PLEASE NOTE THAT THIS DOCUMENT COMBINES THE AUTHOR'S RESPONSE AND THE ANNOTATED MANUSCRIPT

Anonymous Referee #1

Review of Gehlen et al.

We thank the reviewer for his comments and suggestions. We reply to each point below.

This manuscript uses a suite of climate models to predict future changes in pH in deep waters of the North Atlantic. These are then superimposed on the distribution of seamounts and canyons to predict biodiversity threats in 2100. Approximately 17% of the seafloor below 500 m is predicted to experience pH declines of 0.2 pH units. The tremendous stability of conditions in deep water and historical changes recorded in the geologic record, suggest this amount of pH decline is potentially dangerous to deep-ocean biodiversity.

The modeling component of this paper seems sound, although this is not my area of expertise. Work by others including some of the co-authors have predicted seafloor changes in temperature, pH, POC flux and oxygen (Bopp et al. 2013, and pointed out impacts on deep biodiversity (Mora et al. 2013). This paper might want to devote more space to acknowledging and reviewing that earlier work.

We acknowledge the study by Mora et al. (2013) in the introduction section by adding a sentence. Line 106 reads: ”The study complements assessments by Bopp et al. (2013) and Mora et al. (2013) which evaluated large-scale average pH reductions in response to the same RCP pathways, but without a detailed discussion of spatial patterns and their link to circulation.”

Has a similar approach been taken with warming or oxygen?

Mora and co-workers took a multiple stressors approach including temperature and oxygen. Cocco et al. (2013) investigated changes in CO_2 and O_2 in response to a high emission scenario in a set of Earth System Models. We chose to focus on pH only. The North Atlantic is an area of deep water formation and the water column is well oxygenated at present and, according to model projections, will remain so in the future.

Please consider the following issues and suggestions:

Please provide the justification for selection of a 500 m upper limit of analysis. This is not an upper limit for deep-water corals or sponges is it?

The selection of 500 m as an upper limit for analysis follows from model considerations. This study uses output from coarse resolution global ocean models that do not fully resolve processes on the shelf or upper slope. Digitised topographies as used in general circulation models usually average over fine resolution digital data sets by averaging the fine resolution data for use in the coarse grid. Therefore, along the continental shelf break model topographies at around 500 m depth would include also shallower areas, but these cannot be resolved as such.

It seems that a significant component of deep biodiversity may fall between 200-500 m.

We agree that there is significant biodiversity between 200 and 500m. However, we wish to maintain the upper limit due to the reasons as outlined above.

Do the effects of a 0.2 or 0.3 pH unit decline depend on the baseline or starting point?

We thank the reviewer for raising this issue.

The pH is defined as the negative logarithm of the hydrogen ion concentration ($[H^+]$). From the basic properties of logarithms it follows that the difference in pH equals the logarithm of the ratio of hydrogen ion concentrations. For a given pH change, the change in $[H^+]$, $\Delta[H^+]$ is a is a linear function of the initial hydrogen ion concentration ($[H^+]_i$) as $\Delta[H^+] = [H^+]_i ((1/10^{\Delta pH}) - 1)$. Hence, the larger the initial $[H^+]$, the larger the perturbation. We illustrate this point with an additional supplementary figure representing on panel (a) the observed pH at depth and on panel (b) the change in $[H^+]$ corresponding to a pH reduction by 0.2 units.

The dependence of the absolute change in $[H^+]$ on the starting point cautions against a simplistic analysis of pH changes, be it in numerical or laboratory experiments. Contrasting shallow and deep environments highlight that absolute changes in $[H^+]$ are amplified at depth, that is for environments of low natural variability.

In addition to adding a new figure to the supplementary material, we inserted the following text on 186: "The pH is defined as the negative logarithm of the hydrogen ion concentration ($[H^+]$). From the basic properties of logarithms it follows that the difference in pH equals the logarithm of the ratio of hydrogen ion concentrations. For a given pH change, the change in $[H^+]$, $\Delta[H^+]$, is a linear function of the initial hydrogen ion concentration ($[H^+]_i$) as $\Delta[H^+] = [H^+]_i\ ((1/10^{\Delta pH}) - 1)$. Hence, the larger the initial $[H^+]$, the larger the perturbation (Fig. S1). Contrasting shallow and deep environments highlights that absolute changes in $[H^+]$ are amplified at depth or any threshold, that is for environments of low natural variability."

What are the absolute pH values at 500, 1000, 2000 m in the deep Atlantic Ocean?

The absolute mean values of pH in the deep Atlantic:

500 m = 8.015 ; 1000 m = 7.999; 2000 m = 7.994

We decided not to include a pH profile. Its evolution with depth is illustrated on Figure S1, top panel.

Is anything known about natural pH variability in the deep Atlantic and how this changes with water depth, latitude or region?

To our best knowledge, the only published time-series data resolving seasonal variability of pH at different depths across the water column (from 10 m to 3500 m) is by González-Dávila et al. (2010).

There is limited discussion of the mechanisms by which pH might affect biodiversity. Is it through effects on calcification? Acid-base regulation? Energetics (which are discussed somewhat)?

We amended this section of the discussion (lines 397 to 417) so it is more specific and says : "Our knowledge of the ecology of deep benthic communities is still limited and impacts of pH changes on these communities are difficult to evaluate owing to lack of experimental and observational data. Rapid changes in pH will likely lead to disruption of extracellular acid-base balance, impedance of calcification and other physiological effects in deep-water organisms, and whatever acclimation is required may have increased energetic costs (Widdicombe and Spicer, 2008) – e.g. for metabolism/maintenance, growth, reproduction – and could extend to increases in mortality of both adults and juveniles. Changes at the individual and population level will inevitably lead to more widespread ecosystem and community level changes and potential shifts in biodiversity (Hendriks et al., 2010) and ecosystem functioning (Danovaro et al., 2008). Biodiversity reductions could arise from a loss of species, functional, or even taxonomic groups sensitive to pH change. The ecological implications of pH change could be more severe if keystone or habitat-forming species are impacted (Widdicombe and Spicer, 2008), which seems likely (Guinotte et al., 2006). These effects may be likely exacerbated in the presence of other stressors (Walther et al., 2009), such as global warming and projected reductions in deep-sea food supply (Bopp et al., 2013), as well as elevated resource exploitation and pollution. In particular, reductions in food supply to deep benthic communities are projected to result in a decrease in biomass and a shift towards smaller sized organisms (Jones et al., 2013). These changes will modify energy transfer rates through benthic food webs and may leave communities more susceptible to pH reductions. We propose these and future model projections to be taken into account when defining long-term preservation and management approaches to deep-sea ecosystems."

If corals are of major concern, please discuss what a 0.2 or 0.3 pH decline corresponds to with regard to aragonite saturation state.

We chose to mention corals as merely an example group of interest among many, and deliberately chose not to assess changes in aragonite saturation state to maintain an ecosystem-wide focus. Several studies have addressed decreases in saturation state and impacts on cold-water corals. We intend, with this study, to broaden the discussion on impacts of ocean acidification to other communities than calcifiers. The tight control of pH at the cellular scale is an important prerequisite of proper cell functioning and mechanisms of pH control are ubiquitous across many taxa. pH is thus a master variable for biological systems.

It would be appropriate to also calculate and map changes in Omega (aragonite) and determine what fraction of the seamounts or canyons will be exposed to specific omega decline levels. It may be that we have more knowledge of saturation state requirements than pH tolerances.

As stated above, impacts of decreasing aragonite saturation states on calcifiers were the focus of numerous previous studies. From the point of view of biological conservation, pH is the more universal environmental variable as it is not specific to a particular group of organisms.

Several assumptions seem to be made: One is that there is no adaptation potential. . .. Over the next 85 years – is this what the authors believe?

To our knowledge, there is very little (if any information) available on the adaptation potential of deep sea fauna to ocean acidification. There is a pressing need for further biological studies. We do not want to speculate, but rather answer a precise question that is 'likelihood of pH changes affecting deep seafloor'

Do they expect any synergistic interaction with declining oxygen?

This study focuses on the deep North Atlantic, a well-ventilated sub-region of the world ocean. Despite a projected increase in stratification, the region will remain well-oxygenated in the future. This is explicitly stated in the revised version by adding "The North Atlantic is a well-ventilated region of the world ocean and, despite a projected increase in stratification, will remain well-oxygenated in the future (Bopp et al., 2013)." (line 104)

Additional points and considerations that could enhance this work.

a) Are there actual biodiversity data to show that seamount and canyon biodiversity is higher than other settings (continental slope, mid-ocean ridges, vents, basins, fjords, carbonate mounds, or other features).

