



Supplement of

The Northeast Greenland Shelf as a potential late-summer CO₂ source to the atmosphere

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Contents

1	Goal of this supplement	1
2	Water mass fractions on the shelf	2
3	Salinity normalisation of carbonate chemistry	5
4	Modified Z-scores	8
5	Comparison with SOCAT and CARINA data	8
6	Mixed layer variability	9
	References	9

1 Goal of this supplement

The ability of the ocean to dissolve carbon dioxide (CO₂) gas is primarily affected by temperature, salinity, the buffer capacity of the ocean (measured as titrated alkalinity) and the amount of total dissolved inorganic carbon (the sum of all inorganic carbon species in solution once released as CO₂ gas and measured by coulometric titration). To analyse the carbon chemistry from bottle data they are commonly normalised to remove the effect of salinity (S) (Broecker and Peng, 1992; Friis et al., 2003; Yamamoto-Kawai et al., 2005) or temperature (Takahashi et al., 2002, 2009). This allows the analysis of the influence of other processes on the carbon system. Generally, the four main abiotic influences on the carbonate system are temperature, salinity, total alkalinity (TA), and dissolved inorganic carbon (DIC) where the TA is generally considered to be conservative with salinity and the DIC is influenced primarily by autotrophic production and remineralisation (Zeebe and Wolf-Gladrow, 2001). When normalising data with respect to salinity in environments where TA is conservative with salinity, analyses can focus on the biology. For surface water transported to higher latitudes from low and mid latitudes, the increase in gas solubility is associated with the decrease in temperature (Li and Tsui, 1971; Millero, 2013; Weiss, 1970). For an isochemical water mass, the relationship was established by Takahashi et al. (1993) to be $(\partial \ln p\text{CO}_2 / \partial T) = 0.0423 \pm 0.0002 \text{ } ^\circ\text{C}^{-1}$ for water taken from the North Atlantic.

The Northeast Greenland shelf is a unique high latitude coastal environment with more possible influences on the carbonate system than in lower latitude open ocean environments. The environment can not be expected to be isochemical, nor is the surface water all cooled. Water found at the surface and originating in the Arctic Ocean will be exposed to increasing atmospheric temperatures with decreasing latitude in summer which would reduce the solubility of CO₂, while the return Atlantic Water might either heat or cool depending on conditions on the eastern side of Fram Strait, the season during which it arrives on the shelf, and the amount of (melting) sea ice it encounters. Similarly, the other main variables measured to calculate the CO₂ have different sources or are subject to complex processes on the shelf.

This supplement is intended to highlight some details which are relevant to but not directly part of the study. The first is a discussion surrounding the use of water mass tracers on the Northeast Greenland shelf and the errors associated with it. The second is a justification for our choice of using a polynomial fit to normalise the data rather than using more common methods. Finally we provide some detail regarding our use of the modified Z-score, a comparison between our data and that found in the SOCAT and CARINA databases, and overview maps for several integrated mixed layer depth observations.

2 Water mass fractions on the shelf

In an idealised estuarine environment there is a single freshwater source with which incoming ocean water is diluted. This source can be glacial or riverine, and precipitation is considered either negligible or as part of the same catchment. The TA of the freshwater source can be obtained by performing a linear regression between total alkalinity and salinity and finding the TA at $S = 0$. In a northern latitude fjord environment dilution of the surface layer by sea ice melt is an additional process. This makes the analysis more complex since sea ice retains TA in the form of the hydrated mineral ikaite ($\text{CaCO}_3 \cdot 6 \text{H}_2\text{O}$) and so is no longer conservative with the salinity, both in the meltwater influenced layer as well as the underlying water into which the salty but TA-depleted water is mixed. In an idealised fjord with a single meteoric freshwater source and local sea ice formation and melting the sea ice melt influence can be approximated by performing a water mass fraction

analysis. This is most frequently done by using a system of linear equations where 2 tracers are used to obtain 3 unknown water mass fractions. The most commonly used tracers are salinity and stable water oxygen isotopic composition ($\delta^{18}\text{O}$), which are independent from one another both for meteoric as well as sea ice freshwater sources, for end-members of Atlantic Water, Meteoric freshwater, and sea ice melt as shown in Equations 1, 2, and 3.

$$f_{sim} + F_{mw} + F_{aw} = 1 \quad (1)$$

$$\delta^{18}\text{O}_{sim} + \delta^{18}\text{O}_{mw} + \delta^{18}\text{O}_{aw} = \delta^{18}\text{O}_{obs} \quad (2)$$

$$S_{f_{sim}} + S_{mw} + S_{aw} = S_{obs} \quad (3)$$

where subscripts sim, mw, and aw refer to sea ice melt, meteoric freshwater and Atlantic Water end members and obs to the observed (measured) values.

