Cover letter to revised manuscript and review responses

Dear Editor,

We are pleased to send you the revised version of our manuscript. We found that the reviewers provided very valuable inputs which have improved the manuscript.

Please find here a combined pdf-file including:

- our point-by-point response to each of the reviews, along with a list of all relevant changes made in the manuscript (this is the information we uploaded earlier as response to the reviews)
- a marked-up manuscript version.

(In agreement with my correspondence with Svenja Lange at the Editorial Office 9 June 2015, the changes were made in our latest word-version of the manuscript rather than in the *.tex file. We have, therefore, added the few editorial changes that were made before the editorial office uploaded the discussion manuscript (se e-mail of 26 March 2015 10:08). We are very pleased that this solution was possible as it allowed us to make the changes in the manuscript in parallel to replying the reviewers, which saved us time. So again, many thanks!)

Best regards,

Dorte Krause-Jensen

Reply to reviewer 1

Review comments shown in black, reply in blue, original text in red and revised text in green. All references to line numbers refer to the original text (the text file as used by reviewer 1).

Krause-Jensen et al. measure pH, temperature and oxygen concentration across sev- eral scales where pH is expected to vary naturally due to macrophyte metabolic activity. The measurements in this manuscript are comprehensive and impressive, but while some are not novel (it is well established that pH varies due to macrophyte photosynthesis both on a habitat wide scale and at their thallus surface in the diffusion boundary layer), this manuscript will still be of extreme interest to members of the scientific community who study small-scale coastal biogeochemistry, benthic ecology, macroalgal physiology, ocean acidification, and any combination of these themes. What is particularly significant about the manuscript is the compilation pH variability caused by autotrophs at a variety of scales, and even more so, the investigation of pH variability several heights above the substrate within the kelp bed is particularly novel/interesting. These two aspects of the manuscript are extremely useful to the scientific community. As the authors state, measurements such as these are important for forecasting the effects of ocean acidification on future shallow coastal systems. Most critiques I have of this manuscript are of a relatively minor nature.

Moderate comments:

1) The use of saturation state throughout: If total alkalinity or dissolved inorganic carbon was not measured during specific seasons, then I consider it is inappropriate to calculate saturation states from pH and salinity for these sampling periods, regardless of whether correlations between salinity and total alkalinity are known from this region. Since pH and saturation states are so closely correlated, I do not consider that also mentioning and showing rough estimates of saturation data states adds anything to the manuscript. Furthermore, I consider it somewhat simplistic to imply that saturation states below 1 are "corrosive" (e.g. line 51). There is much evidence that this is not the case.

Reply:

We have now restricted the estimation of saturation states to the periods when we had measured total alkalinity and inorganic carbon concentration (September 2013 and September 2014) and, hence, had the best basis for quantifying saturation states. Consequently, Fig. 3C (fjord scale Ω_{arag} as a function of O_2 for the 3 sampling periods) and Fig. A4 (fjord scale Ω_{arag} during the three sampling periods) are omitted and the ranges of Ω_{arag} are mentioned in the text. We have also reworded the description of corrosive states. The text has been revised as indicated below.

l. 22-23

- ".. and large-scale assessments of pH and the saturation state for aragonite (Ω_{arag}) indicate that it is already close to corrosive states ($\Omega_{arag} < 1$)."

- ".. and large-scale assessments of pH and the saturation state for aragonite have let to the notion that the Arctic Ocean is already close to corrosive state.".

- 'however' added in the following line.

l. 35-37

-“Based on pH-measurements combined with relationships between salinity, total alkalinity and dissolved inorganic carbon we also estimated variability of Ω_{arag}.”

-“Based on pH-measurements combined with point samples of total alkalinity, dissolved inorganic carbon and relationships to salinity we also estimated variability of Ω_{arag}.”

l. 41-43

- “Overall, Ω_{arag} was favorable to calcification, and pelagic and benthic metabolism was an important driver of pH and Ω_{arag} producing mosaics of variability from low levels in the dark to peak levels at high irradiance.”

- “Overall, pelagic and benthic metabolism was an important driver of pH and Ω_{arag} producing mosaics of variability from low levels in the dark to peak levels at high irradiance generally appearing favorable for calcification.

l. 50-52

- “Indeed, large-scale assessments of pH and the saturation state for aragonite (Ω_{arag}) indicate that Arctic Ocean seawaters are already in close proximity to corrosive states ($\Omega_{arag} < 1$, Fabry et al., 2009).”

- “Large-scale assessments of pH in combination with saturation states for aragonite (Ω_{arag}) < 1 have led to the notion that the Arctic Ocean is already in close proximity to corrosive state (Fabry et al., 2009).”

l. 165-167

-“Relationships between A_T and salinity (S) were used to verify the published relationship for the Godthåbsfjord system (TA=159+63S, Meire et al. 2014) which was subsequently applied for calculation of A_T based on salinity data collected in April, July and September.”

-“Relationships between the point samples of A_T and salinity (S) were used to verify the published relationship for the Godthåbsfjord system (TA=159+63S, Meire et al., 2015) which was subsequently applied for estimation of A_T for the full September data set.“

l. 256-258

-“Corresponding Ωarag values ranged from minimum values of 1.5, observed in the bottom waters of the inner part of the fjord in July and September, to maximum values of 3, observed in the surface and subsurface waters in April and July (Fig. A4).”

-“Ωarag values were closely coupled to pH and ranged from minimum values of 1.6, observed in the bottom waters of the inner part of the fjord to maximum levels of 2.5 in the subsurface waters in September (Krause-Jensen et al. 2015).”

l. 268-270

-“Hence, overall, pH showed much tighter correlation with O2 levels than with water temperature, and the correlation between pH and O2 was matched by a close correlation between Ωarag and O2-levels (Fig. 3C).”

-“Hence, overall, pH showed much tighter correlation with O2 levels than with water temperature, and the correlation between pH and O2 implied a similar close correlation between Ωarag and O2-levels.”

l. 435-437

- “Overall, the identified Ω_{arag} conditions were favorable to calcification as they were generally well above 1, particularly in illuminated habitats with intense photosynthesis. “

- “Overall, the identified Ω_{arag} conditions were well above 1, particularly in illuminated habitats with intense photosynthesis and, hence, indicated favorable conditions for calcification. “

2) Microprofile methods: Many details are missing with respect to the measurements in the DBL: How long was the micro-electrodes left before the measurements in the DBL began? I.e. was the DBL in steady state or not? If the DBL was not in a steady state then the pH data obtained could underestimate the true values that can be reached (i.e. as time goes by pH at the surface should constantly increase until the steady state is reached). What were the seawater flow velocities used here? Velocity is one of the most important components that modify the pH within the DBL. What was the dimensions of the chamber used during these measurements of pH, and how was flow velocity modified? How many replicates were conducted with each species? If the aim was to determine what pH likely is at the surface of the different species in the field, then the authors need to demonstrate that environmentally realistic conditions were used. From the details here I cannot judge whether the data collected here reflects processes occurring in the real world - see comments below regarding discussion of these data also.

Reply: After the cut specimen was mounted in the aquarium and the sensor positioned at the lowest point (in itself taking some time), we observed a minimum period of 15 minutes before considering the first reading of the Volt sensor. This should have been long enough for the DBL to reach a steady state. The text has been revised to clarify this period.

We agree flow velocity is important and care should be taken to use flow velocities representative of the outside environment. Unfortunately we were not able to conduct measurements in a flume tank, as that would have complicated logistics. We have solved this by mounting a plastic pipette tip at the end of a tube coming from a common aquarium air-pump to generate an air current on the surface. This generated a steady flow visible with the USB microscope (drifting particles). We now have analyzed the videos and estimated the flow velocity in our field of vision. We have added this estimate to the paragraph. Ideally we would like to compare with flow velocities in the field through canopies, but we have no field measurements at this scale and have not encountered literature estimates for flow between 0-2mm above a blade surface for this area. The flow velocity was stable, we did not manipulate it to keep conditions comparable among species and replicates. We believe that the fact that there was a steady, slow flow, comparable for all species and replicas enables us to make valid comparisons between species in this study, although maybe not necessarily with cases measured under different circumstances (with other studies). We used three replicates per species. Aquarium dimensions were approximately 25 x 20 x 10 cm.

l. 221-237

- “The set-up was mounted in a room with climate control and temperature was kept at 2-3ºC. We measured pH from a point close to the leaf surface up until out of the diffusive boundary layer (DBL) where the pH was stable. We used UNISENSE micro-pH sensors with 25 or 50 μm tips, connected to a Volt meter with 1 decimal precision for mV measurements (Consort, R362). pH sensors were calibrated with a three point calibration using NIST buffers of pHNBS 4,0; 7,0 and 10,0 allowing at least 5 minutes between every reading for the sensor to stabilize. A USB microscope (Dinocapture) connected to a PC with on-screen visualization software aided in visually establishing the lowest point of the measurements, as close to the macrophyte surface as possible without breaking the tip of the electrode. A scaled picture from this lowest point allowed for back calculating the actual distance to the leaf surface afterwards. We allowed readings at this lowest point to stabilize for >5 min after which the mV value was written down manually. The microsensor was then raised 20 μm with a precise 1D micromanipulator, afterwards 30 μm, after which we continued with 50 μm increments and then 100 and 500 μm increments until a stable pH was obtained for 3 measurements or more and we considered we were outside the DBL. We evaluated 3 replicas of each species at a light intensity of 200 μmol photons m-2 s-1, and calculated the Δ pH across the boundary layer (defined from the tissue surface to where pH was at 0.99* water-column pH).”

- “The set-up was mounted in an aquarium in a climate-controlled room with temperature kept at 2-3ºC. By gently blowing the water surface above the mounted slide with air supplied by an aquarium pump, we generated a stable, low, current velocity of approximately 0.28 ± 0.02 (SE) mm s^{-1} in our observational area. We measured pH from a point close to the leaf surface up until out of the DBL where the pH was stable. We used UNISENSE micro-pH sensors with 25 or 50 μm tips, connected to a Volt meter with 1 decimal precision for mV measurements (Consort, R362). pH sensors were calibrated with a three point calibration using NIST buffers of pH_{NBS} 4,0; 7,0 and 10,0 before each series of measurements. After each change in species or replica a resting period of >15 minutes was observed to allow the DBL to be fully developed before measurements. A USB microscope (Dinocapture) connected to a PC with on-screen visualization software aided in visually establishing the lowest point of the measurements, as close to the macrophyte surface as possible without breaking the tip of the electrode. A scaled picture from this lowest point allowed for back calculating the actual distance to the leaf surface afterwards. We allowed readings at this lowest point to stabilize for >15 min after which the mV value was written down manually. The microsensor was then raised 20 μm with a precise 1D micromanipulator, afterwards 30 μm, after which we continued with 50 μm increments and then 100 and 500 μm increments until a stable pH was obtained for 3 measurements or more and we considered we were outside the DBL, between subsequent points the sensor was allowed to stabilize for at least 5 minutes. We evaluated 3 replicas of each species at a light intensity of 200 μmol photons m^{-2} s^{-1}, and calculated the Δ pH across the DBL (defined from the tissue surface to where pH was at 0.99* water-column pH).”

Minor comments:

Introduction:

3) Line 78: The sentence that kelp modify pH "as demonstrated for subtropical and tropical vegetated habitats" is a little odd, as this manuscript deals with colder climates, but the introduction does not mention the fact that these types of measurements have been conducted before in colder ecosystems. Given that this manuscript is investigating the ability of macrophytes to modify pH in

colder waters, and that the sentence itself is referring to the ability of kelp to modify pH (which predominately live in temperate and sub-polar ecosystems), I would add citations to two papers that deal specifically with the capacity of kelp to modify pH in a sub-Antarctic and temperate ecosystems (e.g. Cornwall et al. 2013a - referenced below, Delille et al. 2009), both papers which found large variability over a diel cycle. This is strange that the Delille paper is not cited here, as it is cited and discussed in the discussion.

Reply: We agree and have added the suggested references.

l. 78

- "as demonstrated for subtropical and tropical vegetated habitats (e.g. Hofmann et al. 2011, Hendriks et al. 2014)"

- "Such effects have been demonstrated for Antarctic and temperate kelp/macroalgal ecosystems (Middelboe & Hansen 2007, Delille et al. 2009, Cornwall et al. 2013a) as well as for subtropical and tropical seagrass meadows (e.g. Hofmann et al. 2011, Hendriks et al. 2014)."

4) line 106: The term "thallus boundary layer" should be changed to diffusion boundary and a citation that describes what this is and how it is formed is needed, as not all readers will be familiar with this.

Reply: We agree and have changed the text.

l. 106

- "..the thallus boundary layer of key macrophyte species"

- "..the diffusive boundary layer (i.e. the layer in which molecular diffusion is the dominant transport mechanism for dissolved material, see e.g. de Beer and Larkum 2001) of key macrophyte species"

Methods:

5) Study area: Kelp habitats are mentioned here and throughout the methods, but the specific species that are dominant in the study area should be given here; are they the same species investigated in the micro-scale pH measurements? The same comment applies for the macroalgal-dominated intertidal regions. The same comment applies to the figure legends containing photographs of seaweed, these need to have species names on them.

Reply: We have added species names (except for the brown filaments in the photo, which we did not identify to species), and yes, the dominant species of the study area were investigated in the micro-scale experiment.

l. 20-26

- "..subtidal macroalgae form productive benthic habitats along the shores to water depths of ca. 40 m (Krause-Jensen et al., 2012) interspaced with communities of benthic microalgae (Glud et al., 2010, Attard et al. 2014) as well as with scattered eelgrass meadows at 1-3 meters depth (Olesen et al., 2015). Communities of intertidal macroalgae are prominent in the intertidal zone where they form an important habitat for e.g. blue mussel (Blicher et al., 2013)."