We do not infer that the biodiversity of seamounts and canyons is higher than in other settings. We assess pH reductions over the seafloor without discrimination of particular habitats first. We then selected these features as representative examples of specific deep sea environments.

We modified the last sentences of the final paragraph of the introduction (lines 110 to 117) section is modified to: "Future multi-model projections of pH changes over the seafloor are analysed with reference to this threshold and without discrimination of particular habitats first. Next, model results are put into the perspective of ecosystem conservation by evaluating changes in pH against the distribution of seamounts and deep-sea canyons. These features are known as sites of high-biodiversity deep-sea ecosystems, such as cold-water corals and sponge communities (ICES, 2007; Clark MR et al., 2010; De Leo et al., 2010) and are selected as representative examples of deep sea environments. "

b) What fraction of the deep-ocean corals occur on canyons and seamounts as opposed to other features (slopes, mounds, mid ocean ridges etc.)?

We did not detail the distribution of cold water corals, as they were not the focus of this study.

Would the major messages change if these other settings were considered?

It is unlikely that major messages would change given that the ecosystem level response at canyons and seamounts was the focus of the present work rather than the coral group specificly. However, we already assessed impacts on the global deep sea floor as well, which should provide relevant information for the curious reader.

c) The beginning of the paper could do more to justify why the focus is on biodiversity and not, for example on fisheries? Habitat support or other

ecosystem services? Is biodiversity being used as a proxy for something else?

While we appreciate the importance of fisheries as a critical sector of living marine resource sciences, biodiversity is a value by itself and one of the seven criteria retained for the identification of « ecologically or biologically significant areas » (EBSA) by the 10th Convention of the Parties (COP) to the Convention on Biological Diversity (CBD) (see Annex 1 to CBD CoP Decision IX/20 ; CBD, 2008a). These criteria are proposed as a framework for identifying Marine Protected Areas.

d) What is the support for extracting thresholds from the paleoceanographic literature? The time scales seem wrong for comparison with current change. Why wouldn't a 0.1 pH decline over 100 years be more significant than a 0.2 pH decline over thousands or tens of thousands of years?

Done. Thank you for pointing out some ambiguities in the original text. We explicitly state now the implication of paleoceanographic pH data. We modified the text to point out that we consider time scales from multi-annual to millions of years. We do not suggest that a 0.1 pH decline over 100 years is more significant/relevant than a 0.2 pH decline over thousands of years. The text reads now (lines 237 to 250): "Many past episodes of climate change occurred over significantly longer time-scales than the current anthropogenic perturbation of the climate system, allowing carbonate compensation to keep deep-water pH close to constant (Hönisch et al., 2008). This is corroborated by computing pH reduction over glacial-interglacial cycles for a North Atlantic site. Decadal-to-centennial changes are addressed by fresh-water hosing model experiments to simulate effects of circulation changes associated with rapid Heinrich and Dansgaard Oeschger events. In both cases, pH reductions are below 0.15 pH units. Similarly, a small amplitude of natural temporal pH variability at depth emerges from a multi-annual time series stations (González-Dávila et al., 2010) and the analysis of the long pre-industrial simulation "piControl" (Fig. S2 in the Supplement). In summary, natural pH variations on multi-annual, decadal-to-century, and longer time scales were likely smaller than 0.2 pH units on the regional-to-basin scale in the deep Atlantic and at least for the past million years. This suggests that small pH variations of up to 0.2 pH units do not present a risk for marine life."

Summary: This paper addresses issues relevant to Biogeosciences, and presents original data, although the general concept of predicting change and superimposing this on bathymetry is not entirely novel. The writing is generally clear and the authors provide a strong case to substantiate their interpretations. The methods are valid but the assumption that a 0.2 unit decline in pH will alter deep-sea biodiversity remains to be tested broadly.

We agree with the reviewer.

Technical Corrections:

technical corrections have been taken into account while preparing the revised manuscript.

Pg 8609 line 9 the deep benthic environment; also. . .You don't actually report real consequences.

We agree and modified the sentence to: "We report on major pH reductions over the deep North Atlantic seafloor (depth > 500 m) and deep-sea biodiversity hotspots, such as seamounts and canyons."

Pg 8610 line 4 – Mora et al. 2013 should be cited as considering consequences of OA in deep water.

Done

Pg 8610 line 7 deep sea is only hyphenated when used as a double adjective.

Corrected

Pg 8610 line 9 I question whether mineral extraction is dominant in the deep-sea – it has not really happened yet.

We agree with the reviewer that at present only few leases have been granted for mining. One example is the lease granted to Nautilus Minerals Inc. for the exploitation of polymetallic massive sulphide deposits in the territorial waters of Papua New Guinea. We will modify the sentence to "While waste disposal, fishing and, in the future, mineral extraction are well-recognized as human pressures ...".

Pg 8610 line 18. Need a citation after. . . taxa.

Done

Pg 8618 line 18 please define what depths are mean by 'deep water'

Throughout all of the manuscript, pH reductions are reported for depths exceeding 500 m below sea surface. I is stated on p8612, line 15.

Pg 8619 line 16 please define what is meant by ‘climate change’ – is this warming?

We added the definition to line 5 “... physical (climate change, defined here as physical changes in response to warming) ...”

Pg 8620 line 26. Other good citations include Buhl-Mortensen et al. 2010 (Marine Ecology) and other papers by that author.

Done

Pg 8621 line 10. So given the threat to deep protected areas – what do the authors recommend be done? Set aside larger protected areas? Avoid climate change-impacted areas?

The only appropriate reaction would be to curb down CO2 emissions.

Fig. 4 Can you comment on the biology in the regions shown in orange with greatest pH change?

The area with the greatest pH change (in orange) extends around much of the Atlantic margin. This covers a range of depths and climatic zones and has a highly variable biology. Coupled to this, we have very limited data on the fauna of large areas of the deep sea. This means that we would not like to make any generalising statement about the biology of the area with greatest change. To do this properly would be a new study (or serveral) in its own right.

Anonymous Referee #2

Received and published: 10 September 2014

The article “Projected pH reductions by 2100 might put deep North Atlantic biodiversity at risk.”, by Gehlen et al., tries to evaluate the potential impacts of ocean acidification on deep-sea ecosystems by modeling the effects of the IPCC AR5 Representative Concentration

Pathways on an ensemble of seven Earth system models. The work is compelling and original, and the issue addressed of the utmost importance for fellow scientists and policymakers alike. The article itself is competently written, clear and based on good bibliographic support. The work should be accepted for publication, with only the minor changes listed below.

We thank the reviewer for the positive evaluation of our study. We corrected typos and edited the text for clarity during revisions following the recommendations. We modified Figure 5.

195- Where it reads “Atlantic Meridioanl Overturning” it should read “Atlantic Meridional Overturning”

Done

240- The phrase “Projected pH reductionsTime-series of atmospheric. . .” should be corrected.

Done

263- The phrase “. . .that is transfer of. . .” should be edited for clarity.

Figure 5 - The symbols used are too similar at that size, and the use of the same color is visually confusing when they overlap. A change in either or both is suggested.

Done

617- The explanation regarding the different hue of the circles should also be applied to the diamonds.

Done

Projected pH reductions by 2100 might put deep North Atlantic biodiversity at risk.

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Abstract

This study aims to evaluate the potential for impacts of ocean acidification on North Atlantic deep-sea ecosystems in response to IPCC AR5 Representative Concentration Pathways (RCP). Deep-sea biota is likely highly vulnerable to changes in seawater chemistry and sensitive to moderate excursions in pH. Here we show, from seven fully-coupled Earth system models, that for three out of four RCPs over 17% of the seafloor area below 500 m depth in the North Atlantic sector will experience pH reductions exceeding -0.2 units by 2100. Increased stratification in response to climate change partially alleviates the impact of ocean acidification on deep benthic environment. ~~We report major potential consequences of pH reductions for deep-sea biodiversity hotspots, such as seamounts and canyons.~~ We report on major pH reductions over the deep North Atlantic seafloor (depth > 500 m) and at important deep-sea features, such as seamounts and canyons. By 2100 and under the high CO_2 scenario RCP8.5 pH reductions exceeding -0.2, (respectively -0.3) units are projected in close to 23% (~15%) of North Atlantic deep-sea canyons and ~8% (3%) of seamounts – including seamounts proposed as sites of marine protected areas. The spatial pattern of impacts reflects the depth of the pH perturbation and does not scale linearly with atmospheric CO_2 concentration. Impacts may cause negative changes of the same magnitude or exceeding the current target of 10% of preservation of marine biomes set by the convention on biological diversity implying that ocean acidification may offset benefits from conservation/management strategies relying on the regulation of resource exploitation.