The Northeast Greenland shelf is not an idealised northern latitude fjord, it is a complex broad Arctic continental shelf which receives multiple advected watermasses and receives additional local inputs. The water advected onto the shelf is not a pure Atlantic Water end member, it is instead comprised of return Atlantic Water, directly from the West Spitsbergen Current and Eurasian Basin sourced Arctic Atlantic Water which is much colder and may have been subject to processes specific to the Arctic that the return current has not including such things as dense water cascades or sedimentary interactions.

The upper water which includes the cold halocline layer and the surface water is influenced by sea ice melt and by the input of 10-11% of global meteoric river discharge (Shiklomanov et al., 2021). Each of the 6 major rivers discharging into the Arctic Ocean has its own average TA and $\delta^{18}\text{O}$ values which also vary seasonally (Cooper et al., 2008), Due to these complexities we can't assume that TA is conservative with salinity.

The 3 linear equations & solve for 1 unknown system commonly used to determine the water mass fractions is sensitive to the choice of the salinity and $\delta^{18}\text{O}$ for sea ice. Sea ice $\delta^{18}\text{O}$ can vary depending on the water from which it was frozen, whether or not it is covered in snow, and on its age (first year versus multiyear ice) (Mellat et al., 2024). For end member values AW (S=35.0, $\delta^{18}\text{O}$ =0.3‰), MW (S=0, $\delta^{18}\text{O}$ =-20‰) and sea ice melt with S = 2 set to

$\delta^{18}\text{O}$ of -4, -1, and 0.2‰ respectively entered into the system of linear equations, the lowest negative meteoric meltwater fraction (so an indicator of the size of the introduced error) in our data are -9.9%, -8.2%, -7.8% respectively. It is less sensitive to the salinity of the sea ice. For a $\delta^{18}\text{O}$ of 0.3‰, $S = 4$ results in a maximum negative freshwater fraction of -7.7% and remains the same (when rounded to 2 significant figures) at $S = 0$.

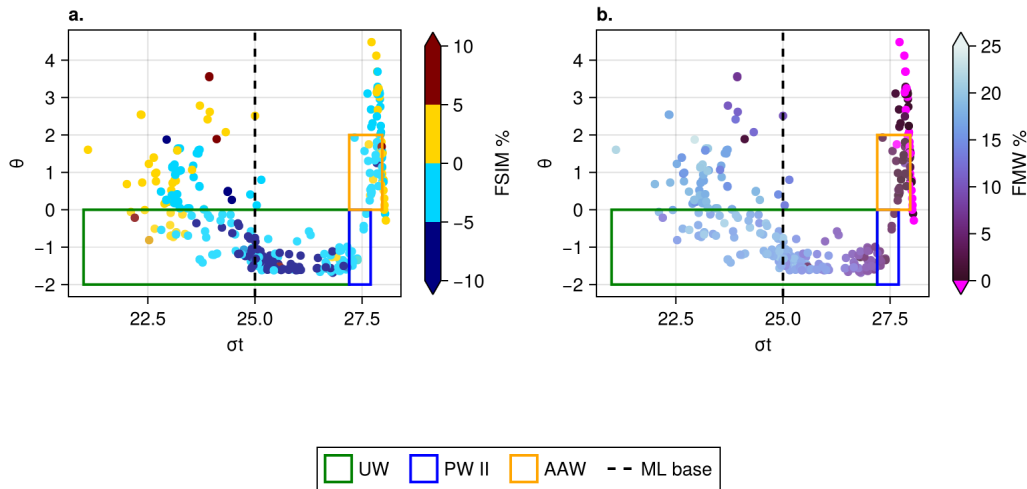


Figure 1: Density against temperature with fractions of sea ice melt (a) and meteoric water (b). Water mass boundaries (Rudels et al, 2022) in colour and the remnant of the winter mixed layer in the black dashed line. Acronyms UW is Upper Water, PW II is Polar Water 2 which refers to the lower halocline & winter mixed layer in the upstream Nansen Basin. Note that the Atlantic Water sea ice melt fraction is close to 0 while simultaneously, the upper water mixes from high in brine (negative melt) to high in sea ice melt crossing through 0 sea ice melt. Meteoric freshwater (FMW) has negative fractions, primarily at high densities which is clearly in error since meteoric freshwater input can't be negative. It is therefore apparent that the system of linear equations with which the water fractions are calculated is lacking the end-members or end-member values required to properly assign these fractions at each data point, likely due to the high variability of input sources.