- "..subtidal macroalgae, dominated by *Saccharina longicruris* and *Agarum clathratum* form productive benthic habitats along the shores to water depths of ca. 40 m (Krause-Jensen et al., 2012) interspaced with communities of benthic microalgae (Glud et al., 2010, Attard et al. 2014) as well as with scattered eelgrass (*Zostera marina*) meadows at 1-3 meters depth (Olesen et al., 2015). Communities of intertidal macroalgae dominated by *Fucus spp*. and *Ascophyllum nodosum* are prominent in the intertidal zone where they form an important habitat for e.g. blue mussel (Blicher et al., 2013)."

l. 207

- pH-variation in vegetated tidal pools and adjacent intertidal habitats on the shore were quantified

- pH-variation in vegetated tidal pools dominated by *Ascophyllum nodosum* and adjacent intertidal habitats on the shore also dominated by *A. nodosum* and *Fucus spp*. were quantified

Fig. 1 legend

- ".. C: Photopanel of benthic habitats: A typical kelp forest habitat and habitat colonized by microalgae/scattered filamentous algae (example from site #1, representative of sites #1-3 in map) and a vegetated intertidal pool and the adjacent vegetated shore (site #4 in map)."

- "..C: Photopanel of benthic habitats: A typical kelp forest habitat (dominated by *Saccharina longicruris*) and habitat colonized by microalgae/scattered brown filamentous algae (example from site #1, representative of sites #1-3 in map) and a vegetated intertidal pool and the adjacent vegetated shore dominated by *Ascophyllum nodosum* and *Fucus spp*. (site #4 in map)."

Fig. A1. Legend

- "..kelp forest"

- "..*Saccharina longicruris*-dominated kelp forest"

6) The study describes the general study area well, but specific details of the de- ployment area of diurnal variation in the kelp bed are needed, in particular with respects to depth and species composition where the deployments took place, as both would likely influence pH. Also, the description of the deployments within and outside kelp beds are somewhat ambiguous as to whether there is spatial pseudo-replication occurring, i.e. are the 3 kelp bed deployments closer to each other than the 3 non-kelp bed deployments? If the deployment locations of pH sensors within and outside of the kelp forests are segregated spatially, then I question whether it is appropriate to test for differences between them. 3 different kelp beds in different locations should have been used, rather than 3 locations within the same bed (as it is written currently).

Reply: We did indeed use three kelp beds situated in three different locations of the fjord and we did kelp bed vs. non-kelp bed deployments in each of the three locations. All kelp beds were dominated by *S. longicruris* with co-occurrence of *A. clathratum*. The water depth was 2-5 m (apparent from Fig. 4). We reworded to make this clear:

l. 178-182

- We conducted 3 parallel deployments of two frames in kelp habitats and two frames in habitats colonized by microalgae and scattered filamentous algae, with each deployment lasting about 48 h. The typical distance between the frames in each habitat was 10-20 m and between kelp forests and habitats colonized by microalgae and scattered filamentous algae approximately 100 m.

- We selected dense (close to 100% cover) three kelp beds located in shallow water (average depth 2-5 m) in different sites of the fjord. All kelp beds were dominated by *S. longicruris* with co-occurrence of *A. clathratum* and were surrounded by habitats colonized by microalgae and varying amounts of scattered filamentous algae. We conducted parallel deployments of frames with loggers in kelp beds vs. surrounding non-kelp habitats in each of the three sites, with each deployment lasting about 48 h. The typical distance between kelp and non-kelp habitats at each site was approximately 100 m.

Very minor changes were added in the surrounding text to improve coherence.

7) Micro-scale pH variability: Not all readers will know what each of the six species of macrophytes are. Mentioning what each are (i.e. Ochrophyta, Rhodophyta etc.) would be helpful.

Reply: Done

l. 216-221

- "pH-variations at a millimeter scale were measured in the laboratory on 6 different species of macrophytes (Ascophyllum nodosum, Fucus vesiculosus, Saccharina longicruris, Agarum clathratum, Ulva lactuca, Zostera marina) occurring in Kobbefjord and collected either there or, for logistic reasons, in another branch of the Godthåbsfjord system.

- "pH-variations at a millimeter scale were measured in the laboratory on 6 different species of macrophytes (the intertidal brown macroalgae *Ascophyllum nodosum* and *Fucus vesiculosus*, the kelps *Saccharina longicruris* and *Agarum clathratum*, the green alga *Ulva lactuca*, and the seagrass *Zostera marina*) occurring in Kobbefjord and collected either there or, for logistic reasons, in another branch of the Godthåbsfjord system.

8) Were there any effects of cutting the macroalgae on the pH data measured? It is known that leached substances from some, but not all, kelp species after they are wounded can reduce pH.

Reply: We do not expect a direct, measurable, effect of possible leached substances on the pH as we used a central measurement spot on the surface that was removed from the cut edges. Also the volume of the water in the aquarium should have diluted any possible effects and we have not visually observed leaching. However we cannot completely exclude the algae affecting aquarium pH in this way. However we think this effect should be negligible compared to the photosynthetic effect on pH.

9) Lines 219 - 221: In nature the macroalgal blades do not exist in isolation, yet here they are examined in this way. Kelp canopies can attenuate water (as mentioned by the authors in the discussion), is it not likely that this could further increase the DBL thickness, leading to larger changes in pH at the thallus surface? Some discussion of how this set-up could influence the results should be mentioned.

Reply: We agree and have expanded the comment already made on this in the discussion:

l. 420-422

- Reduced flows as present in dense vegetation increase the boundary layer thickness and consequently the pH range (Hurd et al., 2011, Cornwall et al., 2013)

- Reduced flows as present in dense vegetation increase the DBL thickness and consequently the pH range (Hurd et al., 2011, Cornwall et al., 2013). The current experiment was, hence, conducted at reduced flow, and, importantly, with the same flow conditions for all species.

10) Line 236: The term "DBL" is defined previously and should be used throughout rather than the more colloquial "boundary layer".

Reply: Done.

11) Line 216: Some mention of how the different species of macrophytes' blade varied in morphology might be useful here, as DBL thickness can be altered by even small undulations (Hurd and Pilditch 2011).

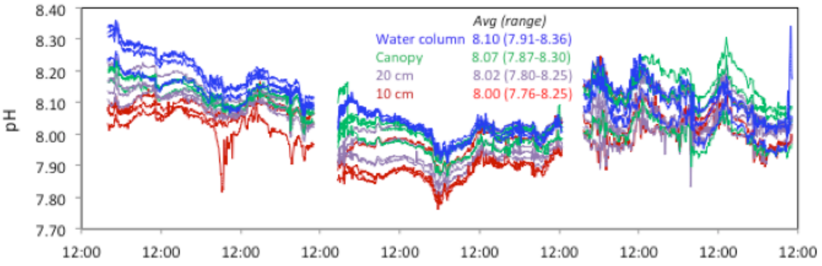
Reply: Done.

- We deleted the following sentence in the results section (l. 329-331) "There were important differences among species, which likely related to their photosynthetic rates and variations in the thickness of their boundary layer."

- and added the following line to the discussion (l. 415): "The interspecific differences likely related to the species' photosynthetic rates as well as to their morphology, which affect the thickness of the DBL (Hurd and Pilditch 2011)."

Results: 12) Figure 7: I consider this the most novel aspect of the study, but it is hard to see the exact differences the authors mention in the results. Is it possible to break this figure down in a second panel that displays the mean of each day, say every hour or so, so that the mean and variability of pH at each time of the day in each location can be observed?

Reply: We have played with various additional presentations of the data and found that the best solution was to provide information on the average and range of pH (after transferring to H+ concentrations and subsequently backtransferring) and provide these in the original figure. We hope you like this solution.



13) Lines 329 - 331. This is more a discussion point, but begs the question of why the DBL

thickness is not presented, or why photosynthetic rates were not measured? DBL thickness should have been easy to calculate with the methods used here to determine pH within the DBL.

Reply: We did not measure photosynthesis. However, we did measure the thickness of the DBL and also measured the DBL at various light intensities. As the focus of this paper is on pH variability at different scales, we found that this information would be too detailed in the context of this paper. We will instead present this information in a separate paper.

Discussion: 14) Lines 363-366: The differences in pH between kelp, and non-kelp, dominated habitats recorded here were small in the paired measurements. In addition, no data is provided showing that the density of kelp influences pH in a particular habitat, nor do the authors conduct manipulative experiments that separated out the effects of kelp and phytoplankton on pH variability. Therefore, I would not consider that the manuscript can support the statement that "mosaics of pH reflected that the density of primary producers...were key drivers of pH variability".

Reply: This summarizing statement on the effect of primary producer density on pH range and variability is aimed broader that at the small difference between pH in the two neighboring submerged benthic habitats (which are both directly, and through advection, affected by the productivity of benthic vegetation). It is certainly also aimed at the much steeper pH gradients/variability in the dense benthic communities (subtidal, intertidal, and in vegetation DBL) as opposed to the less dense pelagic communities. Hence, a pH-variability of e.g. 0.2 units operates over a 10-100 m scale in the planktonic community where the density of primary producers is low while it operates over a cm-m scale in communities of benthic primary producers, which have a much higher density. Further, within each of these communities, the highest pH levels were recorded in the surface layers representing highest concentration of phytoplankton (chl) and the most productive layers of the kelp. The same is true on a temporal scale where the diurnal pH variation in the benthic vegetation matches the seasonal variability of pH in the planktonic community. We have modified the text a bit to strengthen this meaning.

l. 363-368

- The mosaics of pH reflected that the density of the primary producers, and the spatio-temporal separation of photosynthesis and ecosystem respiration in combination with mixing of water masses were key drivers of the variability in both planktonic and benthic communities. Thus, the vertical gradient of declining pH from upper illuminated to lower shaded habitats varied from the 10-100 m scale in the planktonic community to the m scale in the dense kelp forest.

- The mosaics of pH reflected that the density of the primary producers, and the spatio-temporal separation of photosynthesis and ecosystem respiration in combination with mixing of water masses were key drivers of the variability in both planktonic and benthic communities. Hence, the vertical gradient of declining pH from upper illuminated to lower shaded habitats varied from the 10-100 m scale in the planktonic community where the density of primary producers is relatively low to the cm-m scale in dense kelp forests. The same is true on a temporal scale where the diurnal pH variation in the benthic vegetation matches the seasonal variability of pH in the planktonic community.

15) Page 16, 2nd paragraph: Comparing pH variability here with that in other sys- tems is really like comparing apples and oranges unless a multitude of factors are examined. Different depths, seawater retention times, densities of macroalgae, light regimes, species, etc could all play

important roles, making comparisons difficult. The start of this paragraph needs an overhaul, there are a number of unreferenced points, the studies the authors compare their data to are not fully inclusive, and overall I con- sider that the paragraph should make more of an effort to compare the data here to points I have mentioned here, rather than speculating on why there was a slight difference (0.03 units) between the filamentous and kelp habitats.

Reply: We see your point and have revised the text with this in mind.

l. 372-382

- The diel variability in kelp beds was in range with that reported from a Californian kelp forest (Frieder et al., 2012), while greater than reported for Mediterranean seagrass beds (Hendriks et al. 2014), and below the range of up to 1 pH unit reported for dense algal mats (Middelboe and Hansen, 2007). The diel variability in pH in the kelp forest was subjected to a stronger direct biological control than that of the microalgae/filamentous algae, as reflected in stronger pH vs. O2 relationships and steeper pH vs. light relationships, because of the larger density of the kelps and associated faster rates of metabolic activity per unit volume in combination with reduced flow in the dense habitat. The habitat colonized by microalgae/filamentous algae carried a less distinct biological signal reflecting the benthic primary producers at the site in combination with a signal from the planktonic community and the nearby kelp forests in the water masses exchanged with tidal currents.

- Though a multitude of factors including water depth, light regime, season, seawater retention time, density and plant species may all affect pH variability in vegetated habitats, our results match evidence from other latitudes of strong pH variability in macroalgal forests and seagrass meadows. Hence, marked diel pH variability has also been reported from a Californian kelp forest (Frieder et al., 2012), a Mediterranean seagrass bed (Hendriks et al. 2014), and in extreme case for a temperate shallow dense algal bed (diel range ca. 1 unit, Middelboe and Hansen, 2007) and kelp forest (diel range: ca. 0.6-0.8 pH units, Cornwall et al. 2013a). Our pH measurements in benthic habitats neighboring the kelp forest also carried a biological signal, though less distinct, likely reflecting the combined signal of the benthic primary producers at the site, of the neighboring kelp forests and of the planktonic community in the water masses exchanged with tidal currents.

16) Page 17, 2nd paragraph: The first half of this paragraph begins to discuss points of extreme importance to those scientists who study macroalgal habitats. This should be expanded and a separate paragraph should deal with the variability in rockpools, which is a phenomenon that is well known and of less importance to the readers.

Reply: We split the paragraph in two as suggested and added the following sentence in extension of the macroalgal paragraph (l. 398): The fast rates of metabolic activity in combination with reduced flow in such densely vegetated habitats make these 3-D patterns appear in spite of the marked exchange of water masses resulting from the 1-4.5 m tidal range.

17) Line 418: Regarding pH measurements of Sporolithon durum, the review of Roleda and Hurd (2012) should not be cited here, they reproduce the exact figures from Hurd et al. (2011) which is the original source.

Reply: OK. We omitted the Roleda and Hurd (2012) reference.

18) Line 419: The citation to Cornwall et al. (2013) is not in the bibliography, but rather the paper in the bibliography is Cornwall et al. (2012). I suspect that Cornwall et al. (2013b -referenced below) is required in the bibliography. Please check all other references are correct.

Reply: Thank you. We substituted Cornwall et al 2012 by Cornwall et al 2013b.

19) Line 407-408 & Figure 8: I question why pH did not reach a high value for Ulva here, when it is known that Ulva has some of the most efficient CO2 concentrating mechanisms known, and is capable of elevating pH to very high levels in enclosed habitats – as mentioned by the authors. The authors should discuss the possible reasons why pH elevation in the DBL was not high in subsequent sections.

Reply: True. We added this comment in line 419: The pH-range across the DBL of Ulva was surprisingly low considering Ulvas ability to elevate pH to high levels (Björk et al. 2004) but probably the combination of low water temperature and limited nutrient supply limited Ulvas photosynthetic rate.

20) Page 19, 1st paragraph: Though high pH could be an important refuge from po- tential impacts of ocean acidification in the future during the day, what about at night when pH is even more reduced?