Keywords: ocean acidification, climate change, deep-sea ecosystems

1 Introduction

Global ocean anthropogenic carbon inventories suggest that the ocean has taken up ~ 155 ± 31 PgC (10^{15} g of carbon) in 2010 (Khatiwala et al. (2013). This uptake of CO_2 is causing profound changes in seawater chemistry resulting from increased hydrogen ion concentration (decrease in pH, pH = $-\log10[H^+]$) referred to as ocean acidification (IPCC, 2011). Experimental and modelling studies provide compelling evidence that ocean acidification will put marine ecosystems at risk (e.g. Orr et al., 2005; Kroeker et al., 2013). However, with the exception of assessments focusing ~~mostly~~ on cold-water coral systems (Barry et al., 2005, 2013; Fleeger et al., 2006; Guinotte et al., 2006; Tittensor et al., 2010), quantifications of biological ~~impacts~~consequences of ocean acidification ~~have, to date, been limited~~ mostly ~~to the~~targeted surface ocean or coastal environments (Kroeker et al., 2010).

The aim of this study is to extend our understanding of broad scale impacts of ocean acidification from the existing shallow water studies to focus specifically on deep-sea ecosystems. The deep ~~-~~sea is under increasing anthropogenic pressure as technological advances allow exploitation of formerly inaccessible regions (Clauss and Hoog, 2002). While waste disposal, fishing and, in the future, mineral extraction are well-recognized as dominant human pressures (Ramirez-Llodra et al., 2011), expert assessments urge consideration of climate change and ocean acidification impacts in future ecosystem conservation/management strategies (Taranto et al., 2012; Billé et al., 2013).

While previous studies quantified changes in carbonate mineral saturation state as a measure for potential detrimental impacts on deep calcifying communities (Guinotte et al., 2005, 2006; Turley et al., 2007; Fautin et al., 2009), this model-based assessment uses pH. The tight control of pH at the cellular scale is an important prerequisite of proper cell functioning and mechanisms of pH control are ubiquitous across many taxa (Seibel and Walsh, 2003 and references therein). Deep-sea organisms might be particularly vulnerable to changes in seawater chemistry, at least in part owing to limitations on rate processes, caused by low temperature (Childress, 1995; Seibel and Walsh, 2001) and possibly food availability (Ramirez Llodra, 2002), as well as the environmental stability of their habitat in the past (Barry et al., 2011; Seibel and Walsh, 2003). A recent review (Somero, 2012) highlights the link between environmental stability and the capacity to acclimate to future changes in environmental variables such as pH. According to this study, environmental stability might impair the potential for acclimation. This stands in sharp contrast to shallow water or inter-tidal organisms, which are adapted to a dynamic environment with large changes in temperature and seawater chemistry (Hofmann et al., 2011; Duarte et al., 2013).

A model sensitivity study (Gehlen et al., 2008) suggested the potential for large pH reductions (up to – 0.6 pH units) in the deep North Atlantic. Regions of large pH reductions coincided with areas of deep-water formation. Deep-water formation drives the rapid propagation of surface-derived changes in carbonate chemistry to depth as underlined by high vertically-integrated water column inventories of anthropogenic carbon (Sabine et al., 2014), as well as and tritium, chlorofluorocarbon distributions (Doney and Jenkins, 1994). Gehlen et al. (2008) used output from a single model and for a scenario following an atmospheric CO$_2$ increase of 1% per year over 140 years starting from an atmospheric CO$_2$ level of 286 ppm. This rate of increase is about twice as large as the rate typical for a high-end IPCC concentration pathway. The study did not include circulation changes in response to climate change.

Here we extend the study by Gehlen et al. (2008) by analysing pH projections from seven Earth system models that contributed to the 5th Coupled Model Intercomparison Project CMIP5 and for four different Representative Concentration Pathways (RCP, Van Vuuren et al., 2011) ranging from a strong emission mitigation scenario (RCP2.6) to the high-CO$_2$ scenario RCP8.5.— We assess the magnitude of deep-water pH reductions in the North Atlantic (35°N-75°N, 90°W-180°W) over this century in response to atmospheric CO$_2$ increase and climate change. The North Atlantic is a well-ventilated region of the world ocean and, despite a projected increase in stratification, will remain well-oxygenated in the future (Bopp et al., 2013). The study complements assessments by Bopp et al. (2013) and Mora et al. (2013) which evaluated large-scale average pH reductions in response to the same RCP pathways, but without a detailed discussion of spatial patterns and their link to circulation. We define a critical threshold for pH reductions based on evidence from paleo-oceanographic studies, contemporary observations and model results. Future multi-model projections of pH changes over the seafloor are analysed with reference to this threshold and without discrimination of particular habitats first. ~~Finally~~Next, model results are put into the perspective of ecosystem conservation by evaluating changes in pH against the distribution of seamounts and deep-sea canyons. These features are known as sites of high-biodiversity deep-sea ecosystems, such as cold-water corals and sponge communities (ICES, 2007; Clark MR et al., 2010; De Leo et al., 2010) and are selected as representative examples of deep sea environments.

2 Material and methods

2.1 Earth system models

Our study draws on results from 2 types of Earth system models: (1) the Bern3D-LPJ carbon-cycle/climate model (Steinacher et al., 2013; Roth and Joos, 2013) and (2) seven fully-coupled three-dimensional atmosphere ocean climate models that participated in the 5th Coupled Model Intercomparison Project (CMIP5, Taylor et al., 2011) and contributed to the 5th Assessment Report of the Intergovernmental Panel on Climate Change (IPCC AR5). The Bern3D-LPJ is a model of intermediate complexity featuring a 3D geostrophic-balance ocean and 2D atmospheric energy and moisture-balance model. The cycle of carbon and related tracers is represented including prognostic formulations for marine production, a seafloor sediment, and a dynamic global vegetation model. This model is relatively cost-efficient compared to CMIP5 models. It is used to evaluate the order of magnitude of pH reductions associated with past abrupt climate change by analysing results from freshwater hosing experiments (Bryan 1986; Marchal et al., 1999; Matsumoto and Yokoyama, 2013) .

Concerning the subset of CMIP5 models, we selected models for which 3D pH fields were available and that had been part of a published multi-model evaluation (Bopp et al., 2013). We analyse output for four future atmospheric CO_2 concentration scenarios (RCP), along with the corresponding pre-industrial control simulations, piControl. The nomenclature follows CMIP5 recommendations. Historical simulations cover the period between 1870 and 2005 and are followed by climate change scenarios according to RCP8.5, RCP6.0, RCP4.5 and RCP2.6 from 2006 to 2100 (Van Vuuren et al., 2011; Moss et al., 2010). RCP identifiers refer to the additional radiative forcing as target for 2150 AD in the Integrated Assessment Models used to derive the RCP scenarios: RCP2.6, RCP4.5, RCP6.0 and RCP8.5 with corresponding atmospheric CO_2 levels of 421, 538, 670 and 936 ppm. Individual RCPs differ with respect to the temporal evolution of atmospheric CO_2 and range from a stringent emission mitigation RCP2.6 to the high-CO_2 scenario RCP8.5. The complete set of RCPs was not available for all models. Please refer to Table S1 (supporting material) for model name, scenario and references.

2.2 Deep-sea ecosystems

This study uses datasets of seamounts (Yesson et al., 2011) and canyons (Harris and Whiteway, 2011). For seamounts, these data include location, height and surface assuming a conical shape. For canyons, the data consist of a high-resolution vector database of canyon centre lines that was converted into a raster dataset of canyon presence (using ArcGIS v10) for analysis. Data were projected on a 1°x1° regular grid.

2.3 Post-treatment of model output and data

2.3.1 Post-treatment of CMIP5 model output

Model output is interpolated on a regular grid of 1°x1° resolution. Anomalies are computed as the difference between the decade 2090-2099 and the long-term mean of the pre-industrial state. As the focus of this study is on impacts on benthic communities, we quantify pH changes in the deepest model box over a topography range from 500 m to > 4500 m water depth.