For representative end-member values of AW ($S=35.0$, $\delta^{18}\text{O}=0.3$ ‰), MW ($S=0$, $\delta^{18}\text{O}=-20$ ‰), and for SIM $S=2$ and the mean $\delta^{18}\text{O}$ value of sea ice collected and melted during the second cruise: $\delta^{18}\text{O} = -2.34$ ‰ (Willcox et al., 2023). It can be seen that the Cold Halocline Layer (CHL, from the base of the winter mixed layer at $\sigma_t=25$ to the Polar Water II at $\sigma_t=27.2$) is most influenced by negative sea ice melt (generally interpreted as brine) and all other water, the more dense Polar II and Arctic Atlantic Water as well as the surface water have meltwater fractions of 0 ± 5 %. For the surface water this is not a problem since the meteoric freshwater and Atlantic Water fractions are not below 0. It does pose a problem for

the higher density waters ($\sigma_t > 27.2$) where the freshwater and/or Atlantic Water fractions are unrealistically $< 0\%$ (magenta in Figure fig. 1 b) and the sea ice meltwater fraction is lower than those erroneously negative fractions. When Atlantic Water enters the Arctic Ocean, it eventually forms the lower halocline when the warm water is rapidly cooled, by loss of heat to the atmosphere, but also through the melting of sea ice and a meltwater signature in these denser waters could be correct and can not be simply discarded. This issue can't be easily resolved without the use of additional tracers such as the ^{236}U and ^{129}I anthropogenic radionuclides which can differentiate between different Atlantic Waters based on their time spent in transit.

Table 1: End member values used to determine water mass fractions. Meteoric water values for $\delta^{18}\text{O}$ and TA are those of the Lena river according to (Cooper et al., 2008). Sea ice melt values for $\delta^{18}\text{O}$ and TA are from own measurements on the shelf

	Salinity	$\delta^{18}\text{O}$ (‰ VSMOW2)
Sea ice melt	2	-2.344 ± 0.746
Meteoric	0	-20.5
Atlantic	35.0	0.3

3 Salinity normalisation of carbonate chemistry

The TA of return Atlantic Water that has sea ice melted directly into it may be different (say a TA of 2330 diluted with a mean shelf sea ice concentration of $\sim 204 \mu\text{mol/kg}$) to the TA of Arctic Atlantic Water that has a similar salinity but may have had brine and meltwater added during multiple years spent in the Arctic Ocean. Simply correcting with the sea ice meltwater fraction therefore may not be sufficient to describe local processes.

The simplest formulation of the salinity normalisation of marine inorganic carbon system data is given by Equation eq. 4 where the reference salinity normalised to is often 35 (Peng et al., 1987). Several modifications to this have been proposed with time including those which involve corrections for nutrients (Broecker and Peng, 1992).

$$nX = \frac{X_{meas}}{S_{meas}} \cdot S_{ref} \quad (4)$$

where X is the variable to be corrected for, e.g. TA and/or DIC, S is the salinity, and $meas$ and ref subscripts stand for the field measurements and the reference value respectively.

Whether the resulting normalised data are entirely independent of freshwater flux has been questioned (Robbins, 2001). Later iterations were developed specifically for higher latitudes including corrections for a TA estimated by linear regression at the point $S = 0$ (Friis et al., 2003), and for the calculated sea ice melt fraction (Yamamoto-Kawai et al., 2005). Each of these corrections has associated issues and errors and may not provide useful information, especially where there are multiple low salinity sources for TA such as shelf environments host to catchments with differing geology. Although there is an official description of what a reference salinity is (Wright et al., 2010), it is often either chosen to be 35 or a regionally obtained variable, often the mean salinity. This makes any comparison between different geographical regions with different dominant water masses and therefore chosen reference salinity for calculated values subject icomparable. This complexity primarily impacts mixed layer depths (Friis et al., 2003) where the meteoric-influenced layer is highest or multiple different sources such as precipitation, riverine inputs, and sea ice melt, contribute to the dilution. If these normalizations rely on other assumptions such as those underlying the calculation of sea ice melt fraction from $\delta^{18}O$, any error in these assumptions will be propagated into any subsequent application using the normalized data.

