

## Authors Responses

\*Reviewer Comments are in blue

\*\*Authors responses are in black

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The authors feel that the comments made below have improved the manuscript substantially and have added a sentence to the acknowledgements as a token of our appreciation to both reviewers.

### Reviewer #1, Anonymous:

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#### **General comments:**

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This work presents a nice data set from a region where few data has been collected, especially when focusing on the inorganic carbon cycle and how this is impacted by input from land. It is largely well written and the figures illustrate the results. However there are some minor issues that the authors should consider before publication.

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The authors are grateful for this detailed review. Various sections of the paper now have improved wording, and various statements have been added to the discussion section that improve the overall interpretation of the data.

#### **Specific comments:**

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One is an aspect that often is seen in the literature. The sentence that starts in line 25 of page 1 reads that the Arctic Ocean is particularly vulnerable to OA because of . . . low buffer capacity in cold waters. . . The low buffer capacity means that DIC is not changing much for a given change in pCO<sub>2</sub>, which also means that the concentration of CO<sub>3</sub><sup>2-</sup> does not change as much as it will in warmer water of less equilibrium DIC concentration. Thus the saturation state of calcium carbonate changes less in cold water compared to warm water for a given increase in pCO<sub>2</sub>. So even if the saturation state is lower to begin with does this mean that these waters are more vulnerable? It is best to be more specific when making this kind of statement.

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We appreciate this comment and understand the confusion created by the wording of this sentence. In the revised manuscript ([starting line 263](#)), we have clarified between solubility, and the change in solubility. Specifically, we have removed the parts of this sentence that refer to CO<sub>2</sub> solubility and buffering capacity, and instead have described how changes in pH and carbonate ion concentration due to CO<sub>2</sub> uptake differ in cold, low alkalinity waters compared to warm, high alkalinity waters. We have also added a reference to Shadwick et al., 2013, wherein these concepts are discussed in detail.

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A principle issue is that one analyse seawater but determine (or measure) TA, DIC or any other constituent. When analysing TA it means that one determines what TA consists of. One can claim that this is minor thing and that the word “analyse” often is used in this way, but that is not an excuse for not being correct.

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The authors appreciate this point. The word ‘analysis’ is used incorrectly (and overused) throughout the manuscript. The authors have now used the terms ‘measure’ and ‘determine’ in the appropriate places.

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Page 6, line 22. It is suggested that excess TA and salinity is added by brine, and on line 36 that sea ice melt result in a negative deviation of TA. This is highly likely considering the data and other observations from the Fox basin, but can one thus conclude that this result show that no ikaite (calcium carbonate) is formed and trapped in the sea ice. I would urge the authors to expand on this topic.

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The authors had not considered dissolution of Ikaite as a potential source of TA, so we thank the reviewer for bringing this to our attention. A statement relating to this topic has been added (line 448), however, given the limitations of the dataset, we believe that any further discussion on this topic would be rather speculative.

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On page 7 the term “benthic carbonate input” is used. I assume that what is meant that metal carbonate dissolves at the sediment surface and that the carbonate ion is added to the bottom water. If so add “ion” after carbonate.

We appreciate this clarification, and have added ‘ion’ where appropriate.

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Next to last sentence of the first paragraph on page 8. It is extremely important to take samples for salinity determination from the same flask as where the chemical samples are collected in stratified waters. This cannot be stressed enough and this contribution again well illustrates this.

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We thank the reviewer for their appreciation of this result.

The section starting on line 12 at page 9. It would be interesting if the authors discuss how the observed C-13 signal is impacted by either decay of marine produced organic matter or terrestrial produced organic matter. Can the data be used to distinguish these sources?

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The reviewer raises an interesting point here, as this analysis assumes all organic matter is of marine origin. Consequently, authors have added a note of caution to the end of this paragraph. However, we have also noted that the turnover of organic matter in marine systems is relatively rapid, thus a terrestrial signature will be very difficult to detect when sampling within the bay. Overall, these points (starting on line 544) are an interesting addition to the discussion.

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85 Next paragraph. Here I have difficulties to understand how bottom water with high TA and DIC can be mixed up into the surface to give the high omega values without also mixing up salinity. Is it not more likely that the dissolution of metal carbonates occurs in the river drainage basin and is transported out to the estuary? Is there information on the mineral compositions of the different drainage basins that can add to the observations?

90 The authors agree that it is important to state that the majority of the carbonate dissolution likely occurs within the drainage basin, rather than in the estuary itself. However, we cannot rule out dissolution within the estuary entirely, thus in the revised manuscript we now state that carbonate dissolution may occur within the drainage basin and within the estuary (see statements starting at lines 463 and 553)

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**Reviewer #2, Lee W. Cooper:**

**General comments:**

This is a short descriptive paper describing the results of sampling in 2010 for total alkalinity and inorganic carbon, including the isotopic composition of DIC in Hudson Bay, with the use of oxygen isotopes as tool to evaluate runoff and melted sea ice contributions. It follows related studies by Azetsu-Scott et al. 2014 and Granskog et al. 2011, among others in the same region, so it is of value both as a point in a time-series for possible changes in the inorganic carbon system and to fill in the geographical gap for arctic data coverage within Hudson Bay. Because of the limited one time nature of the sampling, it is not clear whether changes can be readily determined, but the scope of the paper seems appropriate for the descriptive nature of the data set presented. I recommend a few improvements and pose some questions below for the authors to consider.

The authors greatly appreciate the thorough and thoughtful comments made in this review. Dr. Cooper clearly understands the scope of the paper, and his comments have led to significant improvements in all areas (text, figures, and tables) of the revised version.

**Specific comments:**

Figure 1. The map could be improved. It is plotted in a Mercator projection, which is not a polar projection, so distances are distorted, and it is not clear where the latitude and longitude markers are. The shaded areas denoting sea ice are also rather awkwardly illustrated and hard to see, such as the northern straits connecting to Hudson Bay. I think this could be easily re-done in a standard GIS program in a more appropriate polar map projection with better labeling. The map figure in the Granskog et al. 2011 paper that is referenced in the text, while still plotted in Mercator projection, is a much more attractive example of how to display the geographical information that is important to the data presentation.

The authors appreciate these comments, and have redone Figure 1. An orthogonal polar projection is now used, providing a less distorted map. The coloring has been altered to make the figure and labels more clear, and the scale of the map has been changed to avoid the northern section, which was not necessary.

Figure 2, and 6c. Why isn't the  $\delta^{13}\text{C}$ -DIC data coverage more complete? Again, as with Figure 1, the quality of these figures is only fair, and it could be improved by exporting out of Ocean Data View into a more robust graphics program, with appropriate labeling undertaken such as of the Nelson River (simply outlined in blue now). Also one of the software license requirements of Ocean Data View is to cite the software developers. "ODV may be used free of charge for non-commercial, non-military research and teaching purposes. If used in scientific papers, reports or posters, ODV must be referenced as follows: Schlitzer, R., Ocean Data View, odv.awi.de, 2015." Please add to the references or acknowledgements.

$\delta^{13}\text{C}$ -DIC was only sampled during the first part of the cruise. For clarity, this has been stated explicitly in

160 the captions of Figures 2 and 6.

As for figure 2, the authors feel that these ODV plots adequately illustrate the key discussion points in the manuscript. Steps were taken to try and improve the quality of the image, such as labeling of the Nelson River, but it was decided to leave this as a descriptive label in the caption in order to maintain a larger text size within the panels.

165 Finally, the authors appreciate pointing out the ODV license requirement, and have added the reference to the acknowledgements.