2.3.2 Computation of the area of seamounts for impact assessment

The area of North Atlantic seafloor impacted by ocean acidification is estimated on the basis of individual grid cells for which the reduction in pH exceeded ≥ 0.2 or 0.3 units. The impacted area follows as the integral of the area of these 1°x1° grid cells. The area of seamounts with a pH reduction ≥ 0.2 or 0.3 units is computed based on distribution and height assuming a conical shape (Danovaro et al., 2008, Yesson et al., 2011). The database provides height above seafloor and base area. The area of the seamount (A) is given by:

$$A = pr^2 \sqrt{r^2 + (h + h')^2} \qquad (1)$$

where, r is the base radius of the seamount and h+h' is the height. The height impacted by a pH reduction exceeding the threshold (h') is diagnosed from the depth of the pH anomaly corresponding to the threshold. The radius of the seamount at the depth of the anomaly (r') is obtained from the Thales theorem:

$$\frac{r'}{r}=\frac{h'}{h} \tag{2}$$

as: $$r'=\frac{h'}{h}r \tag{3}$$

The final expression of r’ is the positive analytical solution of the fourth-order polynomial

$$\frac{A^2}{p^2}=\frac{h^2}{h'^2}r'^2\left(\frac{h^2}{h'^2}r'^2+(h+h')^2\right) \tag{4}$$

as: $$r'=\pm\frac{h'}{h}\left[\frac{1}{2}\left(-1\pm\sqrt{\frac{4A^2}{p^2h^2}}\right)\right]^{\frac{1}{2}} \tag{5}$$

The impacted area of the seamount (A*) follows from the depth of pH anomaly as a function of seamount height:

$$A*p\frac{h'}{h}\left[\frac{1}{2}\left(-1+\sqrt{\frac{4A^2}{p^2h^2}}\right)\right]^{\frac{1}{2}}\left(h'^2+\frac{h'^2}{h^2}\left[\frac{1}{2}\left(-1+\sqrt{\frac{4A^2}{p^2h^2}}\right)\right]\right) \tag{6}$$

where A is the total surface area of the seamount.

3 Results and discussion

3.1 Environmental stability and critical threshold for pH reduction

Considering that environmental stability might impair the potential for acclimation, we assessed pH changes over glacial-interglacial time scales and for past events of rapid climate changes recognized for having driven major reorganizations in North Atlantic circulation and carbonate chemistry.

The pH is defined as the negative logarithm of the hydrogen ion concentration ($[H^+]$). From the basic properties of logarithms it follows that the difference in pH equals the logarithm of the ratio of hydrogen ion concentrations. For a given pH change, the change in $[H^+]$, $\Delta[H^+]$, is a linear function of the initial hydrogen ion concentration ($[H^+]_i$) as

$\Delta[H^+] = [H^+]_i\ ((1/10^{\Delta pH}) - 1)$. Hence, the larger the initial $[H^+]$, the larger the perturbation (Fig. S1). Contrasting shallow and deep environments highlights that absolute changes in $[H^+]$ are amplified at depth for any threshold, that is for environments of low natural variability.

3.1.1 Glacial-interglacial time-scales

The paleo-record permits evaluation of environmental variability of the deep-ocean over the past million years. Available evidence indicates a low variability over this time interval (Elderfield et al., 2012; Yu et al., 2010; Yu et al., 2013). Changes in carbonate chemistry were small in the deep-ocean compared to surface layers (Yu et al., 2010). Recent studies re-evaluated deep-water pH changes between glacial to present (Sanyal et al., 1995), arguing that carbonate compensation kept deep-water pH close to constant (Hönisch et al., 2008). We use data available in Yu et al. (2010) (and associated supplementary material) and follow their reasoning to infer DIC changes from [CO_3^{2-}] and hence alkalinity, to compute associated changes in pH for sediment core BOFS 8K (52.5 N, 22.1 W, 4,045 m). This pH change is computed using CO2sys (http://cdiac.ornl.gov/oceans/co2rprt.html) with alkalinity and DIC as input variables, along with temperature, depth, phosphate and silicate as (Yu et al., 2010). We estimate a pH reduction of ~0.1 pH units for North Atlantic deep-water over the early deglacial (17,500 to 14,500 years before present).

3.1.2 Rapid events associated with fresh-water release: Heinrich and Dansgaard Oeschger events

Model experiments yield maximum pH reductions in North Atlantic deep-water below 0.15 pH units in response to a shut-down of the North Atlantic Meridional Overturning Circulation (AMOC, Fig. 1). To realize an abrupt shutdown of the AMOC different durations of freshwater perturbations in the North Atlantic on top of a pre-industrial steady state have been tested releasing in total $3x10^{15}$ m^3 freshwater (~9 m sea level equivalent). In terms of pH changes in the North Atlantic region, the experiment with a 300 yr lasting freshwater forcing of 0.33 Sv results in the strongest response (Fig. 1(a)). In these experiments, the cause of the pH decrease is not high atmospheric CO_2 (CO_2 only increases a few ppm during the freshwater experiment), but is mainly a result of the decrease in deep ocean ventilation. This leads to the additional accumulation of dissolved inorganic carbon (DIC) by the respiration of organic matter. Although alkalinity is also increased in the deep by the dissolution of carbonate particles settling through the water column, it does not compensate the increase in DIC leading to more acidic waters in the deep. The most extreme negative excursion of the pH averaged over the deep (below 2000 m) Northern Atlantic (45° N – 65° N) occurs ~ 150 years after the end of the freshwater forcing with a decrease of ~ 0.13 pH units relative to the unperturbed pre-industrial state (Fig. 1(b)). The pH-decrease does not exceed -0.18 pH units in any of the individual grid boxes. In Figure 1 (c) and (d) the spatial distribution of the pH-reduction averaged over years 400-450 (i.e., during the maximum of the pH decrease) is shown in terms of pH anomalies at the seafloor and in a section through the Atlantic at 38.5°W.

3.1.3 Critical threshold for pH reductions

For the purpose of evaluating the potential for negative impacts on deep-sea benthic environments, a critical threshold for pH reduction needs to be identified. Reductions of pH exceeding the envelope set by past and present natural variability are considered as critical. Paleo-evidence suggests that the deep-sea fauna has evolved under conditions of environmental variability confined to a narrow range over the past million years (Yu et al., 2010; Elderfield et al., 2012). Many past episodes of climate change occurred over significantly longer time-scales than the current anthropogenic perturbation of the climate system, allowing carbonate compensation to keep deep-water pH close to constant (Hönisch et al., 2008). This is corroborated by computing pH reduction over glacial-interglacial cycles for a North Atlantic site. Decadal-to-centennial changes are addressed by fresh-water hosing model experiments to simulate effects of circulation changes associated with rapid Heinrich and Dansgaard Oeschger events. In both cases, pH reductions are below 0.15 pH units. Similarly, small amplitude natural temporal pH variability at depth emerges from a multi-annual time series stations (González-Dávila et al., 2010) and the analysis of the long pre-industrial simulation "piControl" (Fig. S2 in the Supplement). In summary, natural pH variations on multi-annual, decadal-to-century, and longer time scales were likely smaller than 0.2 pH units on the regional-to-basin scale in the deep Atlantic and at least for the past million years. This suggests that pH variations of up to 0.1 to 0.2 pH units do not present a risk for marine life.

~~Past episodes of climate change mostly occurred over significantly longer time-scales than the current anthropogenic perturbation of the climate system, allowing carbonate compensation to keep deep-water pH close to constant (Hönisch et al, 2008). This is corroborated by computing pH reduction over glacial-interglacial cycles for a North Atlantic site, as well as by model experiments simulating effects the fresh-water hosing associated with a rapid Heinrich and Dansgaard Oeschger events. In both cases, pH reductions are below 0.15 pH units. Similarly, a small amplitude of natural temporal pH variability at depth~~

~~emerges from a multi-annual time series stations (González-Dávila et al., 2010) and the analysis of the long pre-industrial simulation "piControl" (Fig. S1).~~

This leads us to define two thresholds for pH reduction between pre-industrial and the end of the 21st century: -0.2 and -0.3 pH units. Both stand for pH reductions exceeding paleo-record-based estimates of changes in North Atlantic deep-water chemistry over the past ten-thousand years, as well as being much larger than the amplitude of natural temporal variability of pH in the deep North Atlantic (González-Dávila et al., 2010). The first threshold (-0.2) is in line with recommendations by environmental agencies (Schubert et al., 2006) following the precautionary principle, and is reported to increase mortality of deep-sea benthic organisms during in-situ exposure experiments (Barry et al., 2005). The second threshold (-0.3) allows to bracket a range of changes spanning from a ~58% increase in hydrogen ion concentration up to ~100%.

