	2100	2300
Hector	2073.9	2264.1	2357.6	294.7	879.6	1766.5	8.17	7.77	7.50	4.1	2.2	1.4	6.2	3.3	2.1
Δ		0.76	0.47		2.34	4.43		-	-		-	-		-	-0.006
								0.0016	0.0014		0.0076	0.0040		0.0116	
CMIP5	1997.57	2163.16	2298.89	290.47	930.92	1965.23	8.16	7.73	7.45	3.75	2.00	1.36	5.77	3.02	2.04
Δ		0.66	0.68		2.56	5.17		-	-		-	-		-	-0.0049
								0.0011	0.0014		0.0070	0.0032		0.0110	

556

557 **Table 6:** Trends and standard error for carbonate system taken from Bates et al., (2014) . Global
 558 carbonate system parameters for Hector and CMIP5 from 1988-2014.
 559

	DIC ($\mu\text{mol kg}^{-1} \text{yr}^{-1}$)	pCO_2 ($\mu\text{atm yr}^{-1}$)	pH (yr^{-1})	Ω_{Ar} (yr^{-1})
BATS	1.37 ± 0.07	1.69 ± 0.11	-0.0017 ± 0.0001	-0.0095 ± 0.0007
HOT	1.78 ± 0.12	1.72 ± 0.09	-0.0016 ± 0.0001	-0.0084 ± 0.0011
ESTOC	1.09 ± 0.10	1.92 ± 0.24	-0.0018 ± 0.0002	-0.0115 ± 0.0023
Iceland Sea	1.22 ± 0.27	1.29 ± 0.36	-0.0014 ± 0.0005	-0.0018 ± 0.0027
Irminger Sea	1.62 ± 0.35	2.37 ± 0.49	-0.0026 ± 0.0006	-0.0080 ± 0.0040
Hector	0.90	1.82	-0.0017	-0.0089
CMIP5	0.68	1.77	-0.0018	-0.0074

560
 561

562 **Table 7:** Percentage change from reference (RCP8.5) for two Hector outputs a) global pH and b) global
 563 Ω_{Ar} for a $\pm 10\%$ change in eight model parameters. Results are shown for three years, 2005, 2100 and
 564 2300.
 565

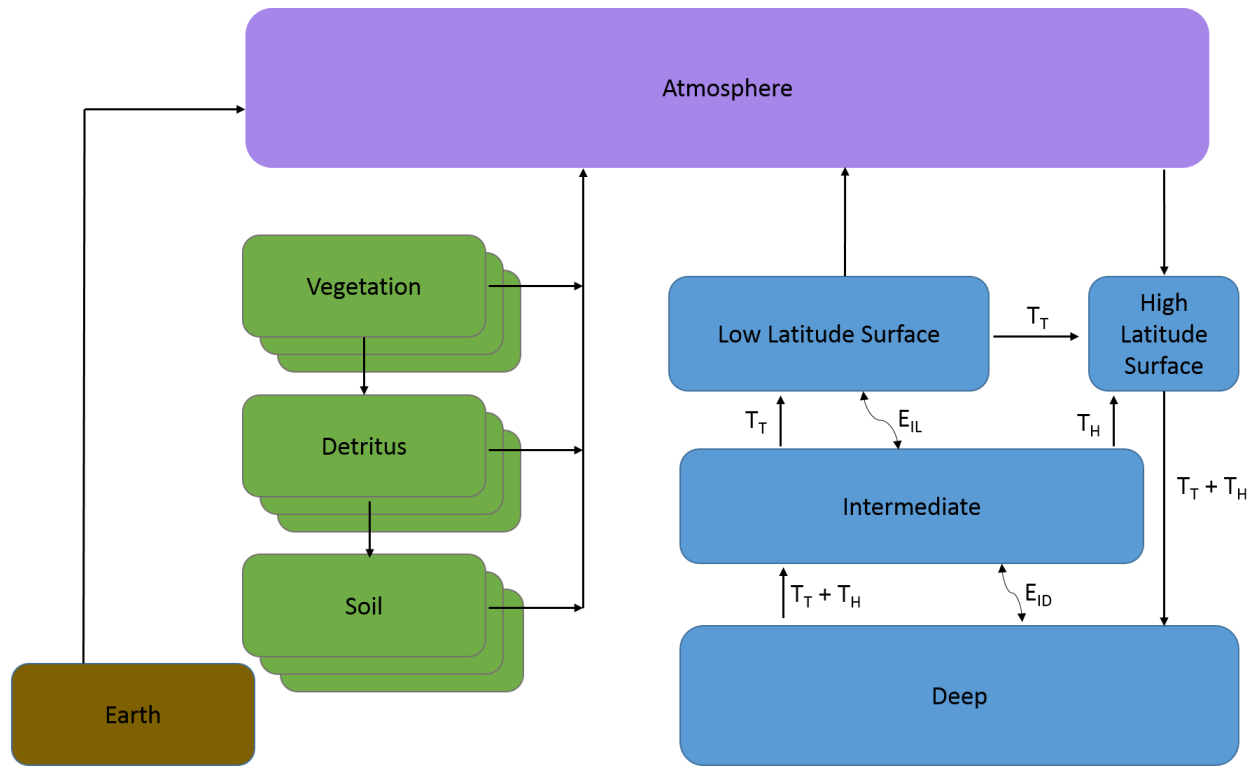
a) Year	Parameter	+10% change	-10% change
2005	Albedo	0.00	-0.00
2100		0.00	-0.00
2300		0.00	-0.00
2005	Beta	0.03	-0.03
2100		0.10	-0.10
2300		0.10	-0.10
2005	Circulation	0.02	-0.02
2100		0.06	-0.06
2300		0.09	-0.10
2005	Q_{10}	-0.01	0.01
2100		-0.06	0.07
2300		-0.18	0.21
2005	Salinity	-0.05	0.08
2100		0.03	0.01
2300		0.11	-0.07
2005	Climate Sensitivity	-0.01	0.01
2100		-0.05	0.05
2300		-0.14	0.15
2005	Surface ocean temperature	-0.00	0.00
2100		-0.01	0.01
2300		-0.02	0.03
2005	Wind Stress	-0.02	0.03
2100		-0.05	0.07
2300		-0.09	0.07

