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Earth System Science Data

CARINA alkalinity data in the Atlantic Ocean

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Abstract. Data on carbon and carbon-relevant hydrographic and hydrochemical parameters from previously non-publicly available cruise data sets in the Arctic, Atlantic and Southern Ocean have been retrieved and merged to a new database: CARINA (CARbon IN the Atlantic).

These data have gone through rigorous quality control (QC) procedures to assure the highest possible quality and consistency. The data for most of the measured parameters in the CARINA data base were objectively examined in order to quantify systematic differences in the reported values, i.e. secondary quality control. Systematic biases found in the data have been corrected in the data products, i.e. three merged data files with measured, calculated and interpolated data for each of the three CARINA regions; Arctic, Atlantic and Southern Ocean. Out of a total of 188 cruise entries in the CARINA database, 98 were conducted in the Atlantic Ocean and of these, 75 cruises report alkalinity values.

Here we present details of the secondary QC on alkalinity for the Atlantic Ocean part of CARINA. Procedures of quality control, including crossover analysis between cruises and inversion analysis of all crossover data are briefly described. Adjustments were applied to the alkalinity values for 16 of the cruises in the Atlantic Ocean region. With these adjustments the CARINA database is consistent both internally as well as with GLODAP data, an oceanographic data set based on the World Hydrographic Program in the 1990s. Based on our analysis we estimate the internal accuracy of the CARINA-ATL alkalinity data to be 3.3 μmol kg^{-1}. The CARINA data are now suitable for accurate assessments of, for example, oceanic carbon inventories and uptake rates and for model validation.

Data coverage and parameter measured

Repository-Reference: doi:10.3334/CDIAC/otg.CARINA.ATL.V1.0
Available at:
http://cdiac.ornl.gov/ftp/oceans/CARINA/CARINA_Database/CARINA.ATL.V1.0/
Coverage: 60° S–75° N; 80° W–34° E
Location Name: Atlantic Ocean
Date/Time Start: 1977-10-7
Date/Time End: 2006-02-02

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(avelo@iim.csic.es)

Published by Copernicus Publications.

Data Product Parameter Name	Data Product Flag name	Exchange File Parameter Name	Exchange File Flag Name	Units
station		STANBR		
day		DATE		
month		DATE		
year		DATE		
latitude		LATITUDE		decimal degrees
longitude		LONGITUDE		decimal degrees
cruiseno				
depth				meters
temperature		CTDTMP		°C
salinity	sf	SALNTY	SALNTY_FLAG_W	
pressure		CTDPRS		decibars
alk	alkf	ALKALI	ALKALI_FLAG_W	micromole kg^{-1}

For a complete list of parameters for the CARINA data base, see Key et al. (2009). Note the different names for the parameters in the Exchange files (the individual cruise files) and the merged data product.

1 Introduction

CARINA is a database of carbon and carbon relevant data from hydrographic cruises in the Arctic, Atlantic and Southern Oceans. The project was formed as an essentially informal, unfunded project in Kiel, Germany, in 1999, with the main goal to create a database of carbon relevant variables in the ocean to be used for accurate assessments of oceanic carbon inventories and uptake rates. Not only the collection of data, but also the quality control of the data has been a main focus of the project, with both primary and secondary quality control (QC) of the data having been performed. The CARINA database consists of essentially two parts:

The first part are the individual cruise files where all the measured data, and their quality flags, are stored. These files are in WHP (WOCE Hydrographic Program) exchange format where the first lines consist of the condensed metadata. There are essentially no calculated neither interpolated values in the individual cruise files, with the exceptions of pressure calculated from depth and some bottle salinities that were taken from ctdsal. No adjustments have been applied to any of these values, with the exception that all pH measurements were converted to the seawater pH scale at 25°C.

The second part of CARINA are three merged quality controlled and adjusted data files; one each for the Atlantic Ocean, Arctic Mediterranean Seas and Southern Ocean regions. These files contain all the CARINA data and include: 1) interpolated values for nutrients, oxygen and salinity if those data are missing and if interpolation could be made according to criteria described in Key et al. (2009) (this special issue); calculated carbon parameters (e.g. if total dissolved inorganic carbon (TCO_2) and Total Alkalinity (A_T) were measured, pH can be calculated). Calculated and interpolated values have the quality flag "0". All the values in the merged data file have been adjusted according to the values in Table 1 and described in Sect. 5. In many cases there are more reported parameters in the individual cruise files that has been included in the secondary QC, such as ^{14}C, ^{13}C and SF_6.

This report describes the consistency analysis of alkalinity measurements of the Atlantic Ocean part of the CARINA database (CARINA-ATL). A more comprehensive description of the complete CARINA data base can be found in Key et al. (2009) (this special issue), for an overview of the North Atlantic CARINA data, see Tanhua et al. (2009a) (this special issue). Alkalinity reports for other areas included in CARINA can be found in the following reports: Artic Ocean by Jutterström et al. (2009), Nordic Seas by Olsen et al. (2009), Atlantic Sector of Southern Ocean by Hoppema et al. (2009), Indian Sector of Southern Ocean by Lo Monaco et al. (2009) and Pacific Sector of Southern Ocean by Sabine et al. (2009).

The Total Alkalinity in sea water is defined as "...the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with a dissociation constant $K \leq 10^{-4.5}$, at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in one kilogram of sample." (Dickson, 1981). A_T is one of the four basic related parameters of the carbon dioxide "CO_2" system in seawater, with the others being total dissolved inorganic carbon (C_T), the fugacity of dissolved CO_2 (fCO_2), and pH. If at least two of these are known, then the remaining parameters can be calculated and the entire CO_2 system determined using thermodynamic constants for a given temperature, salinity and pressure.

High quality seawater carbon data are critical for detecting small changes in the CO_2 system. Both A_T and C_T are used in a number of methods for calculating the anthropogenic CO_2 signal, most specifically those that employ back-calculation techniques. A_T is a key in both determining changes in C_T produced by $CaCO_3$ dissolution (Feely et al., 2002) and establishing concentrations of C_T in surface waters at equilibrium with the atmosphere, whether at historical, present, or future CO_2 levels Furthermore, many measurements of the CO_2 system in seawater have been performed using the

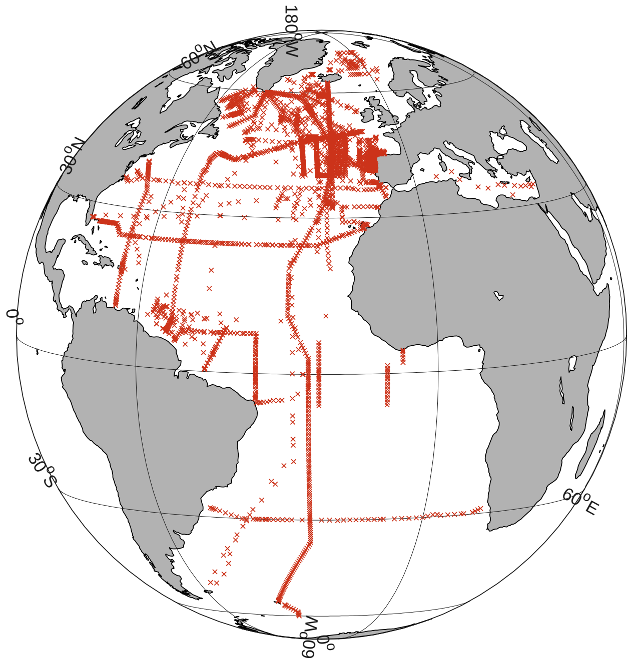

Figure 1. Map of stations with alkalinity data in the CARINA-ATL dataset.

A_T-pH pair for determining C_T. For these reasons, this is a key parameter for the CARINA objectives.

2 Data

Alkalinity data included in the CARINA-ATL dataset originates from a multitude of international research groups using a number of different analysis methods. Whilst most of the A_T data was determined using closed cell potentiometric titrations (Dickson et al., 2007), many measurements were also made by potentiometric titration at end-point in open cell (Mintrop et al., 2000).

The CARINA-ATL dataset has a total of 52 043 alkalinity samples, coming from 4080 stations and 63 cruises. Of these, 46 961 samples came from measurements, and were flagged with a “2”. The remaining 5082 samples came from carbon calculations with the final adjusted data, and so were flagged with a “0”. Figure 1 shows the location of the stations with alkalinity data in CARINA-ATL

For consistency with historical data, a further 12 WOCE/GLODAP reference cruises were included, giving a total of 75 cruises and 65 531 samples. Primary quality control – consisting of outlier and scatter identification – led to 2 cruises and 5738 samples being discarded. For the crossover analyses, only data deeper than 1500 m were used, leading to a number of cruises being omitted from the analyses. In total, 12828 CARINA-ATL samples and 2878 WOCE/GLODAP samples are compared here.