Reply: Yes during night the opposite may certainly be the case. We address this on p. 19, 2nd paragraph.

References cited in this review:

Cornwall CE, Hepburn CD, McGraw CM, Currie KI, Pilditch CA, Hunter KA, Boyd PW, Hurd CL. 2013a. Diurnal fluctuations in seawater pH influence the response of a calcifying macroalga to ocean acidification. Proc. R. Soc. B 80: http://dx.doi.org/10.1098/rspb.2013.2201.

Cornwall CE, Hepburn CD, Pilditch CA, Hurd CL. 2013b. Concentration boundary layers around complex assemblages of macroalgae: Implications for the effects of ocean acidification on understorey coralline algae. Limnol. Oceanogr. 58:121-130.

Cornwall CE, Hepburn CD, Pritchard DW, McGraw CM, Currie KI, Hunter KA, Hurd CL. 2012. Carbon-use strategies in macroalgae: differential responses to lowered pH and implications for ocean acidification. J. Phycol. 48:137-144.

Delille B, Borges AV, Delille D. 2009. Influence of giant kelp beds (Macrocystis pyrifera) on diel cycles of pCO2 and DIC in the Sub-Antarctic coastal area. Estuar. Coast. Shelf Sci. 81:114-122.

Hurd CL, Cornwall CE, Currie KI, Hepburn CD, McGraw CM, Hunter KA, Boyd P. 2011. Metabolically-induced pH fluctuations by some coastal calcifiers exceed projected 22nd century ocean acidification: a mechanism for differential susceptibility? Glob. Change Biol. 17:3254-3262.

Hurd CL, Pilditch CA. 2011. Flow-induced morphological variations affect diffusion boundary-layer thickness of Macrocystis pyrifera (Heterokontophyta, Laminariales). J. Phycol. 47:341-351.

Roleda MY, Hurd CL. 2012. Seaweed responses to ocean acidification. Pages 407- 431 in Wiencke C, Bischof K, eds. Seaweed Biology: Novel insights into Ecophysiology, Ecology and Utilization.

Berlin: Springer Berlin Heidelberg.

Additional changes

p. 4910, l. 9: omitted “comprising about 35% of the World’s coastline (Krause-Jensen and Duarte 2014) as approximately the same meaning appears in l. 26.

Reply to reviewer 2

Review comments shown in black, reply in blue, original text in green and revised text in red. Page numbers refer to the original version (the pdf file as used by the reviewer)

Krause-Jensen et al. measured the inorganic carbon chemistry in a Greenlandic fjord, and by measuring O2 as well, they are able to evaluate and distinguish tidal and photoautotrophic influences. They examined the inorganic carbon chemistry from the planktonic community down to surface of macroalgae and they also examined seasonal differences. It should be pointed out that some previous studies, already measured the fluctuations in inorganic carbon concentrations in coastal habitats (Delille et al. 2000, Middelboe and Hansen 2007) and related them to photoautotrophic activity, but the detailed analysis of this study is completely new. Furthermore, the Arctic with its particularities has in this context never been examined before. The methods are timely and well explained.

Thank you!

Concerning the presentation of the results I would suggest to provide also pCO2-data in the text, to allow an easier comparison with previous works from photosynthesis researchers. For researcher focusing on aquatic photosynthesis the pCO2-value is of particular relevance (This might be a very personal point of view, but still I would like to give this advice).

Reply: We agree that $p\mathrm{CO}_2$ data are of interest and we have added the ranges. As the main point in this paper is the changes in pH we prefer not to enter a detailed description of pCO2. We are providing such detailed description of gas exchange in sub-Arctic and Arctic kelp forests in a separate paper (not yet published)

- p. 14918, l. 4 (fjordscale): Corresponding $p\mathrm{CO}_2$ levels ranged from 162 to 325 µatm in the surface layer across the fjord in September.

- p. 4919, l. 30 (small-scale and diurnal pH variability): Corresponding pCO2-levels ranged from 238 to 536 µatm at the kelp sites and from 258 to 515 µatm at the microalgal/filamentous algal sites.

Generally, but in the discussion I would suggest to pay more attention to the effects of ocean acidication on non-calcifying algae/ animals. These are often overlooked and receive too little attention compared to calcifying species. However, in your study, where you focus on Arctic fjords, where kelps are the most important keystone species you should mention the known OA-effects on kelp and in my opinion even highlight it in your discussion.

Reply: We have added information on OA effects on kelp as specified in the responses below.

The paper is very well written and beside the mentioned suggestions for improvements I only have some minor remarks, which potentially might help to improve the paper and broaden its audience. I hope that you consider them constructive. In Summary, I enjoyed reading the paper and recommend the publication after a minor revision.

Thank you for the constructive criticism.

Page 4909 Line 5: Why do you limit yourself to calcifyers? Also non-calcifying organisms will, in particular photoautotrophs will be strongly influenced by lowered pH? I recommend mentioning them.

Reply: We did the following change of text:

- As most calcifiers occupy coastal habitats, the assessment of risks from OA to these vulnerable organisms cannot be derived from extrapolation of current and forecasted offshore conditions

- Effects of OA on calcifiers and non-calcifying phototrophs occupying coastal habitats cannot be derived from extrapolation of current and forecasted offshore conditions,

Page 4910 Line 20: Gordillo and Mercado 2011 named this problematic in 2011, consider citing them.

Gordillo and Mercado2011, Inorganic carbon acquisition in algal communities:are the laboratory data relevant to the natural ecosystems? Photosynth Res (2011) 109:257–267

Reply: Reference added (it is Mercado and Gordillo 2011) and a line included:

- , the same is true regarding potential effects of OA on coastal phototrophs (calcifying or non-calcifying) (Mercado and Gordillo, 2011).
- L. 24: vulnerability changed to sensitivity

Page 4911 Line 8: A reference to Delille et al. 2000 and Middelboe and Hansen et al. 2007 is much more appropriate.

Reply: We have added references and modified the text:

"Such effects have been demonstrated for Antarctic and temperate kelp/macroalgal ecosystems (Middelboe & Hansen 2007, Delille et al. 2009, Cornwall et al. 2013a) as well as for subtropical and tropical seagrass meadows (e.g. Hofmann et al. 2011, Hendriks et al. 2014)."

Line 14: What about non calcifying organisms, such as the kelp, the key-species of the ecosystem you are investigating. Kelps growth can be stimulated by OA (Olischläger et al. 2012), but its reproduction can be OA-insensitive (Olischläger et al. 2012), or hampered by OA (Roleda et al. 2011, Xu et al. 2015). Furthermore OA affects the competition between understory red algae and kelps (Connell and Russell 2010) You are examining kelp habitats, in my opinion you should mention the known pH-effects on kelp, in particular of species with the Arctic distribution.

Roleda et al. 2012. Ocean acidification and seaweed reproduction: increased CO2 ameliorates the negative effect of lowered pH on meiospore germination in the giant kelp Macrocystis pyrifera (Laminariales, Phaeophyceae) Global Change Biology, 18, pages 854–864

Olischläger et al. (2012) Effects of ocean acidification on differ- ent life-cycle stages of the kelp Laminaria hyperborea (Phaeophyceae) Bot Mar 55, 5, 511–525, DOI: 10.1515/bot-2012-0163,

Xu et al. (2015) Effects of CO2 and Seawater Acidification on the Early Stages of Saccharina japonica Development, Environ. Sci. Technol., 2015, 49 (6), pp 3548–3556, DOI: 10.1021/es5058924

Connell S, Russell BD (2010) The direct effects of increasing CO2 and temperature on non-calcifying organisms: increasing the potential for phase shifts in kelp forests, Proc. R. Soc. B 2010 277, 1409-1415

Reply: We agree and have modified the section to also include mentioning of potential effects of OA on the phototrophs:

p. 4911, l. 8-14

- Calcifiers such as bivalves, brittle stars and sea urchins are ecologically important as they contribute significantly to carbon cycling in both sub-Arctic and high-Arctic areas of Greenland where their distribution range from the intertidal zone to >300 m depth (Sejr et al. 2002; Blicher et al. 2007, 2009, 2013 Blicher & Sejr 2011). Calcifiers, especially bivalves are also important prey items for marine mammals (Born et al. 2003) and sea birds (Blicher et al. 2011).

- Calcifiers such as bivalves, brittle stars and sea urchins, which are potentially vulnerable to OA, are ecologically important as they contribute significantly to carbon cycling in both sub-Arctic and Arctic Greenland where their distribution range from the intertidal zone to >300 m depth (Sejr et al., 2002; Blicher et al., 2007, 2009, 2013 Blicher and Sejr, 2011). Phototrophs such as kelps, while being able to affect the pH regime, may also respond to OA, which has been shown to stimulate their growth (Olischläger et al. 2012) and affect the competition between kelps and understory red algae (Connell and Russell 2010).

Page 4915 Line 1: Can you define kelp habitats, species depth, density? Species would be most important

Reply: yes – we have now added a specification as also requested by reviewer 1. Old and new text are indicated below.

- We conducted 3 parallel deployments of two frames in kelp habitats and two frames in habitats colonized by microalgae and scattered filamentous algae, with each deployment lasting about 48 h. The typical distance between the frames in each habitat was 10-20 m and between kelp forests and habitats colonized by microalgae and scattered filamentous algae approximately 100 m.

- We selected dense (close to 100% cover) three kelp beds located in shallow water (average depth 2-5 m) in different sites of the fjord. All kelp beds were dominated by *S. longicruris* with co-occurrence of *A. clathratum* and were surrounded by habitats colonized by microalgae and varying amounts of scattered filamentous algae. We conducted parallel deployments of frames with loggers in kelp beds vs. surrounding non-kelp habitats in each of the three sites, with each deployment lasting about 48 h. The typical distance between kelp and non-kelp habitats at each site was approximately 100 m.

Page 4916 Line 14: Saccharina longicruris or Saccharina latissima? See figure 8, where you write latissima,

Reply: It is *S. longicruris*. We have corrected the legend of Fig. 8 accordingly.

Page 4918 Line 27: Could you describe the light attenuation underwater, in my experience in Arctic fjords in summer the underwater light regime is strongly influence by melting river plums. You describe a river flowing into your fjord, therefore I asked myself if there were pronounced river sediments plums above your algae habitats? Sometime, kelp algae can even be densely covered by sediments, which might affect their photosynthesis and thereby influence on the local pH.

Reply: The river did not cause pronounced sediment plumes above the algal habitat. K_d at the central station of Kobbefjord has been reported at 0.135 m^{-1} in September (Sejr et al. 2014). This information is now added in the description of the study area.

p. 4912, l. 19

- Light attenuation in the water column has been reported to range from 0.083 in February over 0.197 in May to 0.135 in September (Sejr et al. 2014).

Page 4922 Line 25: The growth season of kelp in the Arctic is difficult to address, since Arctic brown algae accumulate C-storage metabolites during spring summer and grow in winter (Dunton and Schell 1986). In peak summer many adult species do not show vegetative growth and tend to fuel their reproduction. At least in the high Arctic this reproduction phase is decreasing or has already ended in September (Olischläger and Wiencke 2013). Furthermore, arctic kelps tend to store more of their photosynthates in preparation for the polar night. This potentially might affect their respiration rates (Olischläger et al. 2014) and be relevant for your data. Hence algae might be already preparing for the overwintering and growth season, showing reduced metabolic activity. In my opinion you should consider discuss these informations in relation to your pH/O2- profiles.

Dunton KH, Schell DM (1986) Seasonal carbon budget and growth of Laminaria solidungula in the Alaskan High Arctic. Mar Ecol Prog Ser 31:57–66

Olischläger M, Wiencke C (2013a) Seasonal fertility and combined effects of temperature and UV-radiation on Alaria esculenta and Laminaria digitata (Phaeophyceae) from Spitsbergen. Polar Biol 36:1019–1029

Olischläger M, Iniguez C, Gordillo FJL , Christian Wiencke (2014) Biochemical composition of temperate and Arctic populations of Saccharina latissima after exposure to increased pCO2 and temperature reveals ecotypic variation. Planta Volume 240: 1213-1224, DOI 10.1007/s00425-014-2143-x

Reply: Delille et al (2009) whom we refer to here state in the abstract “Daily variations of pCO_2 and DIC are significant in the spring and summer, but absent in the winter, reflecting the seasonal cycle of biological activity in the kelp beds.” So, even though blade extension takes place in winter, the main C-assimilation and, hence, the main effect on pH, occurs during the spring and summer when irradiance is highest. For clarity we have changed “productive season” to “spring and summer”.

Page 4925 Line 10: I remember a talk from Frank Melzner, where he showed that mussels grow at very low pH-conditions, but were in good physiological conditions with well-calcified shells as long as they had enough to eat. This was different when the mussels were starving. I hope this is correct in the way I explained it. Consider, have a look at Frank Melzners papers or contact him.

Reply: Good point! We have expanded the sentence and added the reference:

- “Blue mussels have indeed been observed to abound in intertidal macroalgal habitats (Blicher et al. 2013) and along with other calcifiers to be trophically linked with habitat-forming algae such as *Ascophyllum* (Riera et al., 2009), and have also been reported to tolerate high $p\mathrm{CO_2}$ concentrations when food is abundant (Thomsen et al., 2013)."

Page 4926: Increased primary production? In my eyes depending on the habitat, Fu- cus, subjected to high pCO2 showed a negative growth response (Gutow et al. 2014). Laminaria hyperborea responded with increased growth (Olischläger et al. 2012). Po- tentially, this statement is too general. Consider being more specific and provide references. Furthermore, the response is apparently dependent on the influence of further environmental factors, such as light, nutrients temperature.

Gutow et al. (2014) Ocean acidification affects growth but not nutritional quality of the seaweed Fucus vesiculosus (Phaeophyceae, Fucales) Journal of Experimental Marine Biology and Ecology, 453 , pp. 84-90 . doi:10.1016/j.jembe.2014.01.005

Olischläger et al. (2012) Effects of ocean acidification on different life-cycle stages of the kelp Laminaria hyperborea (Phaeophyceae) Bot Mar 55, 5, 511–525, DOI: 10.1515/bot- 2012-0163

Reply: Rereading the sentence I see that it can be misunderstood as a discussion of OA effects on the vegetation, which is not the intention. The aim was to point to the vegetation as a potential niche of high pH in summer. To avoid this misunderstanding we have now rephrased:

- Under scenarios of ocean acidification such coastal environments of increased primary production should gain increased importance as local refuges for calcifyers.

