Response from the authors

We thank the two referees for their insightful and accurate comments. Here we provide a detailed response to the specific comments made by the referees. The comments by the reviewers are highlighted in yellow. Corrections in the text are shown in italic.

Review 1:

In section 4.2 the authors discuss the effect of glacial meltwater on the carbonate system variables. They suggest that in addition to a “negligible” direct effect on pCO2, glacial meltwater can also induce pCO2 undersaturation through a second mechanism which is due to the non-conservative behaviour of pCO2 during the mixing of fresh water and saline water. To illustrate this point they compute pCO2 for a mixture of glacial meltwater with a TA= 50 & DIC=81.2 and seawater with TA =2220 and DIC=2118 _molkg-1. The result is a pCO2 undersaturation that vary with salinity (or glacier water fraction) (Fig 11a) in a highly non-linear way. The authors argue that this nonlinearity is due to the non-linear effect of salinity on pCO2. I disagree with authors on this point! I believe the strong non-linearity depicted on Fig 11a is due to the fact that DIC of the glacial meltwater is higher than its TA value whereas in the saline water TA is higher than DIC. Thus, both DIC and TA mix conservatively, but the mixing lines have different slopes and they cross at some point. The crossing point is the point with highest pCO2 undersaturation. One simple way to confirm the above is to re-plot Fig.11a with glacier water TA and DIC values such that the mixing lines never cross. For instance, TA =50, and DIC=50 or TA=159 and DIC =60. Note, the latter values are those indicated by the linear regressions reported on page 17938, lines 7-9. I recommend this section to be revised accordingly.

The suggestion made by the reviewer is that non-linearity in the pCO2 in Fig 11a is due crossing mixing lines (DIC of the glacial meltwater is higher than TA whereas in the saline water TA is higher than DIC). But we disagree with the reviewer on this point. To show this, we have made a figure with different end member simulations as proposed by the reviewer (panel 1: TA =50, DIC = 81; panel 2: TA = 50 and DIC = 50; panel 3: TA = 150 and DIC = 50). These three figures all show a DIC deficit that responds non-linearly to the salinity (i.e. the DIC deficit represents the carbon uptake from the atmosphere that would occur when the water is exposed to a 400 ppm atmosphere after mixing). Accordingly, strong undersaturation occurs at any of the suggested TA and DIC combinations from freshwater. The only difference between the three panels is the initial undersaturation of the freshwater endmember. In section 4.2, we have separated these two effects for clarity.

I also find the TA values to be inconsistent within the manuscript and with Rysgård et al (2012). On page17938, lines 7-9: the TA vs. S relationship suggests a TA value of 159 _mol kg-1 for the glacial endmember i.e. with S=0. This is three times the measured value reported on page 17935, line 8). Furthermore, both the above values are different than that obtained from the TA vs. S relationship reported by Rysgård et al (2012) for the same area. The authors need to clarify on this point.

This is a good comment/suggestion: we agree that comparison to previous work was missing and the uncertainty needs to be carefully assessed. The relations of TA and DIC versus salinity (S) are provided below. Confidence intervals widen near the end points of the range covered by linear regression, while due to the lack of data points at low salinities, the uncertainty in these relations at low salinities is further amplified. As a result, a large uncertainty propagates into the estimated DIC and TA values of the glacial endmember. Instead, we only report the actually measured TA and DIC values of the glacial endmember, which are derived from sampling glacier ice. We believe these values are more precise and certain than the endmember values as derived from the TA-S and DIC-S relations. Values of the TA versus S relation are nearly identical with Rysgaard et al. (2012) and only the DIC versus S
relation varies slightly. In this regard, it should be noted that the Rysgaard et al. (2012) dataset only includes 12 data points from 1m meter depth. The current dataset includes 500 data points and many depths.