Of the 53 cruises included in the crossover analysis, alkalinity data from 31 had been generated using certified reference materials (CRMs) to test or calibrate the titration system. The remaining 22 did not use CRM at all, instead using an alternative solution for standardization (Dickson et al., 2007). The most typical reported analytical error was around 1%, ~2.5 μmol kg^{-1}. However, similar crossover exercises (Key et al., 2004; Sabine et al., 2005; Wanninkhof et al., 2003) performed on older data estimated an overall accuracy of ±5 μmol kg^{-1}.

The overall objective of this work was to assess the quality of the Atlantic CARINA alkalinity data in order to generate a mutually consistent database, by checking for apparent offsets for each cruise considering all the information reported by different sources (Tanhua et al., 2009b) For A_T, the minimum adjustment to be applied to the final dataset following the identification of an additive offset was established as ±6 μmol kg^{-1}, as was the case for the previous crossover comparison study for the North Atlantic (Wanninkhof et al., 2003).

3 Methods

The methods and techniques applied here are described in detail in Tanhua et al. (2009b) . In summary, the procedure essentially entails the comparison of data from separate cruises whose tracks cross or at least come close to each other, so-called crossover analyses. Before that comparison, a primary quality control (1st QC) consisting on outlier and scatter identification has been performed (Key et al., 2009). Only data that were flagged “good” during this primary QC procedure were considered in this process. With the application of various software packages (Tanhua et al., 2009b) generating statistical and objective information about the *offsets* between pairs of cruises, as well as the graphics needed to visually verify the computer generated offsets. For each crossover analysis, A_T data from samples deeper than 1500 m were compared on sigma-4 density surfaces generating an offset and a standard deviation of this difference, as well as totaling the number of contributing stations and samples. For alkalinity, additive offsets (and adjustments) were determined.

Slightly different procedures have been performed in the Nordic Seas (Olsen, 2009) due to the lower variability in deep waters in that area.

In this work, the semi-automated crossover procedure was run for all possible pairs of Atlantic cruises. Next, the crossover results were then visually inspected in order to ensure quality and to check the analysis had run correctly. Only “good” quality crossovers were selected, and those results were used for subsequent cruise adjustment calculations. Good crossovers had enough sample data to yield a reasonably uniform additive offset over the entire zone of analysis, leading to parallel cruise profiles. Standard deviations for

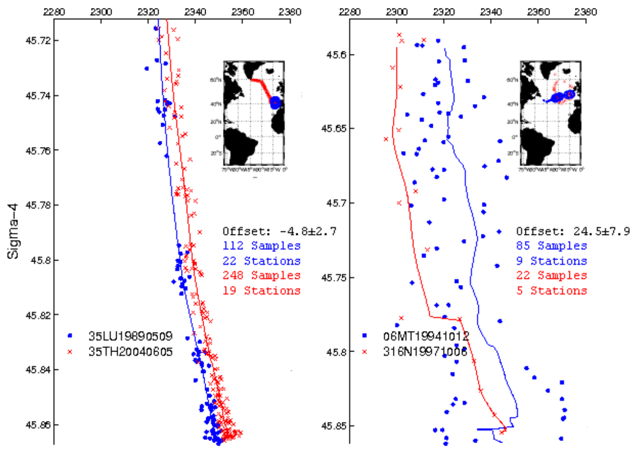

Figure 2. Crossover between the cruises 35LU19890509 and 35TH20040605 **(a)** and the cruises 06MT19941012 and 316N19971006 **(b)**.

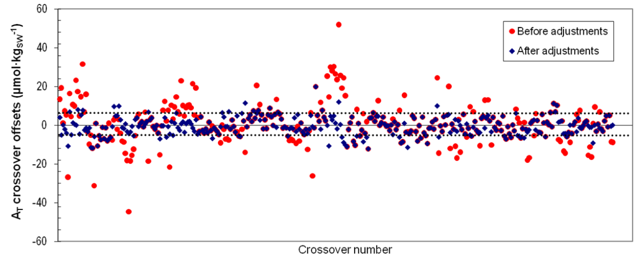

Figure 3. Crossover alkalinity offsets obtained with original database and after adjustments were applied.

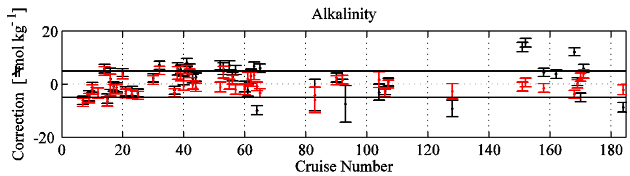

Figure 4. Mean and standard deviation of the offset for each cruise before (black) and after (red) the adjustments were applied.

individual cruise data and difference profiles were also used to provide more information on crossover quality.

In Fig. 2, two examples of A_T crossovers are shown; the contrast between a good crossover (on the left) and a bad one (on the right) can be easily appreciated, as well as the lack of data and dispersion. The quality of the offset is assessed when the standard deviation of the offset is compared (±2.7 versus ±7.9 μmol kg^{-1}).

After this first iteration, automated procedures described by Tanhua et al. (2009b) weighted the crossover quality by statistical parameters for later adjustment calculations for all cruises. This process was applied for all available cruise crossovers in the Atlantic. In total, 337 individual crossovers were obtained for A_T.

The final offsets and statistics were used as the input for an inverse least squares procedure (Tanhua et al., 2009b). Inversion results generated a set of suggested *corrections* for all cruises included in the analysis that minimized the differences. Figure 3 shows the offsets for all A_T crossovers in the Atlantic region before (pink dots), and after (blue dots) the adjustments were applied to each cruise. The convergence to values inside the bounds can be easily appreciated for values after inversions. The standard error for the original crossovers is 10.5 μmol kg^{-1} whereas the standard error for the adjusted ones is 4.7 μmol kg^{-1}.

In order to ensure the highest quality results from the inversion and to help get a more accurate and consistent solution to the system, a small subset of cruises were a priori defined as "core". These were chosen according to their geographical extent (i.e. covering a large distance) and expected high data quality (i.e. WOCE/CLIVAR quality), and were agreed upon by the CARINA Atlantic group. Offsets identified towards "core" cruises received a higher weighting in the inversion minimization process (Tanhua et al., 2009b). Once the full result of A_T offsets for each cruise had been generated, only the suggested corrections that exceeded a predefined limit of ±6 μmol kg^{-1} were applied. These subsets of high values were used as starting point to establish the final adjustment values to be proposed. The decision on final values was made manually and by consensus among the CARINA collaborators. For this decision, subjective factors such as the location, use of CRMs, technique, date, quantity and quality of crossovers, or some particularly relevant crossovers were used. Only those offsets that were strongly supported by the analysis were finally adopted and subsequently applied to the measured results. The corrections that were actually applied to the data product are, in following, referred to as an *adjustment.*

After the need for an adjustment and its magnitude were established for each cruise, the values were applied to the original database, and the full process of crossovers and inversions repeated. The result of this second iteration was a very useful way of validating the proposed offsets. Figure 4 shows the corrections values for each cruise obtained after the first inversion procedures (values in black), and the corrections obtained after the second iteration (values in red). The results from the second inversion clearly show that the remaining offsets are lower, and most of them fit within the chosen minimum error boundary

3.1 Overall accuracy

The offsets for the crossovers applied to the data product were used to estimate the overall accuracy of the alkalinity data (Fig. 5). The weighted mean (*WM*) was calculated for alkalinity by using the absolute value of the offset (*D*) of the

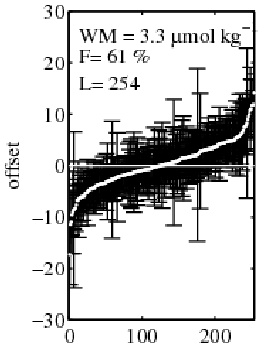

Figure 5. Sorted offsets calculated for the crossovers in the CARINA-ATL data after adjustments have been applied. *WM*: the weighted mean of the offsets (see text); *F*: the percentage of offsets indistinguishable from 1 within their uncertainty; *L*: the number of crossovers.

L crossovers with the uncertainty (σ):

$$WM = \frac{\sum_{i=1}^{L} D(i)/(\sigma(i)^2}{\sum_{i=1}^{L} 1/(\sigma(i)^2} \quad (1)$$

Based on this analysis we have estimated the accuracy of the CARINA-ATL alkalinity data to 3.3 μmol kg^{-1}.

4 Results

Results are summarized in Table 1. This table shows the cruises in the CARINA-ATL dataset with A_T data, and the summary of adjustments applieds. The following data is presented:

- Cruise ID: CARINA assigned identification number for the cruise.
- Cruise Expocode: String identifying the cruise. This is composed by a country code (two numbers), vessel code (two characters or numbers) and the departure date in year, month, day format (YYYYMMDD).
- Region: Location of the cruise. All cruises belong to Atlantic Ocean (NA), but some overlap with the Arctic Mediterranean Seas (AMS) or Southern Ocean (SO) areas.
- Core: Indicates whether or not the cruise is a core cruise for the crossover analysis.
- CRM: Indicates whether or not CRMs were used during instrumental analysis.
- WLSQ adj: Result of the inversion process through the Weighted Least Squares method (Tanhua et al., 2009b).