- Under scenarios of ocean acidification such vegetated habitats may gain increased importance as local refuges for calcifyers.

We have also rephrased the final sentence, which could also be misunderstood:

- Similarly, increased pelagic primary production has been forecasted for parts of the Arctic Ocean (Arrigo et al., 2008; Slagstad et al., 2011, Popova et al., 2012) and may also gain increased importance as local niches of high pH.

- Similarly, increased pelagic primary production as forecasted for parts of the Arctic Ocean (Arrigo et al., 2008; Slagstad et al., 2011, Popova et al., 2012) may also create local niches of high pH.

Macroalgae contribute to nested mosaics of pH variability in a sub-Arctic fjord

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Abstract. The Arctic Ocean is considered the most vulnerable ecosystem to ocean acidification (OA) and large-scale assessments of pH and the saturation state for aragonite (Ω_{arag}) have let to the notion that the Arctic Ocean is already close to corrosive states. In high-latitude coastal waters the regulation of pH and Ω_{arag} is, however, far more complex than offshore because increased biological activity and input of glacial meltwater affect pH. Effects of OA on calcifiers and non-calcifying phototrophs occupying coastal habitats cannot be derived from extrapolation of current and forecasted offshore conditions, but requires an understanding of the regimes of pH and Ω_{arag} in their coastal habitats. To increase knowledge of the natural variability of pH in the Arctic coastal zone and specifically to test the influence of benthic vegetated habitats, we quantified pH-variability in a Greenland fjord in a nested scale approach. A sensor array logging pH, O_2, PAR, temperature and salinity was applied on spatial scales ranging from km-scale across the horizontal extension of the fjord, over 100 m-scale vertically in the fjord, 10-100 m scale between subtidal habitats with and without kelp forests and between vegetated tidal pools and adjacent vegetated shores, to cm-m scale within kelp forests and mm-scale across diffusive boundary layers (DBL) of macrophyte tissue. In addition, we assessed the temporal variability in pH on diurnal and seasonal scales. Based on pH-measurements combined with point samples of total alkalinity, dissolved inorganic carbon and relationships to salinity, we also estimated variability of Ω_{arag}. Results show variability in pH and Ω_{arag} of up to 0.2-0.3 units at several scales, i.e. along the horizontal and vertical extension of the fjord, between seasons and on a diel basis in benthic habitats and within $1 m^3$ of kelp forest. Vegetated intertidal pools exhibited extreme diel pH variability of >1.5 units and macrophyte DBL a pH-range of up to 0.8 units. Overall, pelagic and benthic metabolism was an important driver of pH and Ω_{arag} producing mosaics of variability from low levels in the dark to peak levels at high irradiance generally appearing favorable for calcification. We suggest that productive coastal environments may form niches of high pH in a future acidified Arctic Ocean.

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1. Introduction

The Arctic Ocean is considered to be the most vulnerable ecosystem to ocean acidification due to the combined effects of low temperature, which increases the solubility of CO_2 and, at places, dilution of the buffering capacity of seawater by freshwater inputs (Fabry et al., 2009, AMAP, 2013). Indeed, large-scale assessments of pH in combination with saturation states for aragonite (Ω_{arag}) < 1 have led to the notion that the Arctic Ocean is already in close proximity to corrosive state (Fabry et al., 2009). However, whereas this has been documented for offshore waters, the Arctic contains a massive coastline where the regulation of pH and Ω_{arag} is far more complex than that offshore (Hofmann et al. 2011, Duarte et al., 2013). In coastal waters, the role of air-sea CO_2 exchange in regulating pH operates along with watershed effects driven by the discharge of freshwater and the effects of metabolically intense communities on pH (Duarte et al. 2013). The Greenland Ice Sheet is melting at a rate that has more than doubled in the recent decade (Helm et al. 2014) and Greenland fjords are, hence, potentially among the most susceptible to the effects of freshening and acidification.

As most calcifiers occupy coastal habitats, the assessment of risks of Arctic acidification to these vulnerable species cannot be derived from extrapolation of the current and forecasted offshore conditions alone, but requires an understanding of the regimes of pH and Ω_{arag} in the coastal habitats they occupy, and the same is true regarding potential effects of OA on coastal phototrophs (calcifying or non-calcifying) (Mercado and Gordillo, 2011). Such information is currently largely lacking for the Arctic in general and for Greenland in particular, which calls for efforts to understand variability of pH in the coastal zone informing on the factors controlling pH and ultimately determining the sensitivity of the coastal Arctic Ocean ecosystem to ocean acidification.

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Greenland has a vast and highly indented coastline, extending approximately 44,000 km and representing ca. 12% of the world's coastline (Krause-Jensen and Duarte, 2014). This coastline forms a complex network of fjords and open coasts that contains multiple features contributing to heterogeneity, such as continental ice and freshwater discharge at the headwaters, variable slopes and substrates, differential water residence time conducive to widely distinct temperature regimes within neighboring areas (Olesen et al., 2015), and tides that generate intertidal habitats and force flow patterns. In addition, Greenland fjords often support highly productive kelp forests (Krause-Jensen et al., 2012) and intertidal seaweed communities (Høgslund et al., 2014), which have been suggested to have the capacity to affect pH and Ω_{arag} locally (Krause-Jensen and Duarte, 2014). Such effects have been demonstrated for Antarctic and temperate kelp/macroalgal ecosystems (Middelboe & Hansen 2007, Delille et al. 2009, Cornwall et al. 2013a) as well as for subtropical and tropical seagrass meadows (e.g. Hofmann et al. 2011, Hendriks et al. 2014). Calcifiers such as bivalves, brittle stars and sea urchins, which are potentially vulnerable to OA, are ecologically important as they contribute significantly to carbon cycling in both sub-Arctic and Arctic Greenland where their distribution range from the intertidal zone to >300 m depth (Sejr et al., 2002; Blicher et al., 2007, 2009, 2013 Blicher and Sejr, 2011). Phototrophs such as kelps, while being able to affect the pH regime, may also respond to OA, which has been shown to stimulate their growth (Olischläger et al. 2012) and affect the competition between kelps and understory red algae (Connell and Russell 2010).

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Although the variability in pH and Ω_{arag} in Greenland fjords has not been reported, available oceanography and environmental surveys suggest that this may be substantial. For instance, in Young Sound, Sejr et al. (2011) found that the extent of sea-ice cover and inputs of glacial melt water affect seawater $p\mathrm{CO}_2$ levels and sea-air exchange at spatial, seasonal and inter-annual scales.

Seasonal dynamics of autotrophic and heterotrophic plankton metabolism have also been found to markedly affect pCO_2 levels in Kobbefjord, a sub-Arctic fjord in SW Greenland (Sejr et al., 2014). However, information on scales of variability in pH and Ω_{arag} in Greenland fjords is still lacking, precluding the assessment of their current and future vulnerability to ocean acidification.

Here we quantify pH variability in Kobbefjord, SW Greenland. This sub-Arctic fjord supports dense and productive subtidal kelp forests, intertidal macroalgal habitats and high abundance of bivalves and sea urchins with important roles in the ecosystem (Blicher et al. 2009; Krause-Jensen et al., 2012). We hypothesize that Kobbefjord contains a mosaic of pH environments nested across a range of scales of variability and that primary production in general, and by macroalgae in particular, may be an important driver of pH variability relevant for benthic calcifiers. We first assess seasonal and spatial variability in the pelagic pH at km scale along the horizontal extension and at 100 meter scale vertically in the fjord. We then examine diel variability in pH within subtidal benthic habitats colonized by kelp forest or microalgae/scattered filamentous algae as well as in vegetated tidal pools and adjacent vegetated intertidal shores, with the distance between parallel deployments at the 10-100 m scale. We further explore the pH variability 3-dimensionally at cm- to m-scale within the kelp forest ecosystem and at mm-scale across the diffusive boundary layer (i.e. the layer in which molecular diffusion is the dominant transport mechanism for dissolved material, see e.g. de Beer and Larkum 2001) of key macrophyte species. Whereas our assessment focuses on pH, we also discuss the associated variability of Ω_{arag}.

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2. Methods

2.1. Study area

Kobbefjord is located in the extensive Godthåbsfjord system in south west Greenland (Fig. 1A). The fjord is 17 km long and 0.8–2 km wide and has a maximum depth of 150 m. It is subjected to marked exchange of coastal water driven by a tidal range of 1- 4.5 m (Richter et al. 2011) and receives freshwater mainly from a river in the innermost part of the fjord, leading to a salinity gradient in the surface water. Sea-ice usually covers the inner part of the fjord from December to early May, but the outer part of the fjord is permanently ice free. Light attenuation in the water column has been reported to range from 0.083 in February over 0.197 in May to 0.135 in September (Sejr et al. 2014). Whereas the phytoplankton community is the main primary producer in the central parts of the fjord (Sejr et al., 2014), subtidal macroalgae, dominated by *Saccharina longicruris* and *Agarum clathratum* form productive benthic habitats along the shores to water depths of ca. 40 m (Krause-Jensen et al., 2012) interspaced with communities of benthic microalgae (Glud et al., 2010, Attard et al. 2014) as well as with scattered eelgrass (*Zostera marina*) meadows at 1-3 meters depth (Olesen et al., 2015). Communities of intertidal macroalgae, dominated by *Fucus spp*. and *Ascophyllum nodosum* are prominent in the intertidal zone where they form an important habitat for e.g. blue mussel (Blicher et al., 2013).

Three field campaigns targeting seasonal- and fjord-scale variability in pH in the pelagic zone were conducted in the spring (19 April), mid-summer (18 July) and late summer (3 September) of 2013 (Fig. 1B). The late summer survey was associated with an intensive campaign (27 August- 6 September 2013) exploring pH variability in shallow subtidal kelp habitats and neighboring habitats colonized by benthic microalgae and scattered filamentous algae (Fig. 1C). A final late summer campaign (22-30 August 2014) addressed pH variability in vegetated tidal pools and surface waters of adjacent vegetated shores (Fig. 1C). All pH data from fjord-scale to micro-scale are reported on the total pH scale.

2.2. *Fjord and seasonal scale pH variation*

To determine the large-scale spatial and seasonal variation in physical and chemical parameters in the water column of Kobbefjord, vertical profiles were measured at 11 stations located along a longitudinal gradient following the main central axis of the fjord on 19 April, 18 July, and 3 September, 2013 (Fig. 1B). We used a Seabird CTD (SBE19plus) equipped with sensors for temperature, conductivity, fluorescence (Seapoint Chlorophyll Fluorometer), oxygen (SBE 43, Seabird) and pH (SBE18, Seabird). Alongside CTD profiles, water samples were collected using a 5 L Niskin bottle at 1, 5, 10, 20, 30, and 40 m depth. Water was collected for dissolved oxygen measurement using Winkler titration (Parsons et al. 1984) which was used to calibrate the CTD oxygen optode. The pH sensor was calibrated using NBS buffers and a seawater TRIS buffer prepared according to Dickson (2007). Unfiltered water was transferred to 150 ml borosilicate glass bottles for pH analysis. The samples were poisoned with a saturated mercuric chloride solution, cooled and stored in darkness until arrival. Back in the lab, pH was measured potentiometrically using a glass reference electrode (Orion, Ross Ultra pH/ATC Triode) calibrated with NBS buffers and a seawater TRIS buffer prepared according to Dickson (2007). The measurements were used to correct the offset of the SBE 18 pH measurements.

For estimation of the saturation state of aragonite (Ω_{arag}), samples for analyses of dissolved inorganic carbon (C_T) and total alkalinity (A_T) were collected at 5 stations on one occasion (3 September 2013). Triplicate 12 ml samples were collected at 5, 10, 20, 30, 40 m depth and near the bottom. Samples were carefully siphoned through tygon tubing from Niskin bottles to 12 ml septum-capped glass vial (exetainers) allowing the water to overflow for two volume changes. The samples were poisoned with 100 µl 5% $HgCl_2$ to avoid biological alteration. C_T was analyzed with a C_T analyzer (AS-C3, Apollo Scitech Inc). The accuracy of the analysis was 2.4 µmol kg^{-1} (average numerical deviation from the reference material value) and the precision was 1.4 µmol kg^{-1} (average standard deviation of triplicate samples). A_T was analysed on an alkalinity titrator, AS-ALK2 from Apollo Scitech with verification against the same certified reference material used for pH measurements or a Metrohm Titrando 808 by open cell titration (Dickson et al. 2007) using Batch 136 supplied by the Andrew Dickson lab at UC San Diego for verification. Average analysis accuracy was 2.9 µmol kg^{-1} (average numerical deviation from the reference material value). Relationships between the point samples of A_T and salinity (S) were used to verify the published relationship for the Godthåbsfjord system (TA=159+63S, Meire et al. 2015) which was subsequently applied for estimation of A_T for the full September data set. Ω_{arag} and *p*CO2 were calculated from A_T and pH using the CO_2SYS excel programme version 2.1 (Pierrot et al., 2006) with the K1 and K2 constants from Mehrbach et al. (1973), as modified by Dickson and Millero (1987).