The TA vs S and DIC vs S figures will be included in the appendix. We have adapted the text at P 17942 L10 as follows:

Measurements by Sejr et al. (2011) in a meltwater river in east Greenland also indicated that meltwater is undersaturated in CO$_2$. Ryu and Jacobson (2012) however found CO$_2$ oversaturation in rivers between the Greenland Ice Sheet and the Kangerlussuaq fjord that were fed by meltwater of land-terminating glaciers. However, by the time the water reached the actual fjord, the excess CO$_2$ had evaded and the river water was in equilibrium with the atmosphere. The undersaturation of the freshwater endmember is further confirmed by linear regression of TA and DIC versus salinity of all our carbonate system observations (TA = 159 +63*S; R squared 0.95 and DIC = 61 + 59*S; R squared 0.92). These relations are similar to those obtained by Rysgaard et al. (2012) (TA = 161 + 61*S and DIC = 169 + 55*S). Both these sets of relations show that the freshwater endmember is undersaturated. However, it should be noted that the freshwater endmember values derived from these relations should be interpreted with caution, as confidence intervals widen near the end points of the range covered by linear regression, which is aggravated by the scarcity of data points at low salinities. As a result, a large uncertainty propagates into the estimated DIC and TA values of the freshwater endmember. Therefore, we use here in further calculations the DIC and TA values based on our measurements of meltwater from ice berg samples.

For the measurement of TA, the authors report that they used the Standard Operating Protocol 3b of Dickson et al. (2007) which is suitable oceanic levels of total alkalinity (2000-2500 umol/kg) (Dickson et al., 2007). Did the authors make any modifications to ensure applicability for the much lower TA values in the glacier meltwater? If not, they need to comment the effect this issue on the accuracy of TA values (see e.g. Bates et al 2014, their section 2.2.3).

When measuring TA for freshwater or seawater samples with low salinities, the protocol was modified to make sure a proper titration was obtained (especially concerning the acid addition). As indicated in Bates et al. (2014), no CRMs are available for low salinities and alkalinities so the assumption is made that the calibration fit for TA from higher TA values from CRMs remains robust for low salinities.

The text was changed in the following way:

“As noted by Bates et al. (2014), no CRM are presently available for samples at low salinities and low alkalinities, and so the assumption is made that quality assurance based on CRM remains robust at low salinities.”

What constants were used for the computation of pCO2?

pCO$_2$ data shown in this study were not calculated but measured using the HydroC™ Carbon Dioxide Sensor (Contros, Germany). This sensor was serviced and calibrated yearly by the company. For calculation of pCO$_2$ in the model simulation, the AquaEnv package in R was used. This uses the constants by Roy et al. (1993) as default with adaptation by Millero et al. (1995) for low salinities. Consequently the dissociation constants are valid for a salinity range of 0–45 and temperature range 0-45°C.

The text was changed to clarify this (p 17932 L 17).

We used the constants by Roy et al. (1993) as default with the adaptation by Millero et al. (1995) for low salinities. Consequently the dissociation constants are valid over the salinity range of 0–45 and the temperature range 0-45°C.
On page 17940, lines 5-9: please be aware that Fig 8C also compares the ASE flux from three cruises and it seems that highest flux occurs in May although the strongest CO2 undersaturation was observed in August. This is most probably due to the nonlinear effect of wind speed on ASE and need to be commented.

Indeed, wind speed was higher during May compared to August and this leads to higher fluxes in May even though the surface waters are more undersaturated in CO2 with respect to atmospheric equilibrium in August compared to May. The effect of wind speed is now commented upon in the revised manuscript (p 17940 L10).

The wind however plays also an important role: despite higher surface pCO2 values in May, higher wind speed (Fig. 8a) led to a higher CO2 uptake.

Technical comments: Figure 5: I would encourage the authors to use different symbols for the four curves so that these can be differentiated even on colourless printouts.

Thank you for this suggestion. This will be corrected in the revised manuscript.

Review 2:

In their model, the authors used data of TA and DIC measured on melted glacier ice as the freshwater (FW) endmember. There are some problems in this approach:

* As stated in page 17929 only 60% of the freshwater relates to glacier meltwater and 34% relates to surface runoff. It is unlikely that TA and DIC values for surface runoff are the same as those from the melted glacier ice. Hence, the model should have used two FW end-members.

* 6% of the freshwater comes from precipitation. Is this precipitation directly on the fjord surface? or is this precipitation on the watershed? How can it be distinguished from surface runoff? Isn't possible to account this in model (adding an addition flux in the mass balance for direct rain on the fjord surface)?