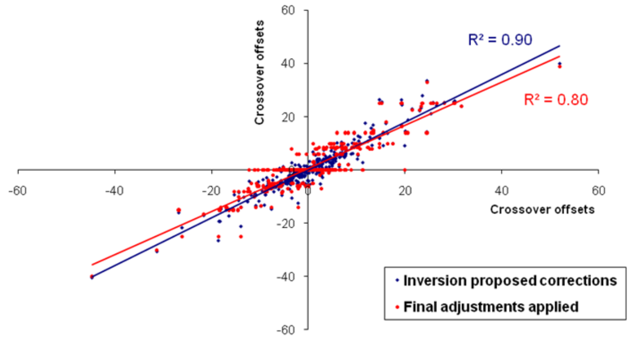

Figure 6. Original (x-axis) versus post-adjust (y-axis) offsets for the all crossover in the Atlantic Ocean after applying the full solution (blue) or the final applied solution given in the last column of Table 1 (pink).

- WDLSQ adj: Result of the inversion process through the Weighted Damped Least Squares method (Tanhua et al., 2009b).
- Adjustment: Adjustments applied for the cruises in the merged data product. All adjustments are fully supported by the CARINA group and no adjustments smaller than $\pm 6\,\mu$mol kg^{-1} are applied.

Figure 6 is a comparison between the original corrections and the final adjustments applied. Blue dots represent offsets obtained by applying full solution (all corrections); pink dots represent offsets obtained with the final adjustments applied to the data product (Table 1). The relation for the applied adjustments (pink dots) has only a slightly lower correlation coefficient than for the full solution.

In the following paragraph a set of figures and comments are presented for each cruise summarizing all crossover offsets with their standard deviation. Each figure shows the following information:

- Green dots: “Offsets”. These values are the offsets taken directly from each crossover. The standard deviation is shown as error bars on these dots.
- Yellow line indicates the additive correction calculated by inversions for the cruise. Note that the correction and offsets are of opposite sign.
- Black stars indicate the correction calculated by inversions for the other cruises that intersect this cruise.
- Blue squares: “Predicted offset” shows the calculated offset that would be obtained by applying all inversion corrections to the cruises.
- Red dots: These are the residuals between the “Offsets” (Green dots) and “Predicted Offsets” (Blue squares)
- c suffix in the upper X-axis labels stands for Core Cruises.

Table 1. CARINA-ATL dataset with alkalinity data and adjustments applied.

Cruise ID	Expocode	Region	Core	CRM	WLSQ adj ±STD	WDLSQ adj ±95%CI	Adjustment μmol kg^{-1}
7	06BE20001128	NA					
8	06GA19960613	NA					
9	06GA20000506	NA					
10	06MT19920316	NA					
12	06MT19920509	NA		x	−27.9±1.3	−25.1±1.6	−25
14	06MT19920701	NA+AMS					
15	06MT19940219	NA					
16	06MT19941012	NA					
17	06MT19941115	NA					
18	06MT19960613	NA					
20	06MT19960910	NA					
21	06MT19970107	NA					
23	06MT19970515	NA					
25	06MT19970707	NA					
26	06MT19970815	NA					
28	06MT19990610	NA					
30	06MT19990711	NA					
32	06MT19990813	NA					
44	06MT20010507	NA	x	x	7.4±0.8	6.2±1.2	6
51	06MT20010620	NA					
52	06MT20010717	NA			6.7±1.0	7.1±1.0	7
53	06MT20011018	NA					
54	06MT20020607	NA					
55	06MT20021013	NA			6.7±0.9	6.5±1.3	6
56	06MT20030626	NA					
57	06MT20030723	NA			4.8±0.9	4.3±1.7	6
60	06MT20030831	NA					
61	06MT20040311	NA		x	−3.9±1.8	−5.1±0.8	−6
62	18HU19920527	NA					
63	18HU19930405	NA					
64	18HU19930617	NA			−10.2±0.9	−9.6±1.1	−10
65	18HU19931105	NA			5.5±0.8	8.1±0.9	8
66	18HU19940524	NA					
68	18HU19941012	NA					
69	18HU19950419	NA					
84	18HU19970509	NA					
85	29CS19771007	NA					
86	29CS19930510	NA					
87	29GD19821110	NA					
89	29GD19831201	NA					
90	29GD19840218	NA					
92	29GD19840711	NA					
93	29GD19860904	NA					
94	29HE19980730	NA					
95	29HE20010305	NA+SO					
106	29HE20020304	NA+SO		x	−4.6±2.6	−6.8±1.6	−6
107	29HE20030408	NA					
108	31AN19890420	NA					
109	316N19971005	NA					
113	316N20010627	NA					
125	316N20030922	NA					
153	316N20031023	NA			13.7±0.9	13.8±0.7	14
154	32EV19910328	NA			15.2±0.7	14.4±1.4	14
158	32OC19950529	NA					
160	33LK19960415	NA			4.1±0.7	5.2±0.7	5
164	33RO19980123	NA					
165	33RO20030604	NA					
168	33RO20050111	NA+SO					
170	33SW20010102	NA			11.9±0.4	14.9±1.6	15
171	33SW20030418	NA					
172	34AR19970805	NA+AMS	x	x	−5.3±0.6	−8.5±0.6	−9
173	35A320010203	NA					
188	35A320010322	NA			−9.3±1.0	−8.1±2.0	−8
	323019940104	NA+SO	x	x	−10.9±2.8	−8.9±0.8	−8

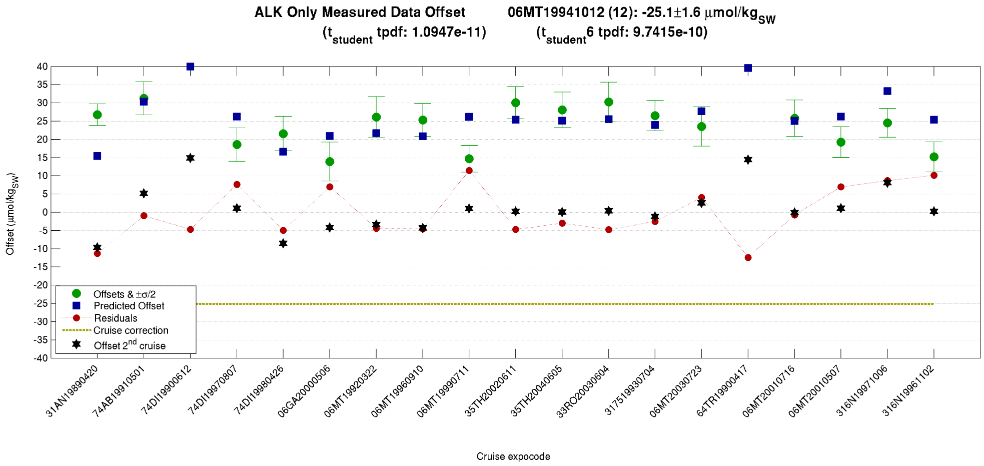

Figure 7. Cruise crossover information plot for 06MT19941012.

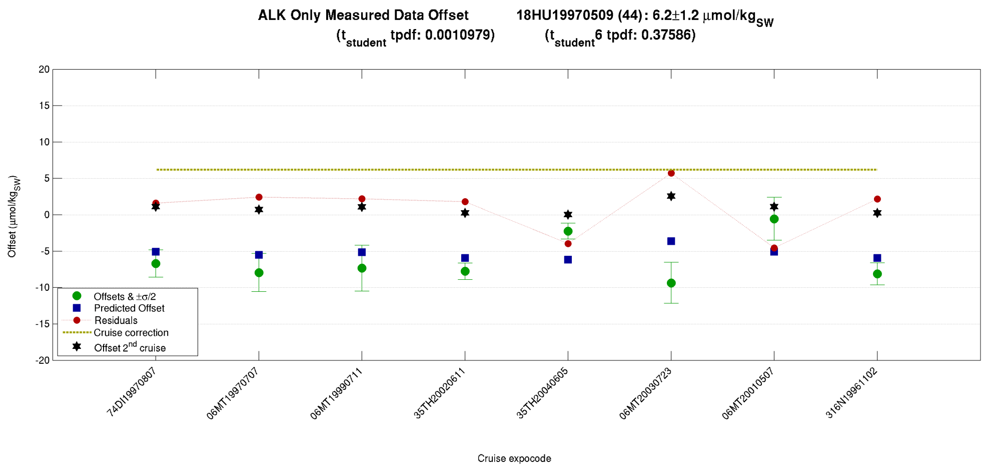

Figure 8. Cruise crossover information plot for 18HU19970509.

5 Cruises

In this section, an assessment and description of the adjustments applied to cruises for CARINA-ATL database is made. CARINA identifiers for the cruises are the numbers indicated between the parentheses. Exact data locations can be found at the CARINA website: http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html.