170 [Figure 5 caption. The discrepancy with rosette bottle salinities can be caused by inadequate flushing time before bottles are closed at depth. Is the flushing time used by the CTD operator known?](#)

The flushing time at each depth was approximately 1 minute, this has been confirmed by the CTD operator. The authors appreciate that this is useful information for the reader, and thus we have added this statement to the methods section (line 324), as well as to the caption in Figure 5.

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[Table 1. The one-time sampling of these rivers is a limitation for this type of study that depends upon integrated and flux weighted data. The table could be expanded and include references to any other available data for these rivers.](#)

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The authors agree and appreciate this recommendation. Table 1 has been expanded to include discharge and dissolved organic carbon (both of which were discussed in the manuscript but not shown in the table), as well as prior  $^{18}\text{O}$  measurements. The required references have also been added to the table.

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[Page 4, line 25. Friedman and O'Neill \(not Friedman et al. 1977\) is really not a very appropriate reference for this method of determining oxygen isotopes. It describes the isotopic fractionation factors associated with equilibration of water with carbon dioxide, but it is not really a description of the method. Epstein and Mayeda, 1953 in \*Geochemica et Cosmochimica Acta\* is the original reference for the oxygen isotope equilibration methodology, but the methods used today that involve flushing of sample vials with small quantities of carbon dioxide in otherwise pure helium are not available as details in these two publications of Epstein and Mayeda and Friedman and O'Neill, which were written well before the technology for continuous flow mass spectrometry was developed. Again, the Granskog et al 2011 paper provides a more accurate description of the methods used. I would start with that.](#)

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The authors tend to agree that the citation to the Friedman and O'Neil paper is outdated, and frankly, unnecessary. We have removed this citation and, instead, have finished describing the method to an adequate degree so as to not require any citation (see paragraph starting at line 361).

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Page 5, second paragraph. It might be worthwhile to reference Smith et al. 2015 (<http://dx.doi.org/10.1080/07011784.2014.9855120>) either here and/or in the discussion, as they have added a significant amount of isotopic data for the Nelson River basin.

205 We appreciate bringing this paper to our attention. Data from Smith et al. 2015 is now presented in Table 1, and is referenced in the revised manuscript (line 477)

210 Page 5, line 17. I understand that a freshwater end-member isotopic value of -14‰ for Hudson Bay as a whole is used, but the more southern rivers such as the Nelson are clearly more enriched in heavy isotopes and this creates an inaccurate result for the sea ice melt contribution (Figure 2e). I am not sure this can be resolved easily but maybe in the future (with more extensive sampling) it would make more sense to divide Hudson Bay into areas influenced by northern rivers versus James Bay and the Nelson River and try to resolve more than one mixing process with runoff and melted sea ice.

215 The authors agree that this oversimplification is an issue, and multiple regional endmembers were discussed during manuscript preparation. However, given the limitations of this ‘snapshot’ dataset and, consequently, the limited scope of this particular section, we believe the simplified method is justifiable here. We do, however, fully understand the necessity to resolve this issue, and have added a sentence to this effect in the conclusion of the revised manuscript (line 583).

225 Page 6, line 15-20. I am not sure why nutrient data, such as nitrate-phosphate ratios, and silicate are not also used to verify the presence of Pacific origin water; this would seem to be much more certain than TA, where multiple freshwater sources are present, although the salinity of 33.1 shown on Figure 3a seems convincing enough for the upper Arctic halocline that is characteristic of Pacific-origin water.

230 The authors do agree that a comparison between alkalinity and nutrients as watermass tracers in the Hudson Bay system would be of interest. However, there is insufficient nutrient data available from this cruise to undergo this comparison, especially given that this is a very complex discussion that may be more suitable as a separate study altogether. For example, nitrate and phosphate are not always ideal watermass tracers due to their relatively non-conservative behaviour compared to the more conservative alkalinity. Also, in shallow systems like the Canadian Archipelago, processes such as denitrification can cause major complications in a nutrient-based watermass analysis.

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# Inorganic Carbon Cycling and Biogeochemical Processes in an Arctic Inland Sea (Hudson Bay)

*(edits relating specifically to the reviewer comments are shown in red)*

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**Abstract.** The distributions of carbonate system parameters in Hudson Bay, which not only receives nearly one third of Canada's river discharge, but which is also subject to annual cycles of sea-ice formation and melt, indicate that the timing and magnitude of freshwater inputs play an important role in carbon biogeochemistry and acidification in this unique Arctic ecosystem. This study uses basin-wide measurements of dissolved inorganic carbon (DIC) and total alkalinity (TA), as well as stable isotope tracers ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{DIC}}$ ), to provide a detailed assessment of carbon cycling processes within the bay. Surface distributions of carbonate parameters reveal the particular importance of freshwater inputs in the southern portion of the bay. Based on TA, we surmise that the deep waters in the Hudson Bay are largely of Pacific origin. Riverine TA end-members vary significantly both regionally and with small changes in near-surface depths, highlighting the importance of careful surface water sampling in highly stratified waters. In an along-shore transect, large increases in subsurface DIC are accompanied by equivalent decreases in  $\delta^{13}\text{C}_{\text{DIC}}$  with no discernable change in TA, indicating a respiratory DIC production on the order of  $100 \mu\text{mol kg}^{-1}$  during deep water circulation around the bay.

**Keywords:** carbon cycling, carbonate system, freshwater, stable isotopes, Hudson Bay System.

## 1. Introduction

The Arctic Ocean is particularly vulnerable to "Ocean Acidification" (defined as the combined results of decreasing pH and increasing calcium carbonate solubility), because changes in pH and carbonate ion concentration in response to a given uptake of atmospheric  $\text{CO}_2$  are more pronounced in cold, low alkalinity waters compared to warm waters with high alkalinity. Furthermore, inflowing Pacific water with naturally high  $\text{CO}_2$  concentrations, as well as dilution from sea-ice melt and river waters, exacerbate the so-called 'vulnerability' of polar waters (AMAP, 2013; Shadwick et al., 2013). Freshwater input can directly reduce the buffering capacity of seawater, and dilute carbonate ions, thereby decreasing the saturation states of calcite ( $\Omega_{\text{Ca}}$ ) and aragonite ( $\Omega_{\text{Ar}}$ ), minerals that many important marine species require to form their shells (e.g., Chierici and Fransson,

2009; Yamamoto-Kawai et al., 2009). Therefore, regions of the Arctic Ocean are predicted to be among the first to experience the damaging effects of ocean acidification (Orr et al., 2005; Fabry et al., 2009).

275 The Hudson Bay system receives nearly one third of Canada's river discharge, and Hudson Bay itself goes from complete ice-cover in winter to open water in summer, culminating in an annual freshwater yield from river runoff and sea-ice melt that is more than double that of the Arctic Ocean (Granskog et al., 2011). Organic matter respiration releases dissolved inorganic carbon (DIC) and consumes total alkalinity (TA), which decreases the  $\Omega_{Ca}$  and  $\Omega_{Ar}$  in deep waters. In addition to the organic matter generated in the euphotic zone by primary producers, local riverine inputs of organic matter are injected into deep waters during sea-ice formation (Mundy et al., 2010; Granskog et al., 2011). Furthermore, at the mouth of Hudson Bay shallow sills restrict the exchange of deep water between the bay and the relatively well-ventilated waters from the adjacent Hudson Strait or  
280 Foxe Strait (Granskog et al., 2011). Given these characteristics, Hudson Bay may be particularly vulnerable to ocean acidification. In support of this, Azetsu-Scott et al. (2014) recently provided the first basin-wide overview of the Hudson Bay carbonate system in fall 2005, reporting that surface waters in south-eastern Hudson Bay, where freshwater inputs are highest, were undersaturated with respect to aragonite ( $\Omega_{Ar} < 1$ ), as were up to two-thirds of Hudson Bay bottom waters.