The reviewer has a very valid point: we agree that our decision to use only one freshwater end-member in the model was not properly substantiated by arguments. To do this, we have now added the following text:

As already noted above, the Godthåbsfjord is also affected by other freshwater sources: 34% originates as surface runoff from the surrounding watershed, while 6% is attributed to direct precipitation on the water surface of the fjord system (Langen et al., 2014). Samples collected from snow indicate an average DIC concentration in snow of 74 μmol kg\(^{-1}\) (Søgaard, unpublished data; TA was not measured). This value is very close to our value measured in ice samples, and indicates that surface runoff could be similar to the glacier meltwater. Direct precipitation has likely different properties than meltwater runoff, but its volumetric input is small. Accordingly, we prefer the use the most parsimonious model, which only considered one type of freshwater end-member, for which we used the measured properties of the glacial meltwater. However characteristics of freshwater are likely characterized by similar properties (low DIC and low TA) compared to the seawater end-member.

* Shouldn't groundwater inputs somehow also be included in the model?

The fjord is mostly characterized a hard bedrock and so groundwater input is considered negligible for the fjord system.

* The glacier ice does not simply melt and mix with seawater. There’s in fact some quite complex water infiltration dynamics (e.g. Olichwer et al. 2012) and weathering below the glacier (Wadham et al. 2010; Graly et al. 2014), so that the FW end-members of TA and DIC are in really different from those used in the model. This in fact appears somehow in the Y-intercept of the linear regressions of DIC and TA vs salinity in the fjord (page 17938) that are different from the FW values (50 vs 159 for TA and 80 vs 61 for DIC). In the end, the CO2 content of Greenland “glaciers” is in fact quite high (Ryu & Jacobson 2012) and not below saturation as stated in page 17942.

This remark is also made by referee 1. See above how we revised the text to accommodate this comment.

P 17935 L 11 : so no seasonality was accounted for the SW end-member? I expect that in such a shallow system DIC increases in bottom shelf waters after the bloom organic matter sinks. I would also expect an enrichment of bottom water DIC in the fjord from remineralization of organic matter that sediments from the surface to the bottom of the fjord. So that DIC concentration transported from bottom to surface (F flux) should be different in each box and increase from Zone 1 to Zone 3.

The reviewer has a valid point. This model assumption was indeed not substantiated. Remineralization of organic matter in deeper water induces very little seasonality in the bottom water. Variability of DIC in bottom water is low, some unpublished data indicate an average concentration in the deeper bottom water of DIC\(_{\text{sw}}\) = 2150 ± 10 μmol kg\(^{-1}\).

We have now added:

“The properties of SW end-member were assumed no to vary throughout the year. The bottom water DIC and TA in the deep part of the fjord shows little seasonality, as the fjord is relatively deep (up to 600 m), and this large volume buffers against fluctuations induced by remineralization of organic matter originating from plankton blooms.”
The attached figure shows a transect of the bathymetry. Despite the fact that the model is run for the upper 40 meter, the water column in Godthåbsfjord is much deeper. This is only shortly mentioned in the Material and Methods.

Is there a possibility that coccolithophores also bloomed in the studied fjord? Coccolithophores are common in high-latitude fjords (Schei 1975; Kristiansen et al. 1994) and this affects CO2 dynamics (Purdie & Finch, 1994).

This is a good point, however, monitoring (http://nuuk-basic.dk/monitoring/marinebasis/) and a study in Godthåbsfjord have shown that diatoms (Krawczyk et al. 2014, in review) are the dominating phytoplankton group in the fjord system, no coccolithophores have been observed in the fjord system.

I suggest that the authors bank their raw data at CDIAC and mention this at the end of the material & methods section.

Data will be made available through CDIAC.

P 17943: The effect of sea-ice meltwater on CO2 dynamics has been shown before in several studies (I picked a recent one by Bates et al. 2014 but there are others), so this is not entirely a complete conceptual revolution of CO2 ocean dynamics, as suggested. Although this might be the first time it is shown for glacier meltwater in a fjord.

The effect has indeed been shown for other systems (rivers and sea-ice) but to our knowledge, the concept has not been applied yet to glacial melt. The reference will be added and it will be indicated in the text that next to rivers, the concept is also applied to sea-ice.

This salinity effect on pH and pCO2 dynamics has been described previously for estuarine systems (Mook and Koene, 1975; Whitfield and Turner, 1986) and sea-ice (Bates et al., 2014) but as yet, the mechanism has not been invoked to explain the low pCO2 in glacier affected systems.