The processes controlling the water mass composition and the associated shelf salinity and alkalinity are complex. In addition, fraction calculations suffer from the ambiguities discussed in the previous subsection, therefore these data might best be normalized with respect to salinity by the simple removal of a polynomial-predicted value from the data, rather than attempting to correct for the assumed representative values for the Northeast Greenland shelf which contains such vastly variable sources in unknown relative quantities. For purposes of comparison and to choose the best representative method for the salinity normalisation of the carbonate system data, four different salinity corrections were applied (Figure 2). The first (Figure 2a) is the direct application of the polynomial in Equation 5:

$$X_{pred} = X_{obs} - X_{poly} + X_{meanS} \quad (5)$$

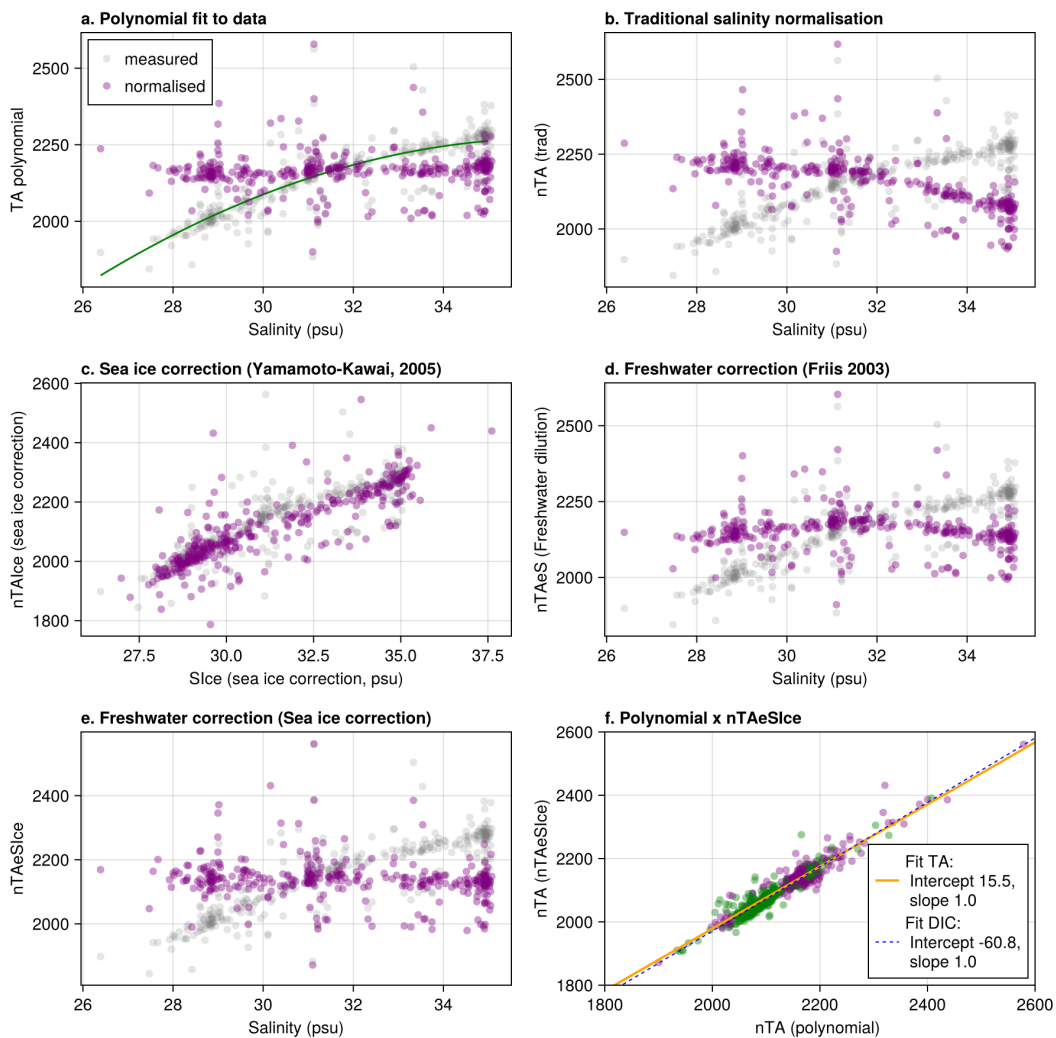


Figure 2: Comparison of normalisation techniques. Application by polynomial fit using the green line with equation $TA = -3631.43 + 324.03 S - 4.45 S^2$ (a), traditional salinity normalisation (b), Sea ice correction (c), Meteoric freshwater correction (d), Meteoric correction applied to sea ice corrected data (e) and finally a comparison between sea ice + freshwater corrections and the polynomial correction indicating a slope of 1 between them.

where pred is the salinity-normalised value estimated by the equation, obs is the observational data, poly is the value predicted by the polynomial fit (green line in Figure 2a), and X_{meanS} the mean salinity for the dataset. This method therefore still relies on an arbitrary choice of reference salinity but it reduces the number of assumptions made about external influences on the data such as the calculated fraction of sea ice melt although these have results that are comparable enough to be used interchangeably (Figure 2f).

4 Modified Z-scores