285 With air temperatures rising, sea-ice coverage declining, and increasing river diversion for hydroelectricity generation, conditions in the Arctic, and Hudson Bay in particular, are changing much more rapidly than in much of the world's oceans. The Hudson Bay system is one of the richest eco-regions for marine mammals in the world and is critical for both resident and migratory species (Wilkinson et al., 2009). Regime shifts in this ecosystem could therefore result in cascading effects impacting multiple organisms and coastal communities. The 2005 fall survey by Azetsu-Scott et al. (2014) provided an initial baseline for understanding of the state of the CO<sub>2</sub> system in Hudson Bay, yet significant uncertainties remain regarding the biogeochemical  
290 processes responsible for the observed state of the marine carbonate system and how the system and its controlling processes have changed, or may continue to change, over time.

Here, we present recent (July 2010) seawater measurements of the marine carbonate system along with stable isotope ratios of oxygen in seawater ( $\delta^{18}O$ ) and carbon ( $\delta^{13}C_{DIC}$ ) across Hudson Bay. Surface distributions highlight the impact of different freshwater inputs on the carbonate system. Relationships of DIC and TA with salinity in deep water provide insight into the  
295 origin of waters in Hudson Bay, while similar relationships in shallow water describe key sources and sinks of carbon. We also evaluate the evolution of water mass properties during transit around Hudson Bay and the importance of precise sampling techniques when working in highly stratified waters.

## 2. The Hudson Bay System

300 The Hudson Bay system, which includes James Bay to the south, and both Foxe and Hudson Straits to the north, is shown in Fig. 1. Hudson Bay, itself, is the largest inland sea in North America (Martini, 1986), covering an area of 841,000 km<sup>2</sup> (Kuzyk et al., 2009). Hudson Bay is relatively shallow, with an average depth of 125 m and a maximum depth of 250 m, while areas of Foxe Strait and Hudson Strait reach depths of 400 m (Prinsenber, 1987; Saucier et al., 2004). Water enters the Hudson Bay system from two channels. Waters that are predominantly of Pacific origin enter from the north, flowing from the Canadian Archipelago into Foxe Basin and Foxe Strait via the Fury and Hecla Strait, while Atlantic waters enter from the east, flowing from the  
305 Labrador Sea into the Hudson Strait (Ingram and Prinsenber, 1998). Hudson Bay is connected to Foxe and Hudson Straits via

four main channels. The narrow channel west of Southampton Island is only 50 m deep but is considered an important source of water to the northwest corner of the bay (Prinsenber, 1986). The majority of water exchange occurs via three channels located between southwest Southampton Island and the east coast of Hudson Bay. The outer channels are only 130 m deep, thus exchange of deep waters is likely limited to the central channel, which contains a sill at 185 m depth (Fig. 1, black star).

310 Within Hudson Bay, the circulation is generally cyclonic (counterclockwise), with a mean summertime current velocity of  $0.05 \text{ m s}^{-1}$  (Martini, 1986; Prinsenber, 1986). During transit, coastal surface waters are substantially modified by river inputs, which total approximately  $760 \text{ km}^3 \text{ yr}^{-1}$  (Déry et al., 2011). The vast majority of this input enters via James Bay (47 % of the total) and from rivers along the southern coast (from the Churchill to the Great Whale, see Fig. 1) that drain directly into Hudson Bay (32 % of the total input). The peak river input ( $\sim 2 \text{ km}^3 \text{ day}^{-1}$ ) occurs in May, while the minimum ( $\sim 1 \text{ km}^3 \text{ day}^{-1}$ ) occurs in  
315 March (Déry et al., 2011). Freshwater is also added to surface waters via sea-ice melt (SIM). Hudson Bay is completely ice covered for 8-9 months of the year and becomes completely ice free in the summer. Sea-ice can reach a maximum thickness of about 1 m in James Bay, 1.5 m in Hudson Bay, and 2 m in Foxe Basin (Martini, 1986). In Hudson Bay, peak inputs from SIM are from June to mid-July, and during this time SIM usually provides more freshwater to surface waters than river runoff (Prinsenber, 1988; Granskog et al., 2011). The pulse of melt water also creates strong vertical stratification, which suppresses  
320 mixing of heat and nutrients into the surface waters (Prinsenber, 1988; Else et al., 2008). Ice formation is also responsible for brine formation due to salt rejection (Saucier et al., 2004, Granskog et al., 2011).

### 3. Methods

We collected samples at 55 stations, including 16 rivers, across the Hudson Bay system from July 7<sup>th</sup> to 30<sup>th</sup>, 2010, during leg 1a of the 2010 ArcticNet Cruise aboard the CCGS Amundsen (Fig. 1). Water samples for salinity, DIC, TA, and stable isotopes of  
325 both oxygen in seawater ( $\delta^{18}\text{O}$ ) and carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) were collected at various depths using 12-L Niskin bottles mounted on a 24-bottle rosette fit with a SeaBird SBE911 Conductivity-Temperature-Depth (CTD) profiler. Niskin bottles were held at each depth for one minute before closing to allow for adequate flushing. A small subset of samples collected in the Nelson River estuary, as well as river samples, were taken using either a single 3-L Niskin bottle hand-lowered to 1 m depth (for DIC, TA, and associated salinities), or using a bucket hand-lowered to less than 1 m depth (for  $\delta^{18}\text{O}$ ,  $\delta^{13}\text{C}_{\text{DIC}}$ , and associated salinities).

330 Samples for DIC and TA determination were taken directly from the Niskin bottles into borosilicate glass bottles: 250 or 500 mL bottles with ground-glass stoppers and elastic closures or 250 mL screw-cap bottles. All DIC and TA samples were poisoned with  $100 \mu\text{l}$  of a saturated  $\text{HgCl}_2$  solution to halt biological activity and were stored in the dark at either room temperature or at  $4^\circ\text{C}$  until being processed ashore. The DIC and TA determinations were conducted at both Dalhousie University in Halifax, Nova Scotia, and the Institute of Ocean Sciences (IOS) in Sidney, British Columbia. Both labs analyzed samples for DIC  
335 coulometrically followed by TA determination from the same bottle using potentiometric titrations. At Dalhousie, both DIC and TA were measured using a VINDTA 3C (Versatile Instrument for the Determination of Titration Alkalinity, Marianda), whereas IOS measured DIC using a SOMMA (Single-Operator Multiparameter Metabolic Analyzer) and TA with a custom-built titration system. The analytical methods followed the recommendations of Dickson et al. (2007). Both labs used Certified Reference Materials (CRM batches 101 and 81) supplied by A.G. Dickson (Scripps Institution of Oceanography) to consistently calibrate  
340 the instruments. Samples measured by the IOS lab have an analytical precision better than  $0.9 \mu\text{mol kg}^{-1}$  for DIC and  $2 \mu\text{mol kg}^{-1}$  for TA. An equivalent precision computation could not be done for samples analyzed at Dalhousie due to a lack of duplicate

samples, but historically, precision of the Dalhousie VINDTA system has been consistently better than  $3 \mu\text{mol kg}^{-1}$  (e.g., Shadwick et al., 2011). We computed the aragonite saturation state ( $\Omega_{Ar}$ ) from the DIC and TA data using the *CO2sys* program of Lewis and Wallace (1998), with the equilibrium constants of Mehrbach et al. (1973) refit by Dickson and Millero (1987).