5.1 Cruise 06MT19941012 (12) (Fig. 7)

This is the so called MT30/2 cruise, on board Meteor and along WOCE leg A02 section, in the North Atlantic. It has 53 stations taken with a 24 place rosette system. A closed cell potentiometric titration method was used on measurements, and CRM Batch #22 was used as reference. The report indicates an estimated precision of $\pm 3\,\mu\text{mol kg}^{-1}$ and an accuracy $\pm 6\,\mu\text{mol kg}^{-1}$. This cruise has 19 crossovers. The inversions suggest a correction of $-25.1\,\mu\text{mol kg}^{-1}$. Most of the residuals fit within $\pm 10\,\mu\text{mol kg}^{-1}$, with half part of them inside $\pm 5\,\mu\text{mol kg}^{-1}$ after corrections applied. No good fit exists with the core-cruises however. The crossovers with 74DI19970807 and 06GA20000506 suggest a minor offset, but the other four core cruises (two of them GLODAP), suggest a correction of around $-28\,\mu\text{mol kg}^{-1}$. Based on this evidence, an adjustment of $-25\,\mu\text{mol kg}^{-1}$ was applied to the alkalinity data.

5.2 Cruise 18HU19970509 (44) (Fig. 8)

This is the AR07Wh, a CCHDO cruise on board R/V Hudson, in the Labrador Sea. It has 13 stations taken with a 24 place Rosette system with ten-liter bottles. CRM analyses were used for standardization and precision was $2.7\,\mu\text{mol kg}^{-1}$. There are eight crossovers giving a fitted correction of $6.2\,\mu\text{mol kg}^{-1}$. The suggested adjustment for this cruise is therefore $6\,\mu\text{mol kg}^{-1}$. Most of the residuals fit very close to 0 and keep inside $\pm 5\,\mu\text{mol kg}^{-1}$ after offsets applied.

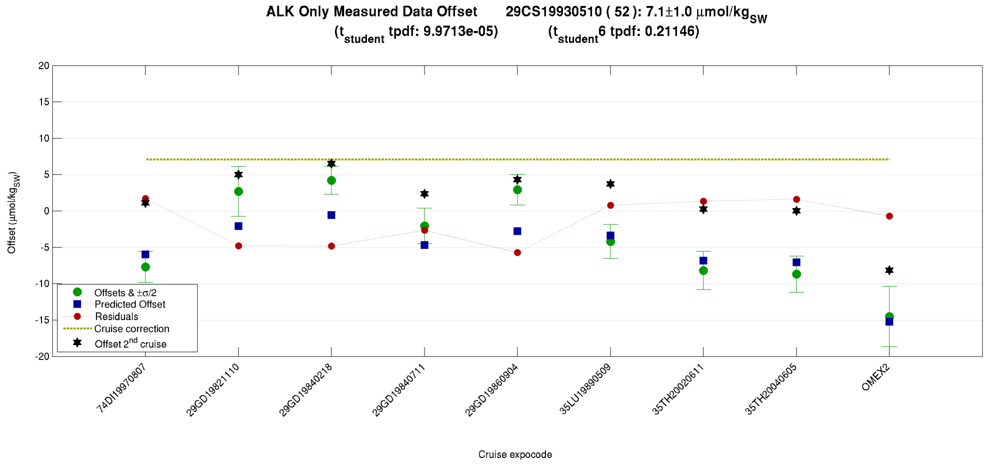

Figure 9. Cruise crossover information plot for 29CS19930510.

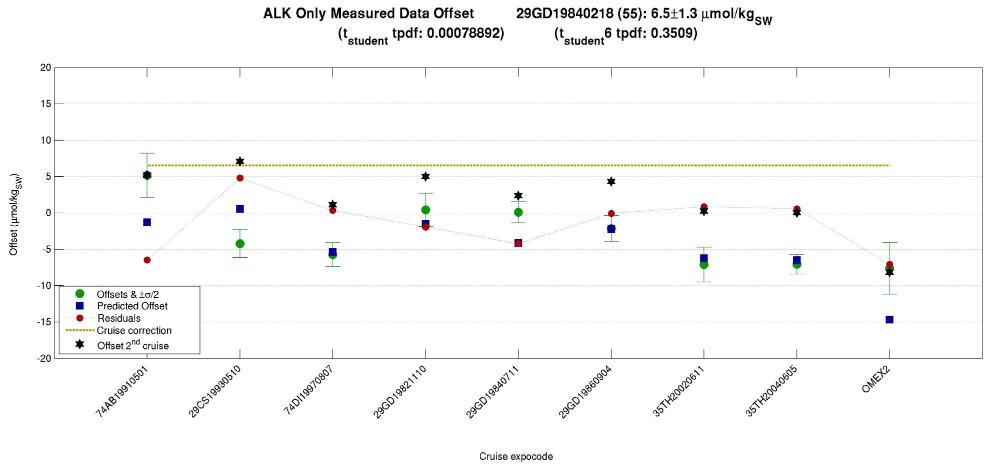

Figure 10. Cruise crossover information plot for 29GD19840218.

There are very good fits with four core cruises. Based on this evidence, an adjustment of 6 μmol kg^{-1} was applied to the alkalinity data.

5.3 Cruise 29CS19930510 (52) (Fig. 9)

This is the so called MORENA-I cruise conducted on board R/V Cornide de Saavedra, along WOCE line AR16e in the Atlantic area, close to NW Spain. It has 92 stations and 24 sampling levels using a rosette system. CRMs were not used for these measurements. There are nine crossovers. The fitted correction of inversions is 7.1 μmol kg^{-1}. The suggested adjustment is therefore 7 μmol kg^{-1}. Crossovers with three core cruises show very low residuals after offset applied. Based on this evidence, an adjustment of 7 μmol kg^{-1} was applied to the alkalinity data.

5.4 Cruise 29GD19840218 (55) (Fig. 10)

This is the so called GALICIA-VII cruise, on board R/V Garcia del Cid in the Atlantic area close to NW Spain. It has 33 stations taken on a hydrocast with 1.7l Niskin bottles.. A precision of 0.1% and accuracy of 1.4 μmol kg^{-1} has been reported. No CRMs were used during the analysis. There are nine crossovers giving a fitted correction of 6.5 μmol kg^{-1}. The suggested adjustment is +6 μmol kg^{-1}. Almost all residuals fit very close to 0 and stay within ±5 μmol kg^{-1} after offsets applied. There are very good fits with three core cruises. Based on this evidence, an adjustment of 6 μmol kg^{-1} was applied to the alkalinity data.

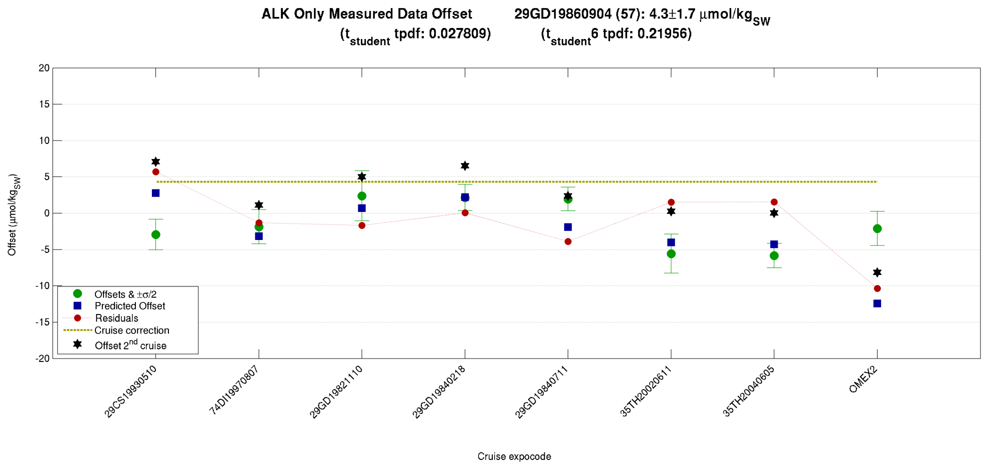

Figure 11. Cruise crossover information plot for 29GD19860904.

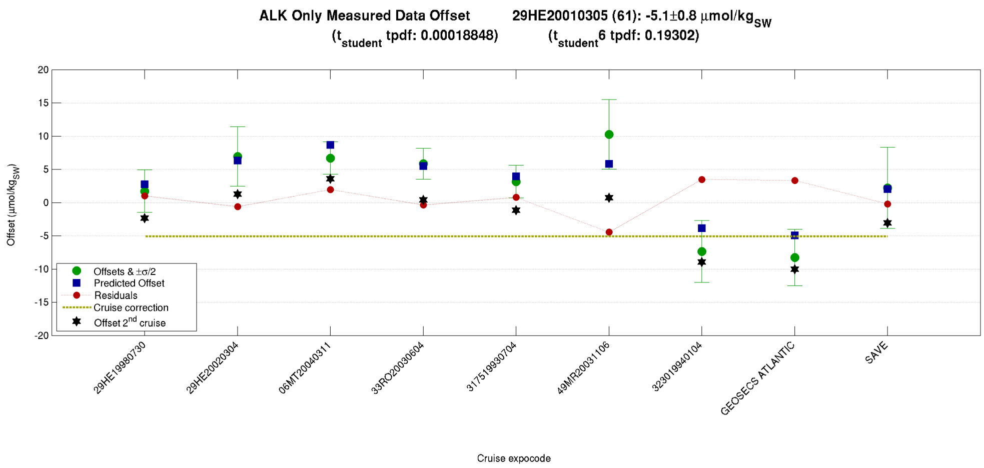

Figure 12. Cruise crossover information plot for 29HE20010305.