Did the surface freeze at some point in the fjord during the annual cycle (sea-ice formation)? If so, shouldn't this be somehow accounted in the mass balance and the air-sea CO2 fluxes?

This is a good point, pinpointing a clear omission in the discussion. We have now added to the text:

The largest part of the Godthåbsfjord is free from sea ice throughout the year. Only in some of the inner stretches, sea ice is present during winter in some years. In the stations and transects sampled in this study, no sea-ice was present during the winter of 2012 and 2013. Although it has been previously shown that calcium carbonate precipitation takes place in the sea ice in Godthåbsfjord (Søgaard et al 2013), the influence of the sea ice melt on the Godthåbsfjord system is very low due to the limited extent of sea ice in the fjord. Therefore the effect of sea ice on the carbonate dynamics and biogeochemistry are not accounted for here.

SPECIFIC COMMENTS

P 17927 L 7: add the months and years of the cruises.

We have added:

Here we present seasonal observations of the carbonate system over the year 2013 in the surface waters of the Godthåbsfjord (west Greenland), which is influenced by tidewater outlet glaciers.
is this the global uptake in oceans or oceans+land?

This is global uptake by the ocean, it is corrected in the manuscript as follows:

The Arctic Ocean plays an important role in the global carbon cycle and contributes 5–14% to the global ocean CO2 uptake (Bates and Mathis 2009).

might be useful to cite some papers that show this fingerprint on other biogeochemical variables in principle more studied than CO2. Salinity, Nutrients, chlorophyll-a.

References have been added to the text to describe the effect on the coastal ocean of glacial meltwater.

Many of the coastal systems in the Arctic are affected by glacial meltwater input, which leaves a unique biogeochemical fingerprint upon their surface waters (Etherington et al., 2007; Bamber et al., 2012; Raiswell 2013).

There’s a mix of units that should all be uniform: tC/month/km², gC/m²/yr, gC/m²/d

This is corrected in the manuscript.

“exact mechanisms : : : not well understood”. Please rephrase: oceanCO2 dynamics isn’t rocket science or quantum physics. There are a handful of thermodynamic and biological processes that control CO2 in the oceans. Whether they’ve been evaluated and quantified in every single part of the ocean is another matter, and indeed there’s some work left.

This is adapted in the manuscript

defined DIC and pCO2 abbreviations first time they’re used:

This is corrected in the manuscript

please provide some information on the precision and accuracy of the pCO2 measurements, and comment on the calibration of the instrument (how and how often?). Paper by Fietzek et al. 2014 might be useful.

pCO2 data shown in this study was measured using the HydroC™ Carbon Dioxide Sensor (Contros, Germany) as stated in the text.

We have added:

The HydroC sensor was serviced and calibrated yearly by the Contros company. The relative standard deviation (RSD) of the pCO2 measurement has been estimated to be 1 % (Fietzek et al., 2014).

define SD

We have now defined RSD (relative standard deviation).

define ICES

The ICES incubator is the type of incubator used in this study (http://www.hydrobios.de/wp-content/uploads/2014/10/hydrobios-ices-incubator.pdf)

This has been adapted in the text:

Incubation bottles were filled with 55mL unfiltered seawater and spiked with 175 μL NaH14CO3 (20 μ Ci mL⁻1) and incubated for two hours in an ICES incubator (Hydro-Bios, Germany).

Yes, the incubations were performed in the dark, this is now added to the text

Triplecate samples (10mL) were incubated at in situ temperature in the dark.

Incubations are quite long. Is this standard procedure? I thought incubations for bacterial production were shorter, e.g. 2 h

Incubations for bacterial production are traditionally shorter, but due to the low rates, longer incubation times where chosen. In a study by Middelboe et al. (2012) in Kobbefjord (a sidefjord of Godthåbsfjord) also 3-5 hours incubations were used.