Modified Z-scores rely on the Absolute Median Deviation (MAD) rather than the mean of a dataset and thus allow for the labeling of outliers in datasets where the mean is too sensitive to outliers. This modified Z-score is calculated according to Equations 6 and 7.

$$MAD = \text{median}_i(|x_i - \tilde{x}|) \quad (6)$$

$$M_i = \frac{0.6745(x_i - \tilde{x})}{MAD} \quad (7)$$

Data can then be flagged as an outlier if $|M_i| > D$. Although Iglewicz and Hoaglin (1993) suggest a D of 3.5, this doesn't adequately flag all outliers in our data. To make sure all outliers based on visual inspection are flagged as such we require $D = 1.5$.

5 Comparison with SOCAT and CARINA data

Limited Surface Ocean CO₂ Atlas (SOCAT) carbon dioxide fugacity measurements and full depth CARbon dioxide IN the Atlantic Ocean (CARINA) total alkalinity (TA) and dissolved inorganic carbon (DIC) data are available for the region of this study, however it is both geographically (Figure 1 a. main text) as well as temporally limited (Figure 4). For the time period (late August and September) of our study in late fall, there is only SOCAT data available from 2009 and CARINA data from 1994 and 2003 and therefore these data are not ideal for comparative purposes.

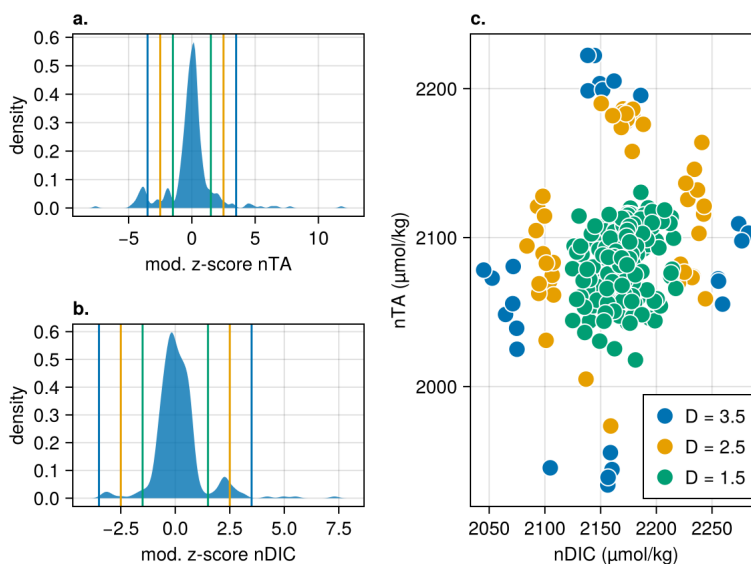


Figure 3: Density plots of the modified Z-scores of normalised TA and DIC (a,b) and of the data not flagged as outliers based on different choice of D

6 Mixed layer variability

Integrated values for measurements obtained at depths shallower than the depth of the maximum Brunt-Väisälä frequency squared (N^2) are shown in Figure 5. Due to the high variability in conditions during the sampling period, these observations cannot be treated as a single snapshot of conditions on the shelf. Since it does not represent the temporal diversity adequately, this figure has been omitted from the main text but is included here for reference.