2.3. Small-scale and diurnal-scale pH variation

To measure small-scale and diurnal-scale variation in pH and physico-chemical variables in kelp forests and adjacent sub-tidal habitats colonized by microalgae and scattered filamentous algae we constructed metal frames measuring approximately 0.90 m × 0.90 m × 1.10 m. Each frame was equipped with instruments that allowed continuous measurements of temperature, salinity, water level, oxygen concentration, photosynthetically active radiation (PAR) and pH at ca 50 cm above the seafloor (Fig. 1S). Measurements were made every 10 min or less. - We selected three dense (close to 100% cover) kelp beds located in shallow water (average depth 2-5 m) in different sites of the fjord. All kelp beds were dominated by *S. longicruris* with co-occurrence of *A. clathratum* and were surrounded by habitats colonized by microalgae and varying amounts of scattered filamentous

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algae. We conducted parallel deployments of frames with loggers in kelp beds vs. surrounding non-kelp habitats in each of the three sites, with each deployment lasting about 48 h. The typical distance between kelp and non-kelp habitats at each site was approximately 100 m. Conductivity, temperature and water level were measured by Hydrolab DS5X and MicroCat (SBE37 Seabird). Oxygen concentration was measured using MiniDot oxygen loggers, Precision Measurement Engineering, and Hydrolab DS5X. PAR was measured using Odyssey PAR loggers from Dataflow Systems Pty Limited. pH was measured using Hydrolab DS5X and SeaFet pH loggers from Satlantic. Hydrolab DS5X pH sensors were calibrated with a routine two-point calibration using NIST buffers of pH_{NBS} 7.0 and 10.0. Before and after each deployment all instruments were placed in a 50 liter tank with sea water to intercalibrate sensors. All pH loggers were offset to the same newly calibrated high-precision seafet pH sensor, calibrated at the Satlantic facility (www.satlantic.com) on the total scale using single-point calibration. Oxygen sensors were calibrated to O_2 concentrations of the tank as determined from Winkler titrations.

To monitor three-dimensional pH variations on a m-scale within the kelp canopy, we deployed a custom built multi-sensor array, consisting of an autonomous data logger (Datataker DT85, serial number 096831) in a water-tight housing (custom built by Albatros Marine Technologies S.I.) with 16 pre-amplified pH electrodes (Omega, PHE-1304-NB). The pH sensors were attached to the submersible logger by 5 m long cables to allow for adjusting their position as needed (Fig. A1). The sensors were configured in-situ in a three dimensional array on the metal frame occupying a volume of approximately 1 m^3, with 4 sensors at 0.1 m from the bottom, 4 sensors at 0.2 m, 4 sensors just underneath the canopy and 4 above the canopy, which typically extended about 0.75 m above the seafloor. All pH sensors were calibrated with a three point calibration using NIST buffers of pH_{NBS} 4.0, 7.0 and 10.0 allowing at least 5 minutes between every reading for the sensors to stabilize. All

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pH loggers were offset to the same newly calibrated high-precision seafet pH sensor as mentioned above. On several occasions triplicate samples for determination of C_T and A_T were collected and analyzed as described above to allow calculation of carbonate chemistry and Ω_{arag}.

pH-variation in vegetated tidal pools dominated by *Ascophyllum nodosum* and adjacent intertidal habitats on the shore also dominated by *A. nodosum* and *Fucus spp.* were quantified over a diurnal cycle through sampling at low tide just after pool formation and prior to pool inundation during day and night. pH and Ω_{arag} were calculated from C_T and A_T samples collected and analyzed as described above and computed using the CO2SYS program (Pierrot et al., 2006) with in situ information on temperature and salinity. Salinity was analysed from water samples based on measurements of conductivity (Orion 3 STAR Conductivity benchtop) while oxygen concentration and water temperature were determined using a portable meter (Hack, HQ40d).

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2.4. Micro-scale pH variation

pH-variations at a millimeter scale were measured in the laboratory on 6 different species of macrophytes (the intertidal brown macroalgae *Ascophyllum nodosum* and *Fucus vesiculosus*, the kelps *Saccharina longicruris* and *Agarum clathratum*, the green alga *Ulva lactuca*, and the seagrass *Zostera marina*) occurring in Kobbefjord and collected either there or, for logistic reasons, in another branch of the Godthåbsfjord system. From each species, a piece of approximately 5 x 2 cm was cut and mounted on a microscope slide in an aquarium with seawater before measurements. The set-up was mounted in an aquarium in a climate-controlled room with temperature kept at 2-3ºC. By gently blowing the water surface above the mounted slide with air supplied by an aquarium pump, we generated a stable, low, current velocity of approximately 0.28 ± 0.02 (SE) mm s^{-1} in our observational area. We measured pH from a point close to the leaf surface up until out of

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the DBL where the pH was stable. We used UNISENSE micro-pH sensors with 25 or 50 µm tips, connected to a Volt meter with 1 decimal precision for mV measurements (Consort, R362). pH sensors were calibrated with a three point calibration using NIST buffers of pH_{NBS} 4,0; 7,0 and 10,0 before each series of measurements. After each change in species or replica a resting period of >15 minutes was observed to allow the DBL to be fully developed before measurements. A USB microscope (Dinocapture) connected to a PC with on-screen visualization software aided in visually establishing the lowest point of the measurements, as close to the macrophyte surface as possible without breaking the tip of the electrode. A scaled picture from this lowest point allowed for back calculating the actual distance to the leaf surface afterwards. We allowed readings at this lowest point to stabilize for >5 min after which the mV value was written down manually. The microsensor was then raised 20 µm with a precise 1D micromanipulator, afterwards 30 µm, after which we continued with 50 µm increments and then 100 and 500 µm increments until a stable pH was obtained for 3 measurements or more and we considered we were outside the DBL, between subsequent points the sensor was allowed to stabilize for at least 5 minute. We evaluated 3 replicas of each species at a light intensity of 200 µmol photons m^{-2} s^{-1}, and calculated the Δ pH across the DBL (defined from the tissue surface to where pH was at 0.99 × water-column pH).

3. Results

3.1. *Fjord-scale and seasonal pH variability*

Large seasonal and spatial variability was observed in pH-values along the longitudinal gradient centrally in the fjord (Fig. 2a). pH_T in surface water increased in April due to CO_2 consumption by the spring bloom as evidenced by a very high fluorescence (Fig. A2), to a maximum value of almost 8.50, most pronounced in the mouth of the fjord with values of around 8.25 in the inner part (Fig. 2). Accordingly, a horizontal gradient of around 0.25 pH units was observed along the main axis of the fjord. pH_T values in upper layers decreased during the summer to around 8.35 in July and with

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the maximum observed towards the inner part of the fjord. A further decrease in pH was observed in September, with more homogenous values in surface waters along the fjord gradient resulting in a horizontal range of only 0.05 pH units. Vertical gradients in pH from the surface to the deeper waters of the fjord ranged from only 0.1 units in April, when the fjord was vertically mixed, over 0.15 units in September to 0.25 pH units in July when maximum pH_T values of 8.35 occurred in a subsurface algal bloom in the inner parts of the fjord with waters supersaturated in oxygen (up to 120 % saturation, Fig. A2, A3) and minimum values of pH_T 8.1 were measured in the deeper sectors (Fig. 2a). Seasonally pH varied between 0.2 and 0.3 units in both surface and deep waters over the 5 months. Ω_{arag} values were closely coupled to pH and ranged from minimum values of 1.6, observed in the bottom waters of the inner part of the fjord to maximum values of 2.5, in the subsurface waters in September (Krause-Jensen et al., 2015). Corresponding pCO$_2$ levels ranged from 162 to 325 µatm, in the range of values recently reported for the fjord (Sejr et al., 2014).

Oxygen saturation at the fjord-scale ranged greatly from 85% to 127% and was strongly related to pH for each of the three periods (Fig. 3a), pointing at strong biological control of pH variability within the fjord. The slope of the pH versus O_2 relationship was steepest for the April survey when the highest pH levels were observed. Examination of pH values in relation to fluorescence and temperature also showed that the warmest waters, of up to 10 °C, observed in July, supported intermediate pH, while the highest pH was observed in the coldest waters, corresponding to the April survey when temperatures were uniformly low across the fjord (Fig. 3b). On a vertical scale, the cold bottom waters with low fluorescence generally supported the lowest pH values across seasons. Hence, overall, pH showed much tighter correlation with O_2 levels than with water temperature, and the correlation between pH and O_2 implied a similar close correlation between Ω_{arag} and O_2-levels.

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3.2. Small-scale and diurnal pH- variability in kelp forests and benthic habitats colonized by microalgae/scattered filamentous algae

The 3 parallel deployments in kelp forest and habitats colonized by microalgae and scattered filamentous algae encompassed 6 complete diurnal cycles which exhibited peak pH_T-levels during the day of 8.11 (8.04-8.19) (avg.(s.d)) and of 8.08 (8.02-8.16), respectively, as opposed to minimum pH_T-levels during night of 8.02 (7.97-8.06) and 8.01(7.94-8.09), respectively, with no significant difference between habitats (t- test, $p>0.05$). The diurnal range of minimum night pH to maximum day pH was slightly higher in the kelp forest (avg.±s.d.= 0.098±0.061) than above the microalgae/filamentous algae (0.073±0.052) (paired, one-tailed t-test, $p=0.041$).

There were large differences in the extent of diel fluctuations in pH among deployments dependent on incident irradiance and the shifting phase of tidal state and the solar cycle (Fig. 4). Diel pH fluctuations were small during dark, cloudy days and when high tide coincided with peak solar radiation, thereby reducing incident irradiance on the benthic habitat. In contrast, diel pH fluctuations were amplified in deployments during sunny days when low tide coincided with peak solar radiation (Fig. 4). Hence, the interaction between tide and the solar cycle controlled incident radiation and thereby induced fluctuations in photosynthetic activity and pH. This was particularly apparent in kelp forests where peak daily pH increased as a function of maximum daily photosynthetic solar radiation reaching the habitat during the day whereas this relationship was not significant in the water column above the microalgae/filamentous algae (Fig. 5). Indeed, biologic control of pH was also reflected in strong relationships between pH and O_2 concentration within each deployment in the kelp forests ($R^2=0.64-0.76$) particularly during high irradiance, as opposed to weaker pH versus O_2 relationships for the microalgae/filamentous algae sites ($R^2=0.05-0.15$)

which also showed much smaller variability in O_2 levels (98-114% saturation) than did the kelp forest (92-128% saturation) (Fig. 6). The diurnal range of O_2 concentrations in the kelp forest matched the range recorded at pelagic fjord-scale on a seasonal basis (85-127%, Fig. 3).

Changes in water masses by the tide, reflected by changes in salinity and temperature, also contributed to variations in pH and O_2 levels. This was visible as incidences of sudden changes in pH paralleling fluctuations in salinity and also as differences in pH levels between deployments in water masses of different salinity (Fig. 4). However, salinity explained much less of the variation in pH than did O_2, except in one deployment in the microalgae/filamentous algae habitat when salinity explained 51% of the variation in pH as opposed to 15% explained by O_2 (R^2=0.04-0.33 in kelp forest; R^2=0.04-0.51 in microalgae/filamentous algae, data not shown). So, overall biological activity had a much stronger influence on pH than had exchange of water masses.

The observed diurnal pH variability also translated into important fluctuations in Ω_{arag}, involving 0.18±0.06 units (from max night levels of 1.77±0.21 to min day levels of 1.60±0.17) in the kelp forest and 0.14±0.07 Ω_{arag} units (from max night levels of 1.72±0.30 to min day levels of 1.58±0.26) at the microalgae/filamentous algae sites. Corresponding $p\text{CO}_2$-levels ranged from 238 to 536 µatm at the kelp sites and from 258 to 515 µatm at the microalgal/filamentous algal sites.

3.3. Meter to millimeter-scale pH variability in kelp forests

Examination of the variability in pH within 1 m^3 kelp forest, sampled from the bottom of the canopy to the overlying water column, using the multi-electrode array, showed very large concurrent pH variability involving about 0.2 to 0.3 pH unit differences at any given time and with a total pH_T range of 7.76-8.36 across deployments (Fig. 7). In general, pH tended to be highest at the top of the canopy and in the water just above the canopy, reflecting that the canopy top is the most photosynthetically active layer, while pH was generally lower in the shaded bottom part of the canopy (Fig. 7) where photosynthetic biomass and incident light are lower and respiration rates higher. The range of pH within 1 m^3 of kelp forest at any one point in time was comparable among deployments, despite the different light conditions, although the absolute values of pH differed among deployments with highest levels observed at peak incident light (Fig. 7). This small-scale variability in pH also translated into a variability in Ω_{arag} of about 0.20 units in 1 m^3 of habitat at any time.

pH also varied significantly within the DBL of the six macrophyte species examined in the light (Fig. 8a), with pH increasing by 0.07-0.85 units, depending on species, from the top of the 0.3-2.2 mm thick DBL to the surface of the plants (Fig. 8b).

3.4. pH variability in intertidal pools

pH and oxygen concentration showed important diel variability in vegetated intertidal pools, with oxygen super-saturation (up to 176%) during the day and under-saturation (down to 11%) at night, compared to far more uniform concentrations in the surface waters on the adjacent vegetated shore (89-111% saturation, Fig. 9). Accordingly, pH_T changed greatly in intertidal pools, reaching maximum values of 9.0 during the day and minimum values of 7.4 during night periods, i.e. a diel range of ca. 1.6 pH units. Diel pH fluctuations in the surface waters of the adjacent shore were much smaller (8.0-8.5) but still high, reflecting the metabolic activity of the intertidal vegetation growing on the shore (Fig. 9). The difference in pH between vegetated intertidal pools and adjacent shores provided an additional example of variability in pH between adjacent habitats.

Data are available in digital form (Krause-Jensen et al., 2015).

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4. Discussion

Our results highlight the nested scales of variability of pH present in the Kobbefjord ecosystem involving (1) seasonal variability, largely driven by the phytoplankton spring bloom as a major event affecting pH; (2) diel variability acting through complex changes in submarine irradiance modulating rates of photosynthesis and respiration of benthic vegetation driven by the interaction of the solar and the tidal cycles; (3) large-scale variability along horizontal and vertical fjord gradients reflecting gradients in metabolic activity in combination with movement of water masses, (4) variability between subtidal habitats with and without kelp forests and between vegetated tidal pools and adjacent vegetated shores reflecting variable degrees of biological control, (5) small-scale three dimensional variability due to heterogeneity in metabolic processes and mixing in vegetated habitats, and (6) micro-scale variability across the DBL of macrophytes (Fig 10).