566

b) Year	Parameter	+10% change	-10% change
2005	Albedo	0.01	-0.00
2100		0.01	-0.01
2300		-0.00	0.00
2005	Beta	0.38	-0.40
2100		1.33	-1.34
2300		1.38	-1.35
2005	Circulation	0.41	-0.45
2100		1.01	-1.05
2300		1.48	-1.55
2005	Q ₁₀	-0.09	0.10
2100		-0.87	0.95
2300		-2.40	3.00
2005	Salinity	3.80	-4.28
2100		5.60	-5.89
2300		7.17	-7.18
2005	Climate Sensitivity	0.07	-0.07
2100		0.55	-0.56
2300		0.43	-0.27
2005	Surface ocean temperature	2.07	-1.99
2100		2.41	-2.29
2300		2.43	-2.27
2005	Wind Stress	-0.18	0.25
2100		-0.65	0.88
2300		-1.13	0.88

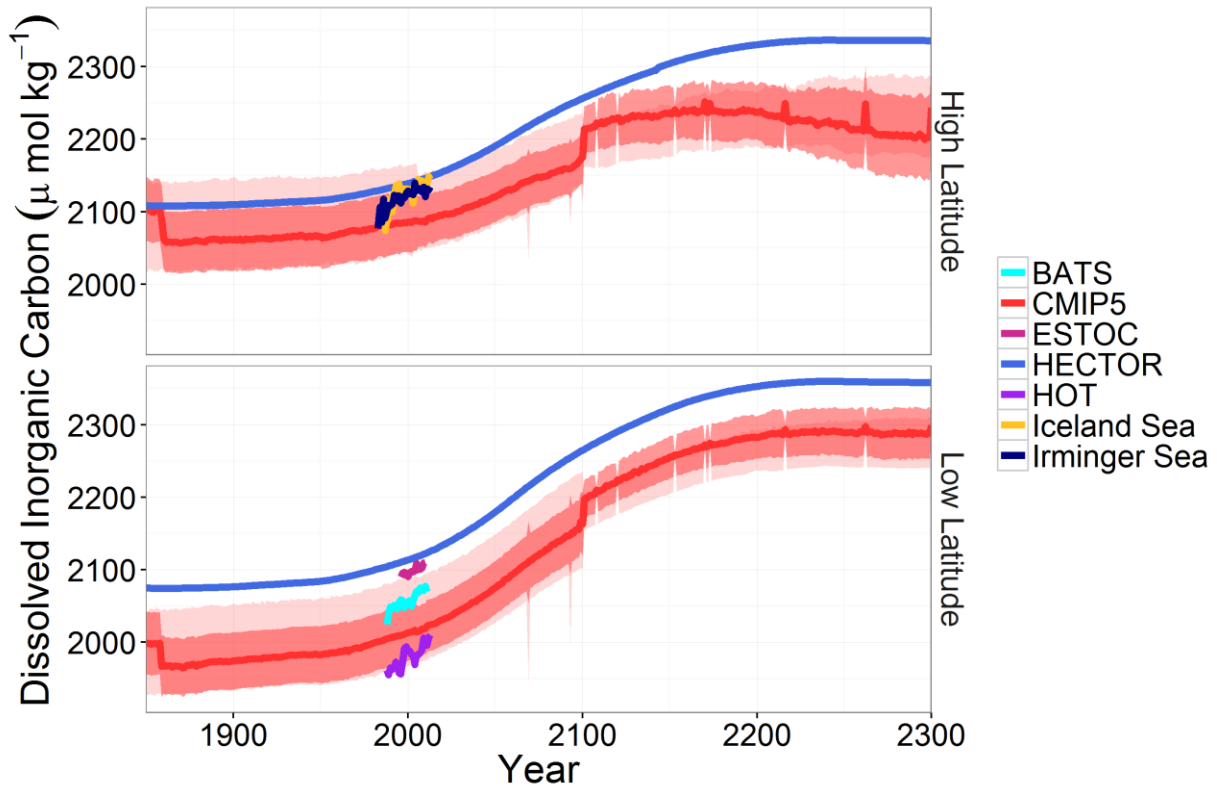
567

568 **Figure 1:** Representation of the carbon cycle in Hector. The atmosphere consists of one well-mixed box,
 569 connected to the surface ocean via air-sea fluxes of carbon. The terrestrial component consists of user
 570 defined biomes or regions for vegetation, detritus, and soil. The earth pool is continually debited to act
 571 as a mass balance check on the carbon cycle (Hartin et al., 2015). The ocean consists of four boxes, with
 572 advection (represented by solid arrows) and water mass exchange (represented by dashed arrows)
 573 simulating thermohaline circulation. The marine carbonate system is solved for in the high and low
 574 latitude surface boxes. At steady state, there is a flux of carbon from the atmosphere to the high
 575 latitude surface box, while the low-latitude surface ocean releases carbon to the atmosphere.
 576