3.2 Projections of pH reductions over the 21st century

Time-series of atmospheric CO_2 (ppm) for three out of four IPCC RCP scenarios between 2006 and 2100 show an increase in CO_2 over this century, only RCP2.6 does not show a general increase with time (Fig. 2 (a)). The corresponding simulated pH reductions for surface and deep North Atlantic waters are presented on Fig. 2(a), respectively Fig. 2 (c). Projected pH changes are indicated as multi-model mean along with the between-model spread. Monitoring at time series stations reveals that the observed surface ocean pH decreases tracks increasing atmospheric pCO_2 (Orr, 2011). This trend is confirmed by the decline in simulated surface ocean pH (Fig. 2(b)) with a small between-model spread. In the surface ocean the extent of ocean acidification is set by the atmospheric CO_2 trajectory, along with physical climate change, namely warming and associated changes in ocean circulation and CO_2 thermodynamic properties. Surface waters, with high levels of dissolved anthropogenic CO_2 and characterised by low pH values, are entrained to the interior ocean during seasonal mixed layer deepening and deep convection episodes. As a result, deep pH changes (Fig. 2 (c)) reflect atmospheric CO_2 to a lesser extent. Because the deep water formation differs between models, the inter-model spread is significantly larger in deep waters than for the surface ocean.

The spatial pattern of pH reductions is exemplified for RCP4.5 and RCP8.5 in Figure 3 (see supplementary material, Fig. S~~2~~3, for RCP2.6 and RCP6.0). Under RCP4.5 (Fig. 3(a) and RCP8.5 (Fig. 3(b)), pH reductions crossing the -0.2 threshold are projected for continental slopes and a latitudinal band extending from 55°N to 65°N. Since the pH perturbation originates at the sea-surface, the continental slope and topographic heights (e.g. mid-Atlantic ridge) experience the largest pH reductions. Increasing impact on the sea floor between RCP4.5 and RCP8.5 for a threshold of -0.2 reflects the depth exposure to the pH perturbation of continental slopes and the mid-Atlantic ridge. In summary, the spatial pattern is set by a combination of topography and North Atlantic circulation pathways. It reflects~~, that is~~the transfer of the surface born anomaly of pH to the ocean interior during deep water formation and downstream transport away from convection sites by the deep western boundary current.

By the end of the twenty-first century, projected pH reductions (Table 1) cross the -0.2 threshold for all scenarios, but RCP2.6. For RCP2.6, deep-water pH reductions remain below thresholds with likely limited impact on benthic environments. Under moderate RCP4.5, a decrease in pH beyond -0.2 units is projected for large areas of the North Atlantic with about 16.7±4.2% of the sea floor area below 500 m being impacted. This estimate increases to 21.0±4.4% of the North Atlantic sea floor area under the most severe scenario (RCP8.5) and is still 14.0±3.3% of the sea floor for a threshold of -0.3. The area impacted does not scale linearly with atmospheric CO_2 (Table 1), but levels off at higher RCPs for threshold -0.2. The -0.3 pH unit threshold (a 100% increase of [H+]) is not reached for RCP4.5 and only modest impacts are projected for RCP6.0 (Table 1). We expect, however, an increase in impacted area for all scenarios and pH thresholds beyond 2100 in response to legacy effects of CO_2 emissions and ongoing downward propagation of the pH perturbation (Frölicher and Joos, 2010).

3.2.1 Opposing effects of climate change and ocean acidification

The progression from RCP2.6 to RCP8.5 corresponds to a series of increasing geochemical (atmospheric pCO_2) and physical (climate change, defined here as changes in ocean dynamics in response to atmospheric warming) forcing with opposing effects on deep ocean acidification.

In order to distinguish between the physical and geochemical drivers of North Atlantic deep-water acidification, we assessed two contrasting simulations available for two Earth system models (GFDL-ESM2M and IPSL-CM5A-LR) for RCP4.5. The first simulation (Fig. 4 (a) includes climate change effects on ocean circulation and geochemical effects on the seawater CO_2 system in response to atmospheric pCO2 increase (RCP4.5). In the second experiment (Fig. 4(b)), the circulation and ocean physics are kept at pre-industrial conditions, but atmospheric CO2 levels following RCP4.5 are used to force ocean acidification (RCP4.5/fixclim). The difference in pH between RCP4.5 and RCP4.5/fixclim (Fig. 4(c)) allows, at first order and within the limits of non-linearities (Schwinger et al., 2014), isolation of the effect of climate change on pH changes. The negative differences in pH on panel (c) indicate stronger acidification in RCP4.5/fixclim, and suggest a slight alleviation of ocean acidification at depth and over the time-scale of this study by climate-change. In the experiment where ocean circulation was held at pre-industrial condition (RCP4.5/fixclim) there was a small increase in the area impacted by pH reductions for all thresholds (Table 1). Largest differences in projected pH values between RCP4.5/fixclim and RCP4.5 co-occur with large negative anomalies in winter mixed layer depth maxima in the Labrador Sea and negative pH anomalies downstream of convection sites following the deep western boundary current (Doney and Jenkins, 1994). This is in line with the projected enhancement of stratification across the North Atlantic in response to increasing temperatures and freshening. It will result in changes in winter mixed layer depth, deep convection and a decrease in the Atlantic Meridional Overturning Circulation (Mehl et al., 2007; Cheng et al., 2013). While increasing atmospheric CO_2 reduces pH, increasing climate change reduces surface-to-deep water exchange. In addition, topography modulates the extent of deep-water acidification. The combination of climate-change, the non-linearities of the carbonate system and topography explains the levelling-off of impacts in Table 1 for pH reductions exceeding -0.2.

3.2.2 Projected impacts on ecosystems

In order to evaluate the risk for specific benthic ecosystems to be affected by pH reductions, we co-located seamounts (Figure 3, black dots) and deep-sea canyons (Figure 3, red dots) -

both of which are key habitats of high biodiversity - and pH changes for RCP4.5 and RCP8.5 separately computed from the multi-model mean (see supplementary material for RCP2.6 and RCP6.0). To further the evaluation of potential impacts of pH reductions beyond pH thresholds, we computed the area of seamounts for which a corresponding decrease is projected. A significant proportion of these habitats will be impacted by pH reductions exceeding -0.2 units by the end of the 21th century under moderate to high emission scenarios (Fig. 5). The geographic pattern results in close to 22.5±5.3% (14.7±4.1%) of North Atlantic deep-sea canyons and 7.7±3.6% (2.7±0.9%) of seamount ecosystems being exposed to pH reductions exceeding -0.2 (-0.3) units under RCP8.5. Under the moderate scenario, RCP4.5, model projections indicate that 21.8±6.0% of deep-sea canyons and 5.0±1.6% of seamounts still will experience pH reductions exceeding the -0.2 threshold. The close to constant impact reflects the use of a diagnostic that is based on counts of features being impacted, in addition to the depth distribution and propagation of the pH anomaly.

Seamounts and deep-sea canyons are known as hotspots of biodiversity and harbour a variety of distinct communities including reef-building cold-water corals, soft coral gardens and deep-sea sponge aggregations (Buhl-Mortensen et al., 2010, 2012; Clark et al., 2010; De Leo et al., 2010; ICES, 2007). Recent assessments reveal a high level of anthropogenic pressures on these ecosystems (Clark et al., 2010, Ramirez-Llodra et al., 2011). While fishing and resource extraction are recognized as the dominant human pressures at present and in the near future, expert assessments highlight the need for an appropriate quantification of the impacts of climate change and ocean acidification (Taranto et al., 2012). Present international conservation targets aim at preserving 10% of marine biomes by 2020 (CBD, 2011). Although not directly comparable to the outcome of model projections, it is nevertheless of interest to confront this preservation target with model results suggesting that ~ 8% of North Atlantic seamounts and 23% of canyons will experience a decrease in pH exceeding 0.2 pH units by the year 2100 for the most severe scenario. Seamounts identified as marine protection areas in the OSPAR region and excluding active venting sites (e.g. Josephine seamount, 36°40.02'N 14°15.00'W; Sedlo seamount, 40°12.8'N 26°15.8'W) fall within the area for which these pH reductions are projected.