5.5 Cruise 29GD19860904 (57) (Fig. 11)

This is the so called GALICIA-IX cruise, on board R/V Garcia del Cid in the Atlantic area close to NW Spain. It has 50 stations taken on hydrocasts with 1.7L Niskin bottles. A precision of 0.1% and accuracy of 1.4 μmol kg^{-1} has been reported. No CRMs were used.

There are nine crossovers giving a fitted correction of +4.3 μmol kg^{-1}. The suggested adjustment is +6 μmol kg^{-1} as t-student statistical checks show that the proposed offset is indistinguishable from 6 μmol kg^{-1}. Almost all residuals fit very close to zero and keep inside $\pm$5 μmol kg^{-1} after offsets applied. There are very good fits with three core cruises. Based on this evidence, an adjustment of 6 μmol kg^{-1} was applied to the alkalinity data.

5.6 Cruise 29HE20010305 (61) (Fig. 12)

This is the so called FICARAM II cruise, conducted on R/V Hesperides along WOCE section A17 in the Western South Atlantic area. It has 29 full depth stations taken with a 24 place rosette system. CRM batches 41 and 51 were used. Uncertainty is 1.4 μmol kg^{-1} according to cruise report. There are 9 crossovers, two of them in the Southern Ocean giving a fitted correction of $-$5.1 μmol kg^{-1}. Analysis of cruise documentation seems to suggest a correction of $-$5 μmol kg^{-1}. The proposed adjustment is $-$6 μmol kg^{-1}, as it is within the offset error and is better supported than no adjustment. All residuals are very close to 0 and fit inside $\pm$5 μmol kg^{-1}. There are very good fits with five core cruises. Based on this evidence, an adjustment of $-$6 μmol kg^{-1} was applied to the alkalinity data.

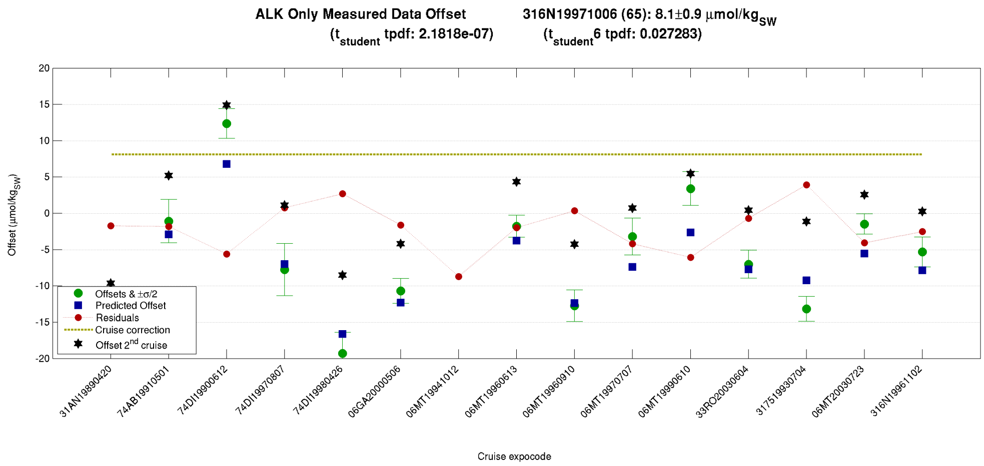

Figure 13. Cruise crossover information plot for 316N19971005.

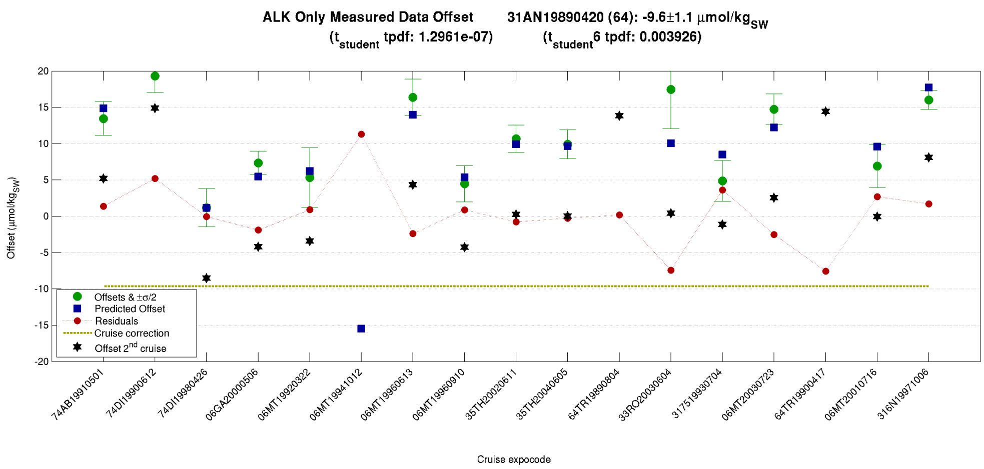

Figure 14. Cruise crossover information plot for 31AN19890420.

5.7 Cruise 316N19971005 (65) (Fig. 13)

This is the so called KN154/2 cruise, on board R/V Knorr along the WOCEAR24b section in the NW Atlantic area. It has 162 stations and 24 sampling levels using a rosette system. No reference to the use of CRM was reported. There are 15 crossovers giving a fitted correction of $+8.1\,\mu\mathrm{mol\,kg^{-1}}$. The suggested adjustment is $+8\,\mu\mathrm{mol\,kg^{-1}}$. Excepting one, all inversion residuals fit inside $\pm 6\,\mu\mathrm{mol\,kg^{-1}}$. The cruise has a good fit with three core-cruises. Based on this evidence, an adjustment of $8\,\mu\mathrm{mol\,kg^{-1}}$ was applied to the alkalinity data.

5.8 Cruise 31AN19890420 (64) (Fig. 14)

This is the so called 31A119 cruise, on board R/V Atlantis II and conducted along a section at about 20° W from 47° N to 60° N. This cruise has 51 stations taken with a rosette system. According the cruise report, the values seem to be about 5 to $10\,\mu\mathrm{mol\,kg^{-1}}$ too high in relation to OACES93 and A16N2003. CRMs were not used. The fitted correction is $-9.6\,\mu\mathrm{mol\,kg^{-1}}$. The inversions suggest an adjustment of $-10\,\mu\mathrm{mol\,kg^{-1}}$. Crossovers with core cruises support the proposed offset very well. In addition, GLODAP 317519930704 supports this adjustment. Based on this evidence, an adjustment of $-10\,\mu\mathrm{mol\,kg^{-1}}$ was applied to the alkalinity data.

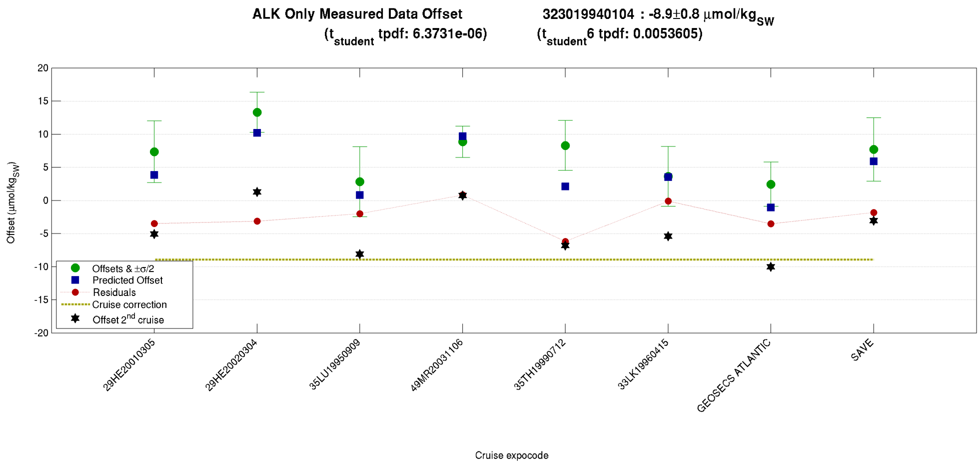

Figure 15. Cruise crossover information plot for 323019940104.