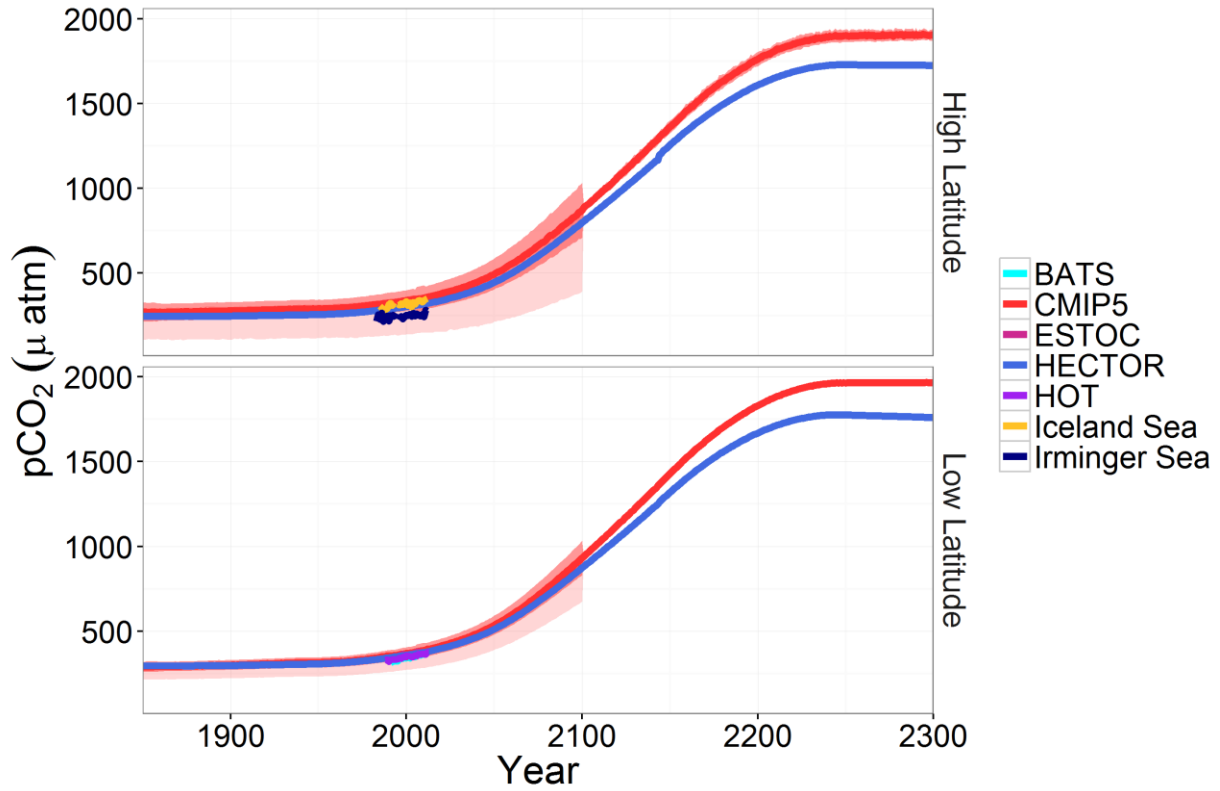
577

578 **Figure 2:** Dissolved inorganic carbon (DIC) for high (top) and low latitude (bottom) surface ocean under
 579 RCP 8.5; Hector (blue), CMIP5 median, standard deviation, and model range (red, $n = 15$ (1850-2100)
 580 and $n = 3$ (2101-2300)); and observations from BATS (teal), ESTOC (pink), HOT (purple), Iceland (yellow)
 581 and Irminger Sea (navy). Note a doubling of CO_2 , from preindustrial values occurs around 2050.
 582



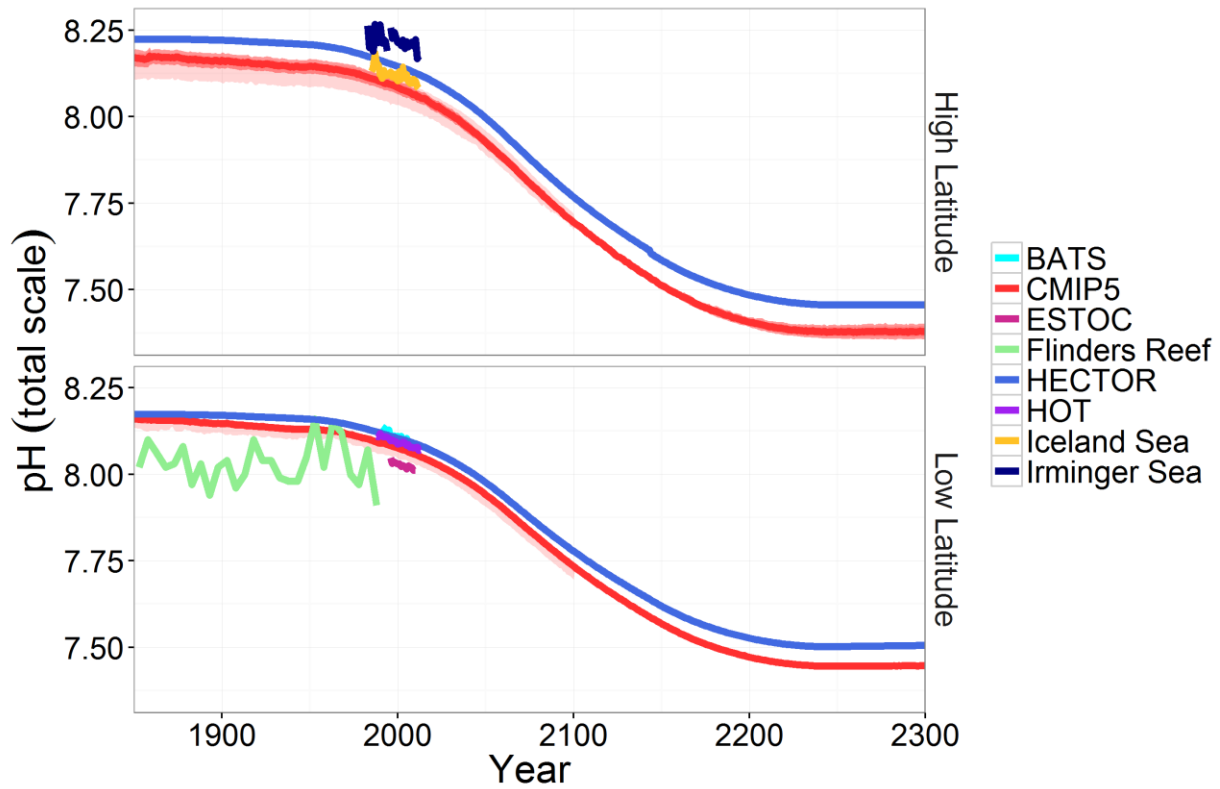
583

584 **Figure 3:** pCO₂ for high (top) and low latitude (bottom) surface ocean under RCP 8.5; Hector (blue),
 585 CMIP5 median, standard deviation, and model range (red, *n* = 15 (1850-2100) and *n* = 2 (2101-2300));
 586 and observations from BATS (teal), HOT (purple), ESTOC (pink), Iceland (yellow) and Irminger Sea (navy).