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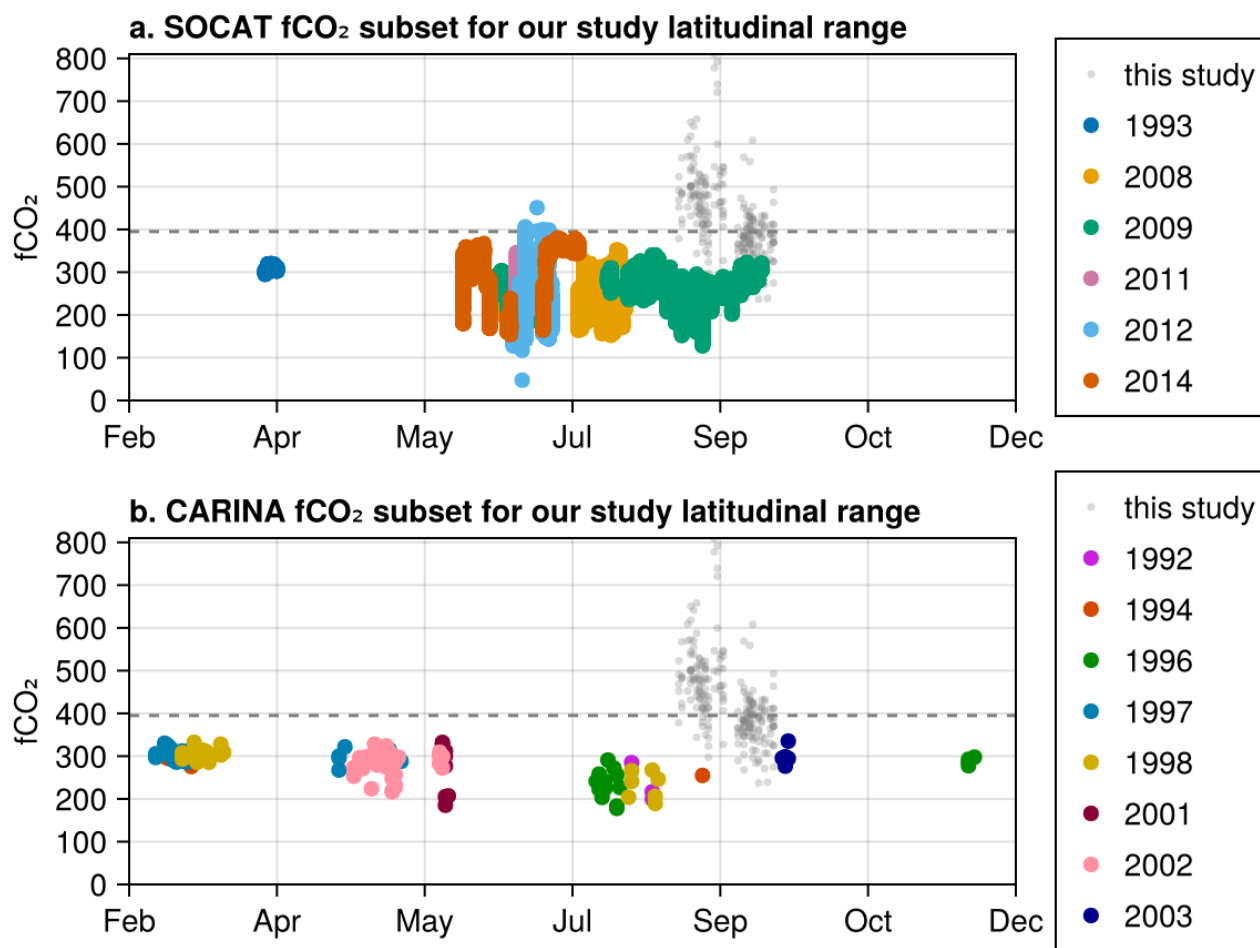