~~Our knowledge of the ecology of deep benthic communities is still limited and impacts of pH changes on these communities are difficult to evaluate owing to lack of experimental and observational data. Whatever acclimation to rapid changes in pH are required for deep-sea organisms, they will often lead to increased energetic costs (Widdicombe and Spicer, 2008) – e.g. for metabolism/maintenance, growth, reproduction – and could extend to increases in mortality of both adults and juveniles. These effects may be likely exacerbated in the presence of other stressors (Walther et al., 2009), such as global warming and projected reductions in deep-sea food supply (Bopp et al., 2013), as well as elevated resource exploitation and pollution. In particular, reductions in food supply to deep benthic communities are projected to result in a decrease in biomass and a shift towards smaller sized organisms (Jones et al., 2013). These changes will modify energy transfer rates through benthic food webs and may leave communities more suceptable to pH reductions. Changes at the individual and population level will inevitably lead to more widespread ecosystem and community level changes and potential shifts in biodiversity (Hendriks et al., 2010) and ecosystem functioning (Danovaro et al., 2008). We propose these and future model projections to be taken into account when defining long-term preservation and management approaches to deep-sea ecosystems.~~Our knowledge of the ecology of deep benthic communities is still limited and impacts of pH changes on these communities are difficult to evaluate owing to lack of experimental and observational data. Rapid changes in pH will likely lead to disruption of extracellular acid-base balance, impedance of calcification and other physiological effects in deep-water organisms, and whatever acclimation is required may have increased energetic costs (Widdicombe and Spicer, 2008) – e.g. for metabolism/maintenance, growth, reproduction – and could extend to increases in mortality of both adults and juveniles. Changes at the individual and population level will inevitably lead to more widespread ecosystem and community level changes and potential shifts in biodiversity (Hendriks et al., 2010) and ecosystem functioning (Danovaro et al., 2008). Biodiversity reductions could arise from a loss of species, functional, or even taxonomic groups sensitive to pH change. The ecological implications of pH change could be more severe if keystone or habitat-forming species are impacted (Widdicombe and Spicer, 2008), which seems likely (Guinotte et al., 2006). These effects may be likely exacerbated in the presence of other stressors (Walther et al., 2009), such as global warming and projected reductions in deep-sea food supply (Bopp et al., 2013), as well as elevated resource exploitation and pollution. In particular, reductions in food supply to deep benthic communities are projected to result in a decrease in biomass and a shift towards smaller sized organisms (Jones et al., 2013). These changes will modify energy transfer rates through benthic food webs and may leave communities more susceptible to pH reductions. We propose these and future model projections to be taken into account when defining long-term preservation and management approaches to deep-sea ecosystems.

4 Conclusions

This study assesses the potential for detrimental pH reduction to occur across the deep North Atlantic by the end of the 21st century. It evaluates results from seven fully-coupled Earth system models and for four representative concentration pathways ranging from RCP2.6 to RCP8.5. In three out of the four scenarios, the multi-model analysis suggests that by 2100 over 17% of the seafloor area below 500m depth in the North Atlantic sector will experience pH reductions exceeding -0.2 units. Enhanced stratification in response to warming and freshening of surface waters slightly counteracts deep-water acidification. pH reductions co-occur with sites of high deep-sea biodiversity such as seamounts and canyons. Model projections indicate that by the end of this century and for the high CO_2 scenario RCP8.5, close to 23% (~15%) of North Atlantic deep-sea canyons and ~8% (3%) of seamounts will experience pH reductions exceeding -0.2 (-0.3) units. Seamounts proposed as sites of marine protected areas are concerned by these pH reductions. The spatial pattern of impacts reflects the depth of the pH perturbation and did not scale linearly with atmospheric CO_2 concentration. Impacts may cause negative changes of the same magnitude or exceeding the current biodiversity target of 10% of preservation of marine biomes implying that ocean acidification may offset benefits from conservation/management strategies relying on the regulation of resource exploitation.

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Table 1. Fraction of North Atlantic seafloor (35°N-75°N, 90°W–180°W) below 500 m experiencing a reduction in pH ≥ 0.2, respectively ≥ 0.3 at the end of the 21st century. Fractions for multi-model mean and standard deviation are given in percentage of impacted surface area relative to the total surface seafloor area of the North Atlantic sector. n=number of simulations available at time of analysis for each RCP

	n	pH reduction ≥ 0.2		pH reduction ≥ 0.3	
		mean (%)	std (%)	mean (%)	std (%)
RCP2.6	6	1.2	1.1	0.0	0.1
RCP4.5	7	16.7	4.2	0.6	0.5
RCP4.5/fixclim	2	18.1	n.a	0.8	n.a
RCP6.0	4	19.9	5.0	4.4	1.5
RCP8.5	7	21.0	4.4	14.0	3.3

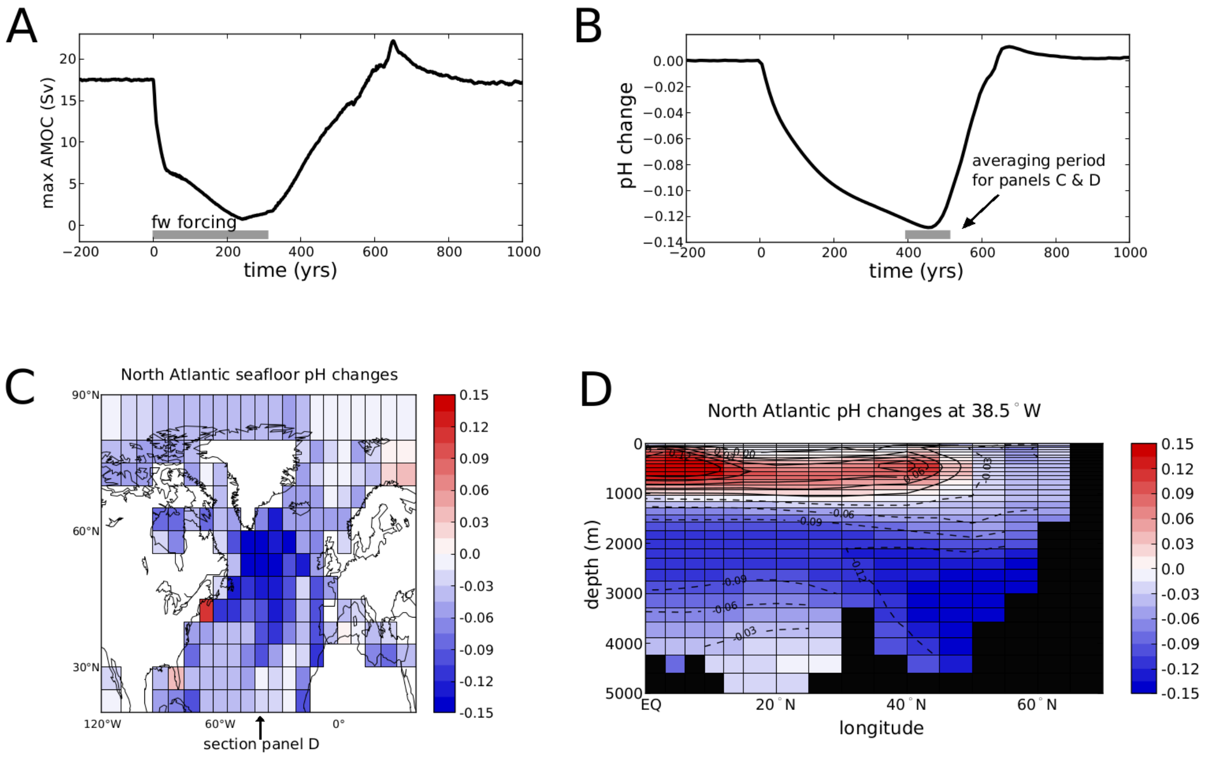

Figure 1. North Atlantic freshwater hosing experiment. (a) Time series of strength of Atlantic Meridional Overturning Circulation (Sv), freshwater release occurred over 300 years (grey bar); (b) times series of pH change relative to pre-industrial averaged over the deep (below 2000 m) Northern Atlantic (45° N – 65° N); (c) spatial distribution of the pH-reduction averaged over experiment years 400-450 (grey bar on panel (b)) in terms of pH anomalies relative to pre-industrial at the seafloor and (d) in a section through the Atlantic at 38.5°W.