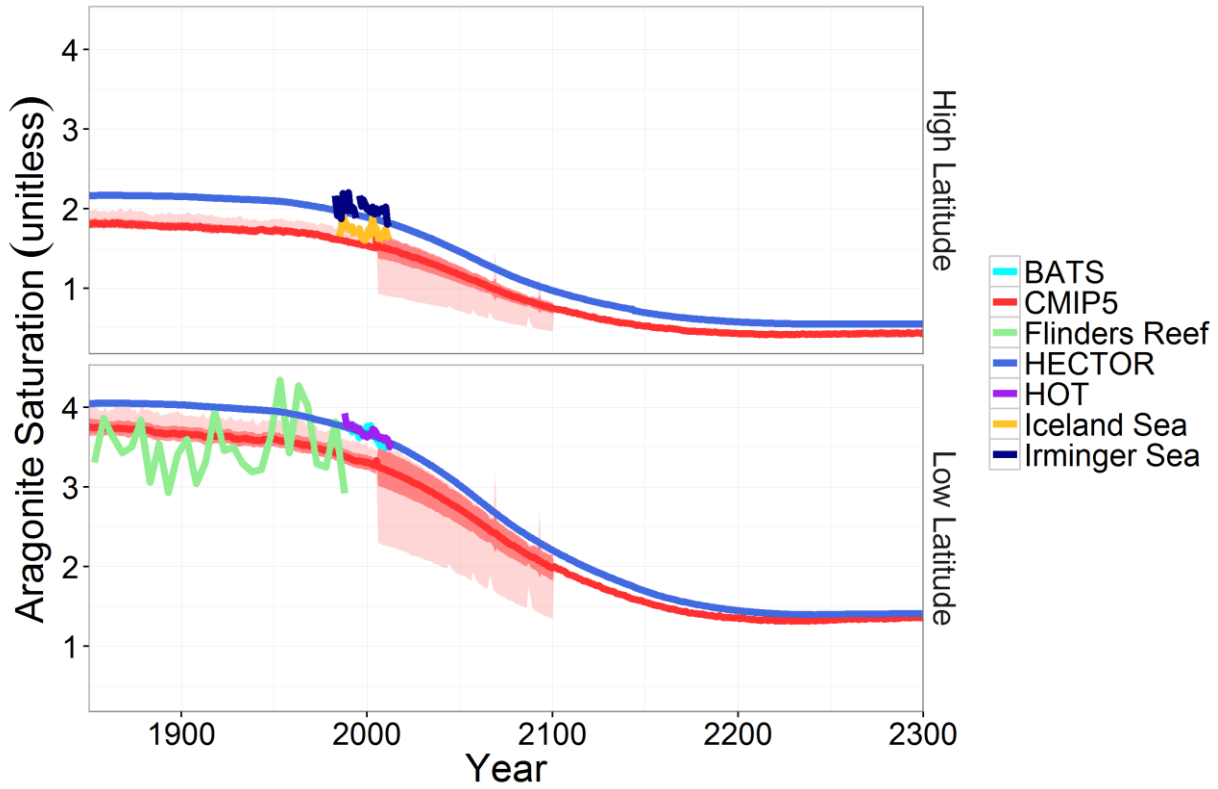
587

588 **Figure 4:** pH for high (top) and low latitude (bottom) surface ocean under RCP 8.5; Hector (blue), CMIP5
 589 median, standard deviation, and model range (red, $n = 13$ (1850-2100) and $n= 2$ (2101-2300)); and
 590 observations from BATS (teal), ESTOC (pink), HOT (purple) Flinder's Reef (green), Iceland (yellow) and
 591 Irminger Sea (navy).



592

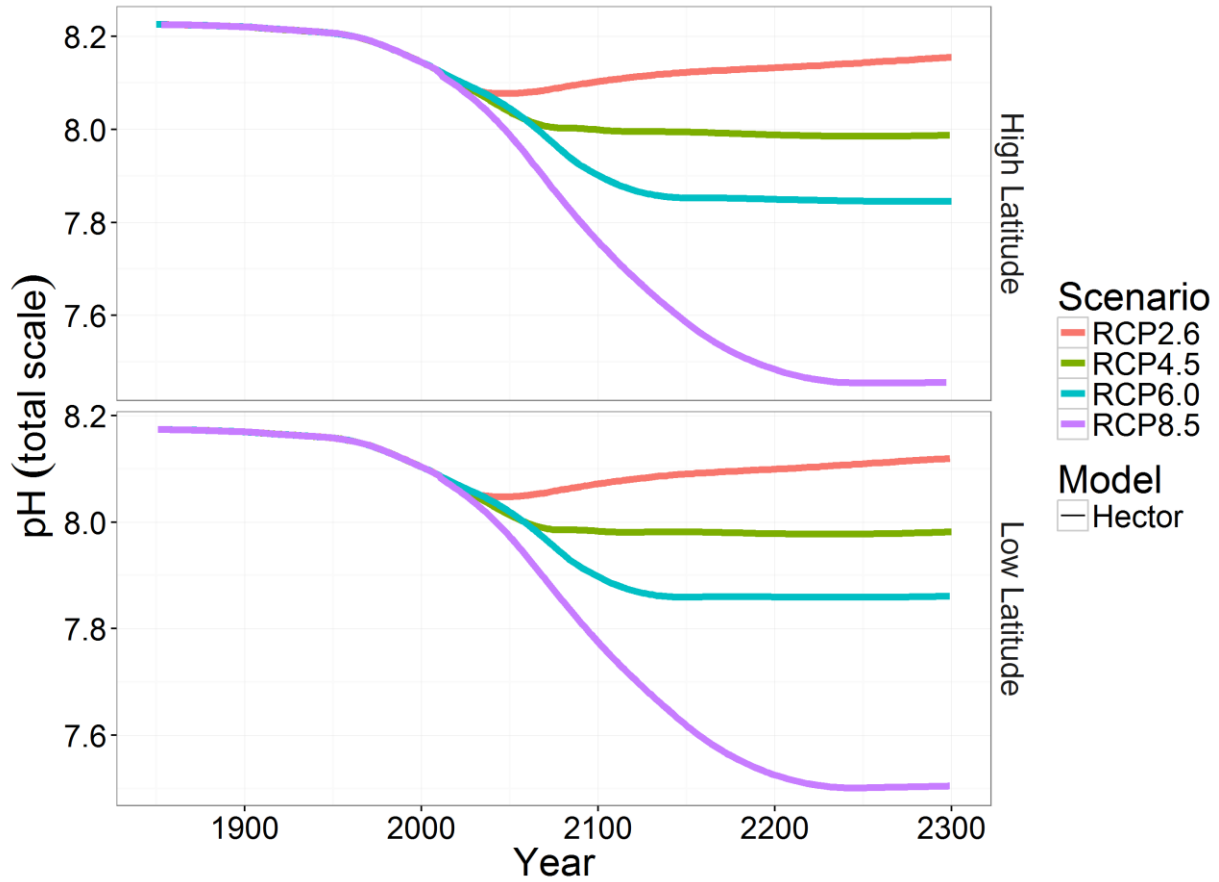
593 **Figure 5:** Aragonite saturation (Ω_{Ar}) for high (top) and low latitude (bottom) surface ocean under RCP
 594 8.5; Hector (blue), CMIP5 median, standard deviation, and model range (red, $n = 10$ (1850-2100) and $n=$
 595 2 (2101-2300)); and observations from BATS (teal), HOT (purple) and Flinder's Reef (green).