There’s increasing evidence that the Wanninkhof & McGillis (1999) parameterization provides over-estimates at high wind speeds, e.g. Ho et al. (2006). This is likely due to strong errors at high wind speeds when the eddy-covariance apparatus is thrown around with ship movement. The use of the Wanninkhof & McGillis (1999) parametrization is a problem in the present study since the fluxes computed at wind speeds of 30 m/s (as stated) will be sky high.
In this study we not only used Wanninkhof & McGillis (1999), but also that of Nightingale (2000). When comparing the fluxes from both parameterizations, the CO\textsubscript{2} uptake rates are quite similar. Presumably this implies that if the Wanninkhof & McGillis (1999) parameterization is susceptible to high wind speeds compared to Nightingale (2000), these high wind speed periods are not dominant in the yearly CO\textsubscript{2} uptake rates that we calculate.

P 17934 L 2 : this equation should be added in Table 1. As it stands, in table 1, there are 7 unknowns (Q1, Q2, Q3, F1, F2, F3, Qg) for 6 equations which is puzzling if you do not carefully read all the M&M, and you'll miss how this was solved.

We understand the issue, but we believe that addition of this equation on P 17934 L 2 will not clarify the issue, as this is not an equation for Q\textsubscript{g}(t). Instead we have now stated in the caption of Table 1 that Q\textsubscript{g}(t) is used as a forcing function upon the model and so it's clear that Q\textsubscript{g} is not a model variable. The caption now states:

*The glacial meltwater input into the fjord Q\textsubscript{g}(t) is imposed as a forcing function upon the model - see the text for details how Q\textsubscript{g}(t) is parameterized as a function of time.*

P 17937 : “strikingly” is a self-evaluation. Let the reader decide what' striking in your work.

This is now corrected in the manuscript

P 17937 L 5: Here and in numerous other places in the ms (17939, 17942, 17943, 17944). The correct phrasing is : “surface waters are undersaturated in CO\textsubscript{2} with respect to atmospheric equilibrium” or “pCO\textsubscript{2} in surface waters is below atmospheric pCO\textsubscript{2}”. The mix of both “pCO\textsubscript{2} undersaturation” or “pCO\textsubscript{2} is undersaturated” is not correct.

This is now corrected throughout the manuscript

P 17930 L 7: Are these relations for all of the data (all stations and all cruises) ? if not please specify. Also, these plots might be included in the paper. Finally, isn't the fact that DIC is conservative contradictory with the fact that NEP seems to control DIC dynamics (Fig. 10) and lead to large temporal changes of DIC (Fig. 10) ? This is probably related to the large salinity variation that obscures the NEP effect on DIC. But some rewording could be useful. Plotting DIC & TA versus Salinity will help to discuss this.

This DIC & TA versus salinity are indeed for all data from all stations and cruises. As mentioned by the reviewer, the large seasonal salinity variation indeed obscures the effect of NEP and temperature on DIC. However it shows how there is a conservative mixing between two end members (the seawater with salinity around 33 and large freshwater input). However due to uncertainty about the DIC relation at low salinity, the section will be deleted. The DIC & TA versus Salinity plots have been added to an appendix.

P 17942 : In page 17935 TAFW is 50, and here it's 54 \_M

This is now corrected in the manuscript.

P 17943 : One way to also demonstrate this is to plot DIC, TA and pCO\textsubscript{2} in surface waters as a function salinity, and compute the theoretical pCO\textsubscript{2} change along the salinity gradient using the two extreme salinity values (DIC and TA end-members) (this gives the thermodynamic effect of salinity change on pCO\textsubscript{2} in a closed system, i.e no air-sea CO\textsubscript{2} exchange).

We do not really understand what the referee is particularly aiming at. In our view this is exactly what is done in Figure 11A and B.

L 17944 : At such low salinities (8) the choice of dissociation constants becomes a problem, as well as the total boron value (computed from salinity), so this should be detailed in the Material and methods.

This was also commented upon by reviewer 1. Calculations of the carbonate system are done using the AquaEnv package. The package was developed using the Scheldt estuary as an example where large variability exist as well in salinity from mouth to upstream regions. Constants of the carbonate system as given in Roy et al. (1993) are used with a freshwater formulation for salinities below 5, as advised in Millero (1995).

Details are added on this in the text (p 17932 L 17):

*The R package CRAN: AquaEnv (Hofmann et al., 2010) was used for acid-base speciation and CO2 system calculations. We used the constants by Roy et al. (1993) as default with the adaptation by Millero et al. (1995) for low salinities. Consequently the dissociation constants are valid over the salinity range of 0–45 and the temperature range 0-45°C.*

References