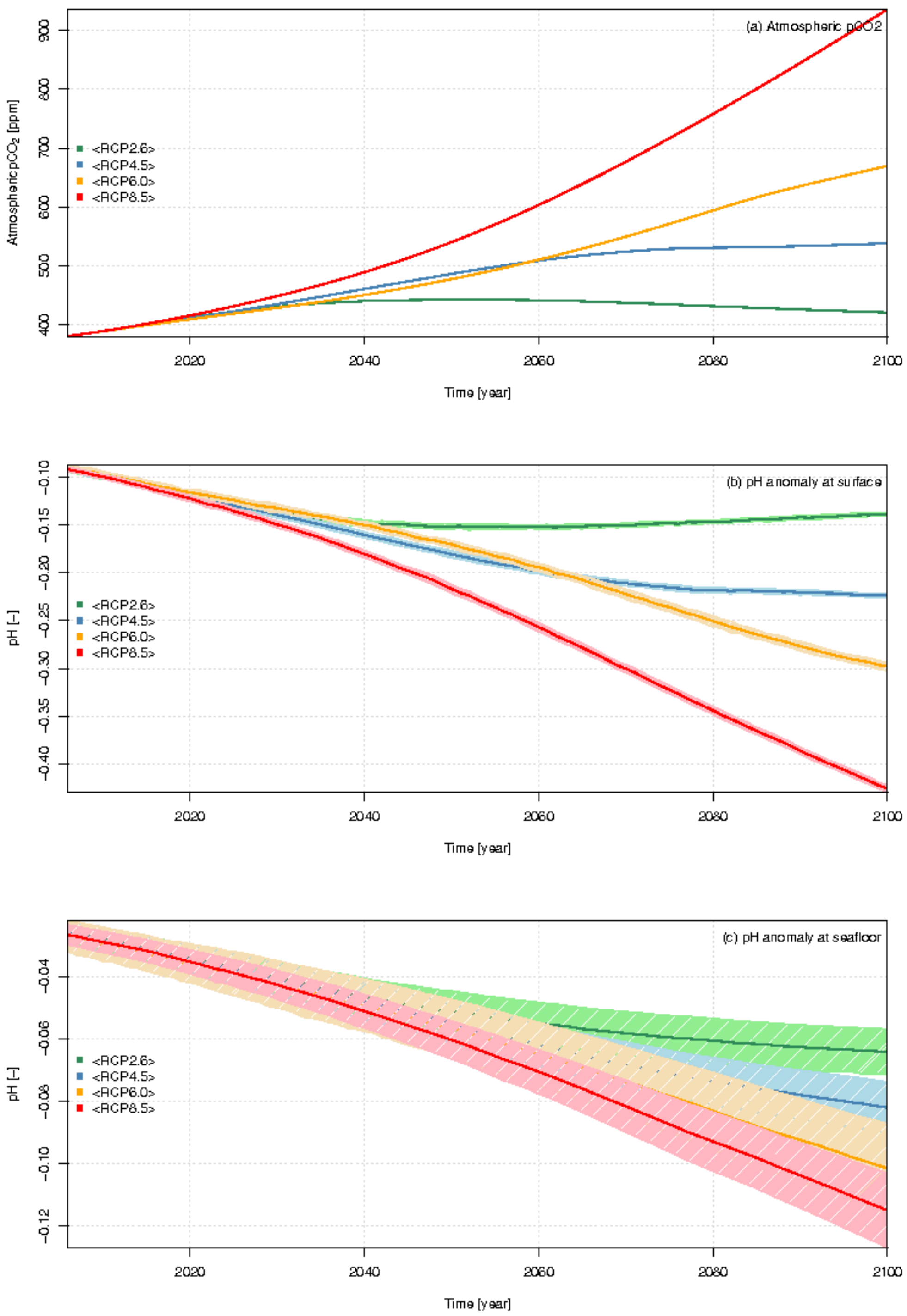

Figure 2. Time-series of (a) atmospheric CO_2 (ppm) for RCP2.6, RCP4.5, RCP6.0 and RCP8.5 scenarios between 2006 and 2100 and corresponding simulated average North Atlantic pH changes relative to the pre-industrial mean for (b) surface waters and (c) deep waters. Hatching indicates the 2.5%-97.5% confidence interval of multi-model averages.

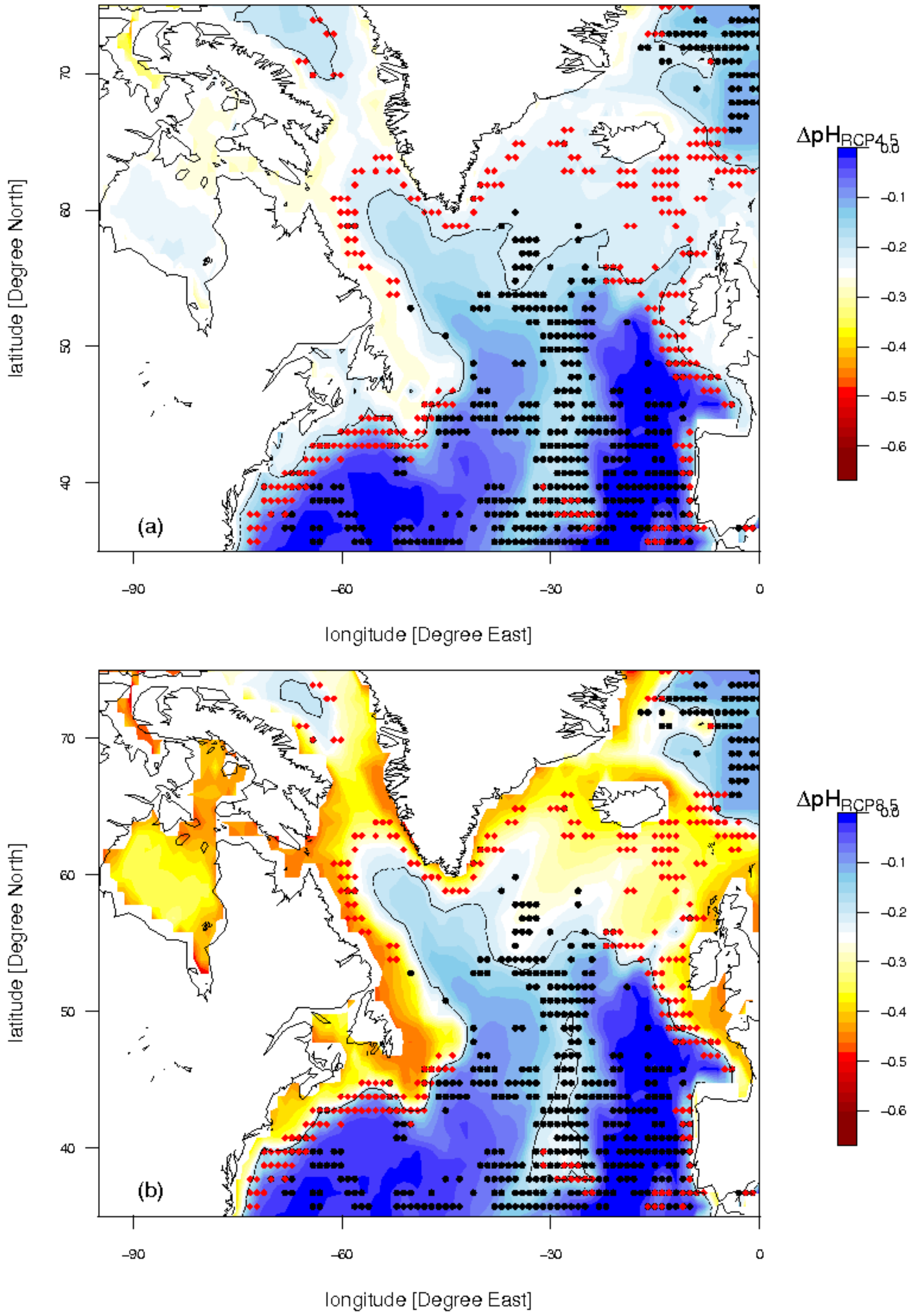

Figure 3. Projected changes in pH between pre-industrial and the experiments forced by IPCC RCP scenarios by 2100. The panels show ensemble-mean differences in pH between the pre-industrial and the 2090-2100 average for (a) RCP4.5 and (b) RCP8.5. Locations of deep-sea canyons and seamounts are indicated as red and black symbols, respectively. The -0.2 pH contour line is plotted to delineate areas experiencing pH reductions beyond this threshold.

