

Interactive comment on “Measurements of the dissolved inorganic carbon system and associated biogeochemical parameters in the Canadian Arctic, 1974–2009” by K. E. Giesbrecht et al.

K. E. Giesbrecht et al.

karinag@uvic.ca

Received and published: 1 February 2014

We thank both reviewers for their positive comments and helpful suggestions in improving this manuscript.

We have copied the reviewer comments in double square brackets below with our relevant responses following each comment.

[[This reviewer feels it important that the remaining samples be analyzed and that the

C294

quality of the samples after the long storage be better assessed. Would salinity determinations indicate that the samples are unaffected by evaporation? If not, could a correction be applied? Subsequently the data from the BSP 1974-1975 samples could be added to the data files.]]

We have been able to analyze all of the 233 remaining viable samples from the 1974 and 1975 BSP cruises that were stored at IOS. We have updated the data files and manuscript accordingly. Specifically, we have added the following lines to the BSP section (page 6, lines 1-13):

Four samples collected from one station from on 1974 cruise were analyzed in 2001, while the remaining 233 viable samples were analyzed in 2013, nearly forty years after collection, using contemporary methods (Fig 5). A headspace correction (Dickson et al., 2007) was applied to the DIC measurements from the 1975 cruise as these samples had varying headspace volumes. To determine the headspace volume, samples were sorted into three classes depending on visual determination of the headspace and a felt pen was used to mark the water level in the bottles prior to analysis. After analysis, headspace volume for each class was approximated as the mean of five gravimetric determinations of headspace volume for samples from each of the three classes. Though samples from these cruises were stored at IOS for nearly forty years, a test of IOS storage methods (see section 3.2.1 below) indicates that the long-term storage of these samples had no effect on DIC or alkalinity.

We also conducted a test to confirm the storage procedure for these samples, adding lines 13-26 on page 10 (see below) as well as an additional table (Table 3). Our test confirms that long-term storage of these BSP samples did not affect the DIC or alkalinity values.

To confirm the integrity of samples stored long-term at IOS, archived deep-water (1000 – 3000 m) samples collected at Station P (50N 145W) in 1976 were analyzed for DIC and alkalinity and compared to recently collected samples from the same depths at

C295

Station P (sampled between 2003 and 2010) (Table 3 in revised manuscript, see attached supplement). Station P is a long-running deep ocean time-series located in the subarctic Northeast Pacific, a region where deep-water (>800-m) DIC and alkalinity are assumed to be virtually constant on decadal time scales (Byrne et al., 2010). Thus, any differences between the deep water DIC and alkalinity values measured in the samples that have been stored for several decades and more recent samples would indicate a bias or error resulting from the storage procedures. There were no significant differences (student's t-test) between the 1976 and more recent samples for both DIC and alkalinity. No systematic bias was observed between samples from these two time periods. These results confirm the viability of long-term storage in the refrigerated sample archive at IOS for seawater DIC and alkalinity samples, for up to forty years.

[[On page 237 the flagging procedures are described and they are compared with those used for the GLODAP and CARINA data collections. GLODAP and CARINA are data collections that have been subject to careful secondary quality control. The data assembled here is subject to primary quality control. It is the opinion of this reviewer that if the primary QC leads to a flag 4 (bad) then the data should simply be deleted as nobody outside the group of authors is likely to know better, ever. Apart from this the flags seem to be used sensibly.]]

While we can understand the reviewer's suggestion to remove any data flagged as '4' (bad), we believe it would be better to leave any flag 4 data points in this primary dataset, but to leave it to the discretion of others as to if the data should be included in any other global data products, as this information, even if erroneous, would be lost forever.

[[It is indicated that in some cases mercuric chloride was used for sample preservation. Is it known when this involved the solid salt and when a solution? Would a dilution factor have been applied if a solution was used?]]

We have clarified this as shown below:

C296

Page 10 lines 5-7

A dilution correction factor was applied to samples where a mercuric chloride solution was used (after 1994).

Page 10 lines 10-12

Sampling according to this protocol used powdered mercuric chloride, and so no correction factor was applied to samples collected prior to 1993.