596

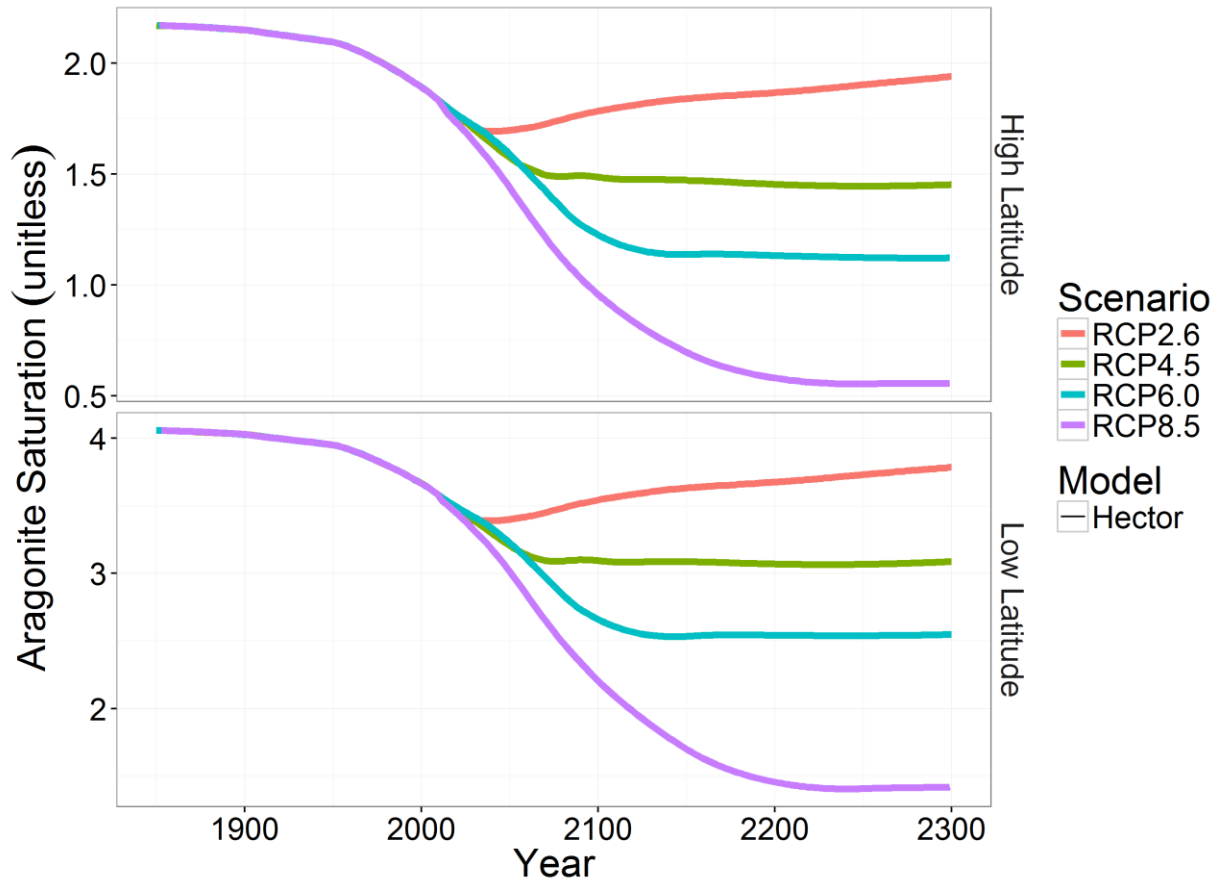
597

598 **Figure 6:** High and low latitude a) pH and b) aragonite saturation (Ω_{Ar}) time series for Hector from 1850-
 599 2300 for RCP 2.6 (red), RCP 4.5 (green), RCP 6.0 (teal) and RCP 8.5 (purple). Note that even under a
 600 strongly mitigated scenario (RCP 2.6), both Ω_{Ar} and pH at 2300 are still lower than preindustrial values.