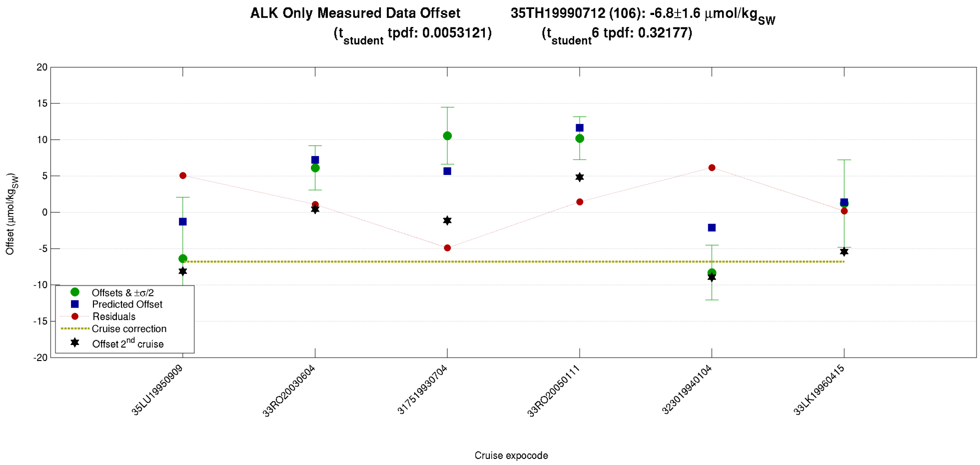

Figure 16. Cruise crossover information plot for 35TH19990712.

5.9 Cruise 323019940104 (Fig. 15)

This is the CITHER2 cruise, on board R/V Maurice Ewing and along the WOCE A17 section in the Western South Atlantic area from 10° S to 55° S. It has 235 stations taken with a 32 place rosette system. In the cruise report, an offset for alkalinity of $-8\,\mu\text{mol kg}^{-1}$ was stated. There are eight crossovers that give a fitted correction of $-8.9\,\mu\text{mol kg}^{-1}$. The suggested adjustment is $-8\,\mu\text{mol kg}^{-1}$ because it agrees with both the fitted result and the cruise report. Most of the inversion residuals fit inside $\pm 5\,\mu\text{mol kg}^{-1}$. There are very good fits with four GLODAP cruises. Based on this evidence, an adjustment of $-8\,\mu\text{mol kg}^{-1}$ was applied to the alkalinity data.

5.10 Cruise 35TH19990712 (106) (Fig. 16)

This is the so called EQUALANT99 cruise, on board R/V Thalassa in the Equatorial Atlantic area. It has 102 stations taken with a 24 place rosette system. Precision is reported as $1.7\,\mu\text{mol kg}^{-1}$. A comparison with WOCE A15 data implies offset values as high as $12.7\,\mu\text{mol kg}^{-1}$. There are six crossovers, giving a fitted correction of $-6.8\,\mu\text{mol kg}^{-1}$. The suggested adjustment is $-6\,\mu\text{mol kg}^{-1}$. All inversion residuals fit inside $\pm 6\,\mu\text{mol kg}^{-1}$ after corrections are applied. There are very good fits with two GLODAP cruises. Based on this evidence, an adjustment of $-6\,\mu\text{mol kg}^{-1}$ was applied to the alkalinity data.

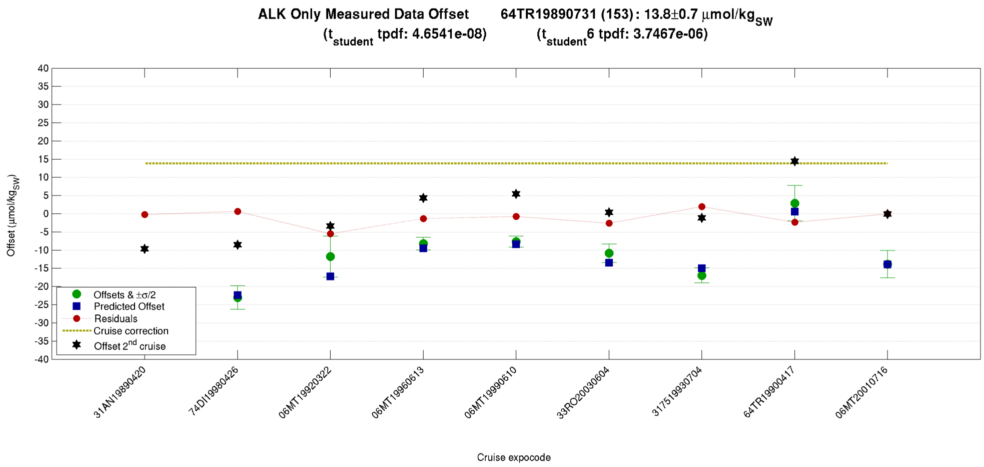

Figure 17. Cruise crossover information plot for 64TR19890731.

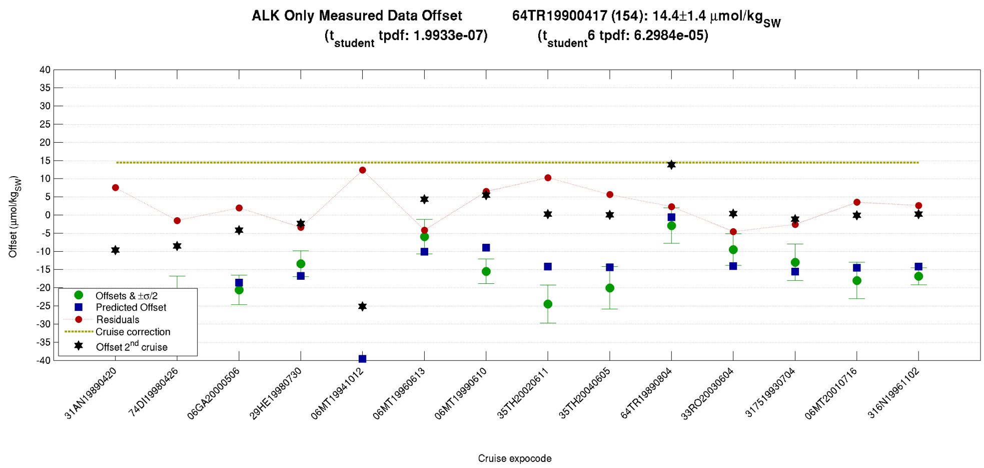

Figure 18. Cruise crossover information plot for 64TR19900417.

5.11 Cruise 64TR19890731 (153) (Fig. 17)

This cruise is also called 64TY8908, on board R/V Tyro along a meridional A16N section at 20° W. The cruise has 73 stations and 12 sampling levels using a rosette system. Nine stations have been flagged 3. There are nine crossovers giving a fitted correction of 13.8 μmol kg^{-1}. The suggested adjustment is 14 μmol kg^{-1}. All inversion residuals are close to zero and fit inside the ±5 μmol kg^{-1} boundary. There are very good fits with two GLODAP cruises. Based on this evidence, an adjustment of 14 μmol kg^{-1} was applied to the alkalinity data.

5.12 Cruise 64TR19900417 (154) (Fig. 18)

This cruise is also called 64TY9001, on board R/V Tyro along a meridional A16N section at 20° W from 30° N to 60° N. This cruise has 23 stations with multiple casts on most of them. The method of Bradshaw et al. (1981), and calculations with constants of Goyet and Poisson (1989) were used. Values are about 20 μmol kg^{-1} low relative to CLIVAR A16N-2003 and have twice the scatter. There are 14 crossovers. The fitted correction is +14.4 μmol kg^{-1}. The suggested adjustment is +14 μmol kg^{-1}. After fitted corrections are applied, 10 inversion residuals fit inside ±5 μmol kg^{-1}. There are good fits with two GLODAP and one core cruise (06GA20000506). Based on this evidence, an adjustment of 14 μmol kg^{-1} was applied to the alkalinity data.

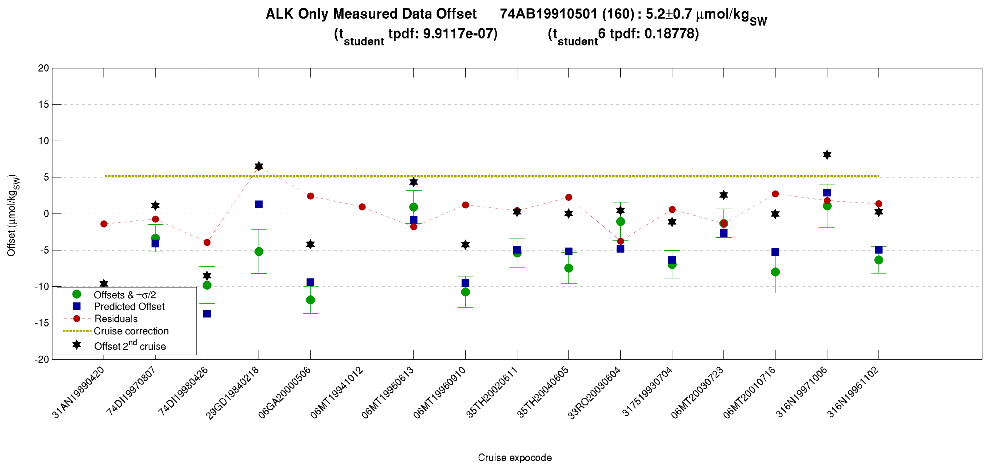

Figure 19. Cruise crossover information plot for 74AB19910501.