345 At station 740 in central Hudson Bay (Fig. 1), an inter-calibration between the IOS and Dalhousie labs was conducted wherein duplicate samples were taken from all 12 Niskin bottles, with each lab producing independent depth profiles of both DIC and TA. Anomalously high deviations in both DIC and TA were measured at the bottom-most sample, and CTD profiles at this station reveal distinct changes in temperature and salinity in the bottom four meters of the water column, suggesting the presence of a bottom nepheloid layer. Given that the bottom Niskin bottle was closed within this layer, the large deviations in both DIC and TA between duplicate samples may be due to large geochemical gradients or high concentrations of suspended material in the Niskin bottle. Not including these bottom samples, mean absolute differences in DIC and TA samples between the two labs were  $2.4 \pm 0.9 \mu\text{mol kg}^{-1}$  and  $12.6 \pm 6.8 \mu\text{mol kg}^{-1}$ , respectively. Deviations in TA between the 11 duplicate samples (bottom sample not included) were not consistently positive or negative, thus an offset correction could not be applied to either dataset prior to merging. Although this average TA difference represents significant variability between the two datasets, TA alterations of this magnitude do not alter the key results of this study and thus are not important in the context of this discussion. For example, a  $\pm 12.6 \mu\text{mol kg}^{-1}$  change in surface water TA at all stations results in an average change in surface water  $\Omega_{Ar}$  of  $\pm 0.12$ , with no visible change in spatial patterns throughout the Hudson Bay and with no stations moving from supersaturation to undersaturation, or vice versa. Also, patterns in  $\Omega_{Ar}$  along the coastal transect in Hudson Bay, including the depth of the saturation horizon, do not change significantly given a  $12.6 \mu\text{mol kg}^{-1}$  change in TA. Furthermore it has to be noted that the sampling strategy used in this study was not ideal for intercalibration purposes, since it took place in highly variable, relatively shallow waters as [opposed](#) to stable deep ocean waters.

360 Samples for  $\delta^{13}\text{C}_{\text{DIC}}$  [determination](#) were collected in 30 mL vacuum-sealed glass vials and spiked with 60- $\mu\text{L}$  of saturated  $\text{HgCl}_2$  solution to halt biological activity. [Measurement](#) of  $\delta^{13}\text{C}_{\text{DIC}}$  was conducted at Yale University using continuous-flow isotope-ratio-monitoring mass spectrometry (CF-irmMS) on Thermo Finnigan MAT 253 gas mass spectrometers coupled to a Thermo Electron Gas Bench II via a Thermo Electron ConFlo IV split interface. The analytical method has a reproducibility of better than  $\pm 0.1 \%$ . Samples for the oxygen isotopic composition of water ( $\delta^{18}\text{O}$ ) were collected in 20 mL borosilicate glass vials, sealed with Parafilm to minimize evaporation, and stored at  $4^\circ\text{C}$ . [Measurements were](#) conducted at the G.G. Hatch Stable Isotope Laboratory (University of Ottawa) using a Finnigan MAT Delta plus XP + Gasbench. A 0.2 to 0.6 mL subsample was flushed with 2 %  $\text{CO}_2$  in helium [before being stored for at least 18 hours to achieve equilibration](#). Stable carbon and oxygen isotope ratios are expressed in the usual delta ( $\delta$ )-notation as per mil (‰) deviation relative to the international VPDB (Vienna Pee Dee Belemnite) and V-SMOW (Vienna Standard Mean Ocean Water) standards, respectively. Salinity samples were analyzed on board the Amundsen using a Guildline 8004B Autosol Laboratory salinometer calibrated with standard seawater from the International Association for the Physical Sciences of the Oceans (IAPSO).

370 The fractions of sea-ice melt water ( $f_{\text{SIM}}$ ) and meteoric water ( $f_{\text{MW}}$ ) are calculated using bottle salinities and  $\delta^{18}\text{O}$  in a three end-member mixing model. The methods, equations, and end-member values (for seawater, sea-ice melt water, and meteoric water) used in the model are identical to those described by Granskog et al. (2011).

## 4. Results and Discussions

### 4.1 Surface Distributions

380 Surface distributions within Hudson Bay (Fig. 2) reveal the dominant role that freshwater input plays in altering the carbonate system parameters of surface waters, particularly in the southern and eastern parts of the bay. Distributions of TA (Fig. 2b), DIC (Fig. 2c), and  $\Omega_{Ar}$  (Fig. 2d) mimic that of salinity (Fig. 2a), with maxima in the high salinity waters of the Hudson and Foxe Straits, and minima along the southern coast of Hudson Bay. One notable exception, however, is near the Nelson River (Fig. 1), where stations exhibit low salinities but relatively high DIC, TA, and  $\Omega_{Ar}$ . The dilution of carbonate parameters by freshwater is more pronounced for sea-ice melt (DIC and TA 300-600  $\mu\text{mol kg}^{-1}$ , e.g., Miller et al., 2011) compared to river outflow (river DIC and TA ~700-1800  $\mu\text{mol kg}^{-1}$ , Azetsu-Scott et al., 2014, and this study), and thus, distributions of DIC, TA, and  $\Omega_{Ar}$  in the southern Hudson Bay likely reflect the variable impacts of river runoff and sea-ice melt on the carbonate system.

390 The Nelson has the highest freshwater discharge of any single river in the Hudson Bay system, and nearly half of the river runoff into Hudson Bay enters via James Bay. These hydrographical features are well illustrated by the distribution of meteoric water fractions ( $f_{MW}$ ) throughout the region (Fig. 2f). In contrast, the fractions of sea-ice melt ( $f_{SIM}$ ) are highest along the southern coast of Hudson Bay (Fig. 2e), near the comparatively small Severn and Winisk rivers (with respective discharges one quarter and one sixth that of the Nelson, Table 1). This region of high  $f_{SIM}$  corresponds well to the observed sea-ice distributions shown in Fig. 1. It is important to note that the high positive  $f_{SIM}$  observed near the Nelson River is due to the use of a single flow-averaged  $\delta^{18}\text{O}$  end-member for meteoric water (-14 ‰, Granskog et al., 2011) near a river with a considerably higher  $\delta^{18}\text{O}$  (-10.8 ‰, Table 1). Overall, riverine  $\delta^{18}\text{O}$  signatures measured here agree well with those observed in previous studies, especially when comparing measurements made in/around the month of July (Table 1). Also note that despite considerable freshwater input near James Bay, aragonite remains supersaturated ( $\Omega_{Ar} > 1$ ) at all stations in surface waters (Fig. 2d).

400 The surface distributions shown in Fig. 2 also align with the general circulation patterns of the Hudson Bay system. For example, differences can be seen between stations in the northern part of Hudson Strait, where Labrador Sea waters with characteristically high salinity, DIC, and TA flow into the Hudson Bay system, and stations at the southern side of the strait, where Hudson Bay outflow with lower salinity and TA, as well as higher  $f_{MW}$ , travels east towards the Labrador Sea. The high salinity water in northwestern Hudson Bay represents water recently introduced from Foxe and Hudson Straits, with salinities generally decreasing in a counterclockwise fashion due to freshwater inputs. At the mouth of James Bay, the salinity and carbonate parameters are higher on the western edge, where waters enter the bay, compared to the eastern edge, where waters altered by large James Bay rivers exit back into Hudson Bay. At the eastern edge of the mouth of James Bay, we recorded the minimum salinity ( $S = 21.71$ ), TA (1705  $\mu\text{mol kg}^{-1}$ ), and DIC (1624  $\mu\text{mol kg}^{-1}$ ), as well as the second lowest  $\Omega_{Ar}$  (1.04), among the “seawater” samples from our entire study.