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Overall, metabolic processes played a fundamental role in driving pH-variability across scales, as reflected in strong relationships between oxygen concentration and pH at the fjord-scale and at both diel and seasonal scales. Primary producers played a major role in the regulation of pH-variability, both in the pelagic zone where, particularly, the intense spring bloom characteristic of Arctic ecosystems (Takahashi et al., 2003, Sejr et al., 2014) induced high pH in the subsurface layers while respiratory process in the bottom waters reduced pH; and in the nearshore benthic environment where the presence of subtidal kelp forests and intertidal macroalgae induced marked spatial and diurnal variability in pH. The mosaics of pH reflected that the density of the primary producers, and the spatio-temporal separation of photosynthesis and ecosystem respiration in combination with mixing of water masses were key drivers of the variability in both planktonic and benthic communities. Hence, the vertical gradient of declining pH from upper illuminated to lower shaded habitats varied from the 10-100 m scale in the planktonic community where the density of primary

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producers is relatively low to the cm-m scale in dense kelp forests. The same is true on a temporal scale where the diurnal pH variation in the benthic vegetation matches the seasonal variability of pH in the planktonic community.

The scale of seasonal pH-variability in the planktonic community (Fig. 10) compared well with previous reports for the Arctic, showing the spring bloom as a prevalent driver of pCO_2 (Sejr et al., 2011, Meire et al. 2015). Though a multitude of factors including water depth, light regime, season, seawater retention time, density and plant species may all affect pH variability in vegetated habitats, our results match evidence from other latitudes of strong pH variability in macroalgal forests and seagrass meadows. Hence, marked diel pH variability has also been reported from a Californian kelp forest (Frieder et al., 2012), a Mediterranean seagrass bed (Hendriks et al. 2014), and in extreme case for a temperate shallow dense algal bed (diel range ca. 1 unit, Middelboe and Hansen, 2007) and kelp forest (diel range: ca. 0.6-0.8 pH units, Cornwall et al. 2013a). Our pH measurements in benthic habitats neighboring the kelp forest also carried a biological signal, though less distinct, likely reflecting the combined signal of the benthic primary producers at the site, of the neighboring kelp forests and of the planktonic community in the water masses exchanged with tidal currents. The marked biological control of pH in kelp forests suggests that diel pH may be even more pronounced during sunny days with more intense photosynthesis than during the generally overcast conditions of our survey. Thus, while the identified pH-range and pH vs. O_2-relationships for the planktonic community covered the full growth season, they solely represented a few overcast September days in the benthic habitats and would likely involve markedly higher levels had they covered the full growth season. For sub-Antarctic giant kelp forests, the diel amplitude in pCO_2 and C_T (Delille et al., 2009) during spring and summer as well as the seasonal amplitude in

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pH, C_T and $p\mathrm{CO}_2$ (Delille et al., 2000) were reported to be markedly higher within kelp forest as compared with unvegetated habitats, underlining the kelps' strong biological control of pH.

We further show, for the first time, significant 3-d variability in pH within 1 m^3 of kelp forest, with pH ranging about 0.2-0.3 pH units at any one point in time and a total variability across deployments of 7.76-8.36 pH_T, resembling the range recorded across the entire growth season in the pelagic. Levels of pH were dependent on the position in the kelp canopy, with the highest pH generally appearing at the top of the canopy and decreasing toward the seafloor, likely reflecting the vertical structure of photosynthetic activity in the kelp bed. The fast rates of metabolic activity in combination with reduced flow in such densely vegetated habitats make these 3-D patterns appear in spite of the marked exchange of water masses resulting from the 1-4.5 m tidal range.

Changes in pH were particularly pronounced in small tidal pools, where photosynthesis of dense seaweed stands of primarily *Ascophyllum nodosum* and *Fucus spp.* drove O_2 levels to heavy super saturation (176%) and forced pH to extremes of up to pH_T 9.0 at low tide during sunny days, corresponding to Ω_{arag} of 4.14 and $p\mathrm{CO}_2$ of 13 µatm compared to night-values of pH_T 7.4, Ω_{arag} of 0.27 and $p\mathrm{CO}_2$ of 1647 µatm driven by community respiration which almost depleted O_2 in the pools (11% saturation). In surface waters of adjacent densely vegetated intertidal shores, we observed a maximum pH_T of 8.5 with corresponding Ω_{arag} 2.23 and $p\mathrm{CO}_2$ of 96 µatm during the day and a minimum pH_T of 8.0, with corresponding Ω_{arag} of 0.54 and $p\mathrm{CO}_2$ of 243 µatm during the night. While intertidal brown macroalgae thrive in such habitats when regularly flushed as in the current study, apparently only *Ulva (Enteromorpha) intestinalis* occurs in isolated, rarely flushed rock pools where it can drive pH to levels >10 (Björk et al., 2004).

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At the micro-scale, pH also showed considerable variability with a range of up to 0.85 pH units across the DBL of the key species of the vegetated shallow ecosystems, with high pH levels at the tissue surface declining towards the bulk water during daytime (Fig. 8). There was substantial variability among species, with intertidal macroalgae (*Ascophyllum* and *Fucus*) showing the largest pH range. The interspecific differences likely related to the species' photosynthetic rates as well as to their morphology, which affect the thickness of the DBL (Hurd and Pilditch, 2011). This microscale pH variability across the DBL compared well previous observations for the calcifying alga *Hamelida discoidea* (pH-range of 0.7 across DBL, de Beer and Larkum, 2001) as well as for the coralline algae *Sporolithon durum* (light-dark pH change at tissue surface 0.9; Hurd et al., 2011) and *Arthrocardia corymbosa* (pH range across DBL e.g. 0.4, depending on flow; Cornwall et al., 2013b). The pH-range across the DBL of Ulva was surprisingly low considering Ulvas ability to elevate pH to high levels (Björk et al. 2004) but probably the combination of low water temperature and limited nutrient supply limited Ulvas photosynthetic rate. The DBL thickness as well as the pH range across it depends markedly on flow conditions. Reduced flows as present in dense vegetation increase the DBL thickness and consequently the pH range (Hurd et al., 2011, Cornwall et al., 2013b). The current experiment was, hence, conducted at reduced flow, and, importantly, at the same flow for all species. Exchange of water masses with different salinity and temperature also added to the variability in pH as indicated for both pelagic (Fig. 3B) and benthic (Fig. 4) systems but showed much weaker correlation to pH than did O_2 concentrations reflecting the biological control.

The processes above resulted in nested scales of pH variability in the Kobbefjord ecosystem (Fig. 10), with variability ranging 0.2-0.85 units across spatial scales and 0.2-1.6 units over diurnal to seasonal scales. This variability provides a dynamic mosaic of niches for organisms. Niches of high

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pH may be particularly important for the more vulnerable larval and juveniles stages of calcifiers under acidic conditions as projected for the future (Kroecker et al., 2013). The suitability for calcifiers is best represented by Ω_{arag}, where calcifiers should be favored by high Ω_{arag} values. The Kobbefjord ecosystems host a number of calcifying species, including bivalves such as blue mussel, scallops and snails, echinoderms, such as green sea urchins, and crustaceans such as *Pseudobalanus balanoides*, calcareous algae and foraminifers. Overall, the identified Ω_{arag} conditions were well above 1, particularly in illuminated habitats with intense photosynthesis and, hence, indicated favorable conditions for calcification. The phytoplankton spring bloom, depleting CO_2 and driving Ω_{arag} to values close to 3, would also provide adequate conditions for pelagic calcifiers, as it would provide the double benefit of adequate environments for aragonite deposition and food supply to support growth and the energetic demands of calcifiers. Canopies of kelp and intertidal seaweed environments may also provide adequate niches for calcifiers during summer, when Ω_{arag} values would be highest through the cumulative action of the processes upregulating pH and Ω_{arag} values discussed above. Indeed, most calcifiers spawn and recruit in early summer (Arendt et al. 2013) when pCO_2 remains low, warmer water temperatures lead to higher Ω_{arag} and high solar radiation and long photoperiod allow seaweeds to draw down CO_2 further (Delille et al., 2000).

The upregulating effect of primary producers on pH is counterbalanced by the opposite effect of respiration and decomposition prevailing in shaded and deeper basins and periods as illustrated by the large scale seasonal variability in the pelagic community (Fig. 2), and paralleled in kelp forests outside the productive period (Delille et al., 2009) as well as during night time and in shaded layers of the kelp forest (Fig. 7) and tidal pools (Fig. 9). These shaded habitats with diurnally low Ω_{arag} could be challenging habitats for calcifyers. Interestingly, however, blue mussels grew in close association with macroalgae even in intertidal pools, where they would experience maximum Ω_{arag}

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values of up to 4.28 when low tide occurred at noon as opposed to levels as low as 0.28 during night (Fig. 9). Blue mussels have indeed been observed to abound in intertidal macroalgal habitats (Blicher et al. 2013) and along with other calcifiers to be trophically linked with habitat-forming algae such as *Ascophyllum* (Riera et al., 2009), and have also been reported to tolerate high *p*CO_2 concentrations when food is abundant (Thomsen et al., 2013). Probably the recurring periods of high Ω_{arag} in combination with adequate food supply can compensate for the potential problems of low Ω_{arag} during night. Laboratory experiments have demonstrated that semidiurnal fluctuations of 0.3 pH units may compensate for negative effects of constantly low pH on the development of mussel larvae (Frieder et al. 2014). Calcareous epiphytic organisms, such as encrusted algae and bryozoans would also experience high variability in Ω_{arag} at the surface of the plant tissue, where periodically high Ω_{arag} values favors calcification, as elegantly demonstrated by de Beer and Larkum (2001).

The existence of a mosaic of environments in the Kobbefjord underlines the importance of metabolic processes along with habitat configuration and interactions among community constituents in affecting pH in coastal ecosystems as opposed to the simpler situation in the open ocean (Duarte et al., 2013, Hendriks et al., 2014). This pronounced influence of metabolic processes occurs in spite of Kobbefjord being a macrotidal area with marked exchange of water masses with the coastal region and is probably also the case in many other shallow coastal areas in the Arctic, as has also been highlighted for areas in the temperate zone (Duarte et al., 2013). While the current study explored pH in benthic habitats under overcast situations in the early autumn of the sub-Arctic, kelp forests are likely to induce much more pronounced increases in pH and Ω_{arag} in midsummer when irradiances are higher and the photoperiod longer, and further north, during high-Arctic midsummer, when the sun does not set for months. Under scenarios of ocean acidification

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such vegetated habitats may gain increased importance as local refuges for calcifyers. The projected poleward expansion of macrophytes into the Arctic with warming and reduced sea ice cover (Müller et al. 2009, Jueterbock et al. 2013) has been hypothesized to provide such niches of elevated pH and Ω_{arag} during summer (Krause-Jensen et al. 2014). Similarly, increased pelagic primary production as forecasted for parts of the Arctic Ocean (Arrigo et al., 2008; Slagstad et al., 2011, Popova et al., 2012) may also create local niches of high pH.

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6. Author contributions

Planning, field work, data processing and writing were carried out jointly, led by D. Krause-Jensen and C. M. Duarte, with L. Meire and M. K. Sejr responsible for fjord-scale surveys, I. E. Hendriks, M. K. Sejr, M. E. Blicher, C. M. Duarte and D. Krause-Jensen responsible for the various small scale measurements, I. E. Hendriks and N. Marba for micro-scale measurements, N. Marba and D. Krause-Jensen for intertidal measurements and M. E. Blicher for Greenland field facilities. Main idea: C. M. Duarte.

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Fig. 1. A: Location of Kobbefjord, Nuuk. B: Location of sampling sites in Kobbefjord: Fjord scale sites (CTD, C_T, A_T: filled circles; CTD: open circles), vegetated subtidal sites (open circles # 1-3), and intertidal sites (open circles (#4). C: Photopanel of benthic habitats: A typical kelp forest habitat (dominated by *Saccharina longicruris*) and habitat colonized by microalgae/scattered filamentous algae (example from site #1, representative of sites #1-3 in map) and a vegetated intertidal pool and the adjacent vegetated shore dominated by *Ascophyllum nodosum* and *Fucus spp.* (site #4 in map).

Fig. 2. Fjord-scale pH-variability in Kobbefjord 19 April, 18 July and 3 September 2013.

Fig. 3. Fjord-scale relationships in Kobbefjord between pH and oxygen (A), and between temperature and fluorescence with associated pH-levels shown with symbol color (B), on three sampling occasions: 19 April, 18 July and 3 September 2013.

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Fig. 4. Diurnal variability in pH, O_2, water depth (all measured by Hydrolab) and light (measured by Odyssey loggers) at ca. 50 cm above the seafloor in kelp forests (Panels A-C) and habitats colonized by microalgae/filamentous algae (panels E-F) during three parallel deployment in Kobbefjord, Nuuk, 27-30 August, 30 August-2 September, 2-5 September 2013. The deployments represent the benthic sites (#1-3, respectively) shown on the map (Fig. 1).

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Fig. 5. Maximum daily pH in a kelp forest (green dots) and above microalgae/filamentous algae (blue dots) as a function of maximum daily incident light over 6 full days as measured during three parallel deployment in Kobbefjord, Nuuk, 27-30 August, 30 August-2, September, 2-5 September

2013. Linear fit and coefficient of determination shown for the significant relationship for the kelp forest.

Fig. 6. pH vs. O_2 concentration for three parallel deployments (#1-3 shown by increasing color intensity) in subtidal habitats colonized by kelp forests (top panel) or microalgae/scattered filamentous algae (bottom panels) in Kobbefjord, Nuuk, August-September 2013. Each deployment represents 10 min loggings by multiloggers (Hydrolab) over ca. 2 diurnal cycles. Linear fits and coefficients of determination are shown.

Fig. 7. pH-variability within 1 m^3 of kelp forest in Kobbefjord, Nuuk, during three deployments in late August-September 2013. 16 pH-sensors were configured in-situ in a 3-d array with 4 sensors at 0.1 m from the bottom, 4 sensors at 0.2 m, 4 sensors just underneath the canopy and 4 in the water column above the canopy, which typically extended about 0.75 m above the seafloor.