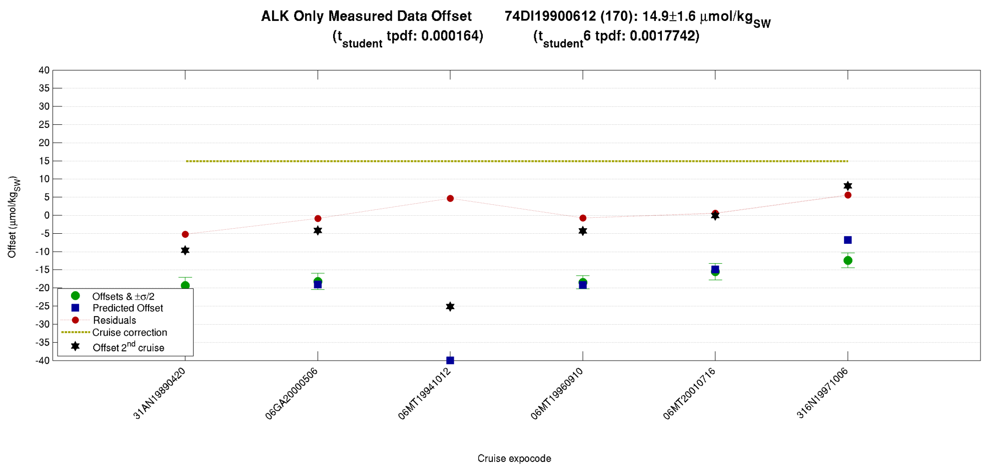

Figure 20. Cruise crossover information plot for 74DI19900612.

5.13 Cruise 74AB19910501 (160) (Fig. 19)

This is the so called Vivaldi expedition, on board R/V Charles Darwin in the NE Atlantic area primarily West of Iberia. It has 614 stations, from which only 34 are deep stations. The samples were taken with a 24 place rosette system. According to the cruise report, the values are low in relation to GLODAP by about 15 μmol kg^{-1}. Good precision is noted. Laboratory-made borax standards were used but no CRMs. There are 16 crossovers giving a fitted adjustment of 5.2 μmol kg^{-1}. The suggested adjustment is 5 μmol kg^{-1} as a student t-test shows that the proposed correction is indistinguishable from 6. Crossovers with six core cruises also support the proposed offset. Furthermore, GLODAP 317519930704 supports this adjustment, as very low residuals are present after the offset has been applied. Based on this evidence, an adjustment of 5 μmol kg^{-1} was applied to the alkalinity data.

5.14 Cruise 74DI19900612 (170) (Fig. 20)

This cruise is also called 74DI192, and was conducted on R/V Discovery in the North Atlantic area from 46° N to 49° N and 17° W to 15° W. This cruise has 20 stations and 12 sampling levels using a rosette system. Comparing with one GLODAP station, values are about 18 μmol kg^{-1} lower. There are six crossovers giving a fitted correction of 14.9 μmol kg^{-1}. The inversions suggest an adjustment of 15 μmol kg^{-1}. Inversion residuals are inside a ±5 μmol kg^{-1} boundary after corrections are applied. Based on this evidence, an adjustment of 15 μmol kg^{-1} was applied to the alkalinity data.

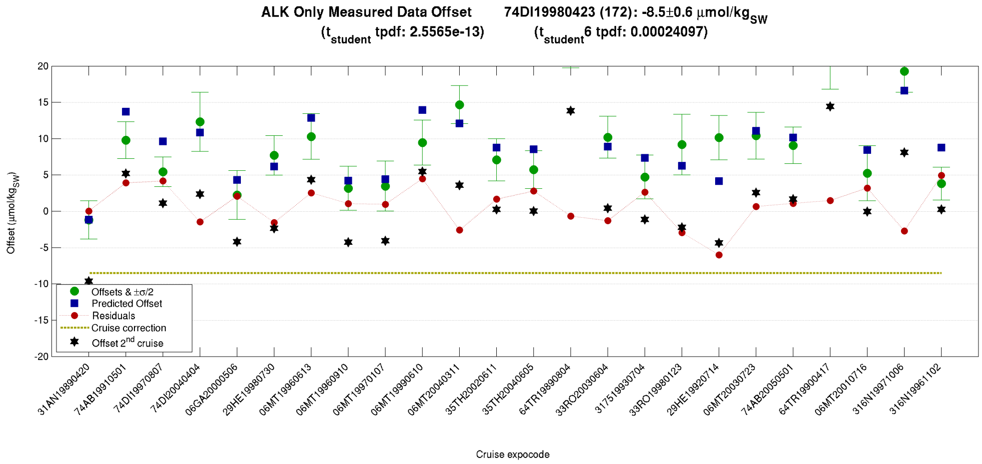

Figure 21. Cruise crossover information plot for 74DI19980423.

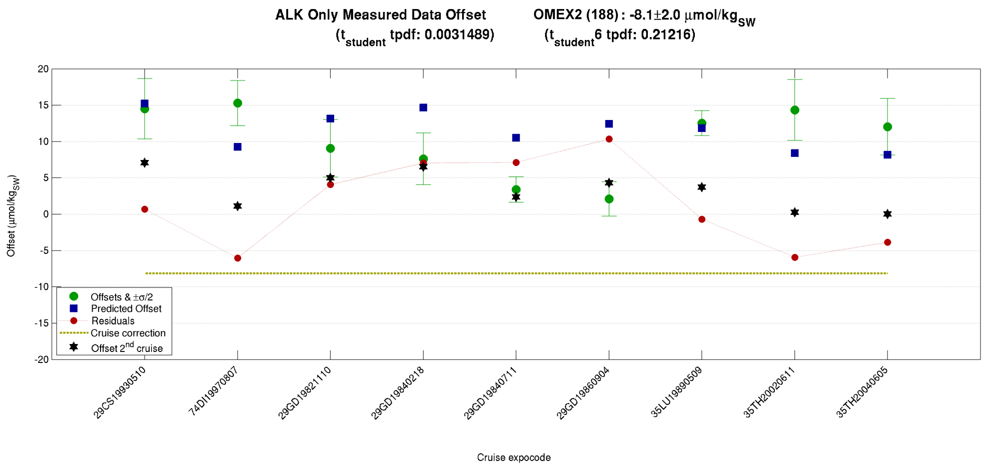

Figure 22. Cruise crossover information plot for OMEX2.

5.15 Cruise 74DI19980423 (172) (Fig. 21)

This is the 74DI233 cruise, also called Chaos, conducted on R/V Discovery, performing a meridional section along 20° W from 20° N to 60° N. It has 44 full depth stations taken with a 24 place rosette system. Data is generally good, with a few data high relative to neighbours and GLODAP. CRMs were used. There are 24 crossovers giving a fitted correction of $-8.5\,\mu$mol kg^{-1}. The suggested adjustment is $-9\,\mu$mol kg^{-1}. Most of the residuals fit very close to zero and keep inside $\pm5\,\mu$mol kg^{-1} after corrections are applied. There are very good fits with core and GLODAP cruises. Based on this evidence, an adjustment of $-9\,\mu$mol kg^{-1} was applied to the alkalinity data.

5.16 Cruise OMEX2 (188) (Fig. 22)

This is also called OMEX2 Project Time Series. Rather than a single cruise, it is a compilation of 12 cruises performed on board R/Vs Belgica, Charles Darwin and Meteor on the NW Iberian margin. There are nine crossovers giving a fitted correction of $-8.1\,\mu$mol kg^{-1}. The suggested adjustment is $-8\,\mu$mol kg^{-1}. With one exception, all inversion residuals fit inside $\pm6\,\mu$mol kg^{-1}. There are three crossovers with core cruises that appear to suggest an even larger offset. Based on this evidence, an adjustment of $-8\,\mu$mol kg^{-1} was applied to the alkalinity data.

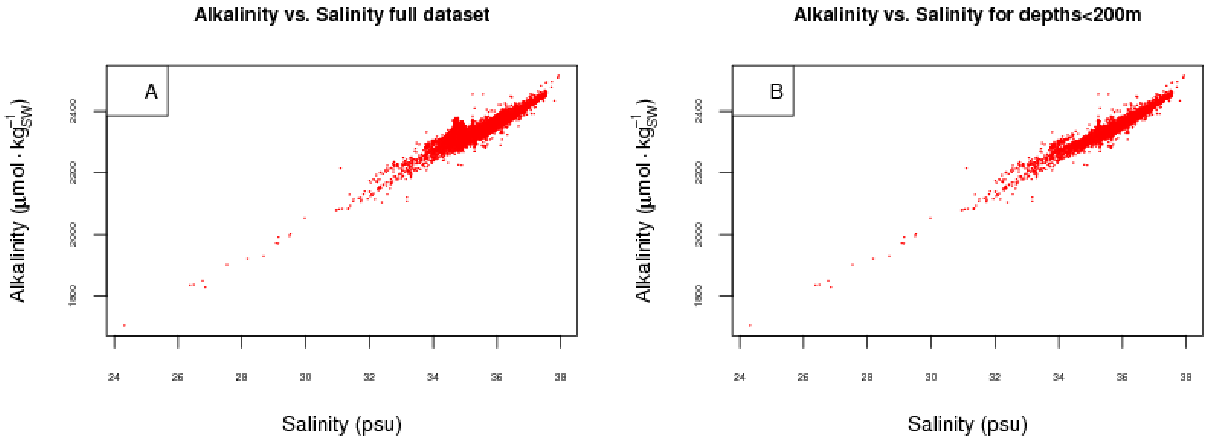

Figure 23. Alkalinity data in CARINA final database versus salinity for: **(A)** data deeper than 200 m **(B)** depths <200 m.