Specific Comments:

Page line

[[235 22: Clarify what a shallow end point means]]

We have changed this sentence (page 13 lines 7-9) to read as follows to better clarify what we meant:

The titration data for samples collected during the CASES cruises were analyzed with a proprietary algorithm specifically designed for shallow slope end-point detection from the titration curves (see Mucci et al., 2010).

[[236 4-10: How much could this offset be and are the data flagged?]]

We have copied our response to reviewer 1 (RC C46) as they also requested we address this issue:

This reviewer's main recommendation was to elaborate on the interconsistency between cruises for the older alkalinity data. Reviewer 2 asks if we can estimate the magnitude of a potential alkalinity offset in their specific comments (specifically in regards to page 236 lines 4-10). We have attempted to address both recommendations with the addition of the text below (page 13 lines 25-32 and page 14 lines 1-4), as well as a new figure (Figure 7 in the revised text, but shown as Fig. 1 below)

A similar evaluation of this dataset is difficult, because of variations in station distribu-

C297

tions (Figure 2b) and a lack of deep samples on many cruises. Nevertheless, a plot of the limited alkalinity data from 2500 m (which roughly coincides with a deep temperature minimum and is slightly deeper than the minimum depth used for secondary quality control crossover analysis in the GLODAP, CARINA and PACIFICA data products; e.g. Tanhua et al. 2009) in the central Canada Basin (Figure 7) indicates that alkalinity measurements may have been high during the 1993 and 1995 cruises. More importantly, however, the alkalinity values at 2500 m show high variability, even after 2000, without any clear offset between individual cruises. Therefore, based on the information available at this time, we can neither rule out nor confidently confirm any analytical bias in the alkalinity measurements between cruises.

This paragraph was originally part of the companion manuscript to this paper (Miller et al., submitted to Polar Research), but we felt it was better placed in this manuscript and hopefully addresses the difficulties of trying to determine the existence or magnitude of such an offset in the alkalinity data.

[[239 5: Is this a mercuric chloride solution?]]

While this is not explicitly written in the protocol, the diagram that accompanied the original documents shows the addition of mercuric chloride as a powder. We have added the word 'powdered' before 'mercuric chloride' in this protocol to be more explicit as we did not include the diagrams associated with the original version of this protocol (we include only a transcription of the text). See page 15, line 5

Technical Corrections: 233 3: DOE (1994) is described We added the word 'is'. Thank you.

Please also note the supplement to this comment:

<http://www.earth-syst-sci-data-discuss.net/6/C294/2014/essdd-6-C294-2014-supplement.pdf>

Interactive comment on Earth Syst. Sci. Data Discuss., 6, 223, 2013.

C298

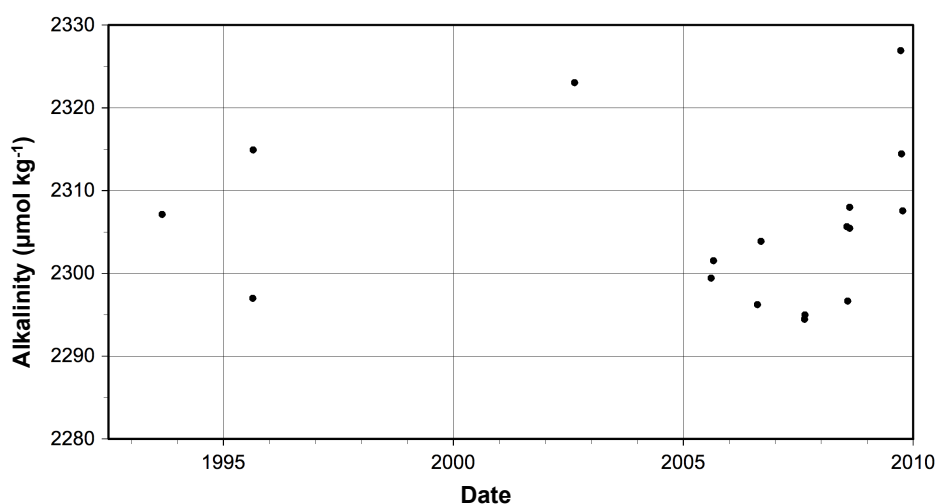


Fig. 1.