Fig. 8. Microscale pH-variability across diffusive boundary layers (DBL) of blades of 6 different macrophyte species illuminated by 200 µmol photons m^{-2} s^{-1}: The kelps *Saccharina longicruris* and *Agarum clathratum*, the intertidal brown macroalgae: *Fucus vesiculosus* and *Ascophyllum nodosum*, the green macroalga *Ulva lactuca* and the seagrass *Zostera marina*. A: pH levels (mean of 2-3 replicate measurements) across blade DBL fitted by an exponential model ($y = y0 + a * exp^{-b*x}$, R^2>0.90 for all individual fits). B: pH range across the DBL of the various species.

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Fig. 9. O_2-concentration and pH in vegetated tidal pools and in surface waters of neighboring vegetated intertidal shores measured at low tide during day and night just after pool formation and before pool inundation.

Fig. 10. Conceptual summary of nested scales of temporal and spatial variability in pH in Kobbefjord, Nuuk. The figure shows the maximum pH range at the various scales examined. From lower left to upper right: 1) micro-scale variability across macrophyte diffusive boundary layers (DBL), 2) small scale variability within kelp forests, 3) diurnal variability in vegetated subtidal habitats and intertidal pools/adjacent shores and variability between habitats at the 100 m scale, 4) seasonal and fjord-scale horizontal variability.

Appendix figures/Supplementary figures

Fig. A1. Photo of deployment frame with loggers shown on the deck of the boat (upper panel) and in situ in the *Saccharina longicruris*-dominated kelp forest (site #1, central panel). Markings in upper panel show the array of 16 pH sensors connected to a common pH logger, the hydrolab measuring salinity, temperature and oxygen and a PAR logger (odyssey).

Fig. A2. Fjord-scale variability in fluorescence in Kobbefjord, Nuuk, 19 April, 18 July and 3 September 2013.

Fig. A3. Fjord-scale variability in O_2-concentration in Kobbefjord, Nuuk, 19 April, 18 July and 3 September 2013.

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Fig. 1

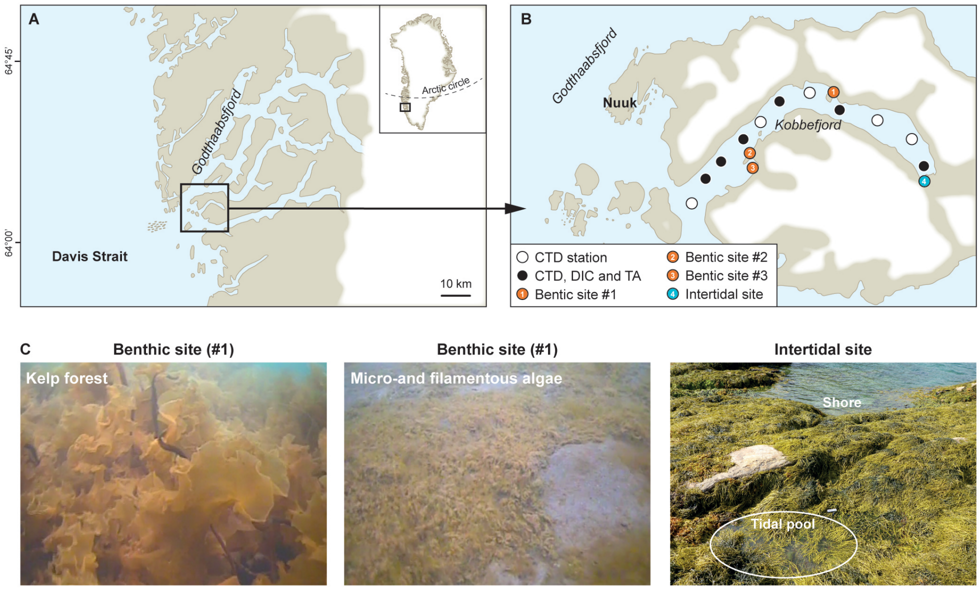
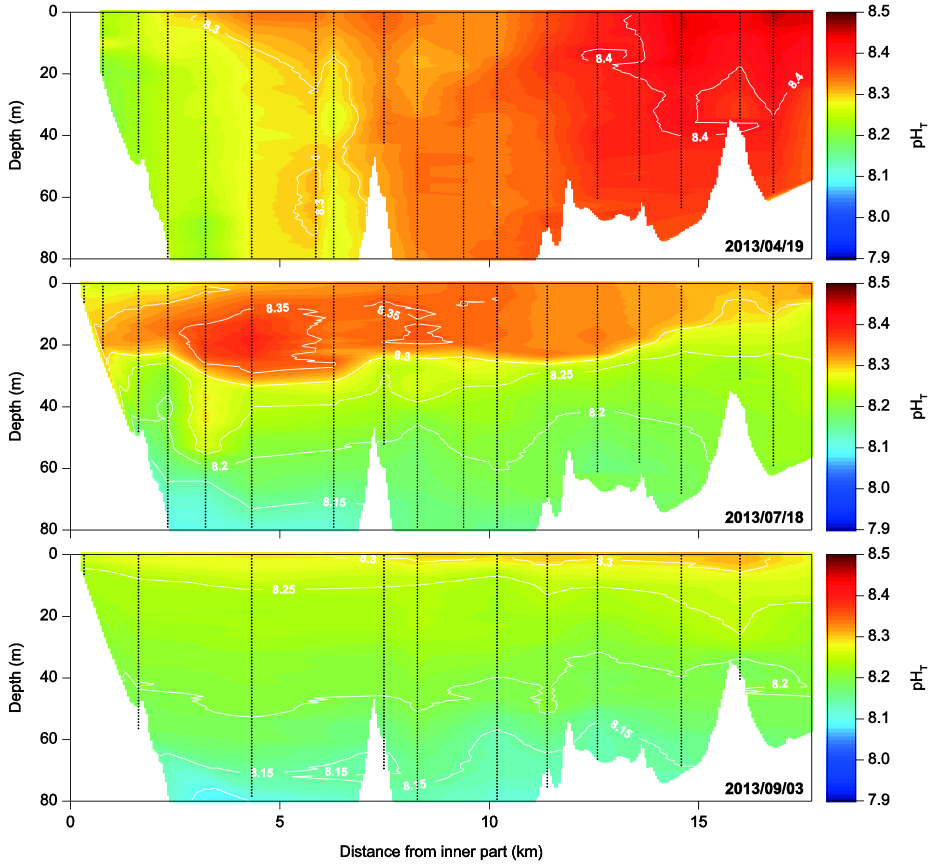
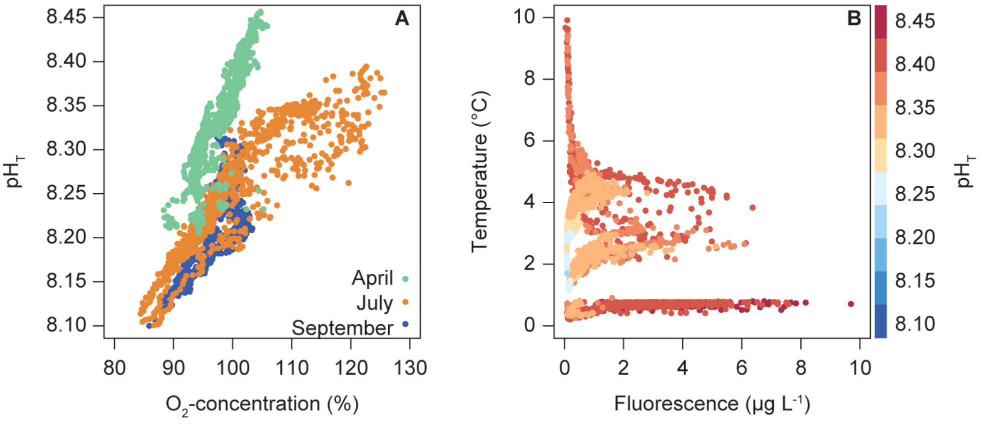

A
64°45'
64°00'
Godthaabsfjord
Arctic circle
Davis Strait
10 km
B
Godthaabsfjord
Nuuk
Kobbefjord
① ② ③ ④
○ CTD station
● CTD, DIC and TA
① Bentic site #1
② Bentic site #2
③ Bentic site #3
④ Intertidal site
C
Benthic site (#1)
Kelp forest
Benthic site (#1)
Micro-and filamentous algae
Intertidal site
Shore
Tidal pool

Fig. 2



Depth (m)
0
20
40
60
80
2013/04/19
2013/07/18
2013/09/03
8.3
8.4
8.35
8.25
8.2
8.15
0
5
10
15
Distance from inner part (km)
8.5
8.4
8.3
8.2
8.1
8.0
7.9
pH_T

Fig. 3



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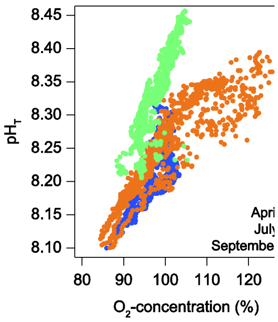
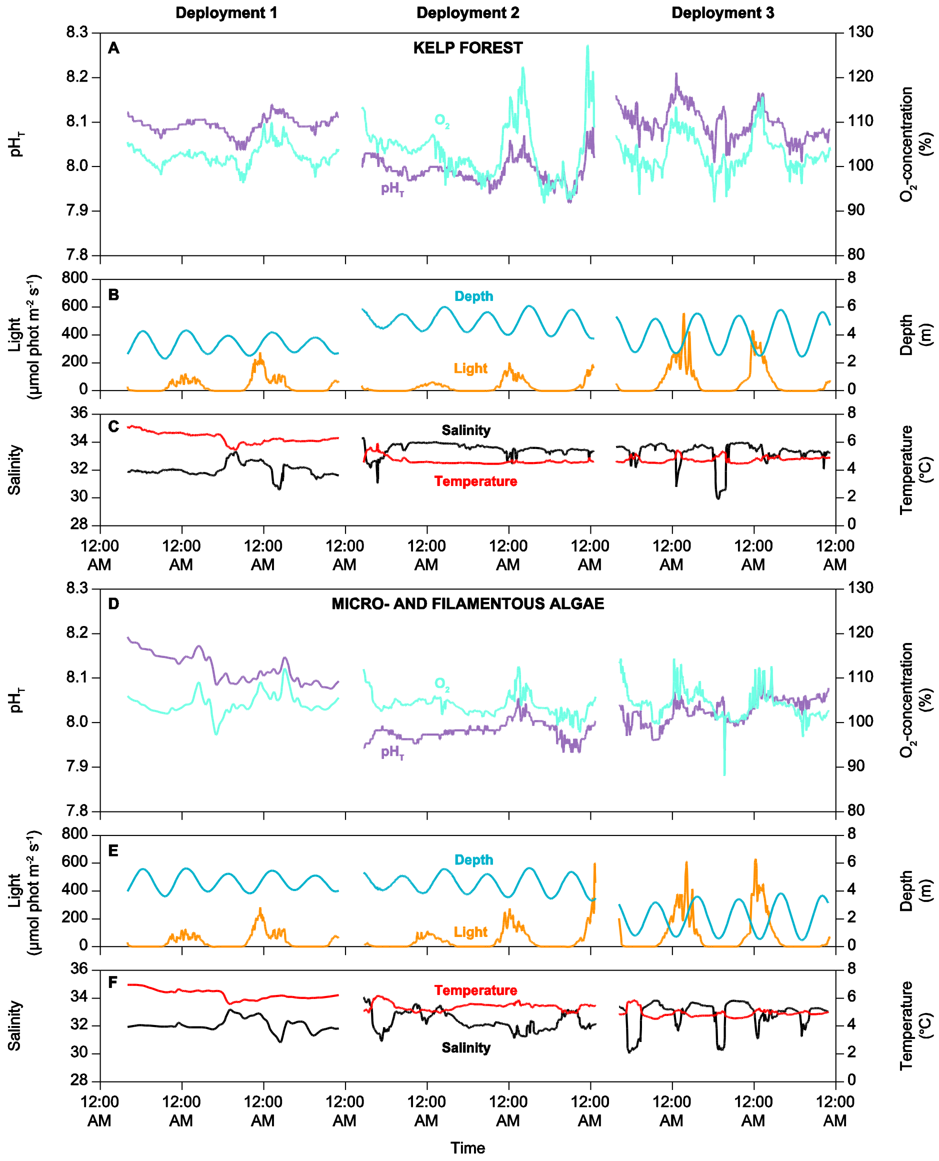


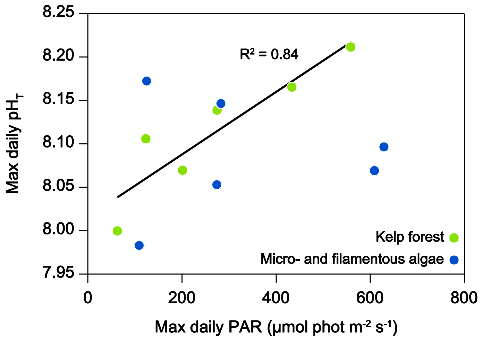
1008 Fig. 4



1009

1010

Fig. 5



8.25
8.20
8.15
8.10
8.05
8.00
7.95
Max daily pH_T
R² = 0.84
Kelp forest
Micro- and filamentous algae
0
200
400
600
800
Max daily PAR (µmol phot m^{-2} s^{-1})