6 Data quality evaluation

As derived from its definition, the salt content of seawater is a determining factor on the A_T. For this reason, salinity is a good parameter to explain some of the A_T variability. In Fig. 23a, alkalinity is shown against salinity for the full CARINA-ATL dataset. As expected, the parameters correlate well, giving a R^2 regression coefficient of 0.77. As near surface formation of water masses is the main process that affects A_T variability, Fig. 23b, represents the variation of A_T versus salinity for the subset of surface waters (depth <200 m). The correlation for this data set is higher than in Fig. 23a, giving a R^2 of 0.94 due to the fact that most of the variability in both salt and alkalinity occurs in the upper few hundred meters. This enforces the idea of the interdependence of both parameters.

To make an overall evaluation of the dataset quality, additional variables that can affect the natural variability of the alkalinity were introduced in the regression. Thus, a Multi-Linear Regression (MLR) was performed with potential temperature (θ), salinity, latitude, apparent oxygen utilisation (AOU), nitrate, phosphate and silicate in order to remove as much natural variability as possible. All of these parameters were included knowing that interdependence exists between many of them. However, the goal here is not to generate a statistical model for alkalinity, but rather a way of getting residuals with natural variability removed to a large extent (about 90%), so that they can be used to test the data quality. This analysis method facilitates a better assessment of scatter and biases in the alkalinity dataset, and even to test the applied adjustments. The MLR procedure can transmit the measurement error of the explanatory variables to the residuals despite being quite lower than the alkalinity error.

In order to improve the quality of the evaluation, the MLR analysis was applied in four density layers, with density at 1000 db (σ_1) being used to divide the ocean. The upper thermocline was set by σ_1 <32.25 kg m^{-3}; intermediate waters (depths from about 1000 to 2000 m) were defined by second layer (32.25<= σ_1 <32.39 kg m^{-3}); water depths between ~2000 to 3000 m were defined by 32.39<= σ_1 <32.53 kg m^{-3} – corresponding to North Atlantic Deep Waters (NADW); and finally, the fourth layer refers to bottom waters, where the presence of Antarctic Bottom Waters (AABW) dominates. This last layer is set by σ_1 >32.53 kg m^{-3}. The surface layer with depths <200 m was removed from this evaluation.

Using this analysis, alkalinity residuals were calculated by the following Eq. (2):

$$A_{T\_\text{MLR}} = \sum_{i=1}^{8} a_i \cdot X_i \\ A_{T\_\text{residuals}} = A_{T\_\text{measured}} - A_{T\_\text{MLR}} \quad (2)$$

where X_i stand for θ, salinity, latitude, AOU, nitrate, phosphate, silicate, and a constant term. This procedure was done with the CARINA-ATL corrected database, and also for the database without any alkalinity adjustments applied.

The alkalinity residuals for each density layer are shown in Fig. 24. This shows a box plot of alkalinity residuals cruise data for each cruise. The box/whiskers represent the typical five number summary (minimum, 25th percentile, median, 75th percentile and maximum), the width of individual boxes corresponds to the number of samples for that cruise, and the numbers on the x-axis are the CARINA cruise IDs as referenced in Table 1.

The best fit (R^2=0.95) is obtained for the shallower waters, with a mean standard deviation of 6.2 μmol kg^{-1}. The other layers have a slightly lower mean standard deviation (5.4, 5.9 μmol kg^{-1} respectively), except for the bottom layer with 6.5 μmol kg^{-1}. The median of mean standard deviations for all cruises is 4.1 μmol kg^{-1} units for each of three deepest density layers. The lower panel in the figure stands for the joined alkalinity residuals of the four density layers.

As can be seen, alkalinity residuals are lower when using the corrected database, in comparison with the uncorrected

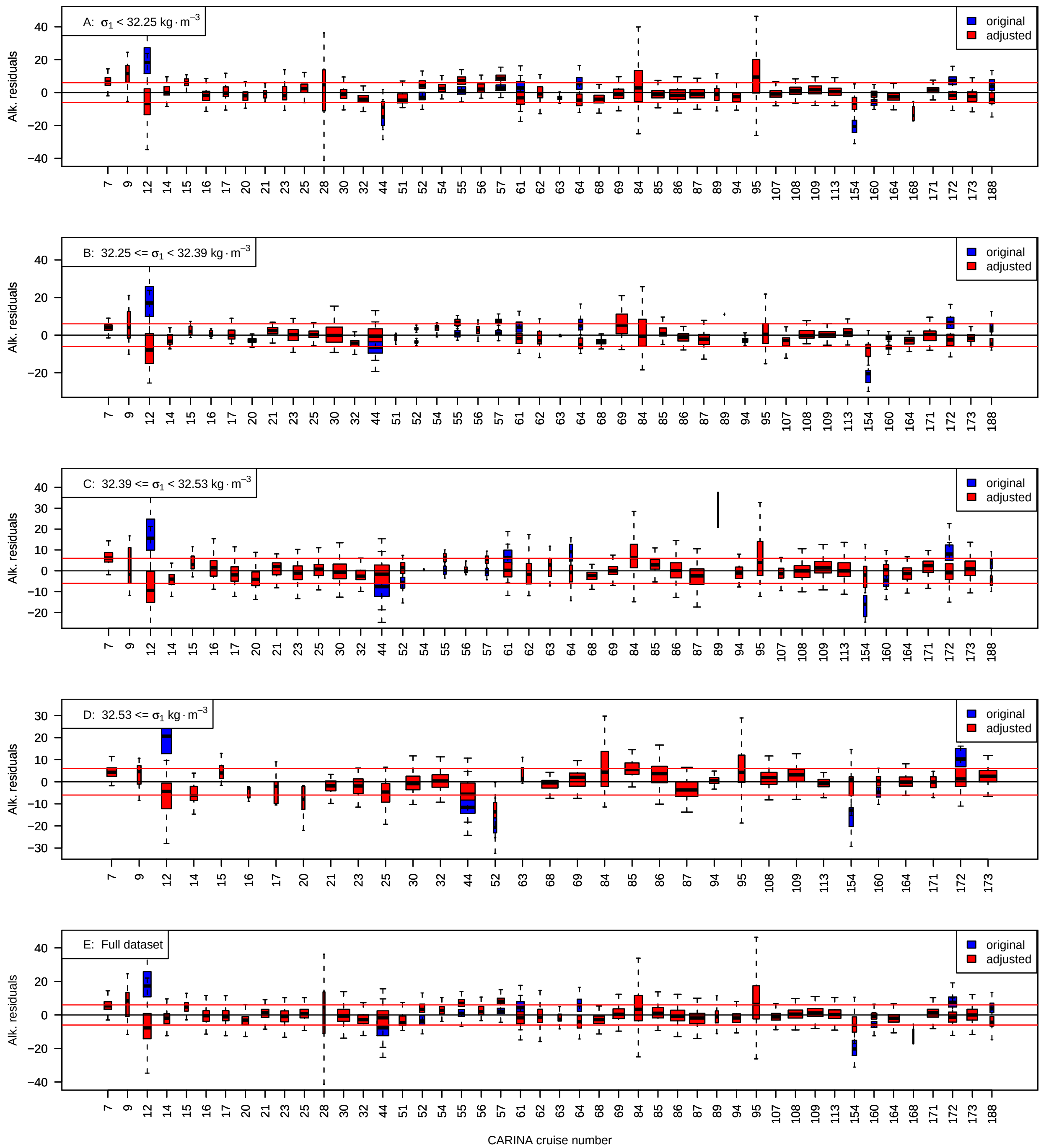

Figure 24. Alkalinity residuals obtained from CARINA-ATL dataset by applying an MLR for alkalinity data against Theta, Salinity, Latitude, AOU, Nitrate, Phosphate and Silicate. (**A** to **D**) are CARINA-ATL subsets for the indicated σ_1 interval, and **(E)** is the join for the full dataset. Blue values are residuals with the original unadjusted alkalinity values, and Red values are the final adjusted alkalinity values. Red lines are the $\pm 6\,\mu$mol kg^{-1} of alkalinity used as lower limit for adjustments in the crossover exercise.

original ones. Most but not all of the cruises have the alkalinity residuals median inside of the $\pm 6\,\mu$mol kg^{-1} boundary, showing that in addition to the alkalinity measurement errors, there are two other sources that increase the variability of the alkalinity residuals: firstly, the MLR is not able to explain all of the naturally observed variability of alkalinity; and secondly, the predictor parameters have their own inherent measurement errors.

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