410 The surface distributions of carbonate parameters throughout the Hudson Bay system are similar to those reported by Azetsu-Scott et al. (2014) for September, 2005. Concentrations within Hudson Strait and Foxe Strait are comparable, and the north-south gradient within Hudson Strait is apparent in both years. Within Hudson Bay, concentrations are distinctively lower than in waters outside the bay, with values decreasing further from the northwest toward the southeast. Aragonite saturation ( $\Omega_{Ar}$ ) in surface waters does not show any significant differences between 2005 and 2010, with surface waters approaching saturation at the mouth of James Bay in both years. However, subtle differences do exist between these datasets. Stations in southern Hudson Bay

have lower salinity, DIC,  $TA_z$  and  $\Omega_{Ar}$  in 2010, whereas stations located further downstream, near the eastern edge of the bay, have lower values in 2005. Rather than reflecting basin-wide changes over the 5-year period, these differences can be ascribed to the seasonal timing of sample collection and general circulation patterns. That is, stations along the southern coast are impacted by substantial SIM in July as the remaining ice is melting, and the cyclonic circulation is capable of transporting such low-salinity water along the eastern edge of Hudson Bay over a two-month period (i.e., from July to September) (cf. Granskog et al., 2009).

#### 4.2 Hudson Bay Source Waters

The main conduits for Pacific and Atlantic waters to the Hudson Bay System (HBS) are Fury and Hecla Strait (located north of Foxe Strait) and Hudson Strait, respectively. Yet it remains unclear whether Hudson Bay is composed primarily of Pacific or Atlantic waters. Jones et al. (2003) surmised that Pacific waters were more prevalent in Hudson Bay but were unable to provide conclusive evidence, due to limitations in the quantity and quality of their data. In regions like Hudson Bay, with multiple seawater and freshwater end-members, mass-balance calculations for unravelling freshwater components are particularly complicated, and in contrast to systems such as the coastal Beaufort Sea, where three rather distinct end-members (the Mackenzie River, sea-ice melt, and a primarily Pacific polar mixed layer) can be defined by two tracers (Macdonald et al., 1995), a similarly rigorous analysis in Hudson Bay would require additional end-members and tracers.

When examining the relationship between TA and salinity throughout the HBS (Fig. 3a), waters below 100 m depth in Hudson Bay are indistinguishable from those in Foxe Strait, and both are distinctly different from deep waters in Hudson Strait.

Furthermore, data from Hudson Bay and Foxe Strait are well aligned with the Pacific water end-member, while data from Hudson Strait falls along a mixing line with the Atlantic water end-member (Shadwick et al., 2011) (Fig. 3a). This indicates that deep water from Hudson Strait does not enter Foxe Strait and that the vast majority of water that flows over the 185 m sill into Hudson Bay is likely of Pacific origin. In addition, some samples in the Hudson Bay/Foxe Strait dataset have higher salinity and TA than the Pacific water end-member, yet still fall along the extension of the general mixing line (Fig. 3a), suggesting an additional source of both TA and salinity. One plausible source of excess TA and salinity in deep waters is from brine rejection. It is known that deep-water formation occurs in Foxe Basin polynyas, and this water can flow into Foxe Strait and potentially further into Hudson Bay (Defosse et al., 2010). However, there is evidence in Hudson Bay that deep waters can also form locally due to brine rejection (Granskog et al., 2011). The same general patterns are shown in a plot of deep water DIC against salinity (Fig. 3b), except that distinctly higher DIC is observed in Hudson Bay compared to Foxe Strait due to the build-up of respiratory DIC in Hudson Bay, which is discussed in greater detail below.

#### 4.3 Freshwater inputs

Prior studies have revealed the importance of watershed geology in governing the highly variable compositions of Hudson Bay rivers (Mundy et al., 2010; Granskog et al., 2011; Azetsu-Scott et al., 2014, see also Thomas and Schneider, 1999), yet relatively little is known regarding the impact of varying river inputs on the inorganic carbon system of Hudson Bay. Variations in TA with salinity in the top 60 m of the water column of Hudson Bay (Fig. 4) reveal two distinct freshwater end-members: a lower TA end-member of  $\sim 700 \mu\text{mol kg}^{-1}$ , corresponding to the vast majority of stations in the bay, and a high TA end-member of  $\sim 1900 \mu\text{mol kg}^{-1}$  for samples collected within the Nelson River estuary (NRE, Figs. 1 and 5). Figure 4 also highlights the various impacts of sea-ice melt, as samples with high  $f_{\text{SIM}}$  (purple circles) show distinct positive deviations from the  $\delta^{18}\text{O}$  vs. salinity mixing line (Fig. 4, inset), as well as negative deviations from the TA vs. salinity mixing line, due to the enriched  $\delta^{18}\text{O}$  signature

450 ( $\delta^{18}\text{O}_{\text{SIM}} = 0 \text{ ‰}$ ) and low TA concentration characteristic of sea-ice melt. The negative TA deviation in sea-ice meltwaters also indicates that there is no significant source of TA from the dissolution of ikaite ( $\text{CaCO}_3$ ) during sea-ice melt (see Rysgaard et al., 2011) in this area.

Considering that samples with potential inputs of brine (i.e., deeper waters) and discernable sea-ice melt input (i.e., stations with  $f_{\text{SIM}} \geq 0.05$ ) are not included in the best-fit regressions, the lower alkalinity end-member (that is,  $\text{TA} = 689 \mu\text{mol kg}^{-1}$ ) likely  
455 represents the average riverine TA for the entire Hudson Bay. This end-member aligns with the prior estimate for “rivers” of  $754 \mu\text{mol kg}^{-1}$ , also derived from regression lines of samples collected within the bay and not from the rivers, themselves, along the eastern shore of Hudson Bay (Azetsu-Scott et al., 2014). Stations in southwestern Hudson Bay, nearest to the Churchill, Nelson, and Hayes rivers (Fig. 4, red squares, ‘705’ stations and station 706, see Figs. 1 and 5), have a similar salinity-TA relationship to that observed throughout Hudson Bay, but are vertically offset to a slightly elevated TA. This TA offset is not related to the  
460 merging of the two TA datasets, as the stations labelled as “SW Hudson Bay” (see Fig. 4) comprise a small subset of the TA data measured at IOS. Also, the magnitude of this vertical TA offset ( $\sim 80 \mu\text{mol kg}^{-1}$ ) is much larger than the average deviation observed between the datasets. Instead, this offset likely indicates input of carbonate ion from the dissolution of carbonate minerals. For salinity vs. DIC, the same offset is visible but is less pronounced, which also points towards benthic carbonate ion addition. Azetsu-Scott et al. (2014) attributed their observations of high TA in the deep waters of southwestern Hudson Bay to  
465 dissolution the carbonate-rich bedrock (defined as the Hudson Bay Lowland) that underlays this area of the bay, as well as much of the Nelson River drainage basin.

We attribute the high TA end-member ( $1870 \mu\text{mol kg}^{-1}$ ) to the Nelson River. A similarly high TA end-member has been reported for the Mackenzie River ( $1540 \mu\text{mol kg}^{-1}$ , Cooper et al., 2008) and time-series measurements collected from the Churchill River (Fig. 1) during the summer of 2007 reveal an average TA of  $1394 \pm 80 \mu\text{mol kg}^{-1}$  (Stainton, 2009). According to Mundy et al.  
470 (2010), the Churchill, Nelson, and Hayes rivers (Fig. 1) have dissolved organic carbon (DOC) concentrations that are 2-6 times greater than other Hudson Bay rivers (Table 1), and these authors attributed variability in riverine DOC to the vastly differing watershed geologies throughout the Hudson Bay region. The weathering of organic rich soils throughout the extensive Nelson River drainage basin would contribute to higher riverine DIC and TA compared to rivers further north with drainage basins in the relatively organic-poor Arctic tundra. Furthermore, weathering processes become more active in subarctic, or even temperate  
475 regions of the Hudson Bay drainage area, yielding higher TA inputs from those regions than from polar regions. This regional dependence on riverine composition is also observed in the  $\delta^{18}\text{O}$  signatures, both across the basin and within a single river catchment, with the south-western rivers having distinctly less depleted  $\delta^{18}\text{O}$  signatures than the rivers further north (Table 1, see also Granskog et al., 2011, and Smith et al., 2015). Nevertheless, the TA end-member calculated here is substantially higher than the prior estimate for the Nelson River ( $1022 \mu\text{mol kg}^{-1}$ , Azetsu-Scott et al., 2014), and we think this discrepancy is due to  
480 sampling depth within this highly-stratified system, as well as to the fact that our samples extended further up the estuary, into fresher waters.