Fig. 6

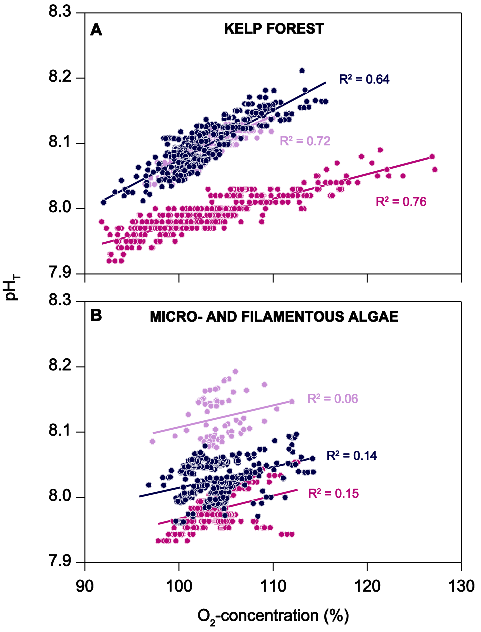
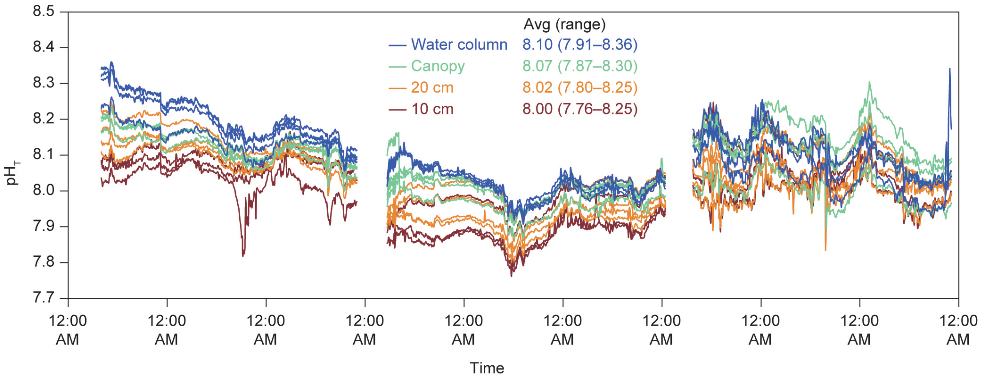

pH$_T$
8.3
8.2
8.1
8.0
7.9
A
KELP FOREST
R² = 0.64
R² = 0.72
R² = 0.76
B
MICRO- AND FILAMENTOUS ALGAE
R² = 0.06
R² = 0.14
R² = 0.15
90
100
110
120
130
O$_2$-concentration (%)

Fig. 7



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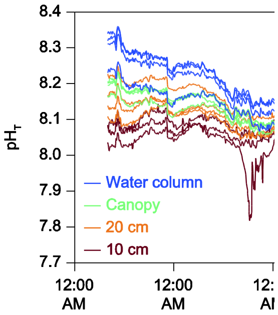

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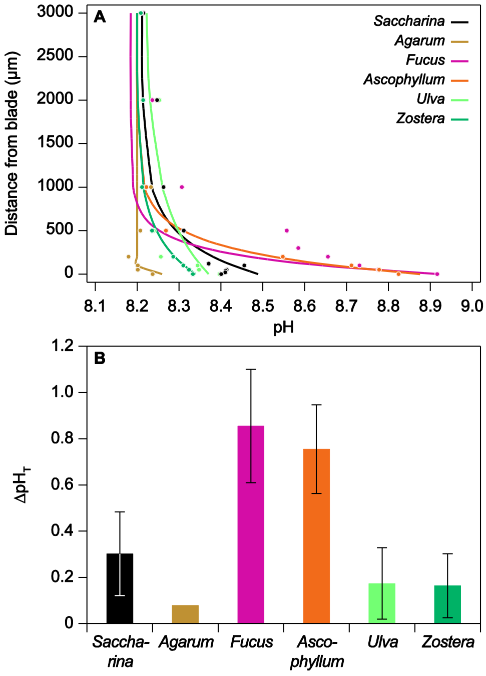
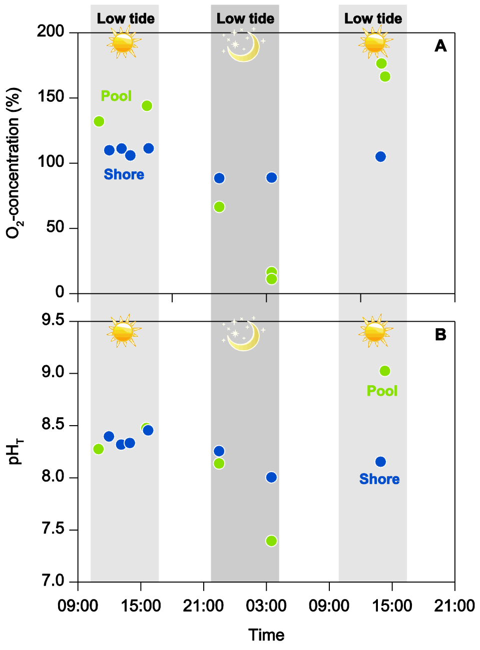
Fig. 8


A
Saccharina
Agarum
Fucus
Ascophyllum
Ulva
Zostera
Distance from blade (µm)
3000
2500
2000
1500
1000
500
0
8.1
8.2
8.3
8.4
8.5
8.6
8.7
8.8
8.9
9.0
pH
B
ΔpH_T
1.2
1.0
0.8
0.6
0.4
0.2
0
Saccha-rina
Agarum
Fucus
Asco-phyllum
Ulva
Zostera

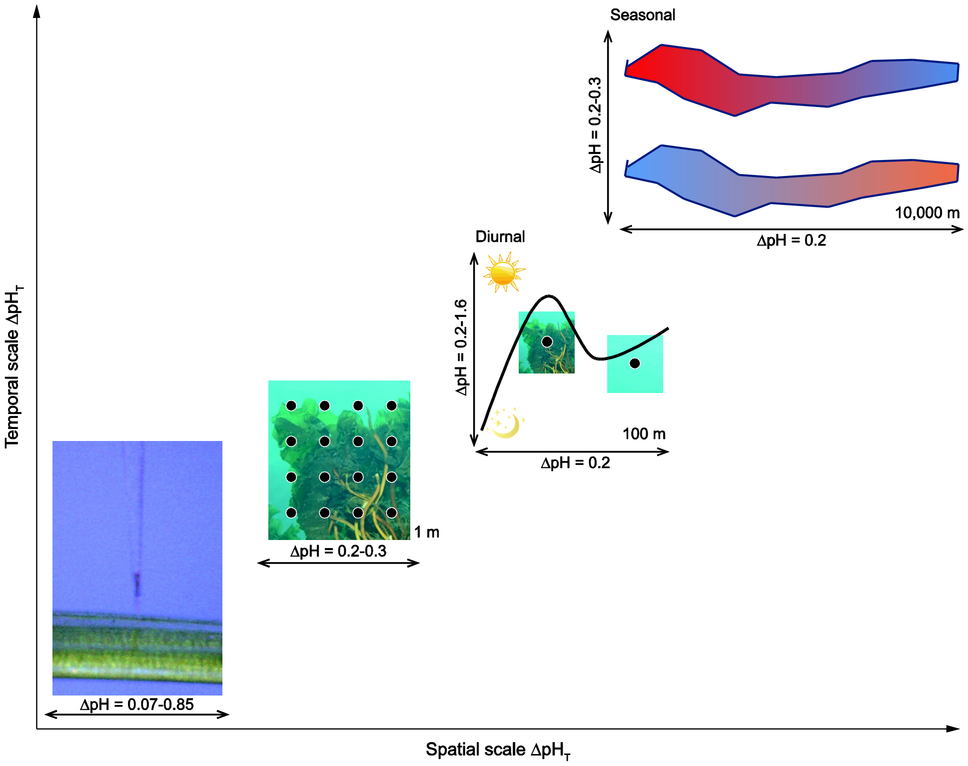
1024 Fig. 9



1025

1026

Fig. 10


Seasonal
ΔpH = 0.2-0.3
10,000 m
ΔpH = 0.2
Diurnal
ΔpH = 0.2-1.6
100 m
ΔpH = 0.2
1 m
ΔpH = 0.2-0.3
ΔpH = 0.07-0.85
Temporal scale ΔpH_T
Spatial scale ΔpH_T

Appendix-figures/Supplementary figures

Fig. A1

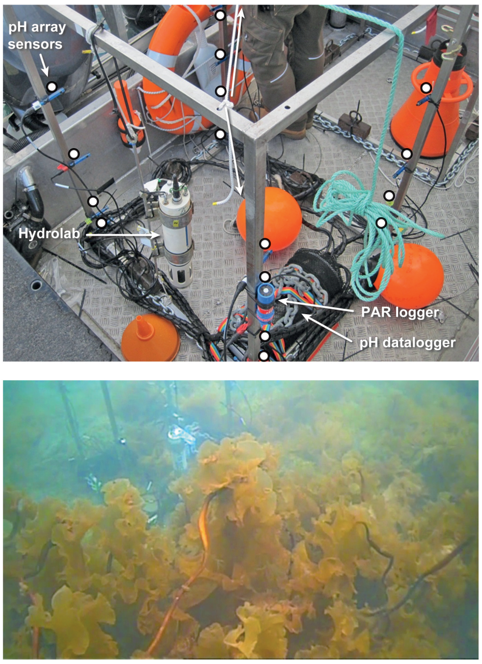


Fig. A2

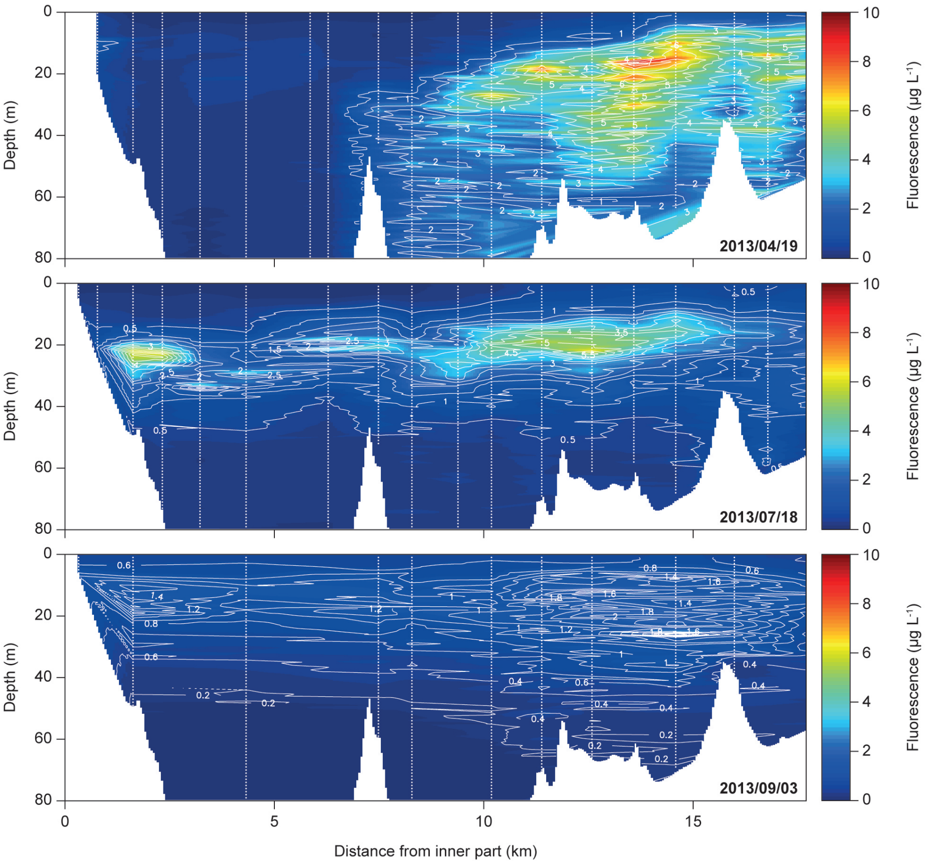
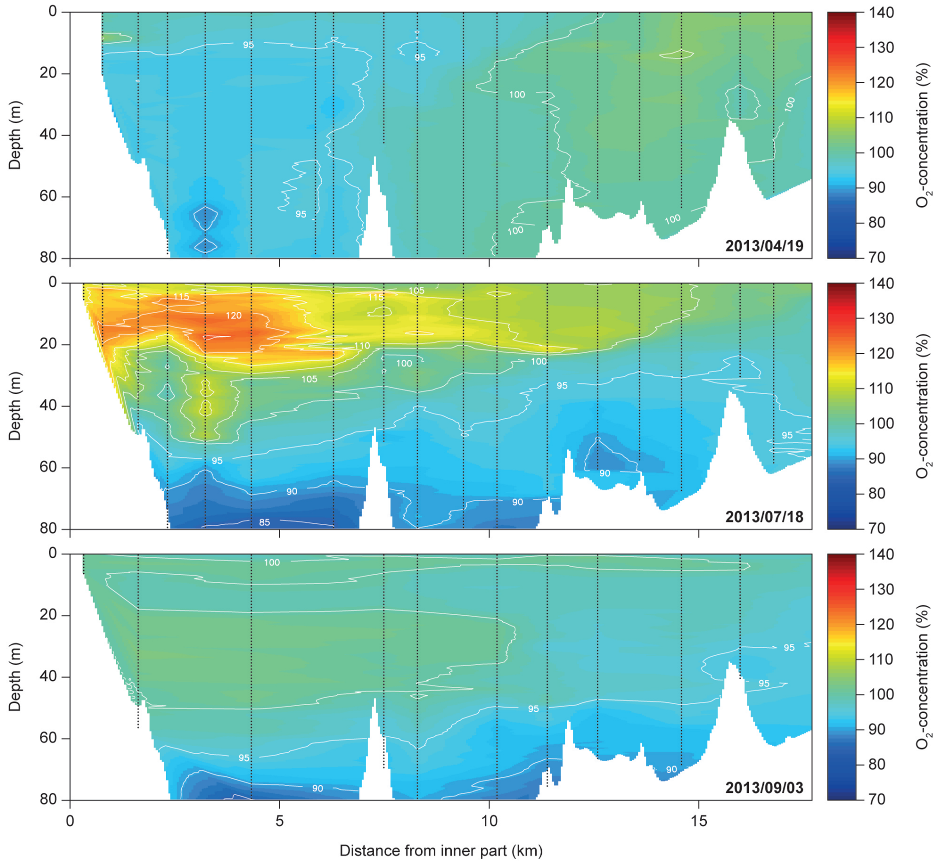

Depth (m)
0
20
40
60
80
Fluorescence (µg L⁻¹)
0
2
4
6
8
10
2013/04/19
2013/07/18
2013/09/03
Distance from inner part (km)
0
5
10
15

Fig. A3


Depth (m)
0
20
40
60
80
2013/04/19
2013/07/18
2013/09/03
95
100
90
85
105
110
115
120
O2-concentration (%)
70
80
90
100
110
120
130
140
0
5
10
15
Distance from inner part (km)

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