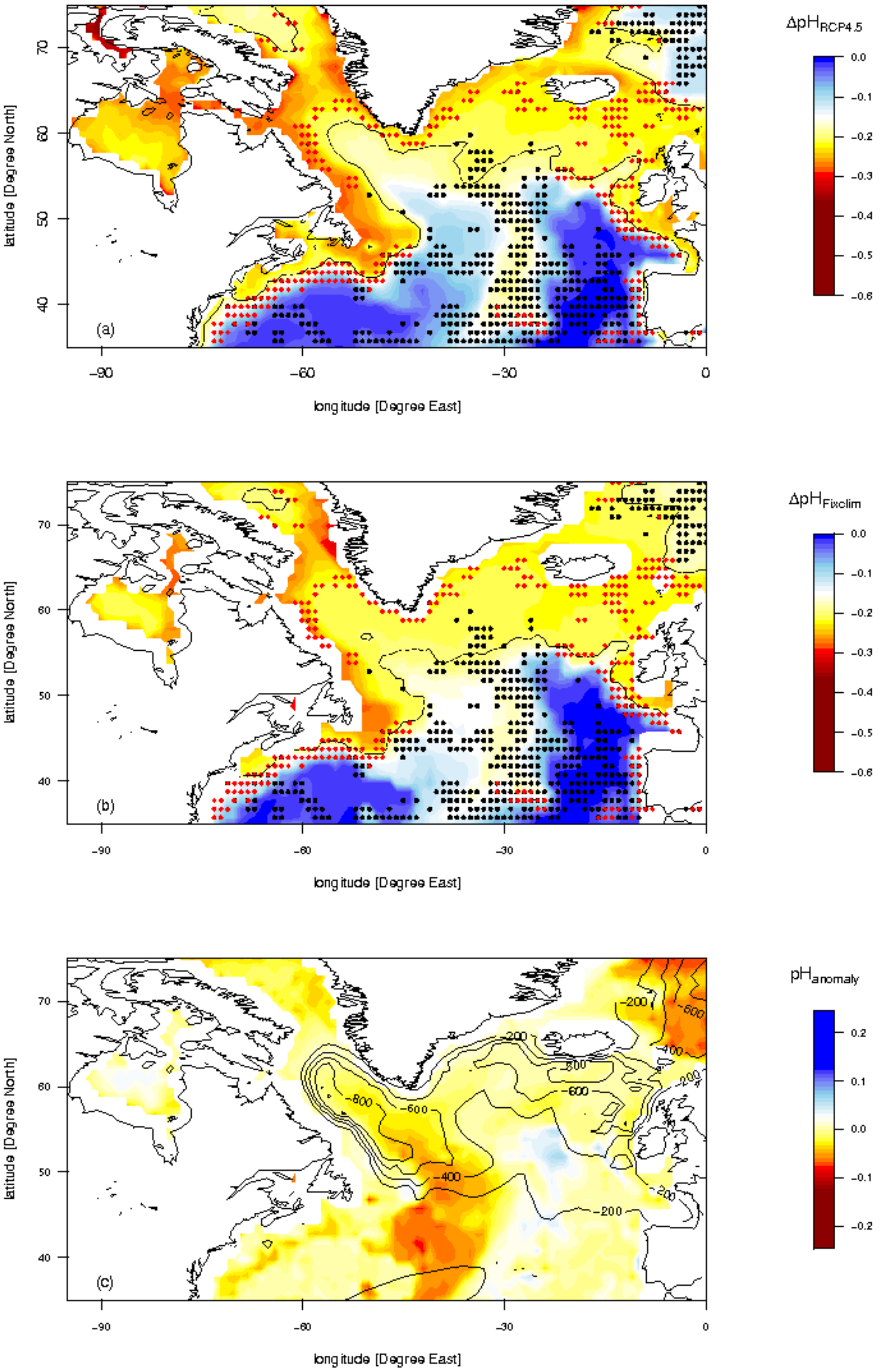

Figure 4. Projected changes in deep ocean pH between pre-industrial and experiments forced with RCP scenarios by 2100: (a) RCP4.5, (b) RCP4.5/fixclim, (c) difference in pH between (a) and (b) together with changes in maximum winter mixed layer depth (contour lines). The

change in pH is computed as the difference in mean pH between the pre-industrial and the 2090-2100 average

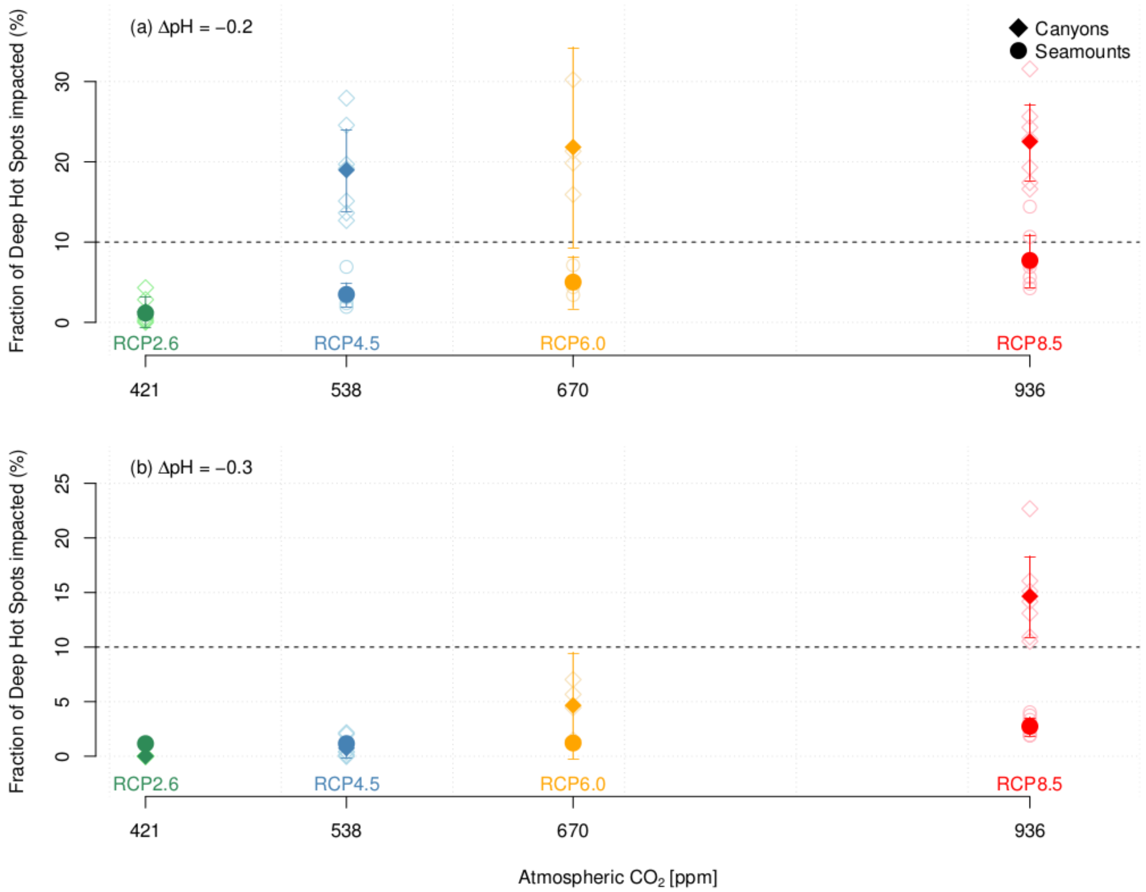

Figure 5. Projected impacts on seamounts (circles) and canyons (diamonds) as a function of atmospheric CO_2 levels by year 2100 for pH reductions exceeding (a) -0.2 and (b) -0.3. Impact is computed as the fraction of the surface area affected by a reduction exceeding the threshold for seamounts, respectively as the number of canyons surrounded by waters for which the reduction in pH exceeding the threshold is projected. Model pH is the decadal mean (2090-2100). Note that the seamount and canyon multi-model averages for the RCP2.6 scenario overlay each other. Light coloured circles: values obtained for each Earth system model; dark coloured circles: multi-model average for each scenario. Vertical and horizontal bars: 2.5%-97.5% confidence interval of multi-model averages.