601
 602

603



604

605

606 REFERENCES

- 607 Albright, R., Langdon, C., and Anthony, K. R. N.: Dynamics of seawater carbonate chemistry, production,
608 and calcification of a coral reef flat, central Great Barrier Reef, *Biogeosciences*, 10, 6747-6758,
609 10.5194/bg-10-6747-2013, 2013.
- 610 Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K., Matsumoto, K.,
611 Munhoven, G., Montenegro, A., and Tokos, K.: Atmospheric Lifetime of Fossil Fuel Carbon Dioxide,
612 *Annual Review of Earth and Planetary Sciences*, 37, 117-134,
613 doi:10.1146/annurev.earth.031208.100206, 2009.
- 614 Bates, N. R.: Interannual variability of the oceanic CO₂ sink in the subtropical gyre of the North Atlantic
615 Ocean over the last 2 decades, *Journal of Geophysical Research: Oceans*, 112, C09013,
616 10.1029/2006JC003759, 2007.
- 617 Bates, N. R., Astor, Y. M., Church, M. J., Currie, K., Dore, J. E., Gonzalez-Davila, M., Lorenzoni, L., Muller-
618 Karger, F., Olafsson, J., and Santana-Casiano, J. M.: A time-series view of changing ocean chemistry due
619 to ocean uptake of anthropogenic CO₂ and ocean acidification, *Oceanography*, 27, 126-141,
620 <http://dx.doi.org/10.5670/oceanog.2014.16>, 2014.
- 621 Bopp, L., Resplandy, L., Orr, J. C., Doney, S. C., Dunne, J. P., Gehlen, M., Halloran, P., Heinze, C., Ilyina, T.,
622 Séférian, R., Tjiputra, J., and Vichi, M.: Multiple stressors of ocean ecosystems in the 21st century:
623 projections with CMIP5 models, *Biogeosciences Discuss.*, 10, 3627-3676, 10.5194/bgd-10-3627-2013,
624 2013.
- 625 Byrne, R. H., Mecking, S., Feely, R. A., and Liu, X.: Direct observations of basin-wide acidification of the
626 North Pacific Ocean, *Geophysical Research Letters*, 37, L02601, 10.1029/2009GL040999, 2010.
- 627 Caldeira, K., Jain, A. K., and Hoffert, M. I.: Climate Sensitivity Uncertainty and the Need for Energy
628 Without CO₂ Emission, *Science*, 299, 2052-2054, 10.1126/science.1078938, 2003.
- 629 Cheng, W., Chiang, J. C. H., and Zhang, D.: Atlantic Meridional Overturning Circulation (AMOC) in CMIP5
630 Models: RCP and Historical Simulations, *Journal of Climate*, 26, 7187-7197, 10.1175/JCLI-D-12-00496.1,
631 2013.
- 632 Cooley, S. R., and Doney, S. C.: Anticipating ocean acidification's economic consequences for commercial
633 fisheries, *Environmental Research Letters*, 4, 024007, 2009.
- 634 DOE: Handbook of methods for the analysis of the various parameters of the carbon dioxide system in
635 sea water, edited by: Dickson, A. G., and Goyet, C., ORNL/CDIAC-74, 1994.
- 636 Doney, S. C.: The Growing Human Footprint on Coastal and Open-Ocean Biogeochemistry, *Science*, 328,
637 1512-1516, 10.1126/science.1185198, 2010.
- 638 Dore, J. E., Lukas, R., Sadler, D. W., Church, M. J., and Karl, D. M.: Physical and biogeochemical
639 modulation of ocean acidification in the central North Pacific, *Proceedings of the National Academy of*
640 *Sciences*, 106, 12235-12240, 10.1073/pnas.0906044106, 2009.
- 641 Ekstrom, J. A., Suatoni, L., Cooley, S. R., Pendleton, L. H., Waldbusser, G. G., Cinner, J. E., Ritter, J.,
642 Langdon, C., van Hooijdonk, R., Gledhill, D., Wellman, K., Beck, M. W., Brander, L. M., Rittschof, D.,
643 Doherty, C., Edwards, P. E. T., and Portela, R.: Vulnerability and adaptation of US shellfisheries to ocean
644 acidification, *Nature Clim. Change*, 5, 207-214, 10.1038/nclimate2508
- 645 <http://www.nature.com/nclimate/journal/v5/n3/abs/nclimate2508.html#supplementary-information>,
646 2015.
- 647 Fabry, V. J., Seibel, B. A., Feely, R. A., and Orr, J. C.: Impacts of ocean acidification on marine fauna and
648 ecosystem processes, *ICES Journal of Marine Science: Journal du Conseil*, 65, 414-432,
649 10.1093/icesjms/fsn048, 2008.

650 Feely, R. A., Sabine, C. L., Lee, K., Berelson, W., Kleypas, J., Fabry, V. J., and Millero, F. J.: Impact of
651 Anthropogenic CO₂ on the CaCO₃ System in the Oceans, *Science*, 305, 362-366,
652 10.1126/science.1097329, 2004.

653 Feely, R. A., Doney, S. C., and Cooley, S. R.: Ocean acidification: present conditions and future changes in
654 a high-CO₂ world, *Oceanography*, 22, 36-47, <http://dx.doi.org/10.5670/oceanog.2009.95>, 2009.

655 Feely, R. A., Sabine, C. L., Byrne, R. H., Millero, F. J., Dickson, A. G., Wanninkhof, R., Murata, A., Miller, L.
656 A., and Greeley, D.: Decadal changes in the aragonite and calcite saturation state of the Pacific Ocean,
657 *Global Biogeochemical Cycles*, 26, GB3001, 10.1029/2011GB004157, 2012.

658 Friedlingstein, P., Meinshausen, M., Arora, V. K., Jones, C. D., Anav, A., Liddicoat, S. K., and Knutti, R.:
659 Uncertainties in CMIP5 Climate Projections due to Carbon Cycle Feedbacks, *Journal of Climate*, 27, 511-
660 526, 10.1175/JCLI-D-12-00579.1, 2014.

661 Fry, C. H., Tyrrell, T., Hain, M. P., Bates, N. R., and Achterberg, E. P.: Analysis of global surface ocean
662 alkalinity to determine controlling processes, *Marine Chemistry*, 174, 46-57,
663 <http://dx.doi.org/10.1016/j.marchem.2015.05.003>, 2015.

664 Gehlen, M., Séférian, R., Jones, D. O. B., Roy, T., Roth, R., Barry, J., Bopp, L., Doney, S. C., Dunne, J. P.,
665 Heinze, C., Joos, F., Orr, J. C., Resplandy, L., Segsneider, J., and Tjiputra, J.: Projected pH reductions by
666 2100 might put deep North Atlantic biodiversity at risk, *Biogeosciences Discuss.*, 11, 8607-8634,
667 10.5194/bgd-11-8607-2014, 2014.

668 Glotter, M., Pierrehumbert, R., Elliott, J., Matteson, N., and Moyer, E.: A simple carbon cycle
669 representation for economic and policy analyses, *Climatic Change*, 126, 319-335, 10.1007/s10584-014-
670 1224-y, 2014.

671 Hansell, D. A., and Carlson, C. A.: Marine dissolved organic matter and the carbon cycle, *Oceanography*,
672 14, 41-49, 2001.

673 Hartin, C. A., Patel, P., Schwarber, A., Link, R. P., and Bond-Lamberty, B. P.: A simple object-oriented and
674 open-source model for scientific and policy analyses of the global climate system – Hector v1.0, *Geosci.*
675 *Model Dev.*, 8, 939-955, 10.5194/gmd-8-939-2015, 2015.

676 Held, I. M., and Soden, B. J.: Robust Responses of the Hydrological Cycle to Global Warming, *Journal of*
677 *Climate*, 19, 5686-5699, doi:10.1175/JCLI3990.1, 2006.