Data obtained via rosette sampling in southwestern Hudson Bay (Fig. 4, red squares) yield a riverine TA end-member of  $710 \mu\text{mol kg}^{-1}$ , and the uncertainty on this value places it in the same range as the end-member calculated for the rest of Hudson Bay. According to the CTD data, samples from southwestern Hudson Bay were collected between 1.4 m and 10.3 m depth, with  
485 the former being considered ‘surface’ samples. In contrast, samples collected from the surface in the inner NRE using the small

barge yield an end-member of  $1870 \mu\text{mol kg}^{-1}$ . Given the close proximity of these inner NRE stations to others in southwestern Hudson Bay, the discrepancy in end-members indicates that surface samples collected via the rosette captured a different water mass than those collected via the small barge. This is illustrated further using a cross-section of salinity in the NRE (Fig. 5).

Salinity across the NRE, as measured in-situ by the CTD attached to the rosette system, and as measured from discrete surface bottle samples collected either from the barge or using a bucket dropped from the bow, is shown in Fig. 5. At stations 705a, b, and c, salinity samples collected from surface waters via bucket have considerably lower salinities than any waters measured by the CTD. Furthermore, according to the CTD pressure data, surface Niskin bottles from stations 705a, b, and c were closed at 1.6, 1.6 and 1.4 m respectively (Fig. 5, black X's), but the salinities measured in these Niskin bottles correspond to the CTD salinities observed at depths of 2.5, 3.6 and 7.1 m respectively (Fig. 5, vertical black arrows), indicating that the Niskin bottles contained some deeper waters entrained into the surface by the upward-moving rosette. This highlights the importance of taking bottle salinity samples from Niskins in parallel with parameters such as DIC and TA, particularly in highly stratified waters. Here, all DIC and TA samples collected in southwestern Hudson Bay are accompanied by a high-precision salinity sample taken from the same Niskin bottle.

At stations B6, B8, and B12 (Fig. 5), salinities measured using the 3-L Niskin bottles (deployed to 1 m depth from the small barge) are very low and show an increasing salinity with distance away from the Nelson River mouth that is consistent with the bucket samples collected at stations 705a, b and c. Clearly, the samples collected from the small boats (barge and zodiac) captured low-salinity waters very near the surface, while the 'surface' rosette bottles captured water from a deeper layer with considerably higher salinities. Assuming the low salinity layer represents the Nelson River plume, this water is only accurately captured using the samples taken via small boats, which explains why samples taken via barge in the inner NRE have a markedly different TA vs. salinity relationship from samples taken via rosette throughout the remainder of Hudson Bay (Fig. 4). Additionally, at station 705c (Fig. 5), the bucket sample near the surface does not appear to have captured the low-salinity river plume, demonstrating the extent to which river inputs are constrained to the coastline during cyclonic transport around the bay (Fig. 1). Large CTD salinity gradients in the upper 2 m were observed at other stations along the southern coast, suggesting that data from the surface Niskin bottle at these stations may also not fully reflect the true "surface water" properties.

#### 4.4 Coastal Transect:

Hudson Bay waters undergo significant compositional changes during their cyclonic transit around the basin (Granskog et al., 2009; Mundy et al., 2010). Here, we focus specifically on changes in the carbonate system along a coastal transect that follows the general counter-clockwise circulation pattern from Northwest Hudson Bay to the Northeast (Fig. 6, transect A-B). For stations within this transect, TA, DIC, and  $\delta^{13}\text{C}_{\text{DIC}}$  are plotted against in-situ density anomaly ( $\sigma_t$ , observed density –  $1000 \text{ kg m}^{-3}$ ) to illustrate deviations at constant density levels (Figs. 6a-c). For TA (Fig. 6a), there is little variability between stations along the transect and the vast majority of the data fall along the river mixing line. There are, however, two notable exceptions: the first being high-TA deviations at stations within the NRE that we attribute to [dissolution of carbonate minerals](#), and the second being low-TA deviations in samples with high sea-ice melt fractions ( $f_{\text{SIM}} \geq 0.05$ ), all of which are measured at or near the surface along the southern coast.

For along-transect DIC (Fig. 6b), the impacts of both freshwater input and biological activity are apparent. Similar to TA, positive deviations from a general river mixing line are observed in the NRE, as are negative deviations along the southern coast,

525 but a distinct increase in DIC is also visible along the transect due to a build-up of respiratory DIC in subsurface waters. The maximum offset between waters along the west coast (blue-purple points) and the east coast (red-yellow points) is between the 24 and 26 kg m<sup>-3</sup>  $\sigma_t$  horizons, indicating that organic matter respiration rates are highest at these density levels. The structure of these density horizons along the coastal transect are shown in Fig. 6d. The lack of any visible offset in bottom water TA suggests that any products of anaerobic respiration that may be produced in sediments are not transported into the water column.

530 Unlike TA and DIC, freshwater input appears to play a relatively minor role in governing variability in the stable carbon isotope signature of DIC ( $\delta^{13}\text{C}_{\text{DIC}}$ ) of Hudson Bay waters (Fig. 6c). This may be due to the fact that Hudson Bay rivers are very isotopically enriched (average  $\delta^{13}\text{C}_{\text{DIC}} = -3.2$  ‰, Table 1) compared to other coastal regions (North Sea  $\delta^{13}\text{C}_{\text{DIC}} = -12$  to  $-16$  ‰; Burt et al., 2016), and thus are much closer to typical seawater values ( $\sim -2$  ‰). Biogenic soils are highly depleted in  $\delta^{13}\text{C}_{\text{DIC}}$  ( $\sim -25$  ‰), while carbonate bedrock has a  $\delta^{13}\text{C}_{\text{DIC}}$  near 0 ‰ (Spiker, 1980). Given that the majority of Hudson Bay rivers have rather low DOC (Mundy et al., 2010) and that much of the bedrock surrounding the bay is carbonate-rich (Ross et al., 2011), it is unsurprising that Hudson Bay rivers are isotopically enriched compared to other regions. However,  $\delta^{13}\text{C}_{\text{DIC}}$  was not sampled along the southern coast, thus the Churchill, Nelson, and Hayes Rivers, which are likely more depleted in  $\delta^{13}\text{C}_{\text{DIC}}$ , are not 535 included in Table 1 and are not well represented in Figs. 6c and d.