Figure 4: SOCAT measured fCO₂ (a) and CARINA CO₂SYN calculated fCO₂ (b) for geographical area on and around the Northeast Greenland shelf compared to data from our study where $D = 1.5$. The grey dashed line is at 395 μatm , which is representative for the time of our study per Fay et al. (2021)

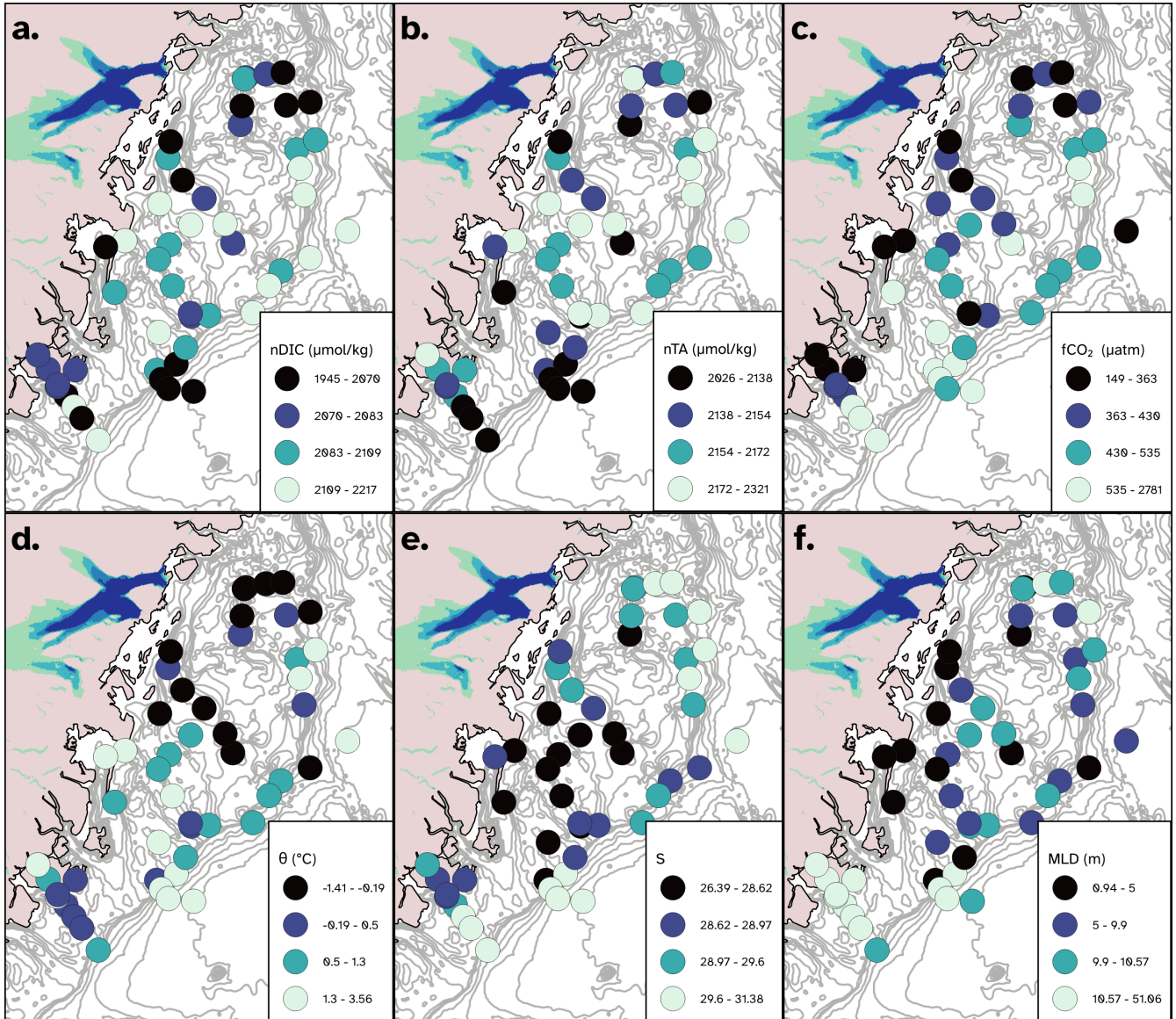


Figure 5: Mixed layer depth values for normalised DIC (a), normalised TA (b), $f\text{CO}_2$ (c), temperature (d), salinity (e). The mixed layer depth itself (per depth of maximum N^2) is shown in f.

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