678 Hönisch, B., Hemming, N. G., Archer, D., Siddall, M., and McManus, J. F.: Atmospheric Carbon Dioxide
679 Concentration Across the Mid-Pleistocene Transition, *Science*, 324, 1551-1554,
680 10.1126/science.1171477, 2009.

681 IPCC: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth
682 Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Stocker, T. F., D. Qin,
683 G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley Cambridge
684 University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp., 2013.

685 Irvine, P. J., Sriver, R. L., and Keller, K.: Tension between reducing sea-level rise and global warming
686 through solar-radiation management, *Nature Clim. Change*, 2, 97-100, doi:10.1038/nclimate1351, 2012.

687 Joos, F., Plattner, G.-K., Stocker, T. F., Marchal, O., and Schmittner, A.: Global Warming and Marine
688 Carbon Cycle Feedbacks on Future Atmospheric CO₂, *Science*, 284, 464-467,
689 10.1126/science.284.5413.464, 1999.

690 Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J.,
691 Mordy, C., and Peng, T. H.: A global ocean carbon climatology: Results from Global Data Analysis Project
692 (GLODAP), *Global Biogeochemical Cycles*, 18, GB4031, 10.1029/2004GB002247, 2004.

693 Kleypas, J. A., Buddemeier, R. W., Archer, D., Gattuso, J.-P., Langdon, C., and Opdyke, B. N.: Geochemical
694 Consequences of Increased Atmospheric Carbon Dioxide on Coral Reefs, *Science*, 284, 118-120,
695 10.1126/science.284.5411.118, 1999.

696 Knox, F., and McElroy, M. B.: Changes in Atmospheric CO₂: Influence of the Marine Biota at High
697 Latitude, *J. Geophys. Res.*, 89, 4629-4637, 10.1029/JD089iD03p04629, 1984.

698 Kump, L. R., Bralower, T. R., and Ridgwell, A. J.: Ocean Acidification in Deep Time, *Oceanography*, 22, 94-
699 107, 2009.

700 Le Quéré, C., Takahashi, T., Buitenhuis, E. T., Rödenbeck, C., and Sutherland, S. C.: Impact of climate
701 change and variability on the global oceanic sink of CO₂, *Global Biogeochemical Cycles*, 24, GB4007,
702 10.1029/2009GB003599, 2010.

703 Le Quéré, C., Andres, R. J., Boden, T., Conway, T., Houghton, R. A., House, J. I., Marland, G., Peters, G. P.,
704 van der Werf, G. R., Ahlström, A., Andrew, R. M., Bopp, L., Canadell, J. G., Ciais, P., Doney, S. C., Enright,
705 C., Friedlingstein, P., Huntingford, C., Jain, A. K., Jourdain, C., Kato, E., Keeling, R. F., Klein Goldewijk, K.,
706 Levis, S., Levy, P., Lomas, M., Poulter, B., Raupach, M. R., Schwinger, J., Sitch, S., Stocker, B. D., Viovy, N.,
707 Zaehle, S., and Zeng, N.: The global carbon budget 1959–2011, *Earth Syst. Sci. Data*, 5, 165-185,
708 10.5194/essd-5-165-2013, 2013.

709 Lenton, T. M.: Land and ocean carbon cycle feedback effects on global warming in a simple Earth system
710 model, *Tellus B*, 52, 1159-1188, 10.1034/j.1600-0889.2000.01104.x, 2000.

711 Liu, C., and Allan, R. P.: Observed and simulated precipitation responses in wet and dry regions 1850–
712 2100, *Environmental Research Letters*, 8, 034002, 2013.

713 Lueker, T. J., Dickson, A. G., and Keeling, C. D.: Ocean pCO₂ calculated from dissolved inorganic carbon,
714 alkalinity, and equations for K₁ and K₂; validation based on laboratory measurements of CO₂ in gas and
715 seawater at equilibrium, *Marine Chemistry*, 70, 105-119, 2000.

716 Matear, R. J., and Hirst, A. C.: Climate change feedback on the future oceanic CO₂ uptake, *Tellus B*, 51,
717 722-733, 10.1034/j.1600-0889.1999.t01-1-00012.x, 1999.

718 Mehrbach, C., Culbertson, C. H., Hawley, J. E., and Pytkowicz, R. M.: Measurement of the apparent
719 dissociation constants of carbonic acid in seawater at atmospheric pressure, *Limnol. Oceanogr.*, 18, 897-
720 907, 1973.

721 Millero, F. J.: Thermodynamics of the carbon dioxide system in the oceans, *Geochimica et Cosmochimica*
722 *Acta*, 59, 661-677, 10.1016/0016-7037(94)00354-O, 1995.

723 Moss, R. H., Edmonds, J. A., Hibbard, K. A., Manning, M. R., Rose, S. K., van Vuuren, D. P., Carter, T. R.,
724 Emori, S., Kainuma, M., Kram, T., Meehl, G. A., Mitchell, J. F. B., Nakicenovic, N., Riahi, K., Smith, S. J.,
725 Stouffer, R. J., Thomson, A. M., Weyant, J. P., and Wilbanks, T. J.: The next generation of scenarios for
726 climate change research and assessment, *Nature*, 463, 747-756, doi:10.1038/nature08823, 2010.

727 Mucci, A.: The solubility of calcite and aragonite in seawater at various salinities, temperatures and at
728 one atmosphere pressure, *Amer. J. of Science*, 283, 781-799, 1983.

729 Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N.,
730 Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar,
731 R. G., Plattner, G.-K., Rodgers, K. B., Sabine, C. L., Sarmiento, J. L., Schlitzer, R., Slater, R. D., Totterdell, I.
732 J., Weirig, M.-F., Yamanaka, Y., and Yool, A.: Anthropogenic ocean acidification over the twenty-first
733 century and its impact on calcifying organisms, *Nature*, 437, 681-686, doi:10.1038/nature04095, 2005.

734 Pelejero, C., Calvo, E., McCulloch, M. T., Marshall, J. F., Gagan, M. K., Lough, J. M., and Opdyke, B. N.:
735 Preindustrial to Modern Interdecadal Variability in Coral Reef pH, *Science*, 309, 2204-2207,
736 10.1126/science.1113692, 2005.