On the other hand, the  $\delta^{13}\text{C}_{\text{DIC}}$  distributions in Fig. 6c do highlight the impact of biological activity along the coastal transect. Waters become isotopically lighter during their transit around the basin, because respiration of organic matter releases isotopically light DIC into the water column. In accordance with Fig. 6b, relative changes between waters along the western shore (blue-purple points) and eastern shore (red-yellow points) are greatest in intermediate waters. In the North Sea, Burt et al. 540 (2016) showed that a respiratory DIC increase of 1  $\mu\text{mol kg}^{-1}$  could be roughly equated to a 0.012 ‰ decrease in  $\delta^{13}\text{C}_{\text{DIC}}$ . Taking this ratio, and assuming that waters are transported along lines of constant density, changes in  $\delta^{13}\text{C}_{\text{DIC}}$  at intermediate depths (between  $\sim 25$ -50 m, at  $\sigma_t = 25$  kg m<sup>-3</sup>, see Figs. 6c and d) between western and eastern waters equate to an addition of approximately 110  $\mu\text{mol kg}^{-1}$  DIC. Observed increases in DIC at the same density level (Fig. 6b) are approximately 90  $\mu\text{mol kg}^{-1}$ , which is comparable given the rough nature of this calculation. In deeper waters (between  $\sim 40$ -100 m, at  $\sigma_t = 26$  kg m<sup>-3</sup>, see Fig. 545 6d), both observed DIC increases shown in Fig. 6b, and increases based on differences in  $\delta^{13}\text{C}_{\text{DIC}}$  (shown in Fig. 6c) equate to  $\sim 70$   $\mu\text{mol kg}^{-1}$ . It is important to note that the ratio taken from Burt et al. (2016) assumes that all respired organic matter is of marine origin, and although the  $\delta^{13}\text{C}_{\text{DIC}}$  derived from respired terrestrial organic matter may have a similar isotopic signature to that of marine-derived material, it is not clear how a significant fraction of terrestrial material in the organic matter pool would affect this first-order calculation. However, in the coastal marine system, the organic matter turnover (i.e., cycles of production and respiration) is generally rapid, and thus any terrestrial signature within the organic matter pool will quickly become difficult to detect.

555 The effects of biological activity, sea-ice melt, and variable riverine input on the carbonate system of Hudson Bay are well summarized in the coastal transect of aragonite saturation state ( $\Omega_{\text{Ar}}$ ) shown in Fig. 6e. In surface waters,  $\Omega_{\text{Ar}}$  is high in the northwest but decreases along the southern coast due to the dilution of both TA and DIC by freshwater input. In the NRE,  $\Omega_{\text{Ar}}$  remains high despite low salinities (see Fig. 2a,d), because of carbonate dissolution either in the drainage basin (as visible in the high alkalinity of the Nelson River), or in the sediments in the estuary (Fig. 4). Surface waters near James Bay show minima in  $\Omega_{\text{Ar}}$ , likely due to the strong sea-ice melt signal in these waters, as well as large inflows of low-alkalinity river waters (see Fig.

2). Along the eastern shore, surface water  $\Omega_{Ar}$  is comparable to (i.e., only slightly lower than) values along the west coast. This is likely due to the fact that the sea-ice melt waters, which dilute TA and DIC to a much greater degree than river input, have yet to be transported to these stations. In September 2005, surface water  $\Omega_{Ar}$  along the southern coast was higher than observed here, while further downstream along the eastern coast,  $\Omega_{Ar}$  was lower than observed here (Azetsu-Scott et al., 2014). This may simply reflect the transport of low- $\Omega_{Ar}$  sea-ice melt waters from the southern coast in July to the eastern shore by September. In accordance with this, Granskog et al. (2009) noted that in October 2005, virtually no sea-ice melt was observed along the southern shore, further suggesting that these waters had been transported northeast by the coastal current.

Focusing on subsurface waters along the transect, the saturation horizon shoals significantly from 60-70 m along the west coast, to 30-40 m along the east coast. Furthermore, deep waters along the west coast are only slightly undersaturated, while deep waters along the east coast are heavily undersaturated. These patterns likely reflect the build-up of respiratory DIC in deep waters during transit around Hudson Bay, as aerobic respiration releases DIC while consuming TA, thus causing a relatively strong decrease in  $\Omega_{Ar}$ . Deep waters along the eastern shore are likely older than waters along the western shore, allowing the products of aerobic respiration to build up over time. Exchange with open ocean waters is limited by the shallow sills at the mouth of Hudson Bay, and very low saturation states are observed at deeper stations in the central Bay, as well as in the coastal transect (Fig. 6e).

Subsurface  $\Omega_{Ar}$ , both along the coastal transect (Fig. 6e) and in a cross-basin section (not shown), is very similar to the 2005 distributions shown by Azetsu-Scott et al. (2014), suggesting that the acidification state of Hudson Bay had not changed discernibly between 2005 and 2010. However, with only two such datasets taken at slightly different times of the year, more information is required to make conclusive statements regarding acidification rates in this region.

## 5. Conclusions:

This work contributes insight into important carbon cycling processes in a region of the Arctic where biogeochemical data are sparse. The Hudson Bay is home to a vast number of ecologically important species, thus an improved understanding of the key processes affecting the carbonate system, and thereby the ecosystem, in the bay is crucial. Surface distributions reveal the importance of variable freshwater inputs from runoff and sea-ice melt in altering the carbonate system, especially in the southern part of Hudson Bay. Rivers draining into Hudson Bay have highly variable DIC and TA, a highly-enriched  $\delta^{13}C_{DIC}$  signature compared to other regions, and  $\delta^{18}O$  signatures that show a strong regional dependence. Given these results, we suggest that future studies in Hudson Bay undergo extensive sampling that is dedicated to making robust estimates of multiple, regionally-defined riverine  $\delta^{18}O$  end-members. This study also shows that the deep Hudson Bay a) is primarily filled with waters of Pacific origin from the Canadian Arctic Archipelago and b) thus has limited interaction with Atlantic waters in the deep Hudson Strait, which supports the preliminary findings of Jones et al. (2003). Within Hudson Bay, the salinity vs. TA relationship indicates mixing between the Pacific waters and river waters with relatively low TA, compared to rivers at lower latitudes. Negative deviations from the mixing line are due to dilution from sea-ice melt, whereas positive deviations in the Nelson River estuary point to carbonate mineral dissolution. Direct sampling of river DIC and TA throughout the bay, as well as detailed surface water sampling (i.e., from multiple platforms) in highly stratified estuarine waters, are needed to better understand exactly how river inputs alter the carbonate system parameters of Hudson Bay. This is especially important given that river input into Hudson Bay

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is likely changing significantly due to climate change and, perhaps more importantly, continued hydroelectric development in the region. Finally,  $\Omega_{Ar}$  in deep waters show no discernable change from 2005 levels, and slight changes in surface water  $\Omega_{Ar}$  can be attributed to seasonal variability.

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**Table 1. Data summary for Hudson Bay rivers**