737 Pietsch, S. A., and Hasenauer, H.: Evaluating the self-initialization procedure for large-scale ecosystem
738 models, *Global Change Biology*, 12, 1-12, 2006.

739 Riahi, K., Rao, S., Krey, V., Cho, C., Chirkov, V., Fischer, G., Kindermann, G., Nakicenovic, N., and Rafaj, P.:
740 RCP 8.5—A scenario of comparatively high greenhouse gas emissions, *Climatic Change*, 109, 33-57,
741 10.1007/s10584-011-0149-y, 2011.

742 Ricciuto, D. M., Davis, K. J., and Keller, K.: A Bayesian calibration of a simple carbon cycle model: The role
743 of observations in estimating and reducing uncertainty, *Global Biogeochemical Cycles*, 22, GB2030,
744 10.1029/2006GB002908, 2008.

745 Ricke, K. L., Orr, J. C., Schneider, K., and Caldeira, K.: Risks to coral reefs from ocean carbonate chemistry
746 changes in recent earth system model projections, *Environmental Research Letters*, 8, 034003, doi:
747 10.1088/1748-9326/8/3/034003, 2013.

748 Riebesell, U., Zondervan, I., Rost, B., Tortell, P. D., Zeebe, R. E., and Morel, F. M. M.: Reduced
749 calcification of marine plankton in response to increased atmospheric CO₂, *Nature*, 407, 364-367, 2000.

750 Riebesell, U., Körtzinger, A., and Oeschlies, A.: Sensitivities of marine carbon fluxes to ocean change,
751 *Proceedings of the National Academy of Sciences*, 106, 20602-20609, 10.1073/pnas.0813291106, 2009.

752 Riley, J. P., and Tongudai, M.: The major cation/chlorinity ratios in sea water, *Chemical Geology*, 2, 263-
753 269, [http://dx.doi.org/10.1016/0009-2541\(67\)90026-5](http://dx.doi.org/10.1016/0009-2541(67)90026-5), 1967.

754 Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S.,
755 Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A. F.: The Oceanic
756 Sink for Anthropogenic CO₂, *Science*, 305, 367-371, 10.1126/science.1097403, 2004.

757 Sabine, C. L., Feely, R., Wanninkhof, R., Takahashi, T., Khatiwala, S., and Park, G.-H.: The global ocean
758 carbon cycle, In *State of the Climate in 2010, Global Oceans. Bull. Am. Meteorol. Soc.*, 92, S100-S108,
759 10.1175/1520-0477-92.6.S1, 2011.

760 Sarmiento, J. L., and Toggweiler, J. R.: A new model for the role of the oceans in determining
761 atmospheric PCO₂, *Nature*, 308, 621-624, 1984.

762 Sarmiento, J. L., and Le Quéré, C.: Oceanic Carbon Dioxide Uptake in a Model of Century-Scale Global
763 Warming, *Science*, 274, 1346-1350, 10.1126/science.274.5291.1346, 1996.

764 Sarmiento, J. L., and Gruber, N.: *Ocean Biogeochemical Dynamics*, edited by: Press, P. U., Princeton NJ,
765 2006.

766 Sasse, T. P., McNeil, B. I., Matear, R. J., and Lenton, A.: Quantifying the influence of CO₂ seasonality on
767 future aragonite undersaturation onset, *Biogeosciences*, 12, 6017-6031, 10.5194/bg-12-6017-2015,
768 2015.

769 Senior, C. A., and Mitchell, J. F. B.: The time-dependence of climate sensitivity, *Geophysical Research*
770 *Letters*, 27, 2685-2688, 10.1029/2000GL011373, 2000.

771 Siegenthaler, U., and Joos, F.: Use of a simple model for studying oceanic tracer distributions and the
772 global carbon cycle, *Tellus B*, 44, 186-207, 10.1034/j.1600-0889.1992.t01-2-00003.x, 1992.

773 Silverman, J., Lazar, B., Cao, L., Caldeira, K., and Erez, J.: Coral reefs may start dissolving when
774 atmospheric CO₂ doubles, *Geophysical Research Letters*, 36, n/a-n/a, 10.1029/2008GL036282, 2009.

775 Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., Hales, B.,
776 Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D. C. E., Schuster, U., Metzl, N., Yoshikawa-
777 Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J.,
778 Arnarson, T. S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C. S., Delille, B., Bates, N. R.,
779 and de Baar, H. J. W.: Climatological mean and decadal change in surface ocean pCO₂, and net sea-air
780 CO₂ flux over the global oceans, *Deep Sea Research Part II: Topical Studies in Oceanography*, 56, 554-
781 577, <http://dx.doi.org/10.1016/j.dsr2.2008.12.009>, 2009.

782 Taylor, K. E., Stouffer, R. J., and Meehl, G. A.: An Overview of CMIP5 and the Experiment Design, *Bulletin*
783 *of the American Meteorological Society*, 93, 485-498, 10.1175/BAMS-D-11-00094.1, 2012.

784 van Vuuren, D., Elzen, M. J., Lucas, P., Eickhout, B., Strengers, B., Ruijven, B., Wonink, S., and Houdt, R.:
785 Stabilizing greenhouse gas concentrations at low levels: an assessment of reduction strategies and costs,
786 *Climatic Change*, 81, 119-159, 10.1007/s10584-006-9172-9, 2007.

787 Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, *Journal of*
788 *Geophysical Research: Oceans*, 97, 7373-7382, 10.1029/92JC00188, 1992.

789 Weiss, R. F.: Carbon dioxide in water and seawater: the solubility of a non-ideal gas, *Marine Chemistry*,
790 2, 203-215, 10.1016/0304-4203(74)90015-2, 1974.

791 Woosley, R. J., Millero, F. J., and Wanninkhof, R.: Rapid anthropogenic changes in CO₂ and pH in the
792 Atlantic Ocean: 2003–2014, *Global Biogeochemical Cycles*, 30, 70-90, 10.1002/2015GB005248, 2016.

793 Yates, K., and Halley, R.: CO₂ concentration and pCO₂ thresholds for calcification and dissolution on
794 the Molokai reef flat, Hawaii, Biogeosciences Discussions, 3, 123-154, 2006.

795 Zeebe, R. E., and Wolf-Gladrow, D.: CO₂ in Seawater: Equilibrium, Kinetics, Isotopes, Elsevier,
796 Amsterdam, 2001.

797

798