| River            | Discharge <sup>(1)</sup><br>[km <sup>3</sup> yr <sup>-1</sup> ] | Date Sampled | Salinity | $\delta^{13}\text{C}_{\text{DIC}}$<br>[‰] | $\delta^{18}\text{O}$<br>This study [‰] | $\delta^{18}\text{O}$ <sup>(2)</sup><br>Previous [‰] | DOC <sup>(3)</sup><br>[μmol kg <sup>-1</sup> ] |
|------------------|---|--------------|----------|---|---|--|--|
| <b>Northeast</b> |   |              |          |   |   |  |  |
| Polemund         | n/a   | 10-Jul-10    | n/a      | -1.82                                     | -14.53                                  | -13.64 (Aug-07)                                      | n/a  |
| Povungnituk      | 11.6  | 10-Jul-10    | n/a      | -4.13                                     | -15.69                                  | -13.97 (Sep-05)                                      | 194  |
| Kogaluc          | 4.9   | 10-Jul-10    | n/a      | -2.56                                     | -14.58                                  | -14.26 (Aug-07)                                      | n/a  |
| Innuksuac        | 3.3   | 11-Jul-10    | n/a      | n/a                                       | -13.85                                  | -12.72 (Sep-05)                                      | n/a  |
| <b>Southeast</b> |   |              |          |   |   |  |  |
| Nastapoca        | 7.9   | 12-Jul-10    | 0.02     | -2.86                                     | -14.27                                  | -14.86 (Jun-06)                                      | 256 (n=2)                                      |
| Little Whale     | 3.7   | 12-Jul-10    | n/a      | -3.69                                     | -14.48                                  | -14.84 (Jun-06)                                      | 304 (n=2)                                      |
| Great Whale      | 19.8  | 13-Jul-10    | 0.33     | n/a                                       | -14.17                                  | -14.64 (Jun-06)                                      | 268 (n=4)                                      |
| <b>Northwest</b> |   |              |          |   |   |  |  |
| Wilson           | n/a   | 18-Jul-10    | n/a      | -2.95                                     | -14.93                                  | n/a  | n/a  |
| Ferguson         | 2.6   | 18-Jul-10    | n/a      | -2.93                                     | -16.22                                  | n/a  | n/a  |
| Tha-anne         | 6.2   | 19-Jul-10    | n/a      | -3.56                                     | -16.82                                  | n/a  | n/a  |
| Thlewiaza        | 6.9   | 19-Jul-10    | n/a      | -4.18                                     | -16.08                                  | n/a  | n/a  |
| <b>Southwest</b> |   |              |          |   |   |  |  |
| Churchill        | 20.6  | 20-Jul-10    | n/a      | n/a                                       | -12.71                                  | -13.59 (Oct-05)                                      | 1180   |
| Severn           | 21.2  | 28-Jul-10    | n/a      | n/a                                       | -11.01                                  | n/a  | n/a  |
| Winisk           | 14.7  | 27-Jul-10    | n/a      | n/a                                       | -10.76                                  | -11.68 (Oct-05)                                      | 199  |
| Hayes            | 18.6  | 24-Jul-10*   | n/a      | n/a                                       | -11.45                                  | -12.40 (Jul-05)                                      | 935  |
| Nelson           | 94.2  | 24-Jul-10*   | n/a      | n/a                                       | -10.81                                  | -10.64 ± 0.52 <sup>#</sup>                           | 814  |

n/a = data not available

\*assumed sampling date (actual sampling date was not recorded)

<sup>#</sup>Average and standard deviation of 344 samples taken between January 2010 and July 2013, from Smith et al. (2015)<sup>(1)</sup>From Dery et al. 2005<sup>(2)</sup>From Granskog et al. 2011. Date (mmm-yy) when sample was collected is shown in brackets.<sup>(3)</sup>From Mundy et al. 2010. Some values are averaged from multiple data sources (indicated with an 'n' value)

715 **Figure 1:** Bathymetric map of the Hudson Bay System showing stations sampled during the 2010 ArcticNet mission (black dots). Shaded areas denote ice-covered regions as of July 12<sup>th</sup>, 2010, determined using weekly regional ice extent maps (Environment Canada, Canadian Ice Service, <http://www.ec.gc.ca/glaces-ice/>). The location of the 185 m sill in the central channel connecting Hudson Bay with Foxe Strait and Hudson Strait is marked with a black star. The dashed box around the Nelson and Hayes River estuaries includes the stations shown in Fig. 5.

720 **Figure 2:** Surface distributions of salinity (a), TA (b), DIC (c), aragonite saturation state ( $\Omega_{Ar}$ ) (d), sea-ice melt fraction ( $f_{SIM}$ ) (e), meteoric water fraction ( $f_{MW}$ ) (f), and  $\delta^{13}C_{DIC}$  (g, samples only collected during first half of the cruise). Nelson River is shown as a blue line. Note that  $\Omega_{Ar}$  (panel d) is above one at all stations.

725 **Figure 3:** Deep (>100 m) water TA (a) and DIC (b) against salinity throughout the Hudson Bay System. The \* represents the end-member properties of Pacific-origin Upper Halocline Water ( $S = 33.1$ ,  $TA = 2283 \mu\text{mol kg}^{-1}$ ,  $DIC = 2236 \mu\text{mol kg}^{-1}$ ) and the black 'x' represents Atlantic Water ( $S = 34.8$ ,  $TA = 2301 \mu\text{mol kg}^{-1}$ ,  $DIC = 2154 \mu\text{mol kg}^{-1}$ ), as defined by Shadwick et al. (2011). Hud Bay = Hudson Bay samples, Foxe = Foxe Strait samples, Hud Strait = Hudson Strait samples.

730 **Figure 4:** Hudson Bay TA vs. Salinity (S) in the upper 60 m of the water column (which should contain seasonal freshwater inputs, see Granskog et al., 2011). Hudson Bay stations (black diamonds, regression line  $TA = 48.8*S + 689.2$ ) do not include the station located northeast of the sill in the central channel (see Fig. 1). Stations in southwestern Hudson Bay (red squares, regression line  $TA = 50.9*S + 225.8$ ) refer to '705' stations (see Fig. 5), and station 706 slightly further north (see Fig. 1), while Inner-Nelson River estuary stations (blue triangles, regression line  $TA = 9.3*S + 1870.0$ ) refer to 'B' stations shown in Fig. 5. Riverine end-members (TA at zero-salinity, or  $TA_{S=0}$ ) and their corresponding uncertainties are calculated using linear least-squares regression and the error associated with the linear fit, respectively. Inset: Hudson Bay  $\delta^{18}O$  vs. Salinity with same sample legend as the main figure (symbols are filled for clarity). The regression line ( $\delta^{18}O = 0.3*S - 11.6$ ) is placed through Hudson Bay samples. It is important to note that for some surface water samples,  $\delta^{18}O$  and its corresponding salinity were collected independently from TA and its corresponding salinity, therefore high  $f_{SIM}$  (calculated using  $\delta^{18}O$ ) may not be present in TA samples. This may explain why some samples with high  $f_{SIM}$  show little to no negative deviation in TA (purple circles).

740 **Figure 5:** Salinity cross-section (top 10 m) in the Nelson River estuary (NRE). Location of transect is shown by the inset map in the lower right (see Fig. 1 for location of the NRE within Hudson Bay). Vertical black lines represent CTD profiles, while black dots (depths  $\leq 1$  m) represent samples taken independently using the single 3-L Niskin (~1 m depth, stations B6, B8, B12) and samples taken using the bucket (~0.3 m depth at stations 705 a,b,c). Black X's show the depth where surface Niskin bottles were closed, as recorded by the CTD's pressure sensor, while the black vertical arrows extend to the depth where salinities in the Niskin bottles match the salinity recorded by the CTD. Prior to closing each Niskin bottle, the rosette was held at the target depth for 1-minute to allow for adequate flushing and stabilization (Y. Gratton, pers. comm.). At all three rosette stations (705 a,b,c), Niskin bottle salinities are markedly higher than the CTD salinities at the closure depth, suggesting that higher-salinity waters were entrained into surface waters by the rosette system.

750 **Figure 6:** Variations in TA (a), DIC (b) and  $\delta^{13}C_{DIC}$  (c) with in-situ density anomaly ( $\sigma_t$ , observed density - 1000 kg m<sup>-3</sup>) along the northwest-northeast (A-B) coastal transect (inset map of transect is shown in lower panel). Dashed ellipses surround data within the NRE, while solid ellipses surround data with  $f_{SIM} \geq 0.05$  (located along southern coastline). Vertical arrows illustrate differences in DIC and  $\delta^{13}C_{DIC}$  between waters in western Hudson Bay (blue/purple points) and eastern Hudson Bay (red/yellow points). Note that  $\delta^{13}C_{DIC}$  was not sampled during the latter part of the cruise (i.e. along the southern coast). (d) Cross-section of  $\delta^{13}C_{DIC}$  along the coastal transect with isopycnals of in-situ density anomaly ( $\sigma_t$ , kg m<sup>-3</sup>). (e) Cross-section of  $\Omega_{Ar}$  with solid line representing the aragonite saturation horizon ( $\Omega_{Ar} = 1$ ).